TECHNISCHE UNIVERSITÄT BERGAKADEMIE FREIBERG

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Trace elements in magmatic systems and geochemical modelling

(an introduction)

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Literature basically used:

Books

- H. Zou: Geochemical modelling. Imperial College Press.
- H. Rollinson: Using geochemical data. Longman.
- A. Philpotts & J.J. Ague: Principles of Igneous and Metamorphic Petrology, Cambridge University Press.
- M. Wilson: Igneous Petrogenesis. Oxford University Press.
- G. Faure: Principles of Isotope Geology. Wiley & Sons.
- F. Albarède: Geochemistry: An Introduction. Cambridge University Press
- F. Albarède: Introduction to Geochemical Modeling. Cambridge University Press.
- William White: Geochemistry. (http://www.imwa.info/white-geochemistry.html)

Other sources

- John D. Winter‘s webpages and lectures: http://www.whitman.edu/geology/winter/
- Heinz-Günter Stosch, Uni Karlsruhe: Skripte

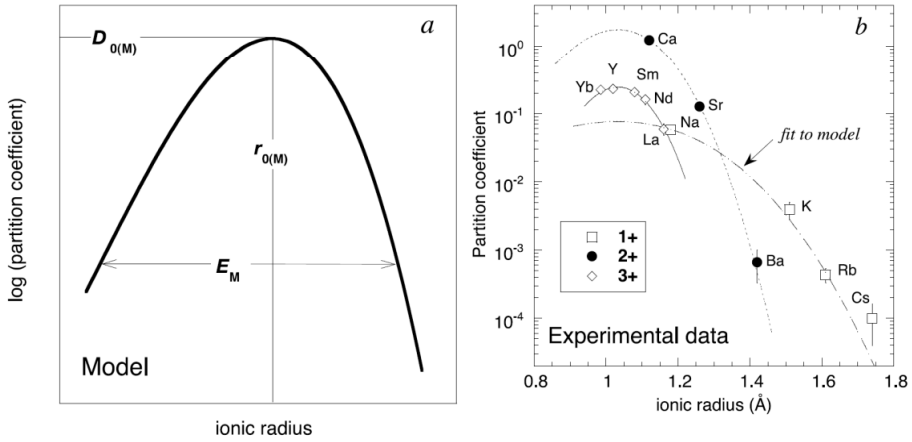
Literature basically used:

Selected papers (amongst thousand others...)

- Salters & Stracke (2004) Composition of the depleted mantle. G-cubed, 5, doi:10.1029/2003GC000597
- Stracke, Bizimis, Salters (2003) Recycling oceanic crust: Quantitative constraints. G-cubed, 4, doi:10.1029/2001GC000223
- Hofmann (1988) Chemical differentiation of the Earth: the relationship between mantle, continental crust, and oceanic crust. Earth. Planet. Sci. Lett., 90, 297314
- Sun & McDonough (1989) Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. Geological Society, London, Special Publications, 42, 313-345
- McDonough & Sun (1995) The composition of the Earth. Chem. Geol., 120, 223-253
- Rudnick & Fountain (1995) Nature and composition of the continental crust: A lower crustal perspective. Reviews of Geophysics, 33, 267-309
- Plank & Langmuir (1998) The chemical composition of subducting sediment and its consequences for the crust and mantle. Chem. Geol. 145, 325-394
- DePaolo (1981) Trace element and isotopic effects of combined wallrock assimilation and fractional crystallization. Earth Planet. Sci. Lett., 1981, 189-202
- Spera & Bohrson, 2001: Energy-constrained open-system magmatic processes I: General model and energy-constrained assimilation and fractional crystallisation (EC-AFC) formulation. J. Petrol., 42, 999-1018.

Chapter 1

B A S I C S



$$D_i = D^{n+}_{0(\mathrm{M})} \times \exp\left\{\frac{-4\pi \mathrm{N_A} \mathrm{E_M}^{n+}\left[\frac{1}{2}r^{n+}_{0(\mathrm{M})}\left(r_i - r^{n+}_{0(\mathrm{M})}\right)^2 + \frac{1}{3}\left(r_i - r^{n+}_{0(\mathrm{M})}\right)^3\right]}{\mathrm{R}T}\right\}$$

What are trace elements (compared to major elements)**?**

- ✓ **Trace elements** occur in only **very limited concentrations** in natural rocks and minerals (in the ppm range), and commonly **do not form own phases** – *some important trace-elements are, for example, are Ba, Nb, Th, U, Hf, Ta, Zr, Rb, Sr ...*

- ✓ Other important trace elements are the **Rare Earth Elements**, **REE**: *La, Ce, Pr, Nd, Pm, Sm, Eu, ... Yb, Lu*

- ✓ But note that sometimes trace elements are indeed major constituents (i.e. become major elements) in minerals, i.e. form own phases, typically named **accessory phases**:

  Zircon: $Zr[SiO_4]$, Monazite: $(La,Ce,Nd)PO_4$, Xenotim: $(Y,Yb)PO_4$, Columbite-Tantalite, Allanite, ...

With this definition, trace-elements behave steady (or continuous) in magmatic systems, major elements do not .....

Concentration units.... can be defined in different ways:

- as **mass per mass**, e.g. µg/g, or mg/kg, or g/to, ...
  Note that the percent notation is usually also used as mass per mass unit, where 1 wt% = 1g/100g
- as **mole per mass,** e.g. mol/g, or mmol/mg, ...
- as mass per volume, e.g. mg/l
- as mol per volume, e.g. mol/l

Note that the ppm notation equals the percent notation, where:

1% = 1 part out of hundred parts

1 ppm = 1 part out of one million parts

Frequently, ppm is used equivalent to mass per mass, where

1 ppm = 1 µg/g and 0.1% = 1000 ppm

but note that this is ambiguous, and thus should be avoided !!

Better use mass per mass, such as µg/g !!

Why using trace elements?

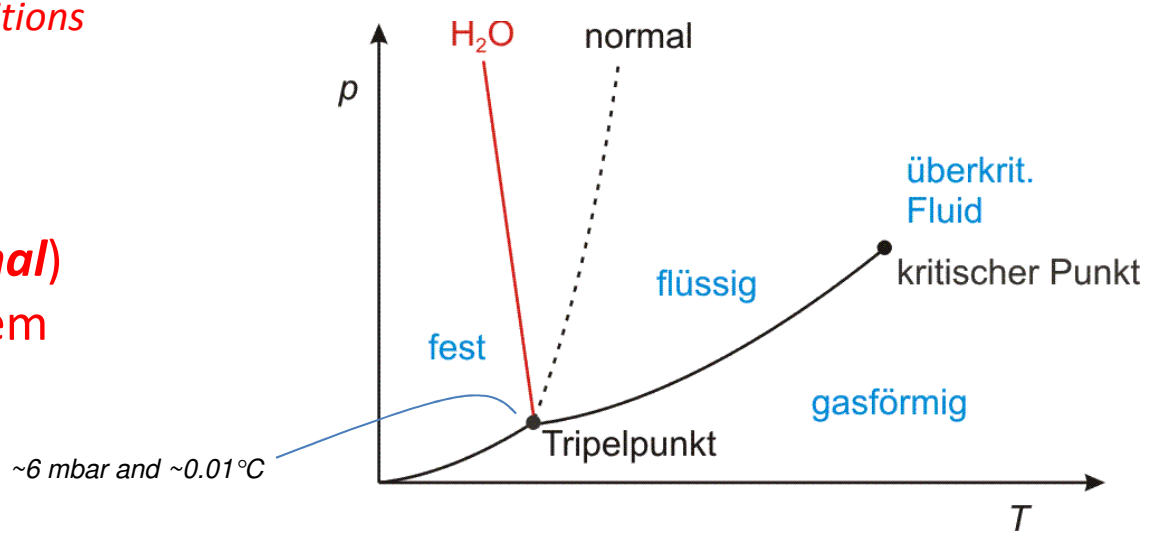
Trace elements are, other than major elements, not components with respect to the *Gibbs' phase rule*, and thus do not follow this *law*:

$$F = C - P + 2$$

F = *degrees of freedom*
C = *components in the system*
P = *phases in the system*

In other words, trace-elements can not appear or disappear if conditions (p, T, X, ...) change!

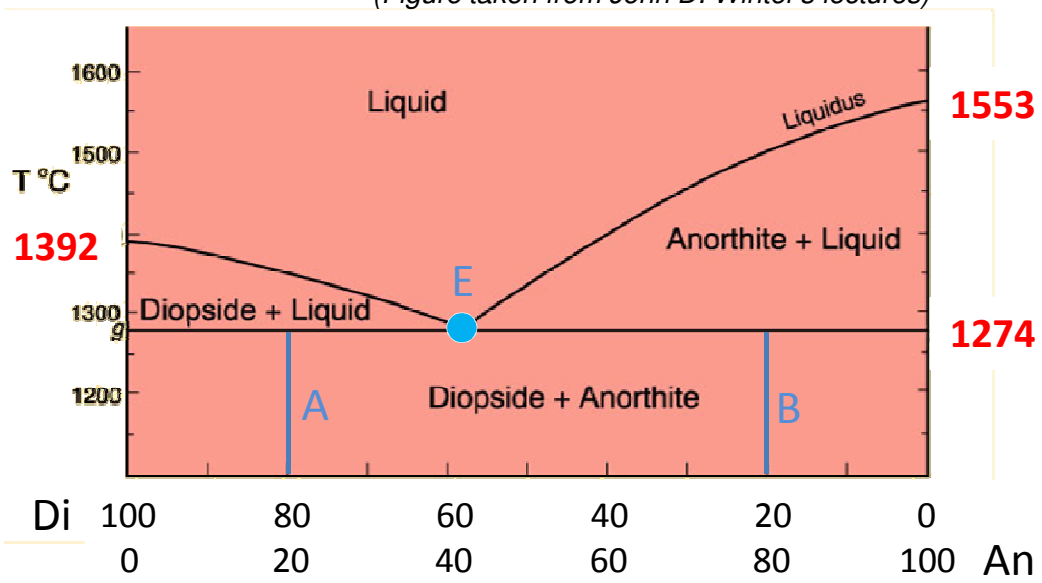
Therefore, they provide other (or better: ***additional***) information about a system than major elements!



Why using trace elements?

Example: Melting in the binary system Di - An

(Figure taken from John D. Winter's lectures)



Eutectic melt composition does **not** provide any information about the **degree of melting** or about the **source composition** (i.e. the source mineralogy expressed as ratio between **Di** and **An** in the source!)

In contrast: The **concentration ratio** of two incompatible trace elements in a melt (for example **Th** and **La)** very closely reflects the ratio in the source rock:

Basalt composition ≈ melt composition!

$$\left(\frac{Th}{La}\right)_{melt} \approx \left(\frac{Th}{La}\right)_{source\ rock}$$

Characteristics of trace elements:

(AFFINITY • MOBILITY • VOLATILITY • COMPATIBILITY)

Trace elements are:

- **sidero**phile (e.g. Ni, Re, Os, W)
- **chalko**phile (e.g. As, Sb, Sn, Se)
- **litho**phile (e.g. Zr, Nb, La, Sm, Rb)
- **atmo**phile (e.g. N, O, He, Ne, Ar, Kr)

- **mobile** (e.g. Rb, Cs, Sr, Pb)
- **immobile** (Nb, Ta, Hf, Zr, Yb)

- **refractory** (Nb, Ta, Ti, Hf, Zr)
- **volatile** (Rb, Cs, Pb, Li)

- **compatible**
- **incompatible**

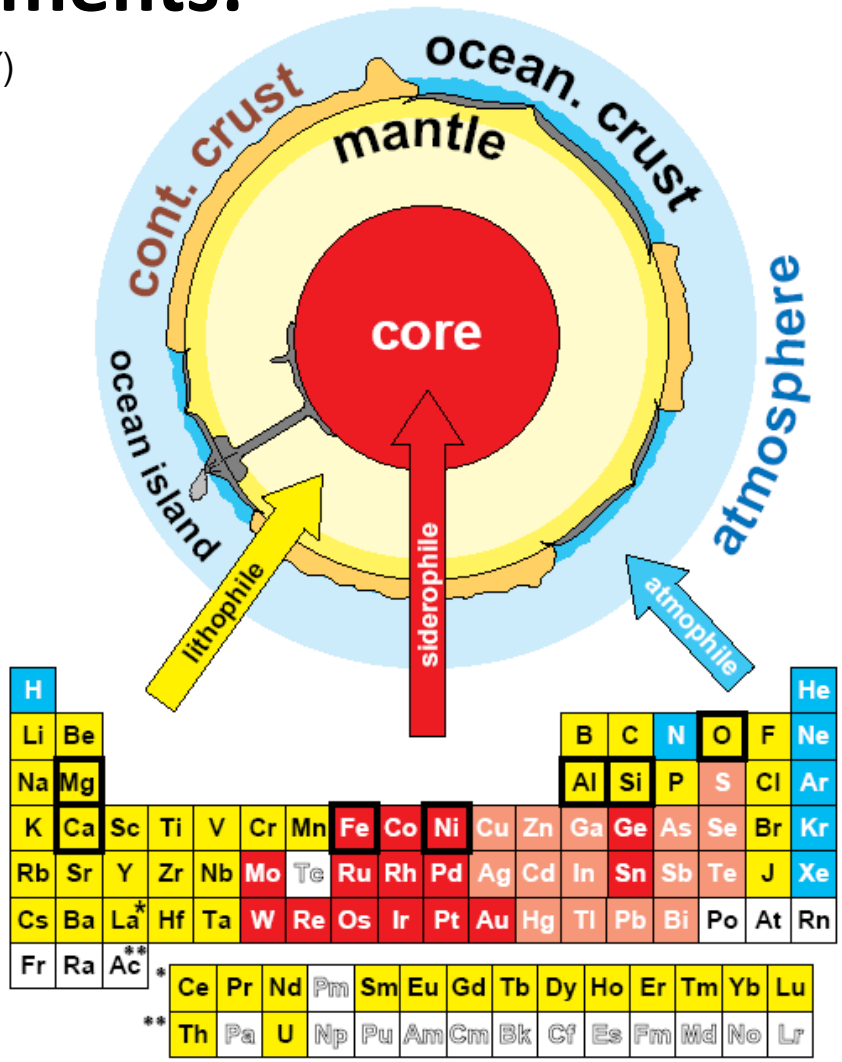


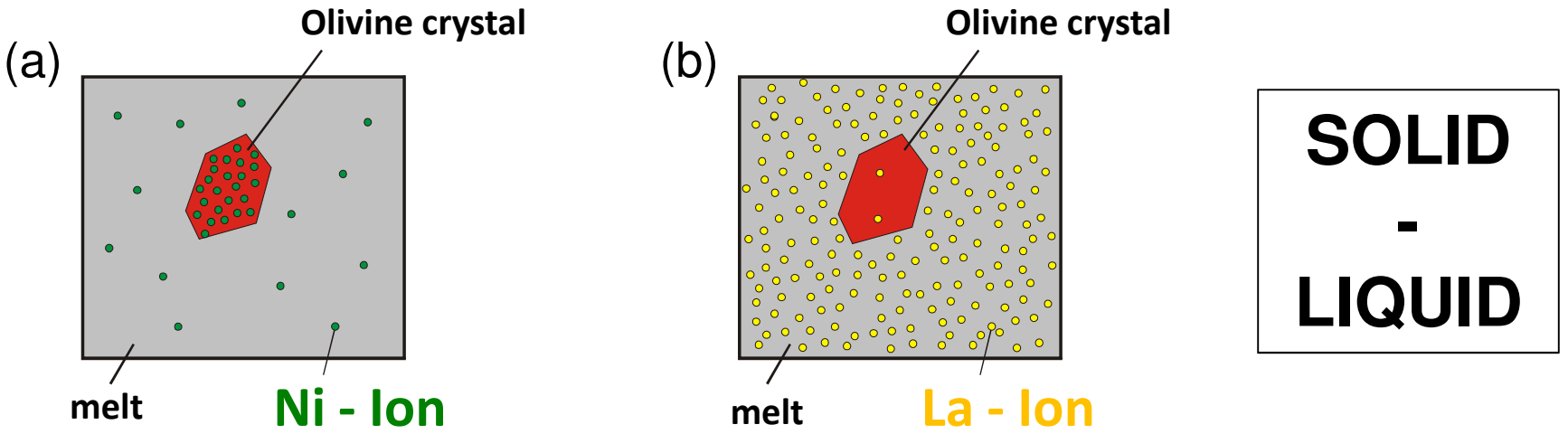
Figure from K.P. Jochum, Max Planck Institut für Chemie, Mainz, Germany

Characteristics of trace elements:

Partitioning between two phases: Solid – liquid distribution

(a) **Compatible** trace elements prefer the solid phase in a solid-liquid system (e.g. mineral – melt in a two-phase system)

(b) **Incompatible** trace elements prefer the liquid phase in a solid-liquid system (e.g. mineral – melt in a two-phase system)

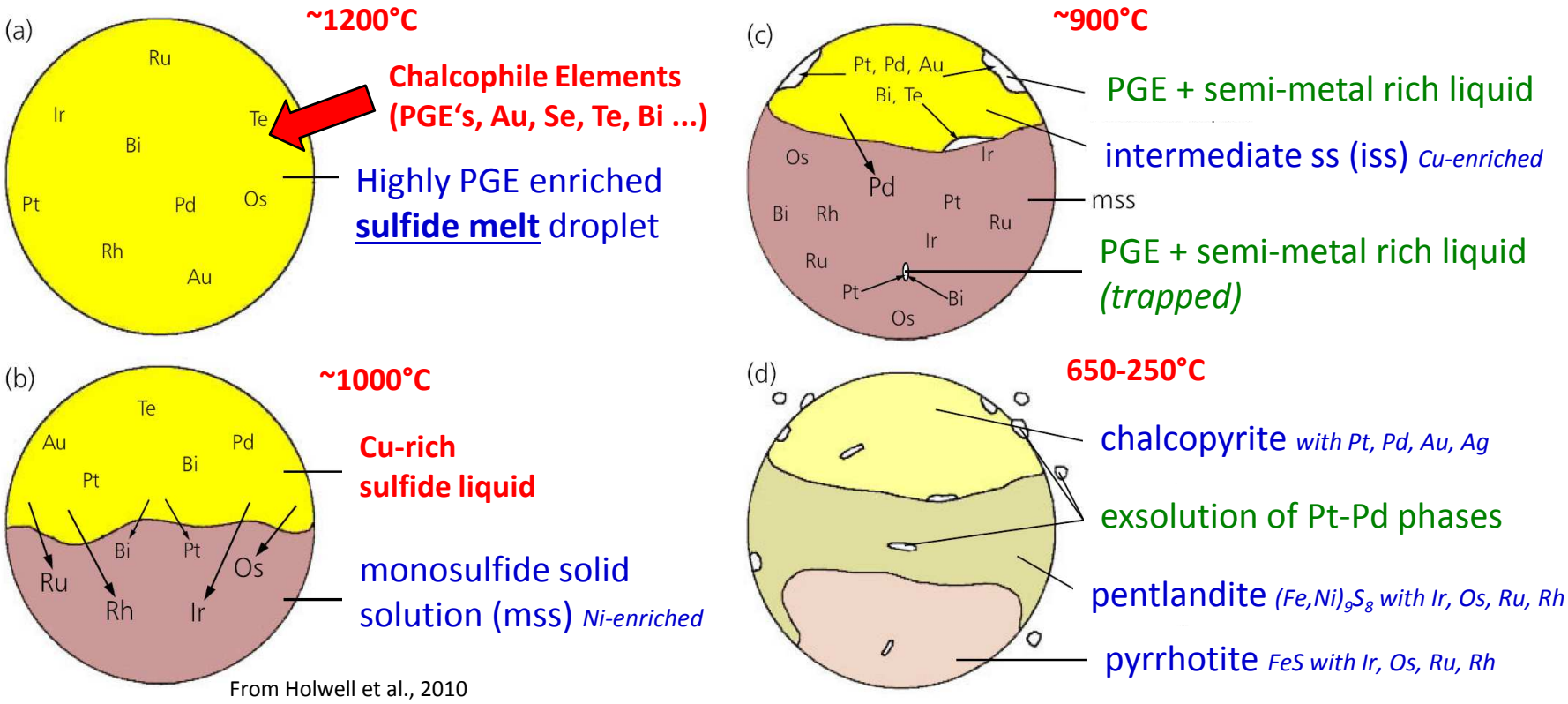


Only valid under **equilibrium conditions** (dynamic equilibrium) !!!!!!!!!!

Characteristics of trace elements:

Partitioning between two phases: Liquid - liquid & solid - solid distribution

Distribution of PGE's (Pt, Pd, Ir, Os, Rh, Ru) and Au between **sulfide** and **silicate** liquid during **sulfide melt segregation** from mafic magmas

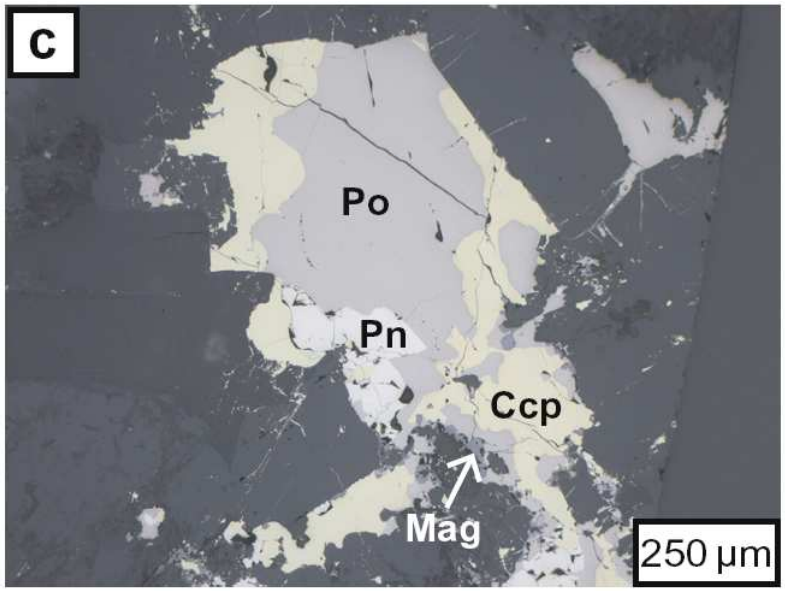


From Holwell et al., 2010

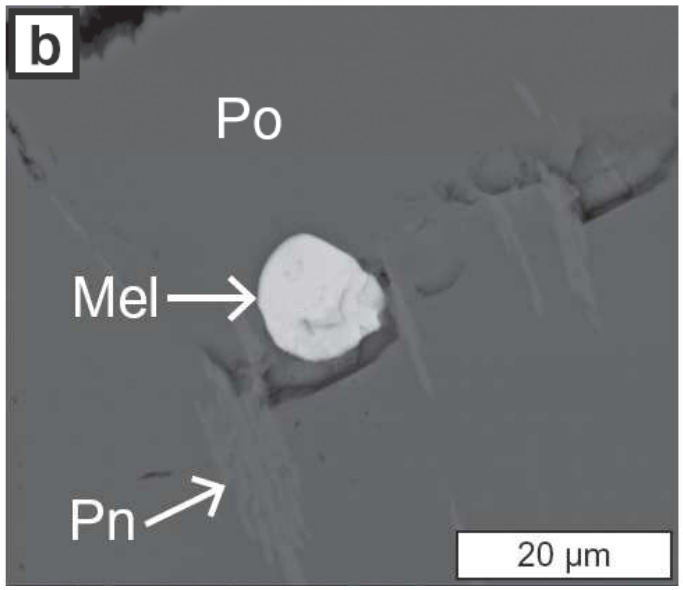
Characteristics of trace elements:

Partitioning between two (or more) phases

Liquid-magmatic sulfid parageneses in optical and SEM images



Massive sulfide phases
in Ol-Hbl-gabbronorite



Melonite ($NiTe_2$) exsolution
in pentlandite-pyrrhotite

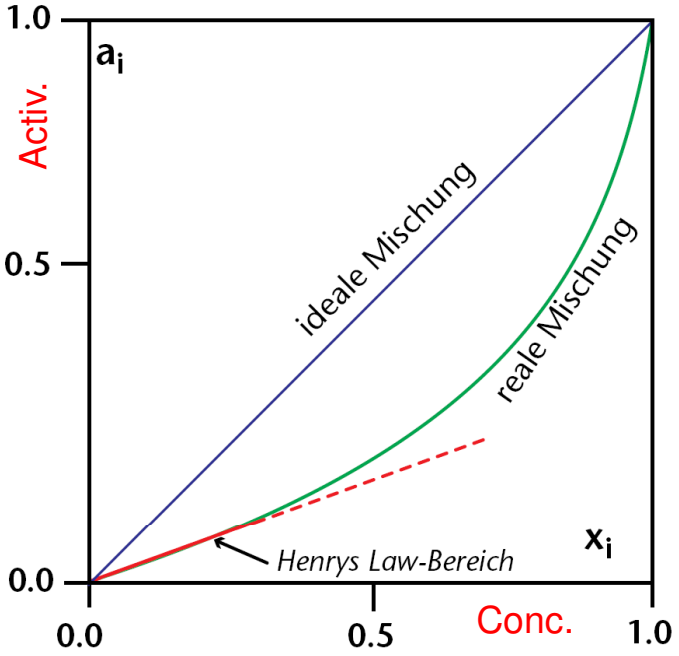
Po = pyrrhotite
Pn = pentlandite
Ccp = chalcopyrite
Mel = melonite

From Járóka et al., 2019

Partitioning – quantitative:

Relationship between concentration (given as mole fraction X) and activity for component **i** (e.g. trace element i).
In the **„Henry's range"** there is a linear relation between **a** and **X**:

$$a^i = \gamma^i X^i$$



$$If\ X^i \to 0,\ then\ \gamma \to 1$$

Exchange equilibrium of a component (i.e. trace element **i**) between two phases (here: solid-liquid, e.g. mineral-melt):

$$K^i = \frac{a^i_S}{a^i_L} = \frac{\gamma^i X^i_S}{\gamma^i X^i_L}$$

K^i = *equilibrium constant for component i*
a^i = *activity of component i*
γ = *activity coefficient =f(X,p,T)*
X = *molar concentration (mole fraction)*
*S denotes **solid** phase*
*L denotes **liquid** phase, i.e. melt*

Partitioning – quantitative:

As trace element concentrations in geological systems are (very) low, their activity is directly proportional to their concentration **C** (or X) (**Henry's law**):

$$a^i \sim C^i \quad \text{yielding} \quad D^i = \frac{C_S^i}{C_L^i}$$

*D^i is the **partition coefficient** for element i, sometimes termed K_d or K_D*

(Note: K is used for the activity ratio, D for the concentration ratio)

valid at low concentrations only !!!

Implications:

If the concentration **C** (or X!) of a trace element **i** in a system (i.e., an infinite melt volume) **doubles**, **C** of this trace element in **ALL phases** (i.e. minerals in equilibrium with this melt) will **double**!

BUT: Trace element ratios will not be affected!

Partitioning – quantitative:

Summary:

Incompatible trace elements: $D^i < 1$

Compatible trace elements: $D^i > 1$

Example:

$$D^{Ni}_{Ol-melt} = \frac{c_s}{c_l} \sim 5 - 30$$

Concentration of **Ni** in an **olivine** crystal in equilibrium with a basaltic melt having 150 ppm Ni:

$D^{Ni}_{Ol\text{-}melt}$ = 10.9 for Fo ~ 0.9

Ni content in this olivine is then:

10.9 x 150 ppm = 1635 ppm (= 0.16%)

Parameters that control D:

Ionic charge and ionic radius

V.M. Goldschmidt (1888-1947)

Goldschmidt rules:

Ion species with identical **radius** and identical **charge** enter a lattice side equally, i.e. an ion can replace another one if it‘s charge and radius are (nearly) the same.

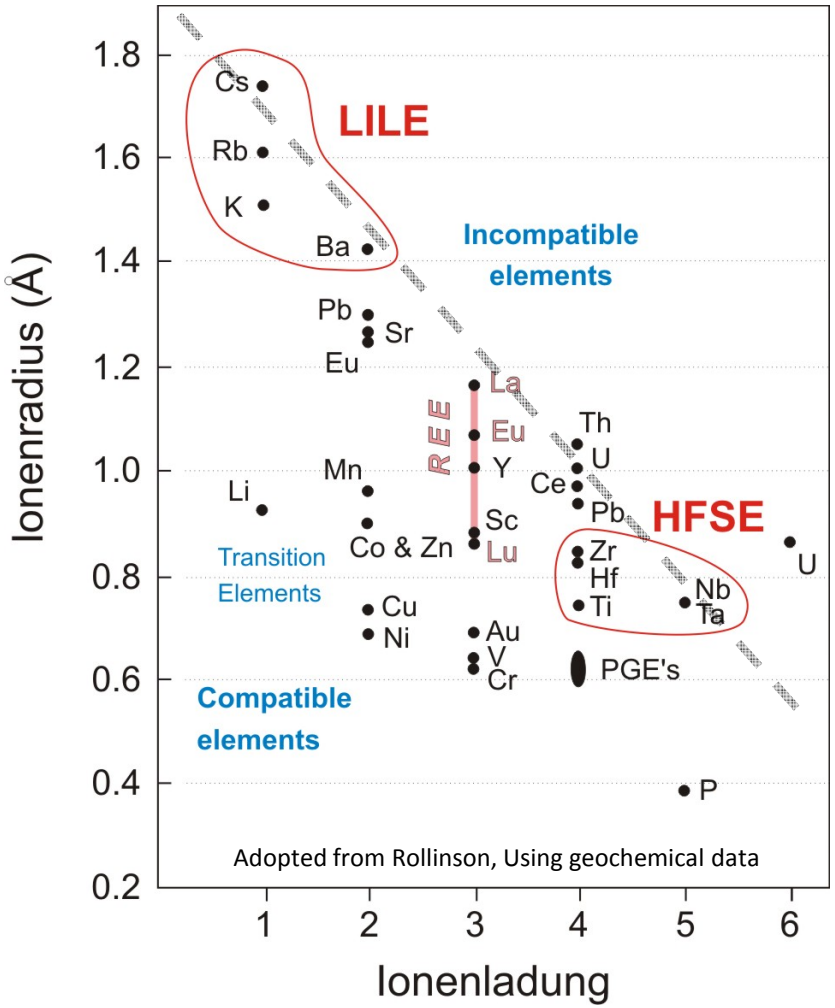
If two ion species have **identical charge** but **different ionic radii**, the species with the **smaller radii** will enter a lattice preferentially (not fully valid!)

If two ion species have **identical radii** but **different charge**, the species with the **higher charge** will enter a lattice preferentially

THE RATIONALE BEHIND IS ION EXCHANGE EQUILIBRIUM WITH RESPECT TO A LATTICE SIDE IN A CRYSTAL (solid solution model)

Parameters that control D:

Ionic charge and ionic radius



For incompatible elements:

The larger the **ionic radius**, the more incompatible!

The higher the **ionic charge**, the more incompatible!

HFSE: Nb, Ta, Zr, Hf, Ti

LILE: Cs, Rb, Ba, K

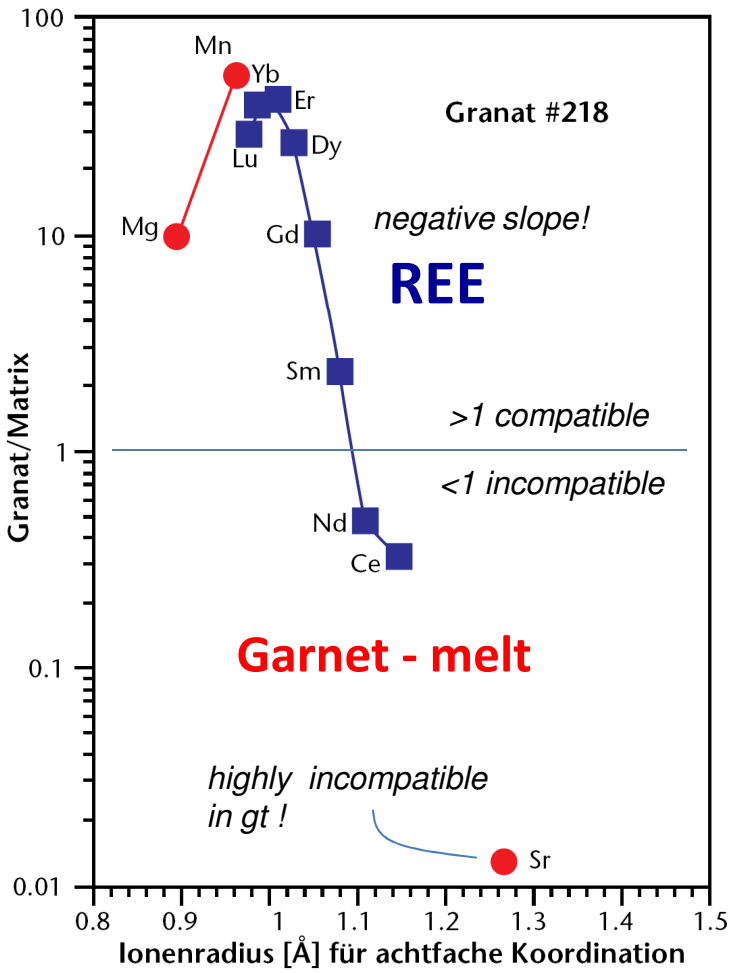
REE: La, Ce, Nd, ... Yb, Lu

Highly incompatible: Th, U, Nb, Ta

Moderately incompatible: HREE

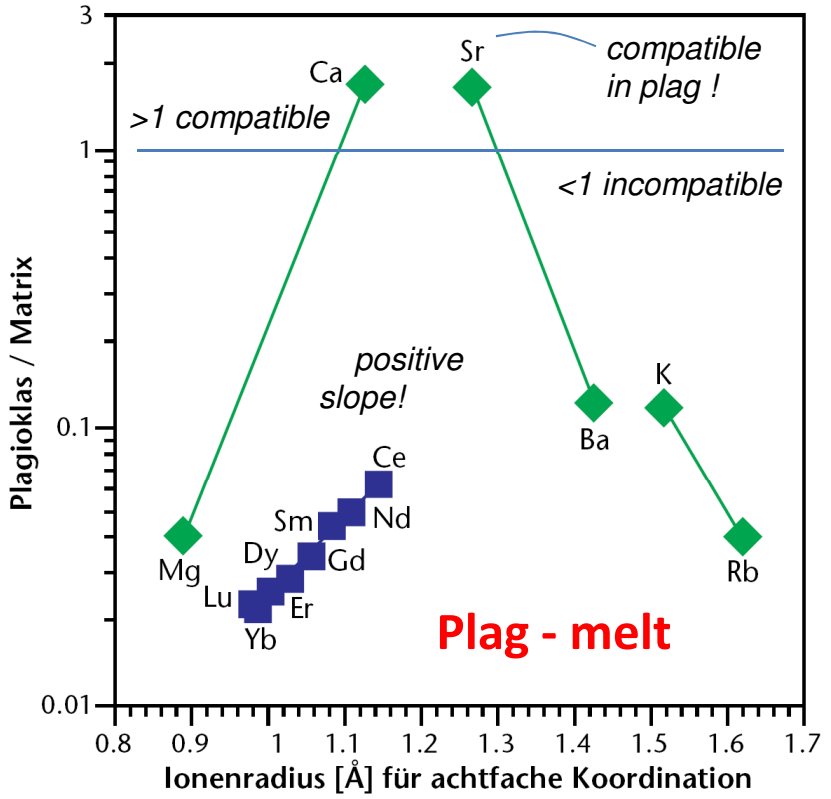
Parameters that control D:

Ionic charge and ionic radius



Onuma diagrams:

D-values vs. ionic radius for **garnet – melt** and **plagioclase – melt**

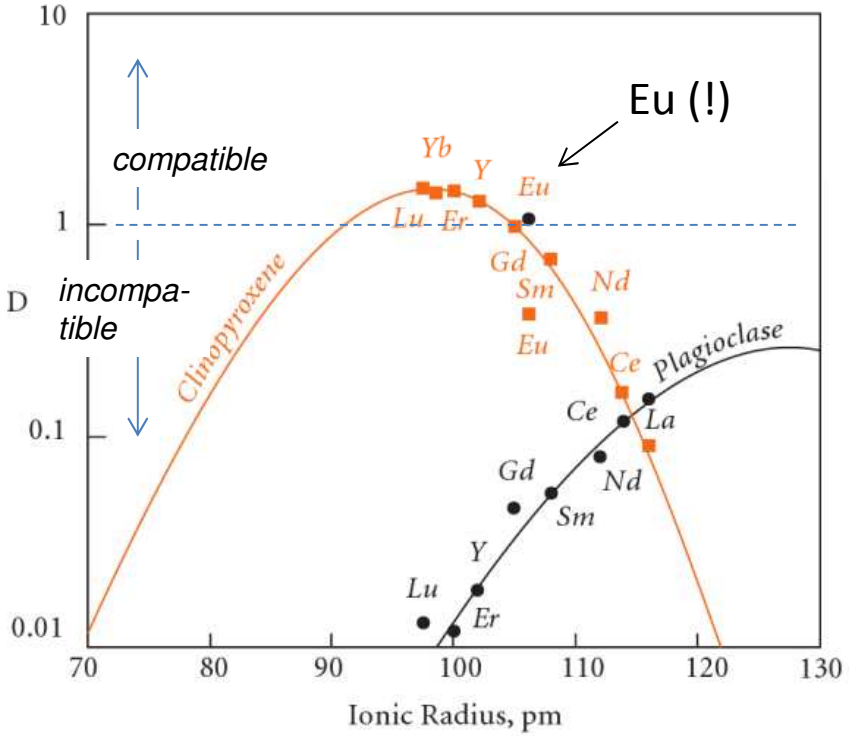


Taken from Stosch: Skripte zur Geochemie

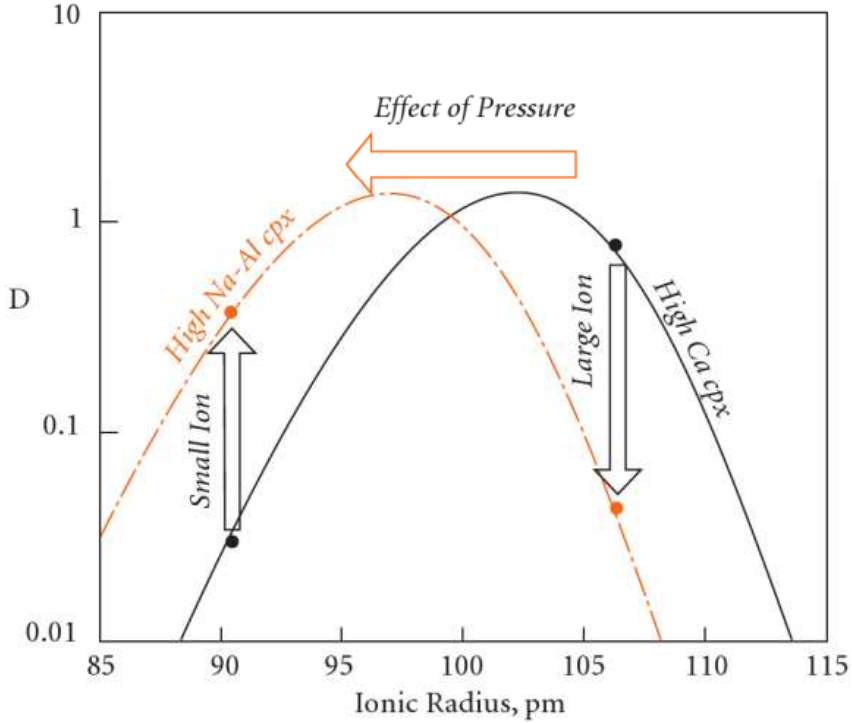
Parameters that control D:

Ionic charge and ionic radius

Onuma diagram: REE for cpx and plag



Effect of composition & pressure

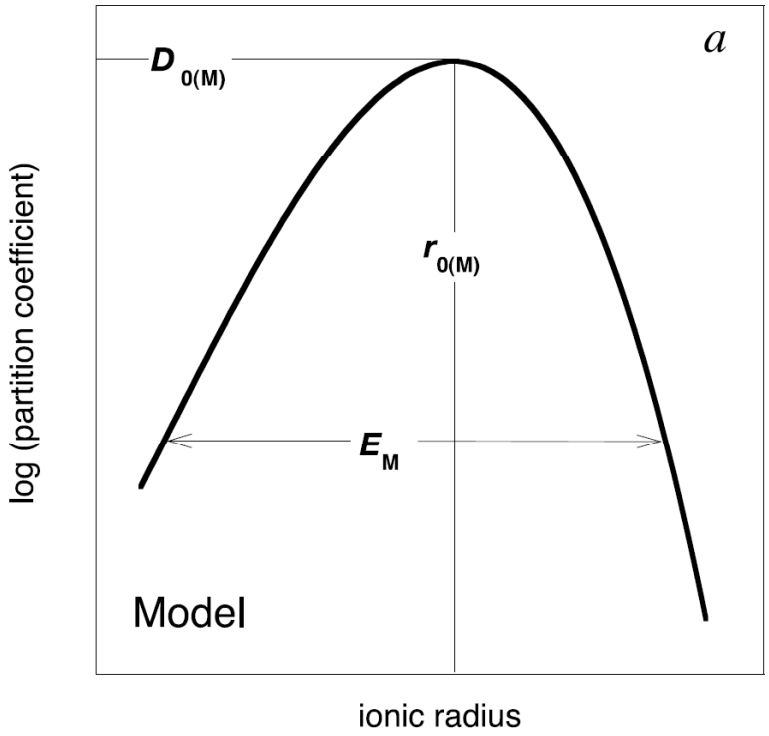


From: W.M. White, Geochemistry, Wiley - Blackwell

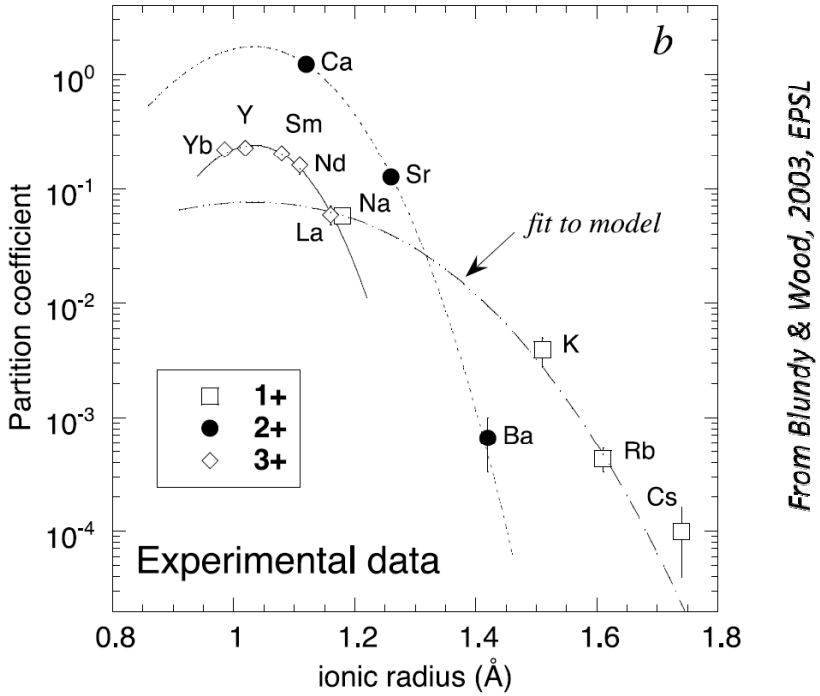
Parameters that control D:

Ionic charge and ionic radius

Lattice strain model: Describes the **D value** of an ion as a function of the radius of a crystal lattice site and the „lattice strain“ produced by this ion. The lattice strain is a function of charge and radius of the ion.



Graphical representation of the lattice strain model



Cpx – melt D-values for the **M2 site in cpx** for isovalent cations along with calculated curves

Parameters that control D:

Ionic charge and ionic radius

Lattice strain model for a series of (isovalent) ions charged n^+:

Blundy and Wood, 2003, EPSL

„elastic response“ of the lattice site of interest (Young‘s modulus)

ionic radius

radius of crystal lattice site M

„strain-compensated“ partition coefficient

$$D_i = D_{0(\mathrm{M})}^{n+} \times \exp\left\{ \frac{-4\pi \mathrm{N_A} \mathrm{E_M^{n+}} \left[\frac{1}{2} r_{0(\mathrm{M})}^{n+} \left(r_i - r_{0(\mathrm{M})}^{n+} \right)^2 + \frac{1}{3} \left(r_i - r_{0(\mathrm{M})}^{n+} \right)^3 \right]}{\mathrm{R}T} \right\}$$

Avogadro‘s number

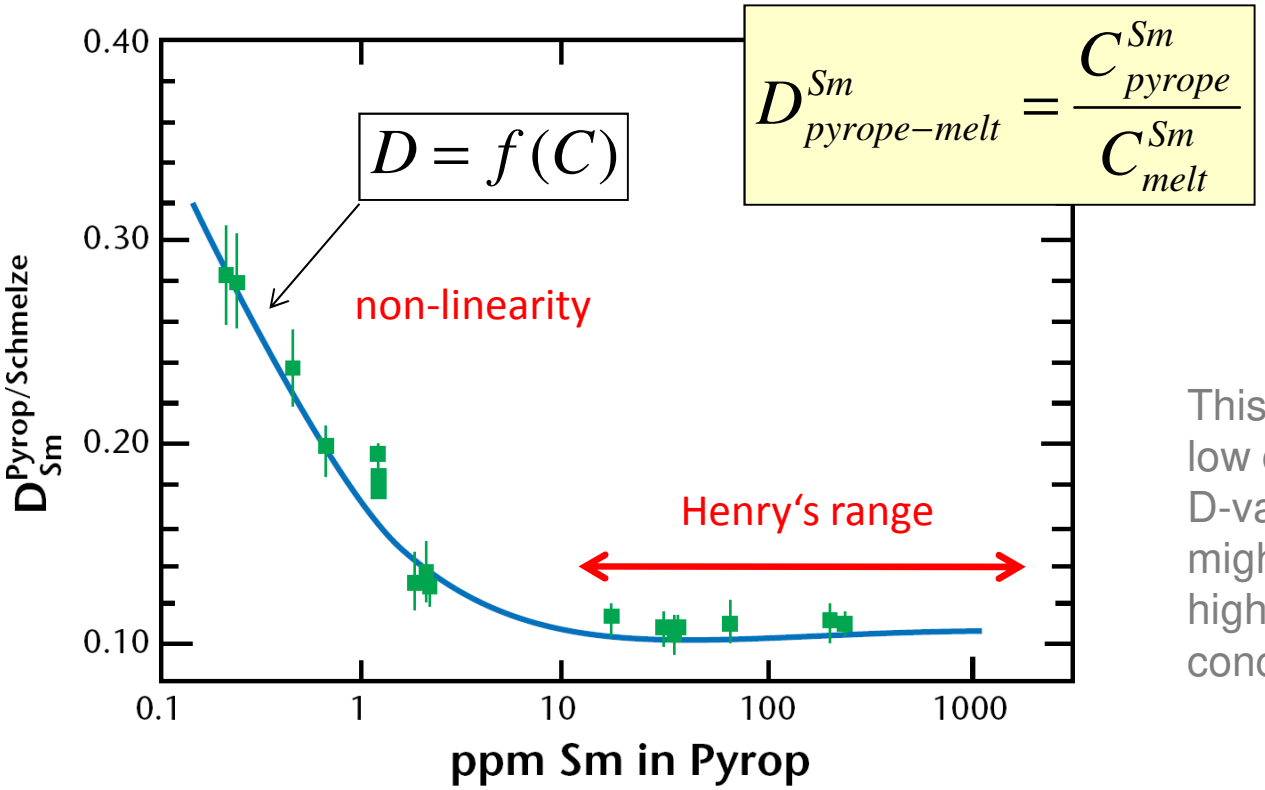
universal gas constant and absolute temperature

This approach allows to calculate D_i of an ion solely from its ionic radius, if the lattice parameters $D_{0(M)}$, E_M and $r_{0(M)}$ are known (e.g. from other elements)!!!

Parameters that control D:

Ionic charge and ionic radius

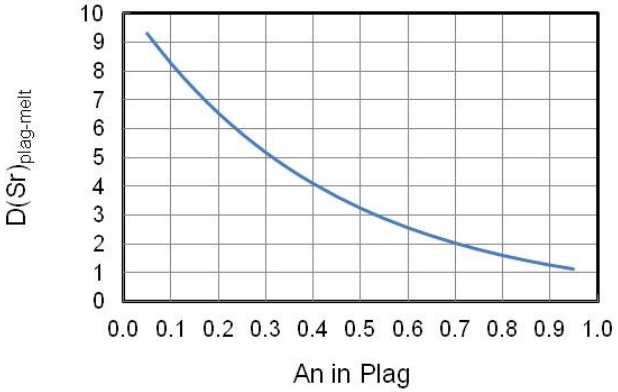
In some cases, at very low concentrations, deviations from Henry's law are observed, e.g. for the partitioning of **Sm** between **pyrope -** $(Mg_3Al_2)[SiO_4]_3$ - and (mafic) **melt**



This means that at very low concentrations the D-value of a mineral might be significantly higher than at higher concentrations

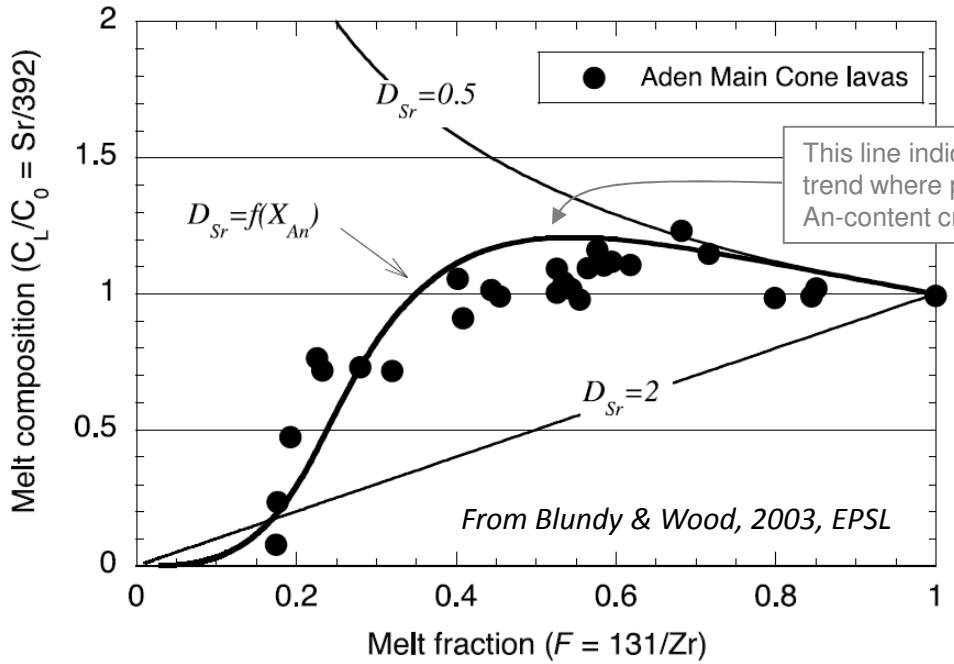
Parameters that control D:

Major element composition of minerals, e.g. partitioning of **Sr** between Plagioclase and melt is a function of the An content in Plagioclase:



$$R\,T\ln D^{Sr}_{plag\text{-}melt} = 26.8 - 26.7\,X_{An}$$

$$D^{Sr}_{plag\text{-}melt} = e^{\frac{26.8 - 26.7\times An}{0.008314\times T}}$$

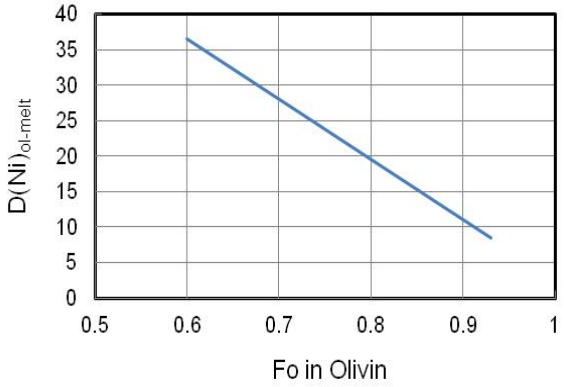


Starting composition:
392 ppm Sr and 131 ppm Zr

An = Anorthite content as molar ratio
R = universal gas constant (0.008314 kJ/mol K)
T = absolute temperature in K

Parameters that control D:

Variation of the partition coefficient of **Ni** between Olivine and basaltic melt as a function of **molar Fo** in Olivine:

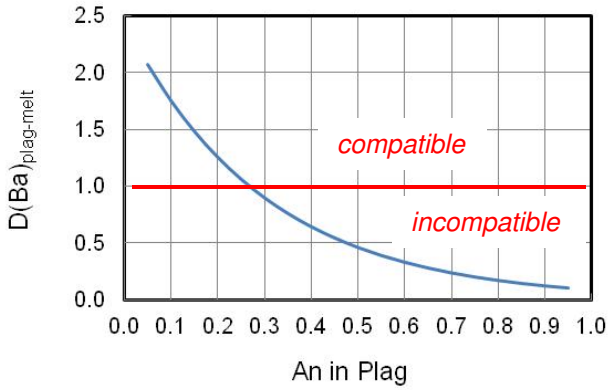


Fo in olivine > 0.65:

$$D^{Ni}_{Olivin/melt} = -0.8480769 \times (100 \times Fo) + 87.373$$

Variation of the partition coefficient of **Ba** between Plagioclase and basaltic melt as a function of **molar An** in Plagioclase:

$$D^{Ba}_{Plag/melt} = e^{\frac{10.2 - 38.2 \times An}{T \times 0.008314}}$$



Equations from Bédard 1994, Chem. Geol., 118, 143 – 153 and from Blundy and Wood 1991, Geochim. Cosmochim. Acta, 55, 193 - 209

Parameters that control D:

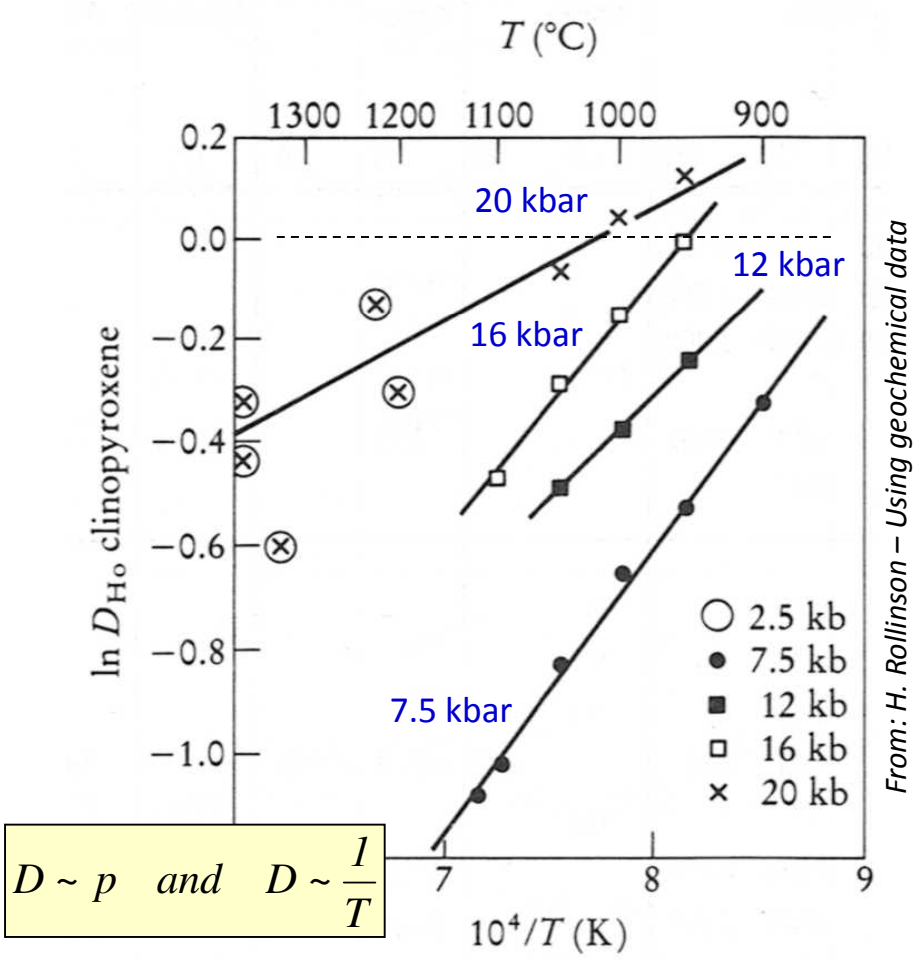
Pressure and temperature have a strong influence on partition coefficients

Combined effect of **p and T** on the partitioning of **Ho** between **cpx** and a **basaltic melt** (at 50 wt% SiO_2).

With increasing temperature, Ho is getting more incompatible in cpx at a given pressure (**D ~ 1/T**)

> kinetic energy of the atoms/ions in the lattice

With increasing pressure, Ho is getting less incompatible (or even compatible) in cpx at a given temperature (**D ~ p**), **but .....**

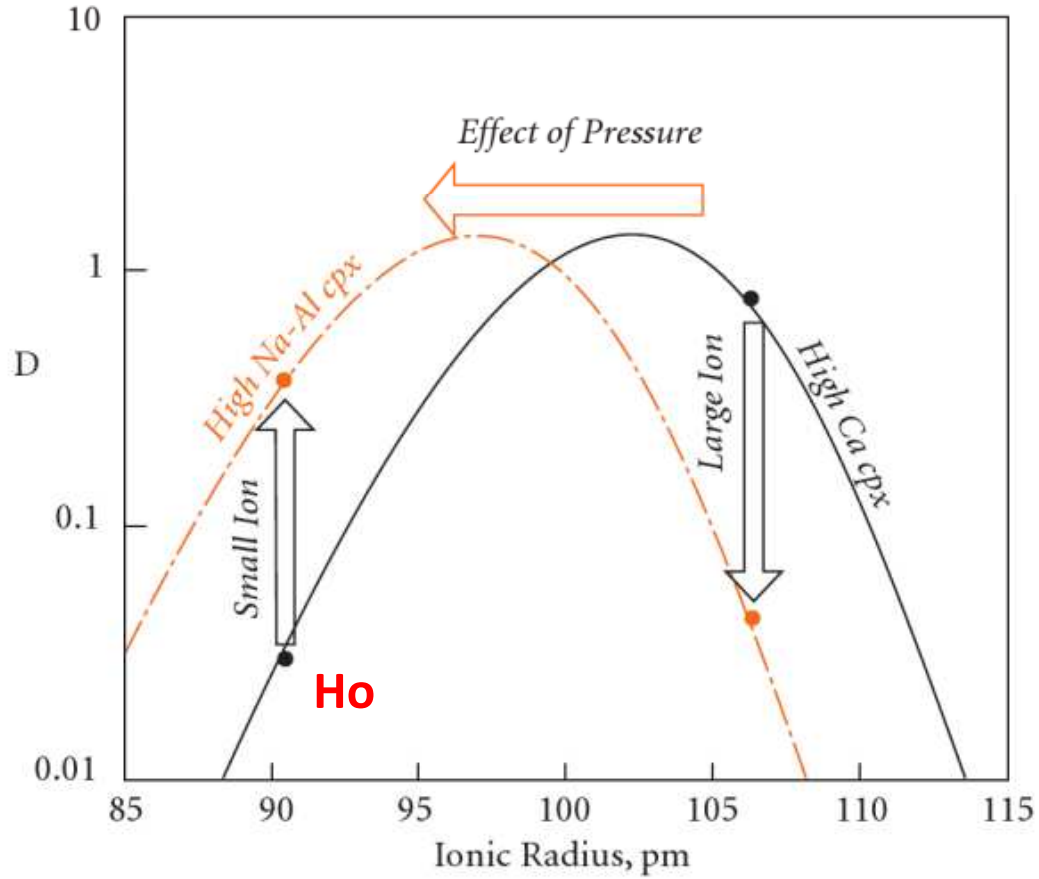


From: H. Rollinson – Using geochemical data

Parameters that control D:

..... note, that the effect of pressure depends on the position of an ion with respect to the D-value-parabola maxima *(or, with respect to the ideal lattice site radius)*!

From: W.M. White, Geochemistry, Wiley - Blackwell

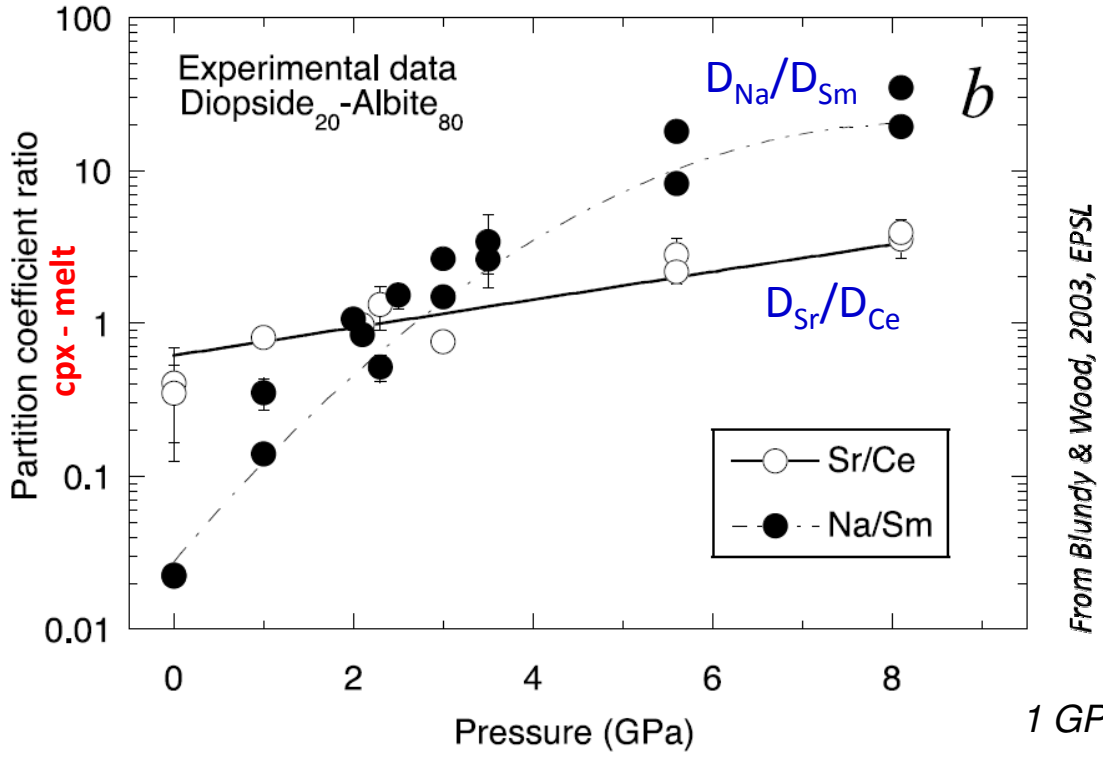


In other words, if an ion is ‚too small' with respect to a lattice position, it is becoming more compatible with pressure, if it is ‚too large', it is becoming more incompatible !!

> compressible lattice model

Parameters that control D:

Variation of **D-values** and **D-ratios** with pressure between **cpx - melt**



D_{Sr}/D_{Ce} variation of ~ 10

D_{Na}/D_{Sm} variation of ~2000

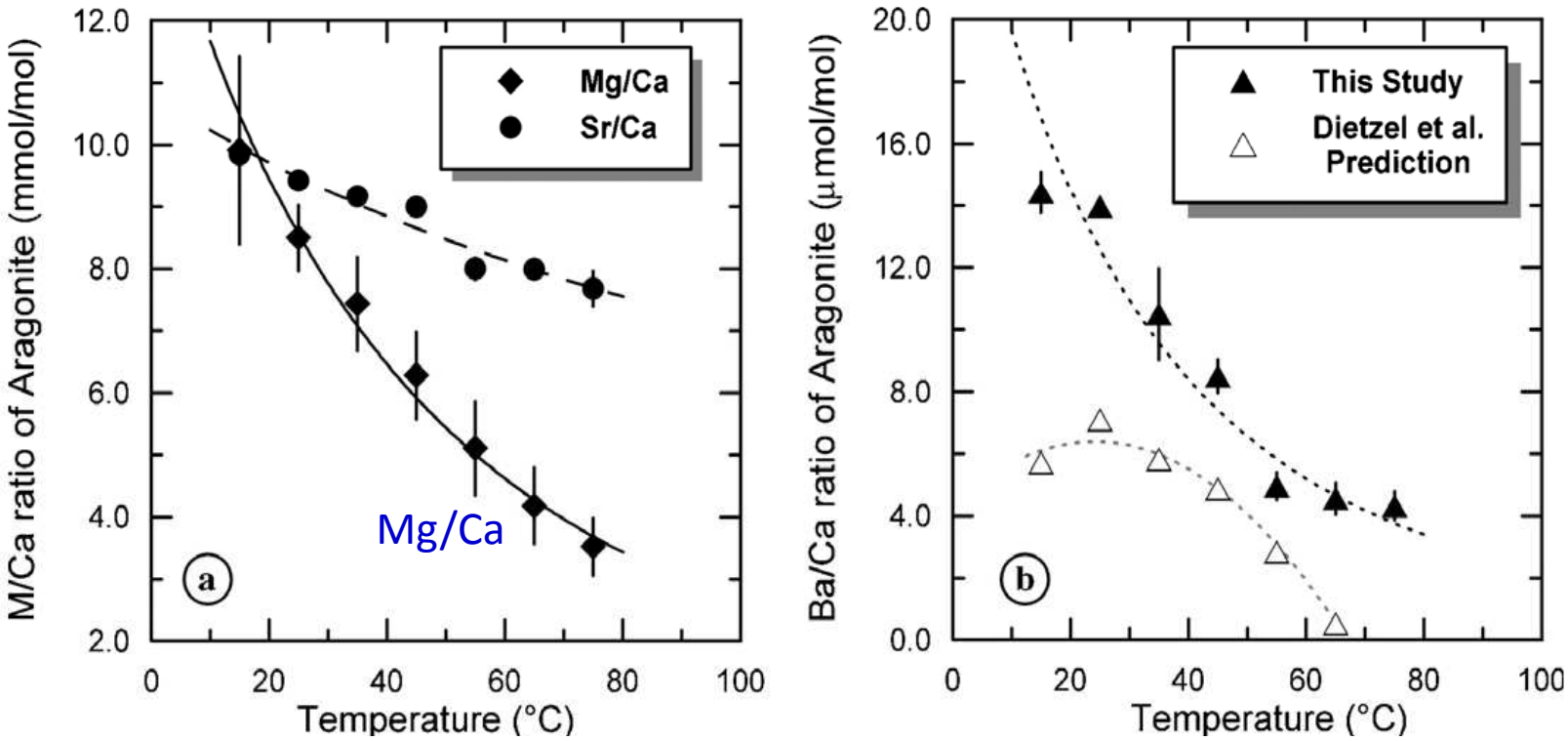
over the pressure range 0 – 9 GPa

1 GPa ~ 33 km

This effect will lead to a strong pressure dependent fractionation of specific trace element pairs (i.e., ratios)! *Think about melt inclusions in olivine!*

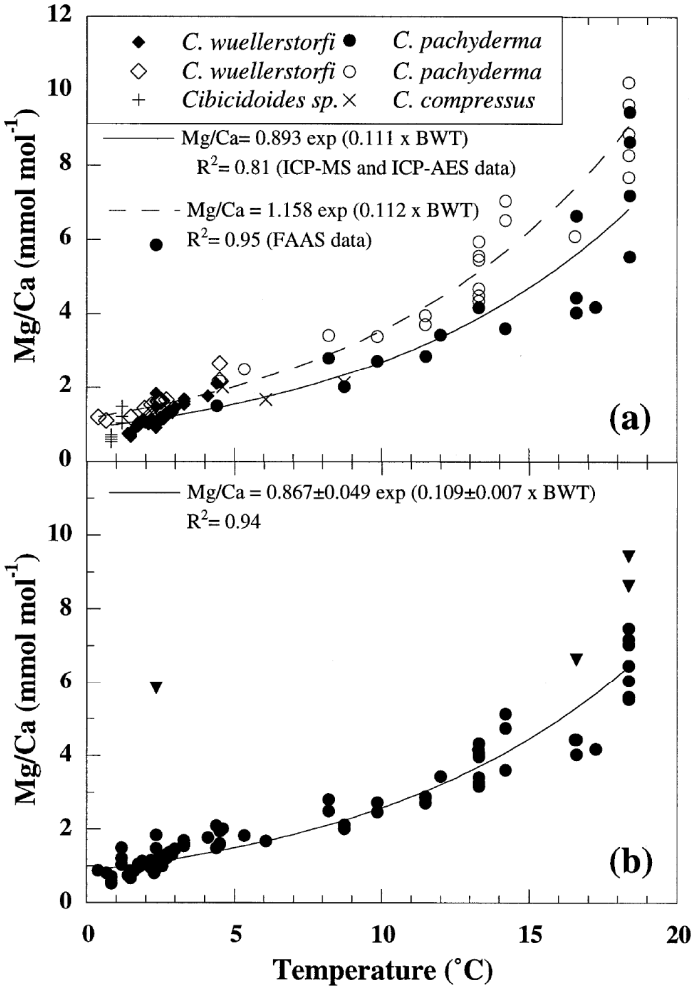
Parameters that control D:

Temperature dependent distribution of **Mg-Ca, Sr-Ca and Ba-Ca** between precipitated aragonite and sea water *(experimental constraints)*:



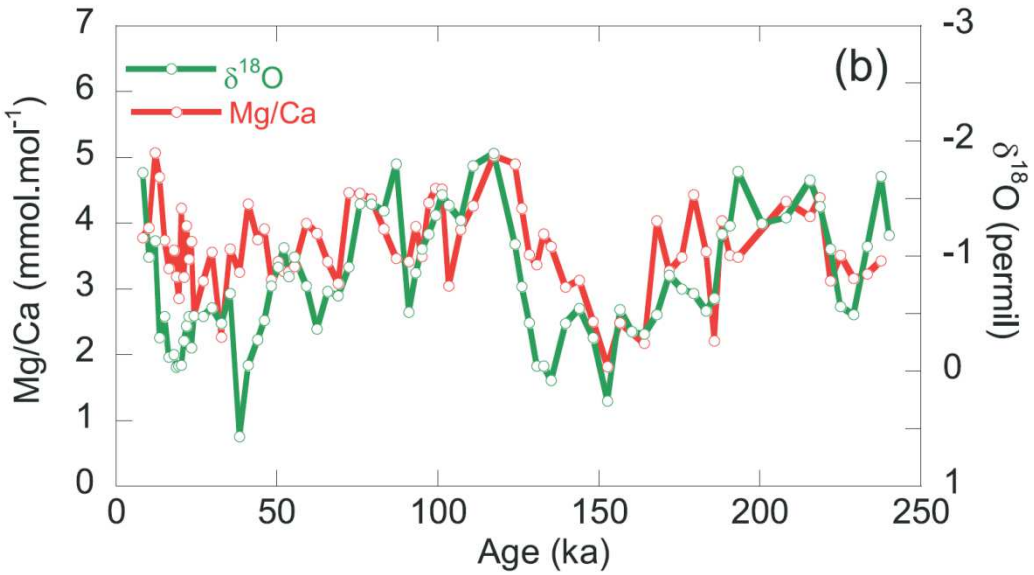
From: Gaetani & Cohen, 2006, Geochim. Cosmochim. Acta

Parameters that control D:



Left: Mg/Ca of benthic foraminifera sampled in different ocean basins as a function of bottom water temperature (from Lear et al., 2002, GCA)

Below: Downcore **Mg/Ca** and **$\delta^{18}O$** of planktic foraminifera (*Globigerinoides ruber)* recovered from a drill core of the Arabian sea (from Barker et al., 2003, Geochem. Geophys. Geosys.)

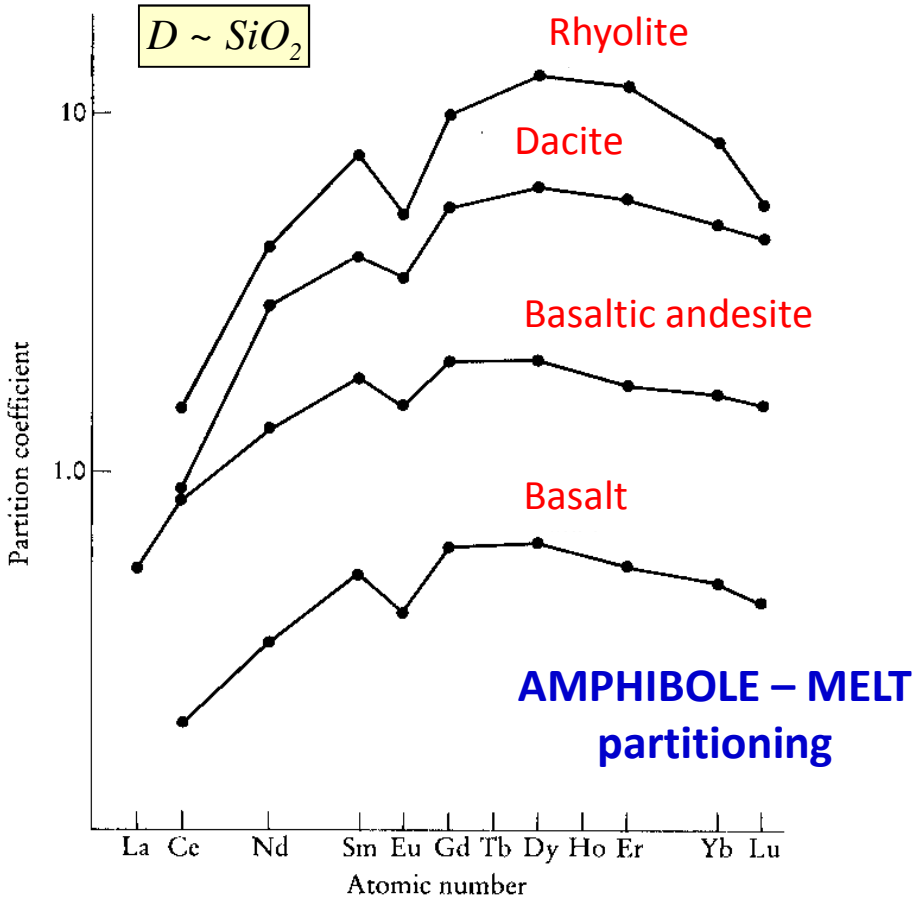


Parameters that control D:

Melt composition has a strong influence on partition coefficients

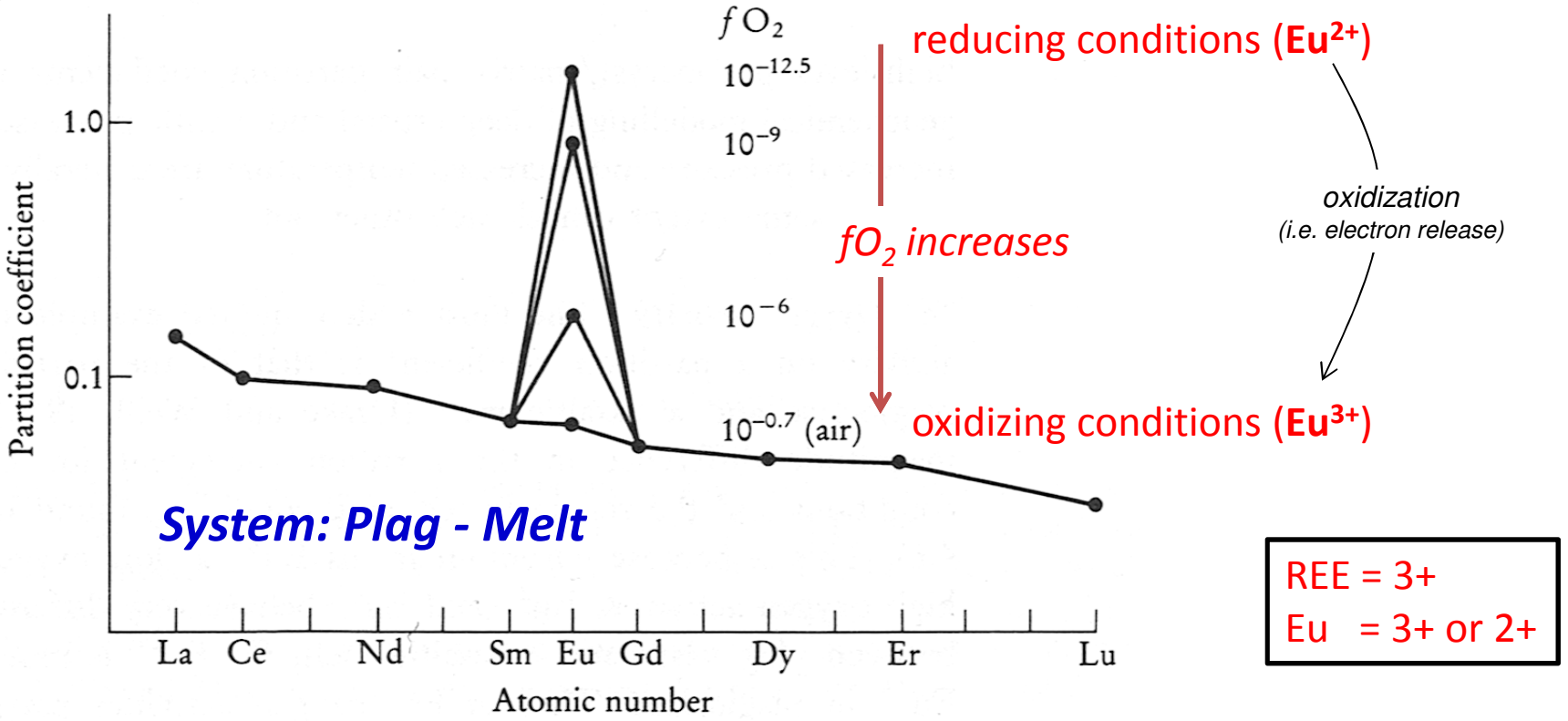
Partitioning of REE between amphibole and silicate melts

REE's are getting less incompatible and compatible, respectively, in amphibole with increasing silica content of the melt!



Parameters that control D:

Oxygen fugacity – many elements have different valence states dependent on the redox conditions in the system, e.g. Eu^{2+} and Eu^{3+}:



Parameters that control D:

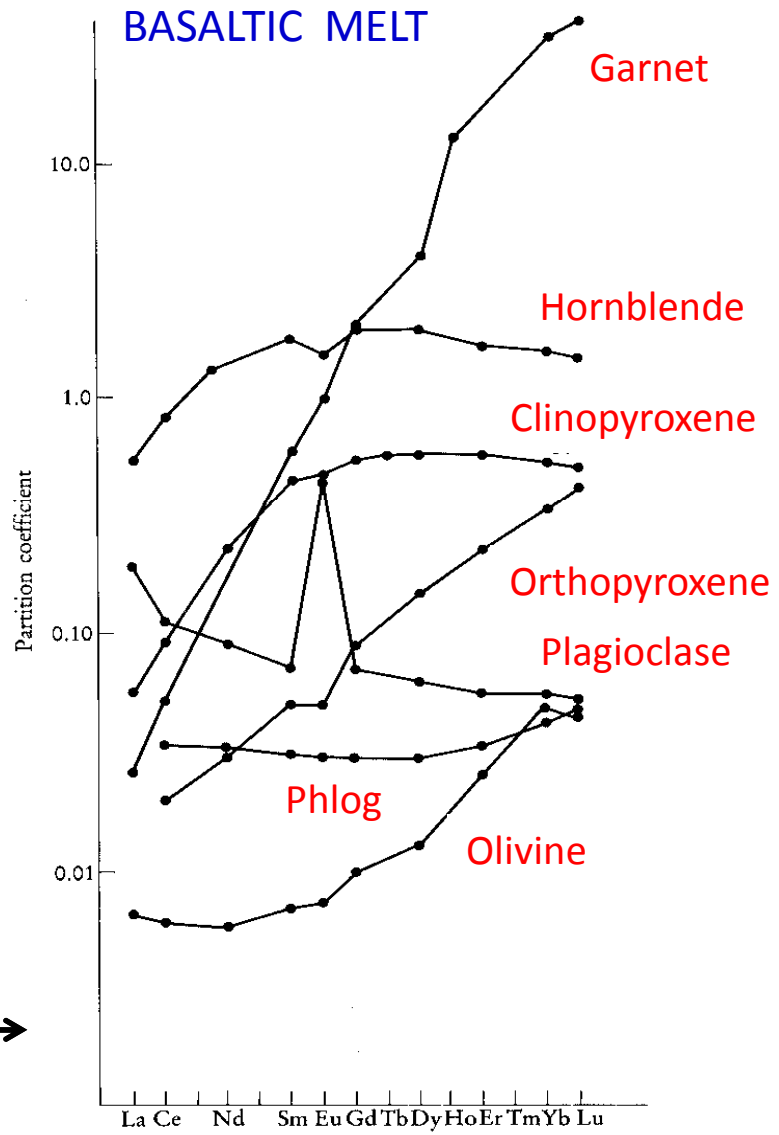
Presence of phases and their abundances in a ***multi-phase system*** (= rock) will influence the effective D-value of this system:

$$\overline{D}^i = \sum x^m D^i_m$$

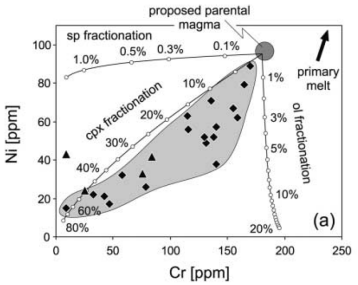
x = modal abundance of mineral m
i = element, e.g. Nd, Sm, Rb, ...
m = mineral, e.g. cpx, opx, ...

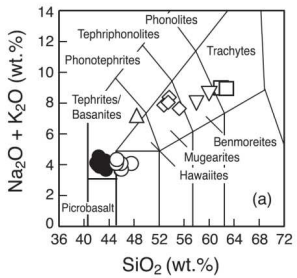
Example: D_{Ce} = 0.08 for cpx – melt and 0.03 for plag – melt. D between a gabbro having 60% cpx (0.6) and 40% plag (0.4) is therefore 0.6 x 0.08 + 0.4 x 0.03 = **0.06**

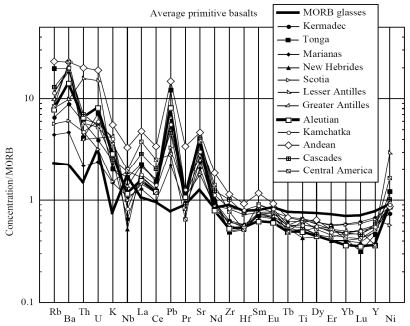
Partitioning of REE between different phases and a basaltic melt →

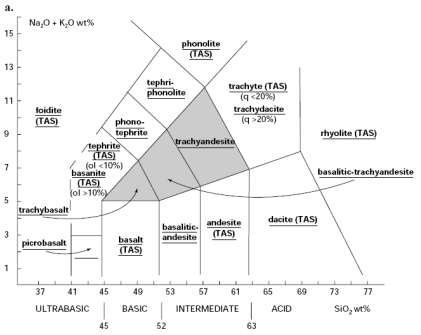


How to present the major- and trace element composition of a rock sample, or better, of a <u>series</u> of rock samples?



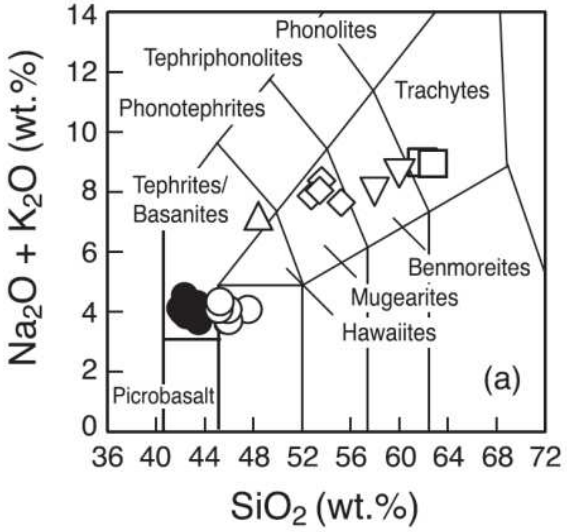




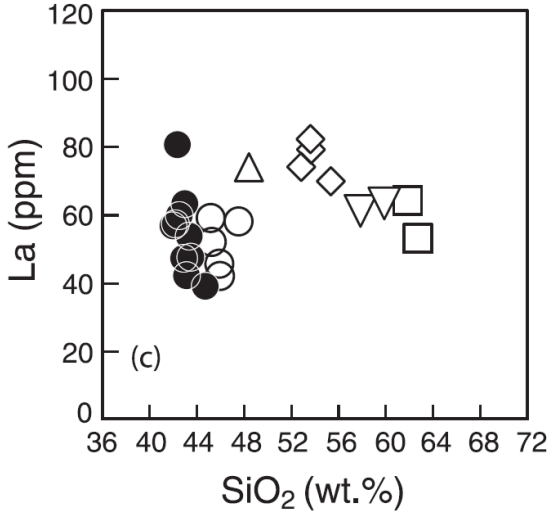


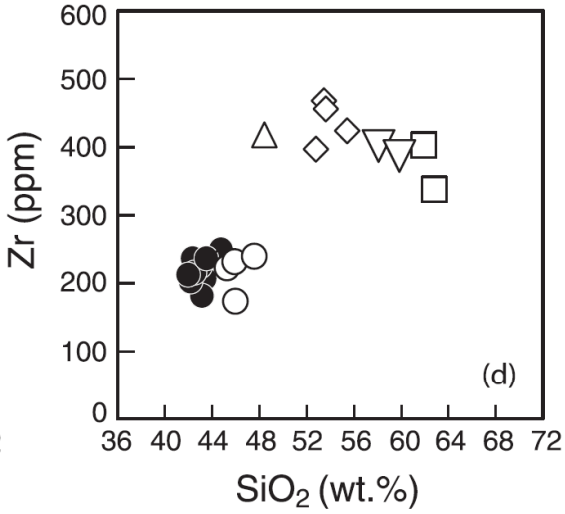
Presentation of geochemical data

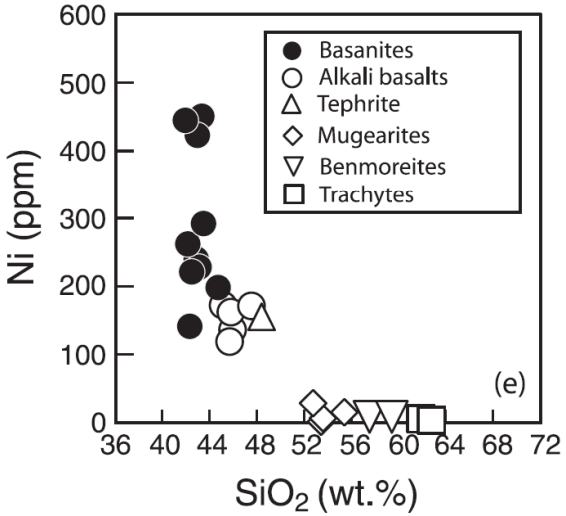
In **X – Y diagrams**, here SiO_2 content of **Siebengebirge lavas** vs. trace element concentration

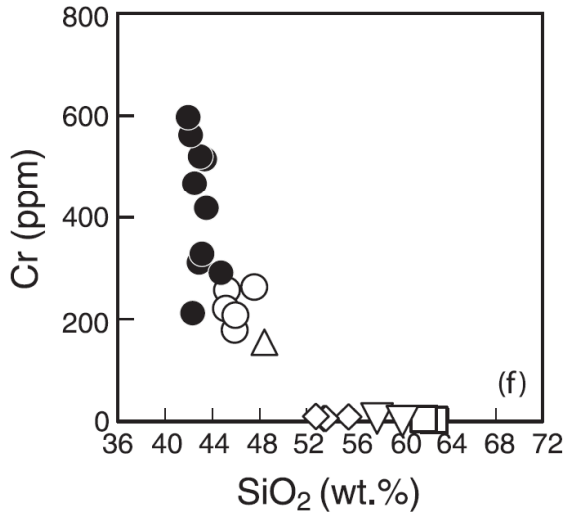


TAS diagram: **T**otal **A**lkali vs. **S**ilica





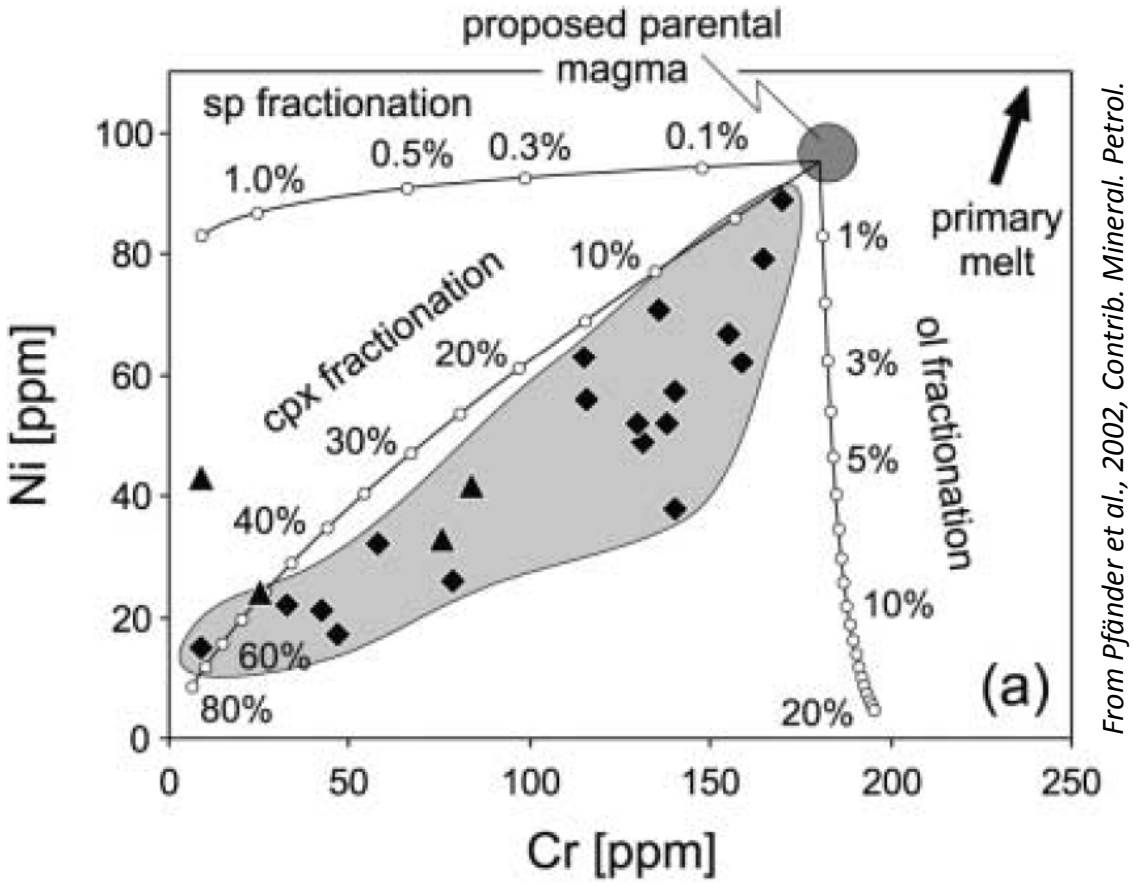




From Jung et al., 2012, J. Petrol.

Presentation of trace element data

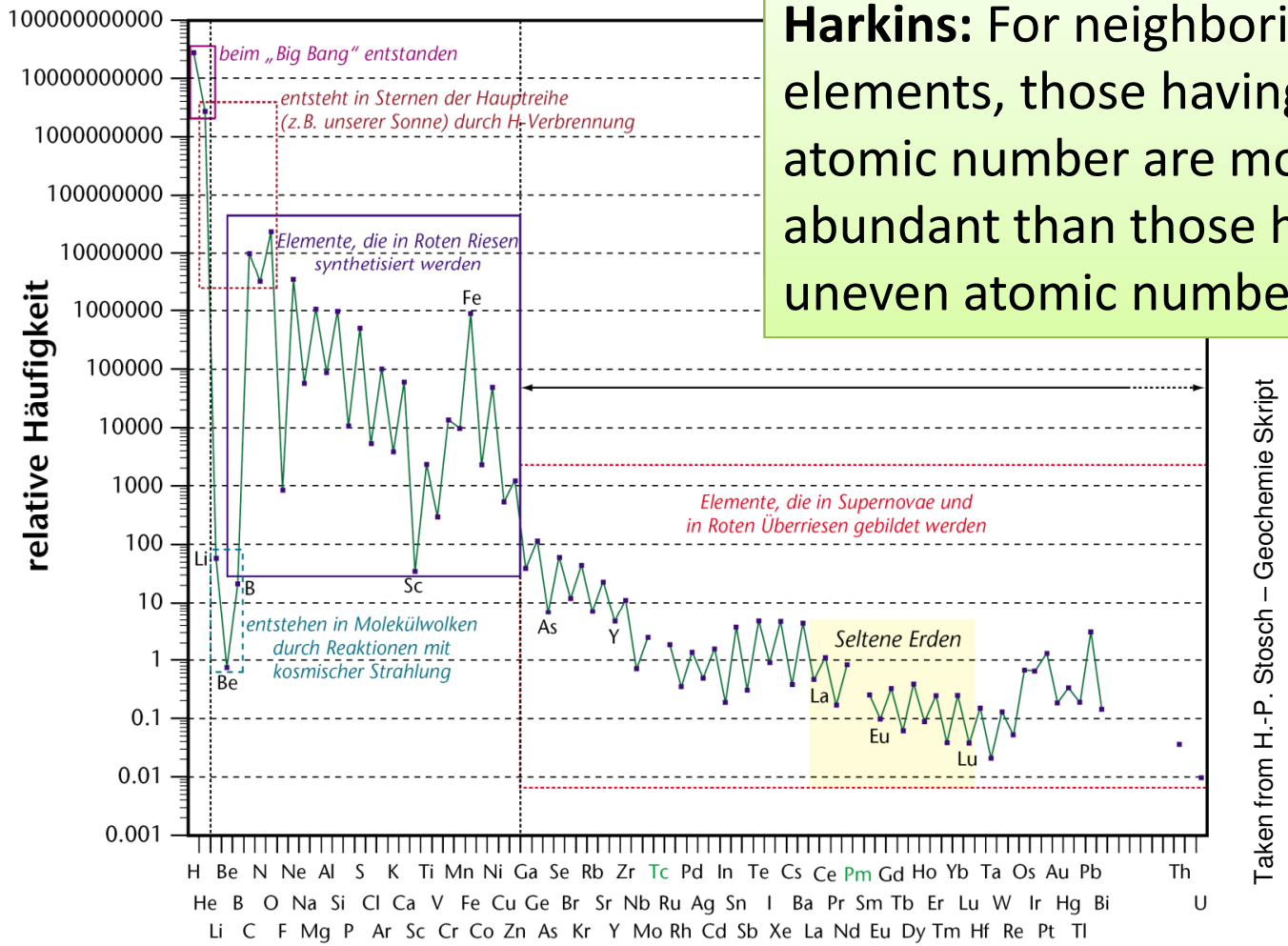
In **X – Y diagrams**, here trace element vs. trace element concentration of a series of **basaltic rocks** from Southern Siberia



From Pfänder et al., 2002, Contrib. Mineral. Petrol.

Presentation of trace element data

Abundance of the chemical elements in the **solar system**



Harkins: For neighboring elements, those having an even atomic number are more abundant than those having an uneven atomic number ...

Taken from H.-P. Stosch – Geochemie Skript

Presentation of trace elements

... therefore, trace element concentrations are usually normalized to a „***reference composition***“, e.g.:

Tschuri with Rosetta and lander Philae (source: SPIEGEL ONLINE, Nov. 2014)

Chondritic composition

(e.g., Sun & McDonough, 1989; McDonough & Sun, 1995)

*Commonly used are **carbonaceous chondrites** (particularly CI)*

PRIMA = Primitive Mantle Composition

(e.g., Sun & McDonough, 1989; McDonough & Sun, 1995, Hofmann 1988; see also references therein!)

> for refractory lithophile elements derived from the composition of CI chondrites (PRIMA ~ 2.75 x CI)

TABLE 1. *Element concentrations (ppm) in C1 chondrite, primitive mantle, N-type MORB, E-type MORB and ocean island basalts (OIB)*

Element	C1 chondrite[a]	Primitive mantle[a]	N-type MORB	E-type MORB	OIB
Cs	0.188	0.032[b]	0.0070	0.063	0.387
Tl	0.140	0.005	0.0014	0.013	0.077
Rb	2.32	0.635	0.56	5.04	31.0
Ba	2.41	6.989	6.30	57	350
W	0.095	0.020	0.010	0.092	0.560
Th	0.029	0.085	0.120	0.60	4.00
U	0.008	0.021	0.047	0.18	1.02
Nb	0.246	0.713	2.33	8.30	48.0
Ta	0.014	0.041	0.132	0.47	2.70
K	545	250	600	2100	12000
La	0.237	0.687	2.50	6.30	37.0
Ce	0.612	1.775	7.50	15.0	80.0
Pb	2.47	0.185[b]	0.30	0.60	3.20
Pr	0.095	0.276	1.32	2.05	9.70
Mo	0.92	0.063	0.31	0.47	2.40
Sr	7.26	21.1	90	155	660
P	1220	95	510	620	2700
Nd	0.467	1.354	7.30	9.00	38.5
F	60.7	26	210	250	1150
Sm	0.153	0.444	2.63	2.60	10.0
Zr	3.87	11.2	74	73	280
Hf	0.1066	0.309	2.05	2.03	7.80
Eu	0.058	0.168	1.02	0.91	3.00
Sn	1.72	0.170	1.1	0.8	2.7
Sb	0.16	0.005	0.01	0.01	0.03
Ti	445	1300	7600	6000	17200
Gd	0.2055	0.596	3.680	2.970	7.620
Tb	0.0374	0.108	0.670	0.530	1.050
Dy	0.2540	0.737	4.550	3.550	5.600
Li	1.57	1.60	4.3	3.5	5.6
Y	1.57	4.55	28	22	29
Ho	0.0566	0.164	1.01	0.790	1.06
Er	0.1655	0.480	2.97	2.31	2.62
Tm	0.0255	0.074	0.456	0.356	0.350
Yb	0.170	0.493	3.05	2.37	2.16
Lu	0.0254	0.074	0.455	0.354	0.300

[a] The compositions of C1 chondrite and primitive mantle are from McDonough & Sun (in prep.) Values for N-type and E-type MORB and OIB are based on a literature survey and internal consistency of elemental ratios.
[b] For mantle-normalized diagrams, the recommended normalizing values for lead and caesium are 0.071 and 0.0079, respectively.

Table 1 from Sun & McDonough (1989)
(see also McDonough & Sun, 1995)

Table 1 from Hofmann (1988)

TABLE 1
Major and trace element abundances in the Earth's primitive mantle, the continental crust and MORB

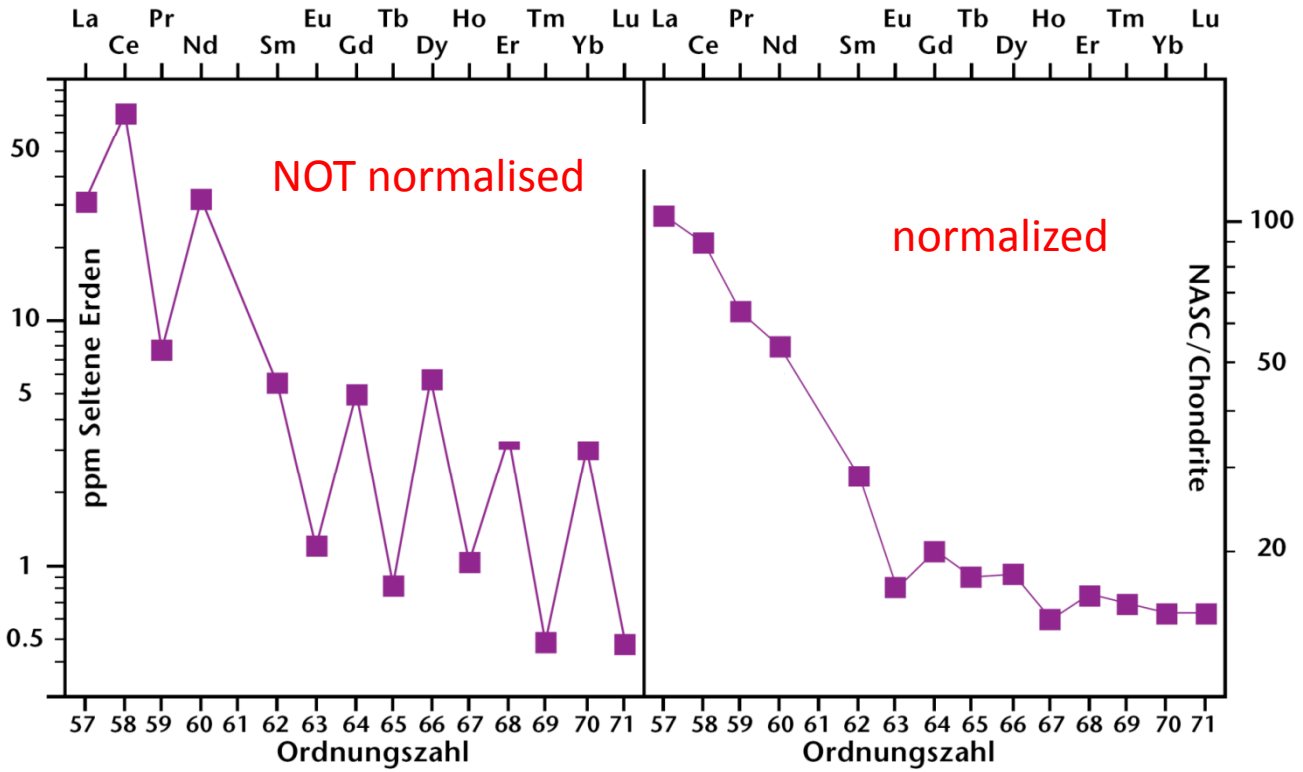
Element	Primitive mantle	MORB			Estimated bulk continental crust		
		N-MORB avg. (n)	N-MORB normalized	percent std. dev.	TM1	TM1 normalized	TM2 normalized
SiO_2 (%)	45.96	50.45	1.098	1.8	57.3	1.247	1.262
Al_2O_3	4.06	15.255	3.757	8.0	15.9	3.916	4.433
FeO	7.54	10.426	1.383	14.8	9.1	1.207	0.995
MgO	37.78	7.576	0.201	12.2	5.3	0.140	0.093
CaO	3.21	11.303	3.521	7.2	7.4	2.305	2.336
Na_2O	0.332	2.679	8.070	13.3	3.1	9.337	10.542
Na_2O (MgO = 8.0%)	0.332	2.526	7.608	15.2			
TiO_2	0.181	1.615	8.925	34.0	0.901	4.978	4.420
La (ppm)	0.6139	3.895	6.345	41.4	16	26.06	30.95
Ce	1.6011	12.001	7.496	40.1	33	20.61	23.73
Pr	0.2419	2.074	8.574	39.0	3.9	16.12	17.78
Nd	1.1892	11.179	9.401	37.8	16	13.45	13.45
Sm	0.3865	3.752	9.708	37.0	3.5	9.06	9.57
Eu	0.1456	1.335	9.167	30.1	1.1	7.56	7.56
Gd	0.5128	5.077	9.901	36.5	3.3	6.44	7.02
Tb	0.0940	0.885	9.412	38.1	0.60	6.38	6.81
Dy	0.6378	6.304	9.884	34.5	3.7	5.81	5.80
Ho	0.1423	1.342	9.433	36.6	0.78	5.48	5.76
Er	0.4167	4.143	9.944	34.3	2.2	5.28	5.52
Tm	0.0643	0.621	9.663	34.7	0.32	4.98	4.98
Yb	0.4144	3.900	9.411	33.8	2.2	5.31	5.31
Lu	0.0637	0.589	9.246	33.8	0.30	4.71	4.71
K	258.2	883.7	3.422	46.0	9100	35.24	48.41
Rb	0.5353	1.262	2.357	76.2	32	59.78	78.46
Cs	(0.0268)	0.01408	(0.53)	71.9	1.0	(37.3)	(63.43)
Sr	18.21	113.2	6.216	24.1	260	14.28	21.97
Ba	6.049	13.87	2.293	71.9	250	41.33	57.86
Hf	0.2676	2.974	11.116	42.7	3.0	11.21	11.21
Zr	9.714	104.24	10.705	40.0	100	10.29	10.29
Ta	0.0351	0.192	5.467	55.0	(1.0)	(28.49)	–
Nb	0.6175	3.507	5.679	55.1	11.0	17.82	17.82
U	0.0203	0.0711	3.496	52.3	0.91	44.76	61.49
Th	0.0813	0.1871	2.300	69.3	3.5	43.04	59.03
Pb	0.175	0.489	2.794	30.7	8.0	45.71	57.14
Y	3.940	35.82	9.091	31.2	20.0	5.08	5.58
Sc	14.88	41.37	2.784	9.8	30.0	2.02	2.02
Co	104	47.07	0.453	7.9	29.0	0.279	0.24
Ni	2080	149.5	0.072		105	0.050	0.014
Cu	28.0	74.4	2.657	29.1	75	2.679	2.14
Sn	0.150	1.382	9.213	32.4	2.5	16.67	–

The data for the primitive mantle and N-MORB average are taken from Jochum et al. [4]. The N-MORB average represents 26 fresh MORB glasses, defined as N-type MORB by their light-REE depletion [5]. The values for the primitive mantle are taken from Hart and Zindler [6] for the major elements, and their factor of 2.51 is used to obtain the mantle values of the refractory trace elements from the abundances in C1 charbonacous chondrites. The sources of the C1 chondrite data are: REE [7], Ba, Sr, Hf [8], Zr, Ta, Nb, Y, Sc [9], U [10]. Other elements were obtained as follows: Th = 4·U; Cu, Ni, Co [11], K = 12,700·U [12], Rb = Ba/12.3 [13], Cs = Rb/20 [14], Sn [15], and Pb from $\mu = 8.88$ [1]. Most of these values are believed to be correct within about 10%, except for Cs, for which different estimates differ by a factor of 4 [13,14,16].
The data sources for the two continental crust averages are: TM1 [17, table 3.5, p. 67]; TM2 [17, table 3.3, p. 62] (this is the so-called andesite model).
All normalized values are derived by division of the concentration through the primitive mantle value.

Presentation of trace element data

Example I: REE abundances in „North Atlantic shale“ plotted against atomic number (corresponding to the order of “decreasing incompatibility”):

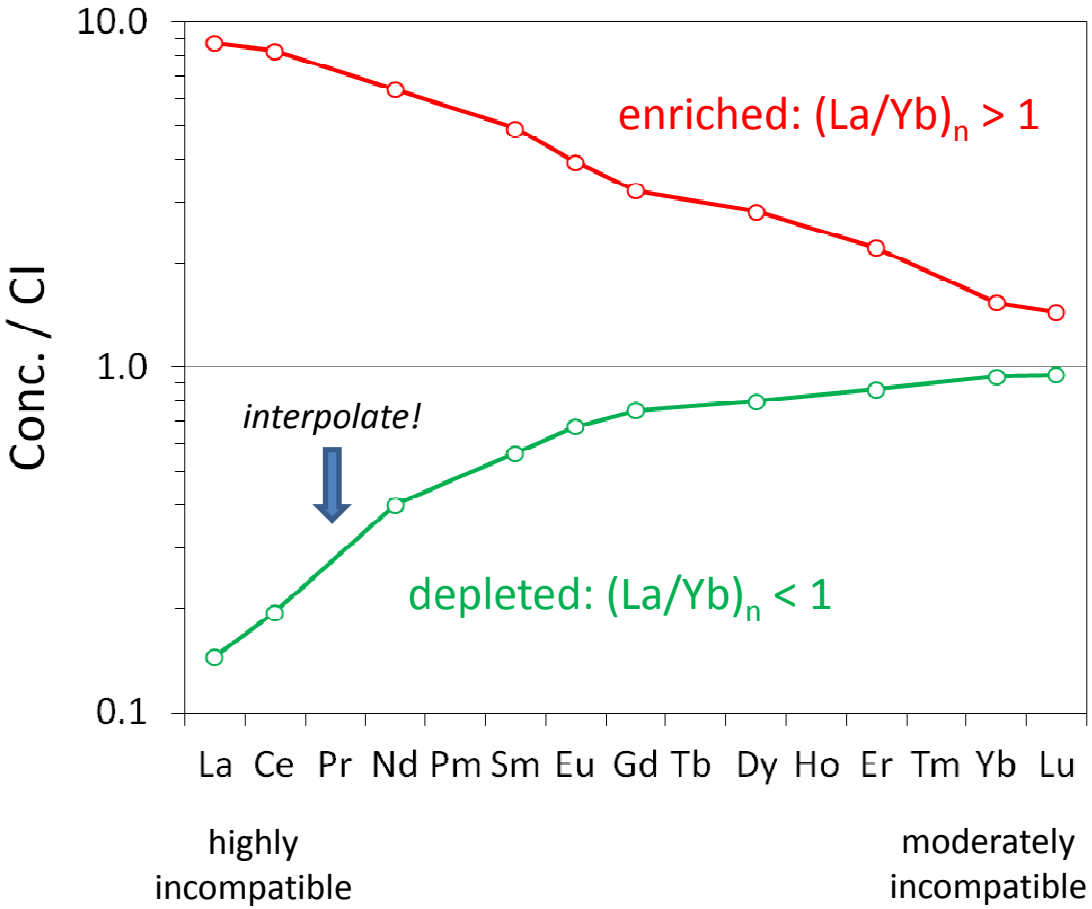
$$c^{i}_{norm.} = \frac{c^{i}_{sample}}{c^{i}_{CI}}$$



Taken from H.-P. Stosch – Geochemie Skript

Presentation of trace element data

Example II: A „typical" REE Diagram



Features:

REE's are given in an order according to increasing ordering numbers (that is decreasing ionic radius)

Concentration values are **normalised** !

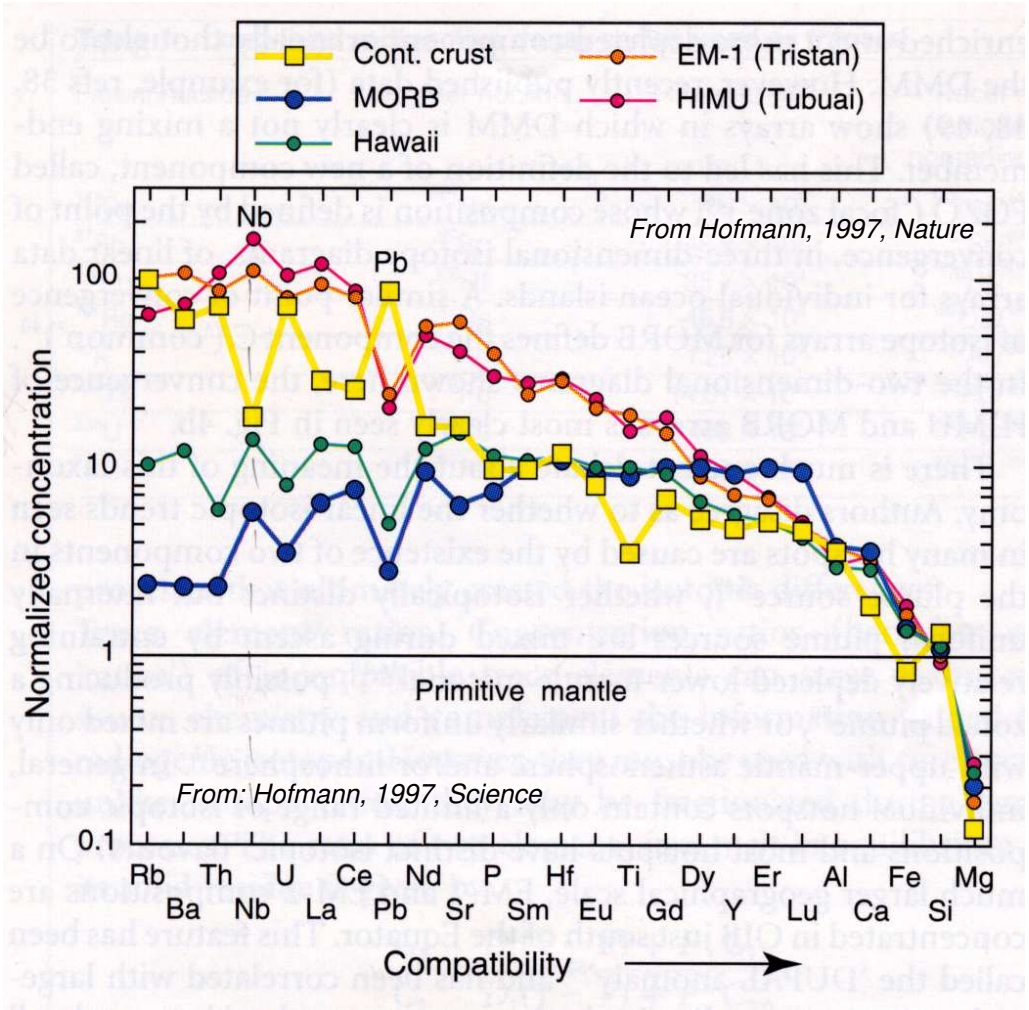
Concentration axis is **logarithmic** !

Missing values are **interpolated** !

$$c^{i}_{norm.} = \frac{c^{i}_{sample}}{c^{i}_{CI}}$$

Presentation of trace element data

Example III: Trace element abundances in major Earth "reservoirs"



This type of diagram, called **„multi-element concentration diagram"**, displays the trace elements on the X-axis in the order of **„decreasing incompatibility"** (from left to right).

Normalised trace element **concentrations** are given on the Y-axis in a **logarithmic** scale.

$$c^{i}_{norm.} = \frac{c^{i}_{sample}}{c^{i}_{PRIMA}}$$

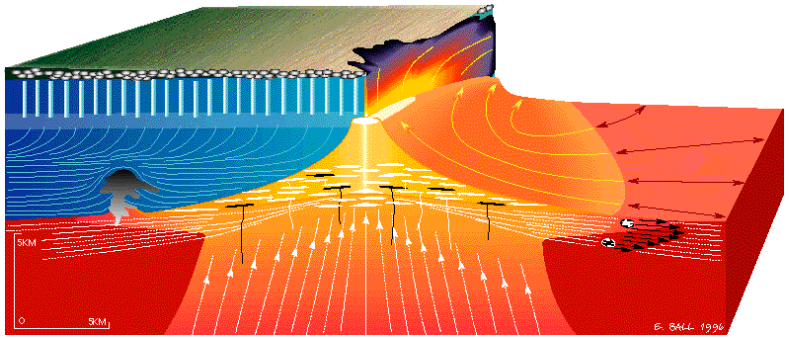
Presentation of trace element data

Brief excursion on the composition of the **bulk-Earth (BE)** and the **bulk-silicate Earth (BSE)**:

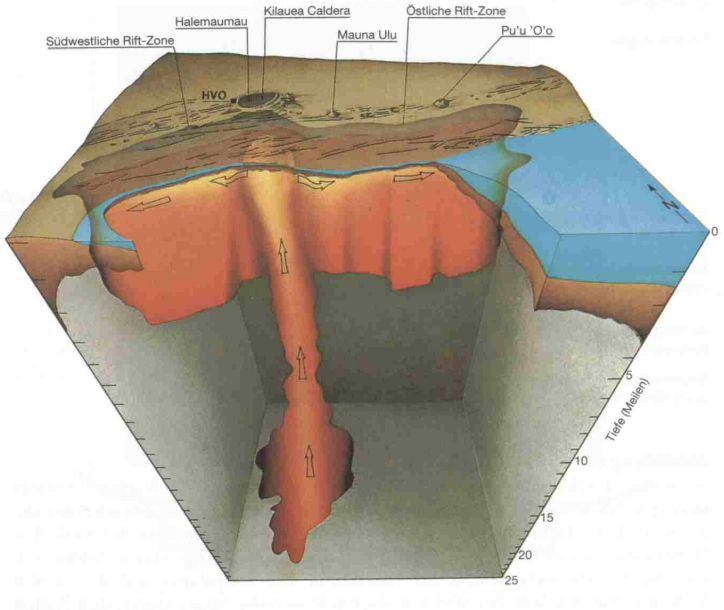
➡ **see „Supplementary Information“**

Chapter 2

PARTIAL MELTING



Melting beneath a mid-ocean ridge (from A. Nicolas, Montpellier)



Melting in a mantle plume (Hawaii)

Classification of ultramafic rocks

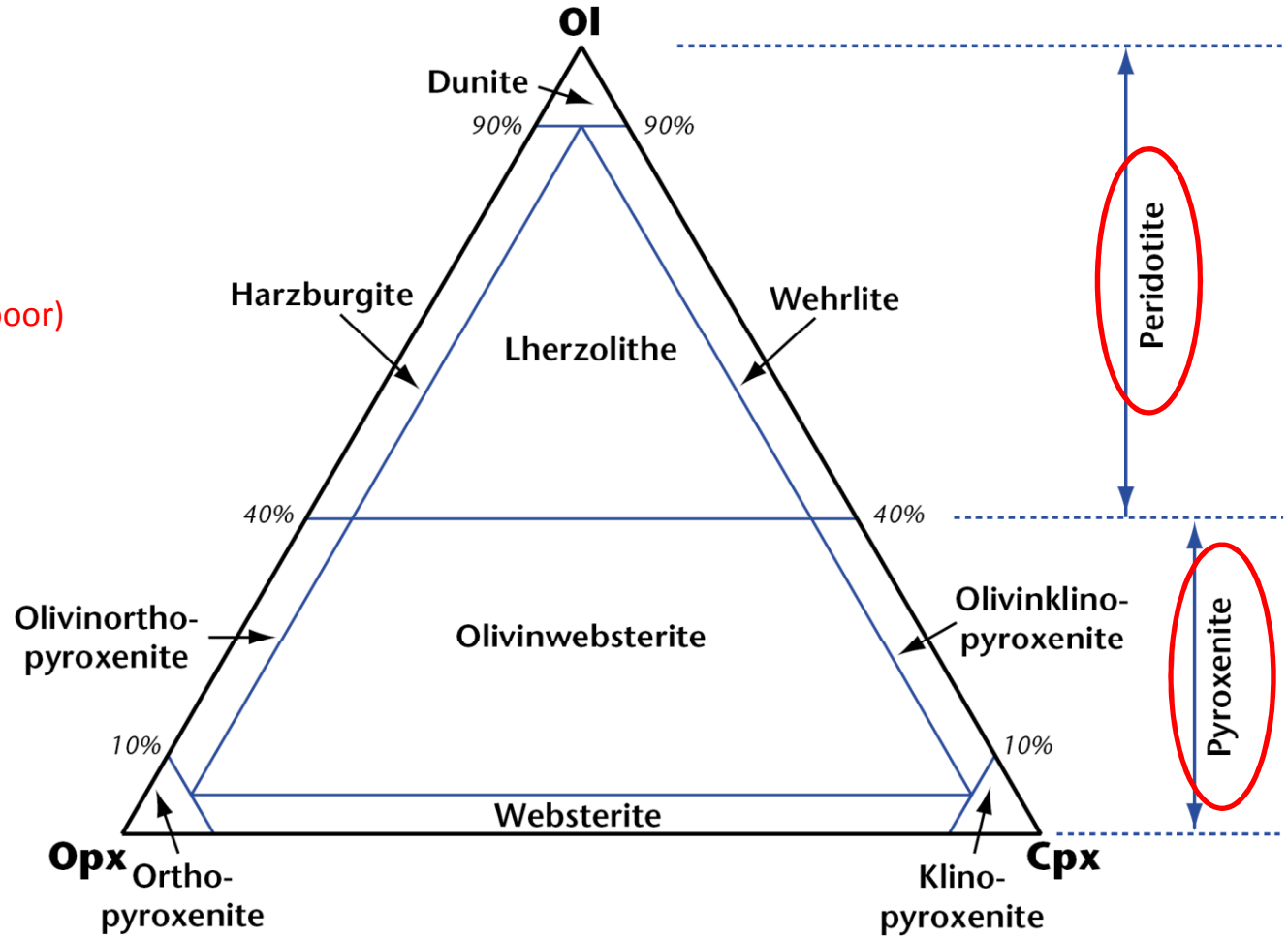
Terms used:

Mineralogy:

- fertile (Cpx rich)
- refractory (Cpx poor)

Chemistry:

- enriched
- depleted



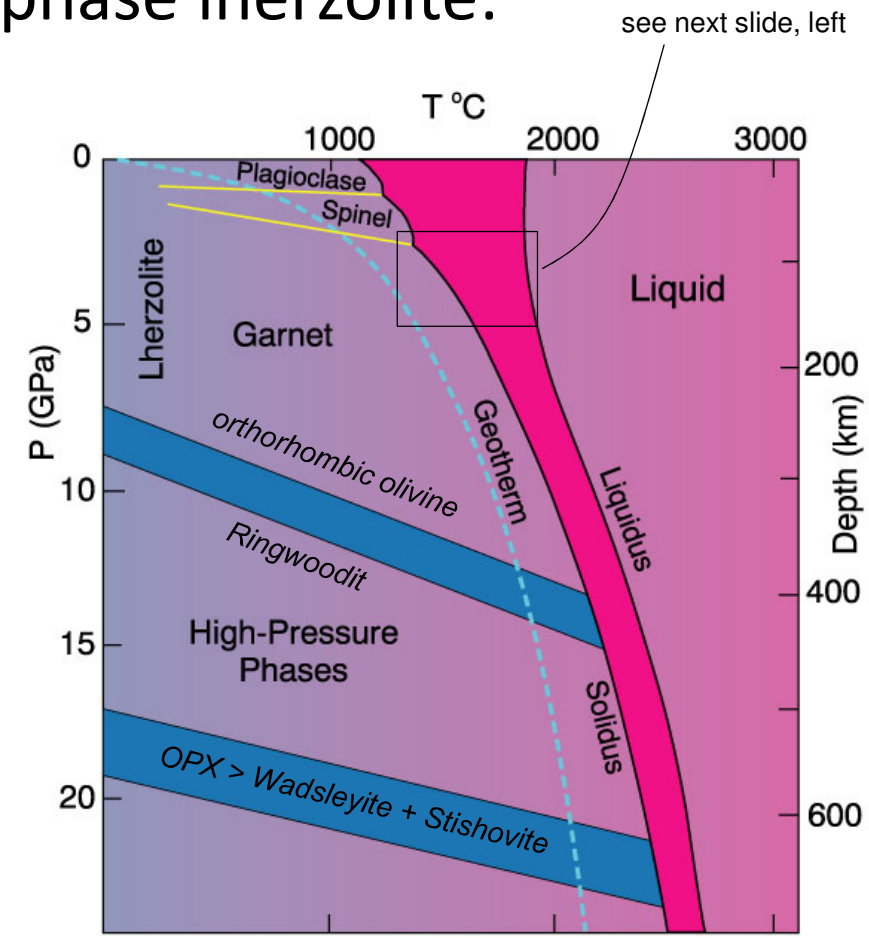
Ultramafic rocks might be fertile or refractory mantle rocks (‚peridotites'), or ultramafic cumulates (‚wehrlites & pyroxenites')

What will be molten (in the mantle)?

P-T diagram for aluminous 4-phase lherzolite:

Al-phases are:

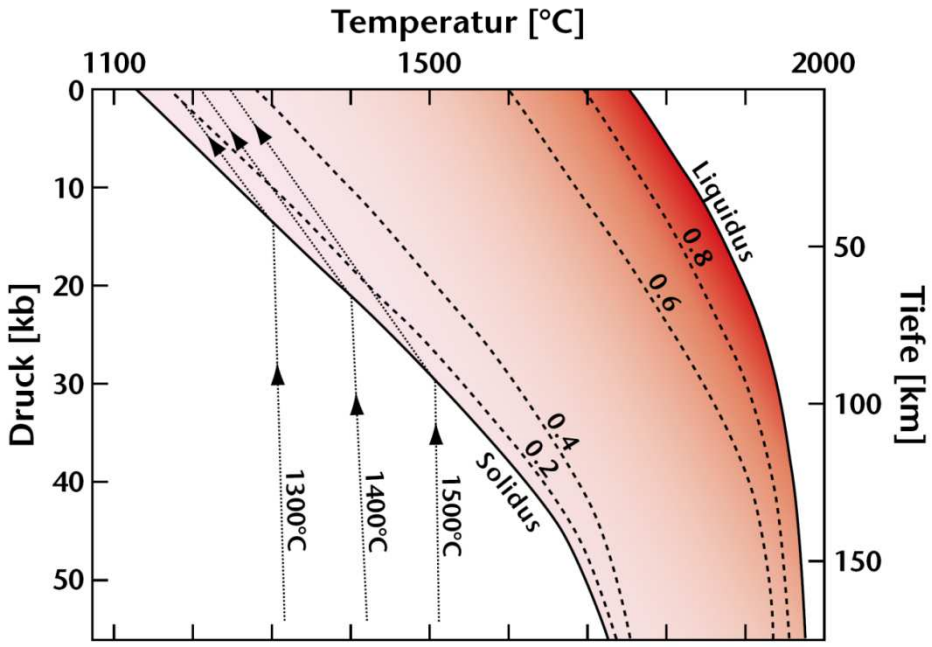
- **Plagioclase** $(Na_2,Ca)Al_2Si_2O_8$
  - ☞ shallow (<50 km)
- **Spinel** $(Mg,Fe)Al_2O_4$
  - ☞ 50-80 km
- **Garnet** $(Mg,Fe)_3Al_2(SiO_4)_3$
  - ☞ 80-400 km

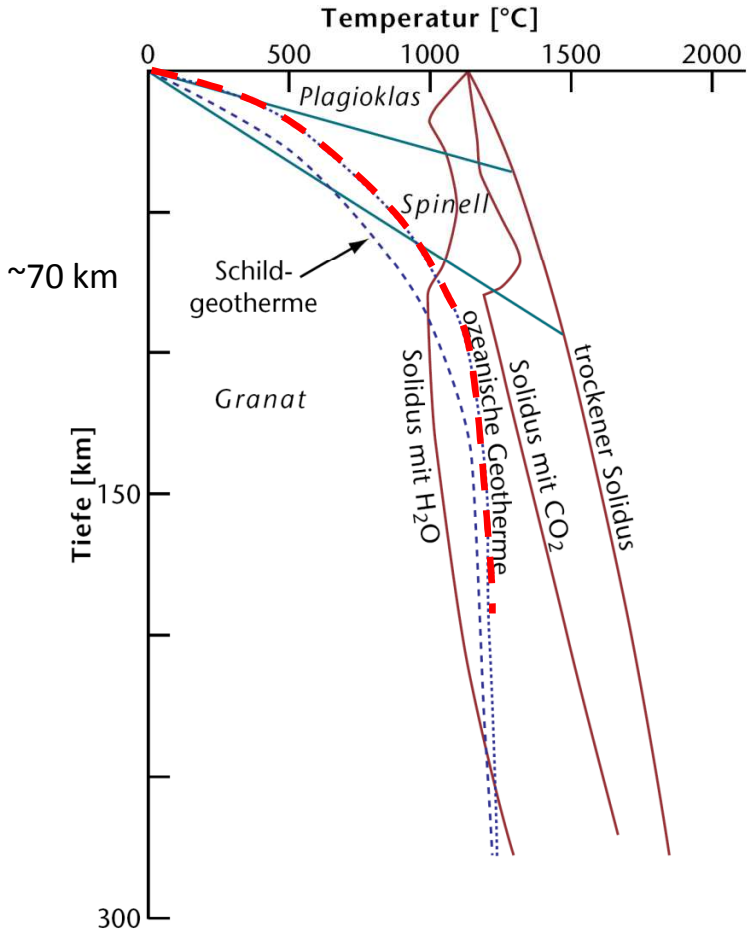


Taken from John D. Winter's petrology lecture (after Wyllie, P. J. (1981). Geol. Rundsch. 70, 128-153)

Conditions required to initiate partial melting:

- Geothermal gradient intersects solidus („*heating*“), *or*
- Addition of fluids („water“), *or*
- Adiabatic decompression





Figures taken from H.-G. Stosch – Geochemie Skript

Partial melting (simplified) is:

- **modal**

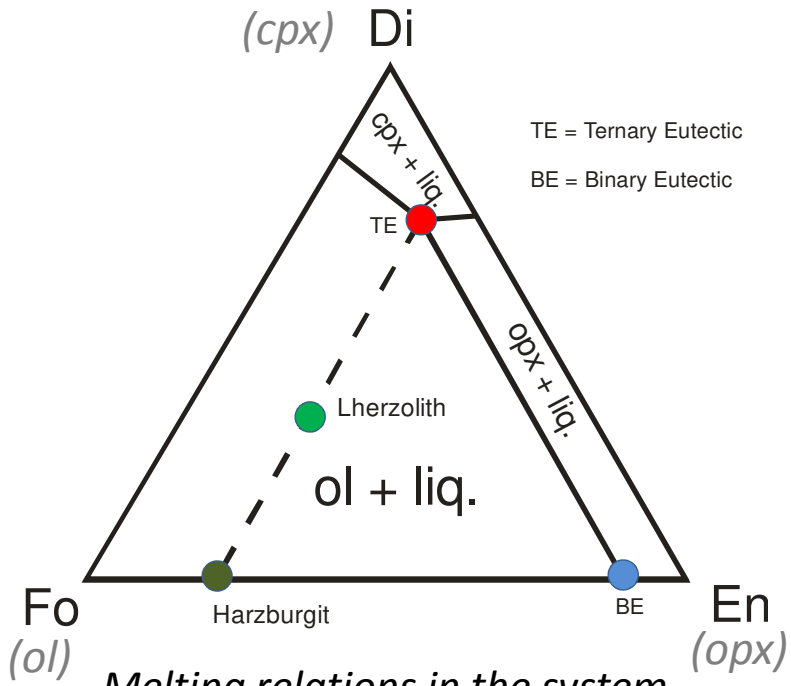
  (source and melt share the **same** modal proportions)

- **non-modal** (eutectic)

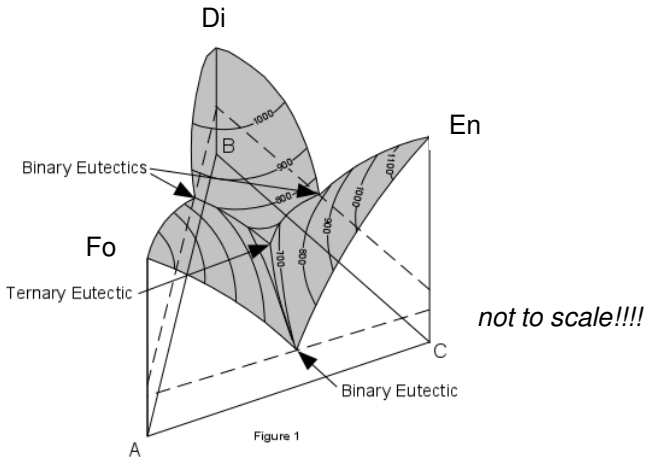
  (source and melt have **different** modal proportions)

- **incongruent**

  (melting produces not only melt but also one or more solid phases)



Melting relations in the system Fo – En – Di (eutectic melting)



not to scale!!!!

Incongruent melting - examples:

Incongruent melting of **spinel lherzolite** at 10 kbar (1 GPa; ~30 km depth; *Kinzler & Grove, 1992*):

0.82 cpx + 0.40 opx + 0.08 sp ----> 0.30 ol + 1.00 melt

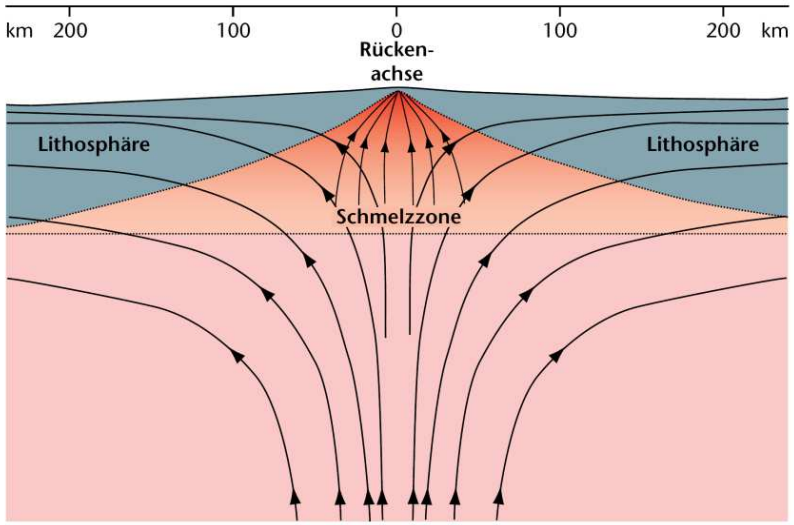
Incongruent (anhydrous) melting of **biotite - sillimanite – gneiss** (crustal anatexis; *Zeck, 1970*):

0.43 bt + 0.30 sil + 0.27 qtz ----> 0.72 cordierite + 0.28 melt

Melting models:

- batch melting
- fractional melting
- dynamic melting

(„polybaric“)



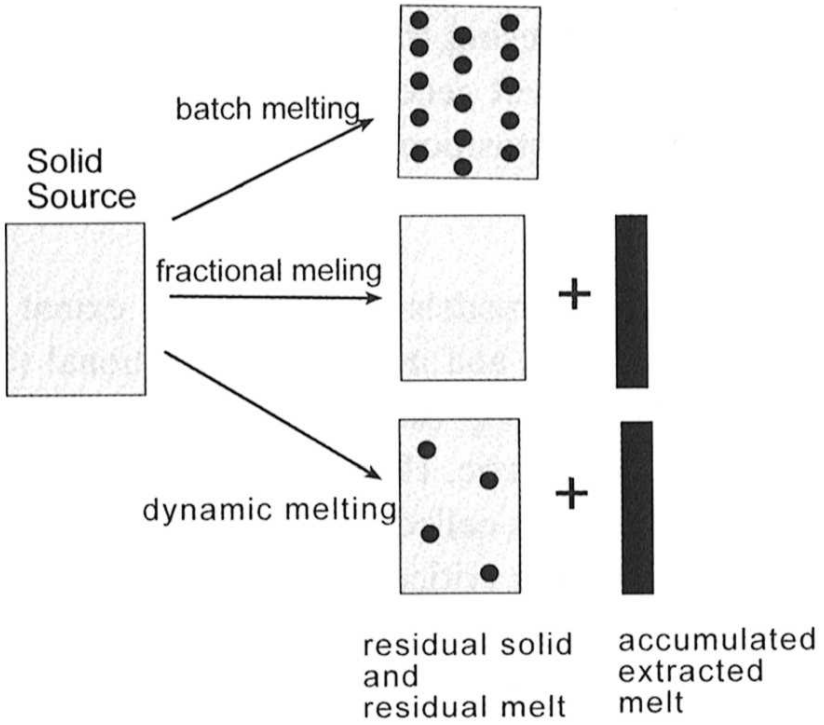


*Illustration of **decompression melting** beneath a mid-ocean ridge. The degree of melting increases continuously upwards (polybaric melting). The arrows are **mantle flow lines**, NOT melt migration paths!*

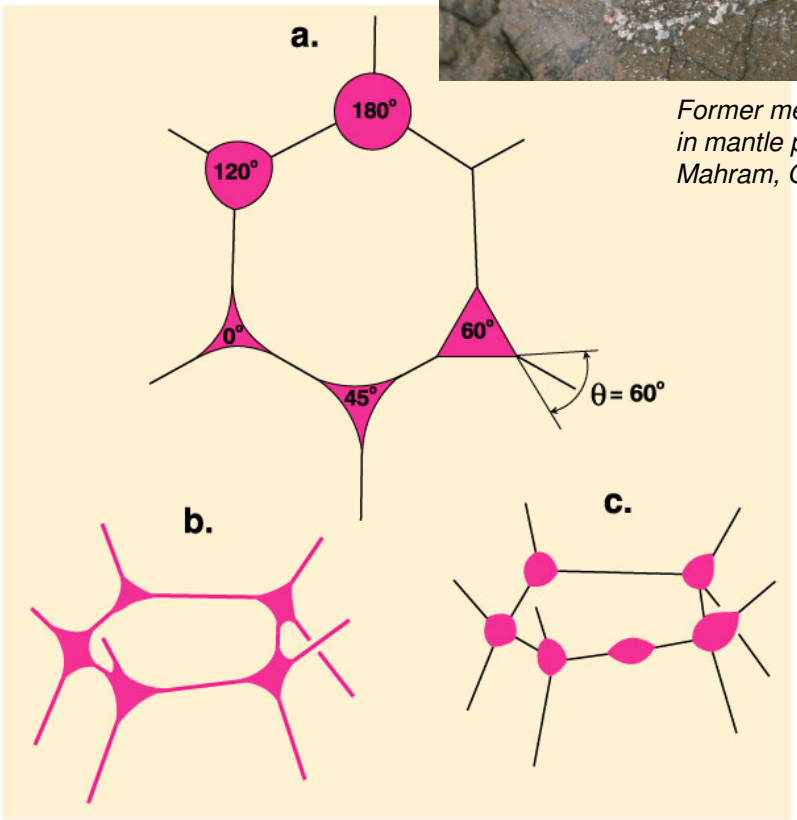
How does a melt leave it's source?

Melt migration starts if a connected melt network has formed. To do so, a **critical volume** of melt has to be generated by **partial melting**.

The critical volume is a function of the **dihedral angle θ** and thus of the surface energy of the melt.

$$\theta = f(p,T,X)$$

Former melt impregnations in mantle peridotite, Mahram, Oman Ophiolite



Taken from John D. Winter's petrology lectures (after Hunter,1987, in I. Parsons (ed.), Origins of Igneous Layering. Reidel, Dordrecht, pp. 473-504)

Quantitative relations during melting:

Conservation of total mass:

$$M_0 = M_S + M_L = 1$$

mass of source rock = mass of residual solid + mass of melt (at any time!)

M_0 = *total mass (of source rock before melting started)*
M_L = *mass of liquid phase (melt)*
M_S = *mass of residual solid*

Introducing **F** this transforms to:

$$M_0 = \underbrace{M_0(1-F)}_{M_S} + \underbrace{M_0 F}_{M_L}$$

M_0 = *total mass (of source rock)*
F = *degree of melting or melt fraction (F=0-1, i.e. 0-100%)*

Keep in mind: F is the portion of melt in the system! If F=0.1, we have 10% of melt in our system!

Quantitative relations during melting:

Conservation of the mass of an **element i**:

$$C_0^i M_0 = C_S^i M_0 (1 - F) + C_L^i M_0 F$$

total mass of element i in the melt

total mass of element i in the residual solid

total mass of **trace-element i** in the system

C_0^i = *concentration of element* ***i*** *in the system* ***before*** *melting (i.e. in the source rock)*

C_L^i = *concentration of element* ***i*** *in the melt (liquid)*

C_S^i = *concentration of element* ***i*** *in the residual solid*

As $M_0 = 1$ *(i.e. always 100%)* this simplifies to:

$$C_0^i = C_S^i (1 - F) + C_L^i F$$

Quantitative relations during melting:

Relation between C_L and C_S for element i:

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

D^i = *partition coefficient of element* ***i*** *(e.g. La) between a specific* ***mineral*** *and melt*

But, source rocks are usually **multi-mineral assemblages**, therefore D^i has to be replaced by the **bulk partition coefficient** defined as:

$$\overline{D}^i = \sum x^m D_m^i$$

$\overline{D}^i$ = *bulk partition coefficient of element* ***i*** *between* ***source rock*** *and melt*

x^m = *modal proportion of mineral* ***m*** *in the source rock (0-1; i.e. 0-100%)*

Therefore: $\overline{D}^i = \frac{C_S^i}{C_L^i}$

the solid is now a rock, not only a mineral

Quantitative relations during melting:

Combination and rearrangement yields the fundamental equation for **modal batch melting**:

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

$\overline{D}^i$ = *bulk partition coefficient of element* ***i*** *between* ***source rock*** *and melt*

the source rock after the melt has been removed

As $\overline{D}^i = \frac{C_S^i}{C_L^i}$ the composition of the **residue** is:

$$C_S^i = \frac{C_0^i \overline{D}^i}{F + \overline{D}^i(1-F)}$$

Quantitative relations during melting:

Set of **partition coefficients** used by Stracke et al. (2003) to calculate the composition of **ocean island basalts** (OIBs):

	Cs	Rb	Ba	Th	U	Nb	Ta	La	Ce	Pb	Nd
Dol	0.0003	0.0003	0.0000	0.0000	0.0000	0.0001	0.0001	0.0002	0.0001	0.0003	0.0004
Dcpx	0.0004	0.0004	0.0003	0.0140	0.0127	0.0040	0.0040	0.0490	0.0700	0.0720	0.1780
Dopx	0.0002	0.0002	0.0000	0.0000	0.0000	0.0030	0.0030	0.0031	0.0021	0.0014	0.0005
Dgt	0.0000	0.0000	0.0001	0.0014	0.0059	0.0031	0.0031	0.0016	0.0050	0.0003	0.0520
Dsp	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

	Sr	Zr	Hf	Sm	Eu	Ti	Gd	Dy	Y	Er	Yb	Lu
Dol	0.0000	0.0010	0.0011	0.0011	0.0005	0.0150	0.0011	0.0027	0.0082	0.0109	0.0240	0.0200
Dcpx	0.1283	0.1190	0.2000	0.2930	0.4300	0.3400	0.4400	0.3800	0.4120	0.3900	0.4000	0.4490
Dopx	0.0007	0.0120	0.0044	0.0016	0.0090	0.0860	0.0065	0.0110	0.0150	0.0210	0.0380	0.0400
Dgt	0.0025	0.2700	0.2400	0.2500	0.4000	0.2900	1.2000	2.2000	3.1000	3.6000	6.6000	7.1000
Dsp	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

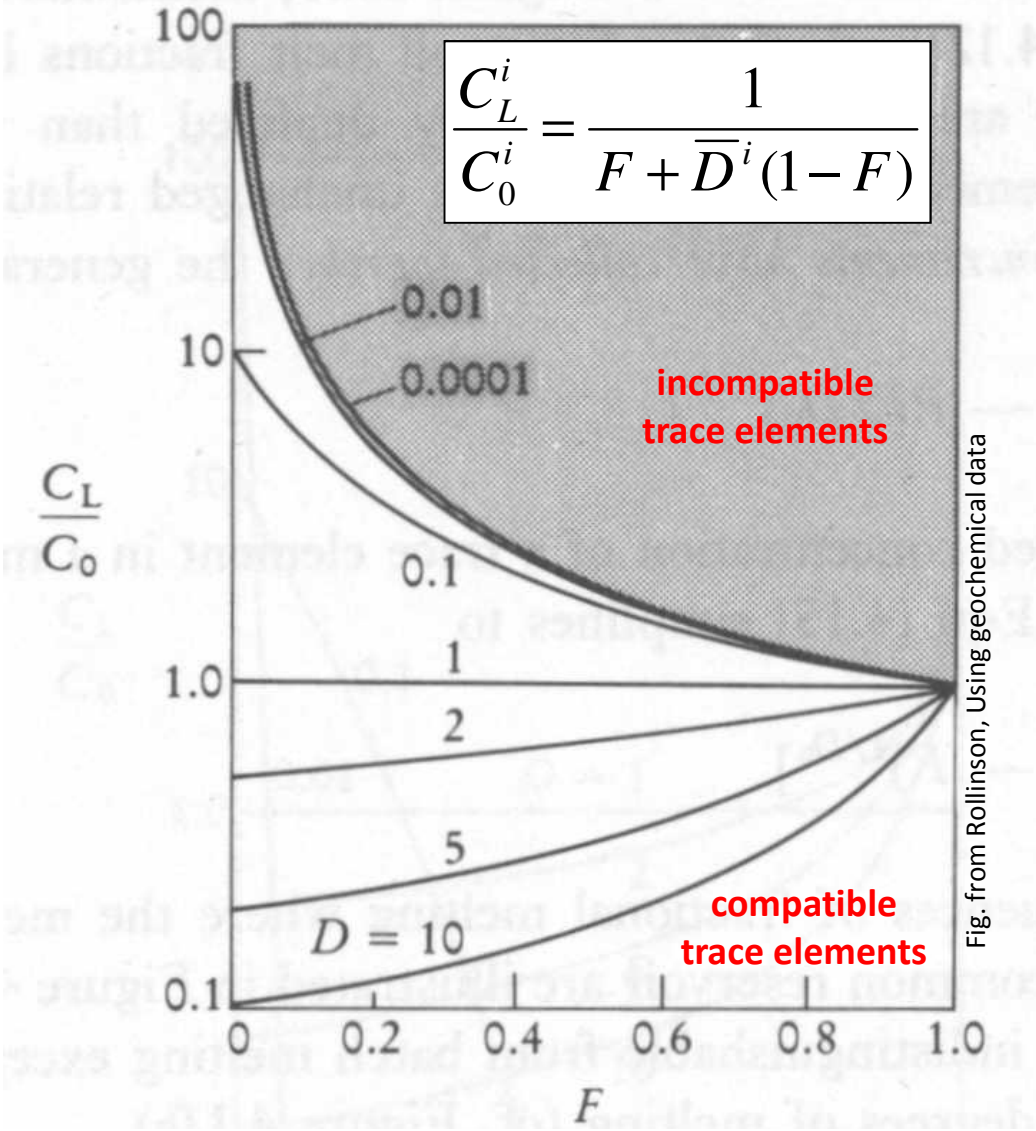
A **web database** providing a comprehensive compilation of published partition coefficients can be found here: earthref.org or directly here: earthref.org/kdd

Quantitative relations during melting:

How will the **concentration** of a **trace element** in a melt evolve with increasing degree of melting?

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

Modal batch melting equation



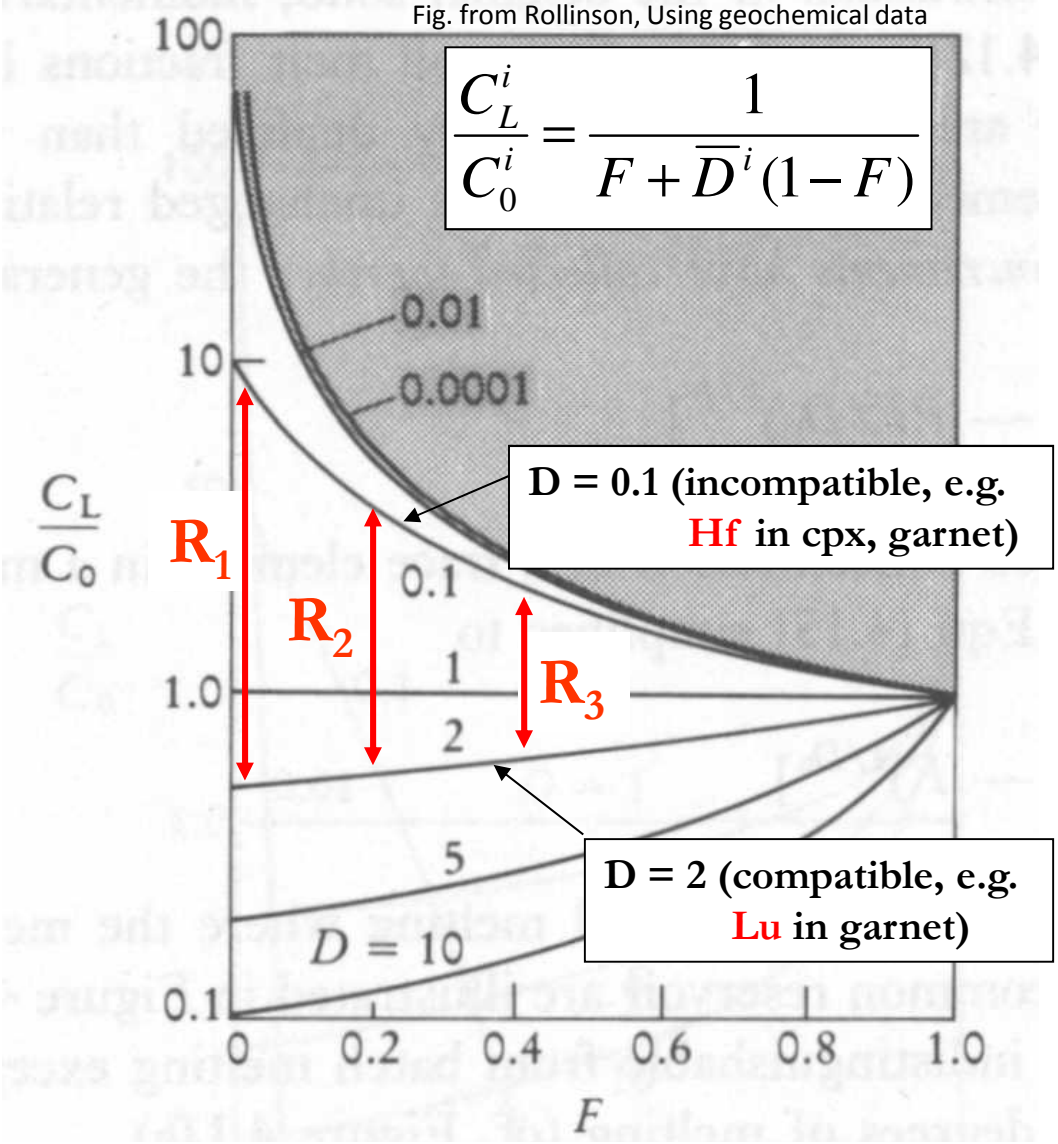
Quantitative relations during melting:

How will a **trace element ratio (R)** in a melt evolve with increasing degree of melting (F)?

$$R = f\left(\frac{1}{F}\right)$$

Geochemists call this effect **„trace element fractionation“** .... but....

Fig. from Rollinson, Using geochemical data



Quantitative relations during melting:

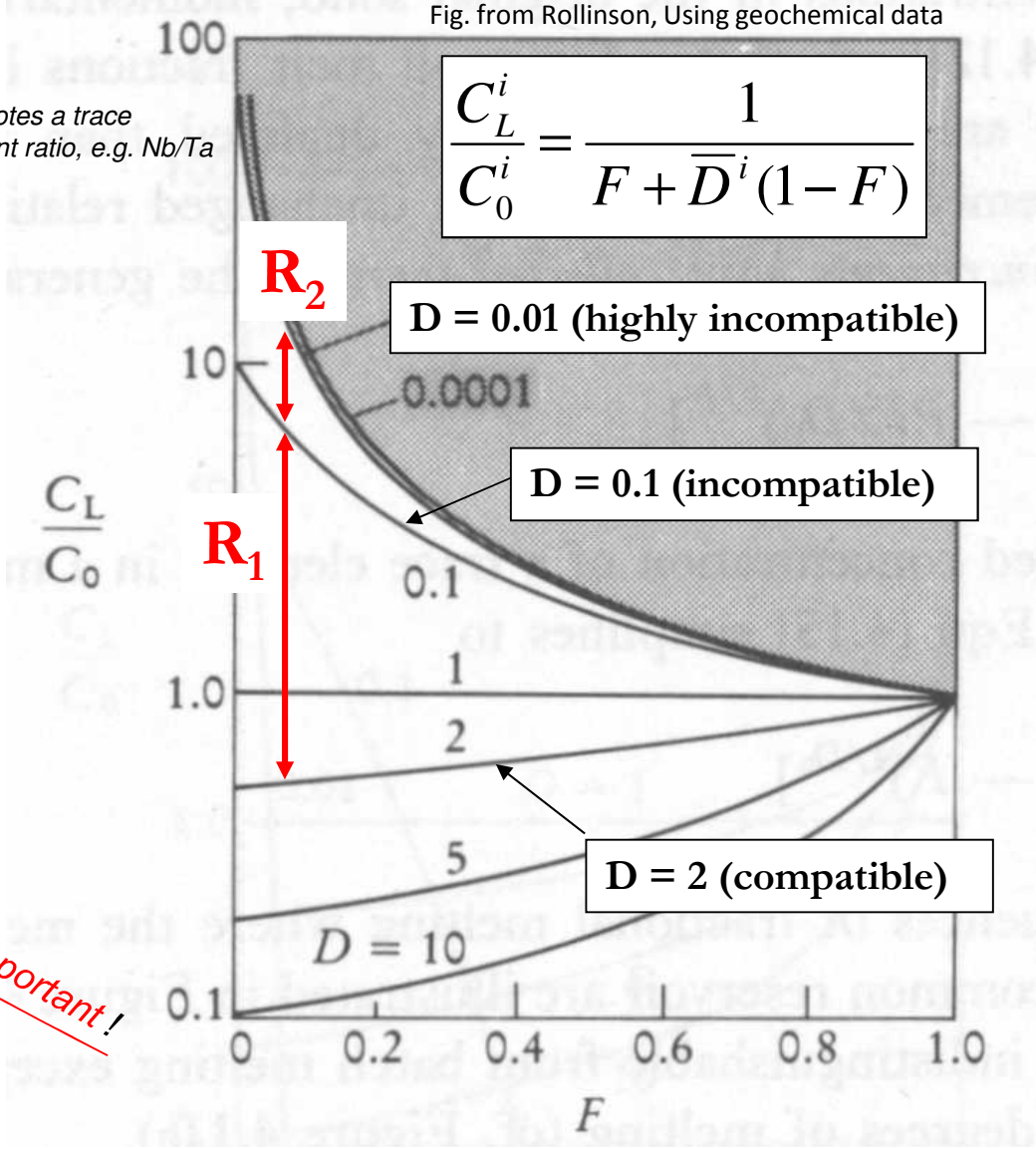
...., at a given F, the **degree** of fractionation depends on the **absolute values** of the D's involved!

The lower than unity the D-values are, the lower is the fractionation of the respective elements!

e.g. Th/U, Nb/U, Nb/La, Nb/Ta are all difficult to fractionate!

important!

Fig. from Rollinson, Using geochemical data



Quantitative relations during melting:

Summary:

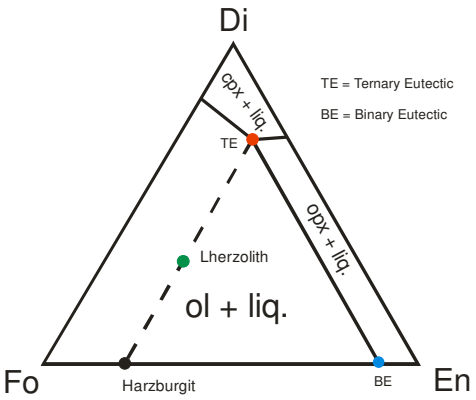
- With increasing degree of melting, the **concentration** of an *incompatible* trace element in a melt decreases!
- The **fractionation** of two trace elements is decreasing with increasing degree of melting! But …
- The **fractionation** of two trace elements is also a function of the absolute D-values and the difference between them!

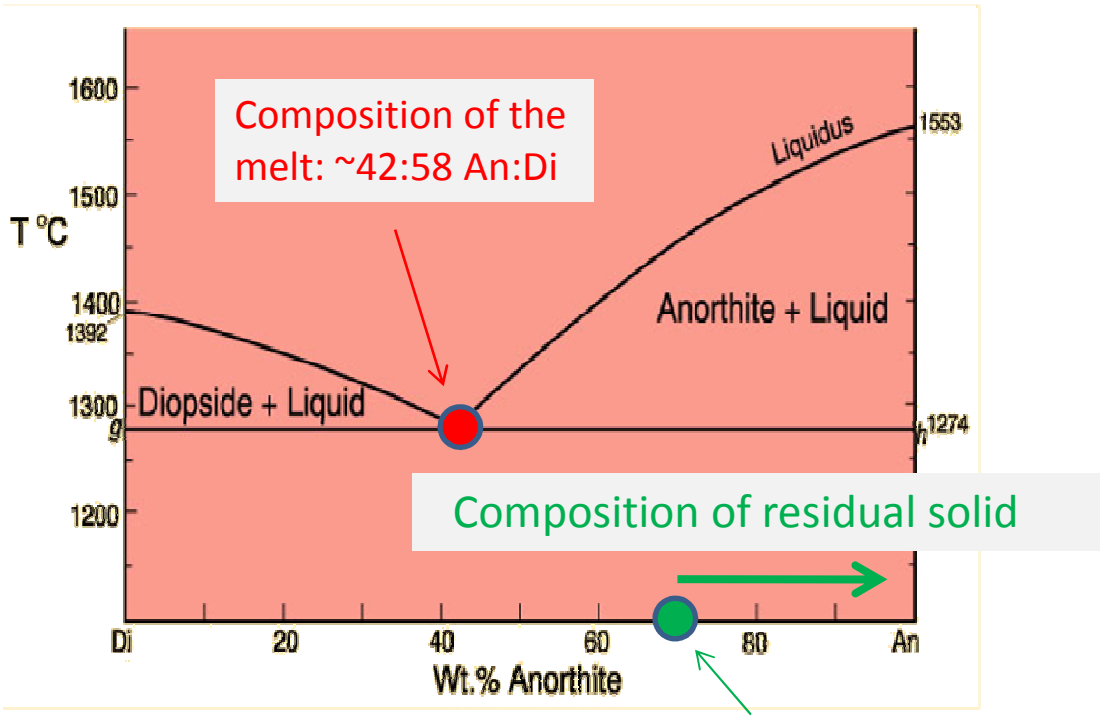
  In other words and very important: At **very low** D-values (<0.01), the **fractionation** between **two** trace elements is negligible !!!!!!!!!!!!!

Quantitative relations during melting:

As melting is commonly **non-modal** or **incongruent**, the *modal proportion* of the minerals (x^m) in the residual solid *changes* during melting, i.e. $\mathbf{x^m}$ is a function of **F**, and thus $\mathbf{\bar{D}^i}$ **also becomes a function of F**:

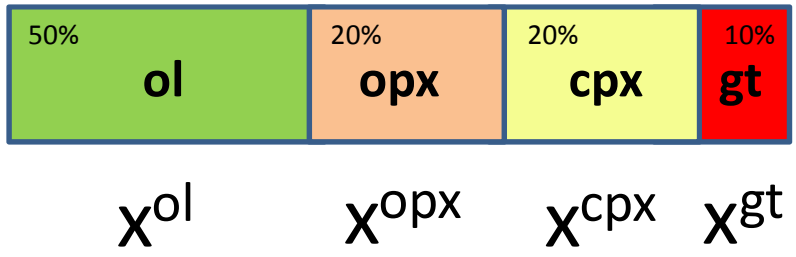
$$\overline{D}^i = f(F)$$



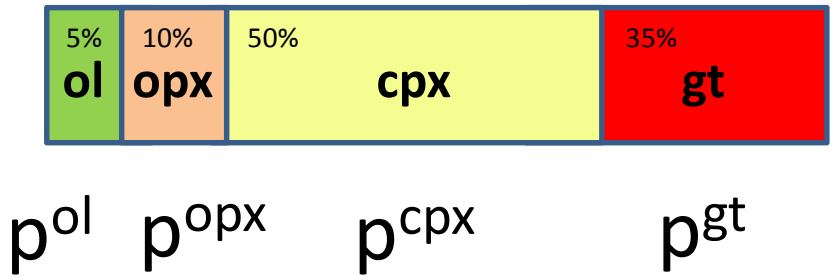


Quantitative relations during melting:

This changing residual composition needs to be accounted for by considering the **modal composition of the „melt“**, i.e. the *modal proportion* of the minerals ***entering*** the melt (i.e. the **eutectic composition**):



Modal composition of the **solid** (here: Lherzolite, or "Pyrolite")



"Modal composition" of the **melt** (i.e. eutectic composition, here: basaltic melt)

Quantitative relations during melting:

Balancing the mass (or mode) of each **mineral** between **residual solid** and **melt** yields:

$$x_0^m = x^m X + p^m F \qquad and \qquad X + F = 1 \qquad yields:$$

$$x_0^m = x^m (1 - F) + p^m F$$

$$x^m(F) = \frac{x_0^m - p^m F}{1 - F}$$

x^m = modal portion of mineral **m** in the ***solid*** phase
p^m = modal portion of mineral **m** in the ***liquid*** phase
x_0^m = modal portion of mineral **m** in the starting solid, i.e. in the solid ***before melting*** has started
X = portion of solid phase
F = degree of melting (= portion of liquid phase!)

This equation describes the modal amount of a mineral in the residual solid as a function of F (note that p^m is constant!)

Quantitative relations during melting:

Combination with $\overline{D}^i = \sum x^m D^{m,i}$ where $x^m = f(F)$

m = mineral, e.g. cpx
i = trace element, e.g. La

results in:

$$\overline{D}^i = \sum x^m D^{m,i} = \sum \frac{x_0^m - p^m F}{1-F} D^{m,i} = \frac{\sum x_0^m D^{m,i} - F \sum p^m D^{m,i}}{1-F}$$

Defining: $\overline{P}^i = \sum p^m D^{m,i}$ $\overline{D}^i$ becomes:

‚Bulk' partition coefficient of the ‚eutectic composition'

Constant during melting for each mineral

$$\overline{D}^i = \frac{\overline{D}_0^i - F\overline{P}^i}{1-F}$$

This equation describes the partition coefficient of trace element i as a function of the degree of melting (F)!

Quantitative relations during melting:

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

modal batch melting

Combining this equation with the equation for **modal batch melting**, i.e. replacing the constant bulk partition coefficient by the **partition coefficient of the initial solid** and the **partition coefficient of the „melt“** yields the equation for **non-modal batch melting**:

$$C_L^i = \frac{C_0^i}{\overline{D}_0^i + F(1-\overline{P}^i)}$$

$\overline{D}_0^i$ = *bulk partition coefficient of element* ***i*** *between* ***source rock*** *and melt* ***before*** *melting has started (i.e. for F=0)*

$\overline{P}^i$ = *normative ‚bulk partition coefficient' of the* ***melt*** *for element* ***i*** *(constant during melting!)*

In this equation, initially introduced by *Shaw (1970)*, the *variable bulk-D value* of the melting solid is replaced by two **constant** partition coefficients!

Quantitative relations during melting:

Note, that the non-modal batch melting equation can also be used for **incongruent melting**, if the stoichiometry of the melting reaction is considered!

Example:

Incongruent melting reaction of **spinel peridotite** in the depth range 60 - 75 km (Salters, 1996):

0.375 ol + 1.125 cpx ----> 1.0 melt + 0.5 opx

Therefore:

$$\overline{P}^i = \sum p^m D_0^i = 0.375\ {}^{ol}D_0^i + 1.125\ {}^{cpx}D_0^i - 0.5\ {}^{opx}D_0^i$$

Partition coefficients for some trace elements and **stoichiometry of melting reactions** for **incongruent melting** *(from Salters, 1996)*:

	Olivine	Orthopyroxene	HP Diopside	LP Diopside	Spinel	Garnet
Distribution coefficients						
La	0.000031	0.00004	0.01	0.0536	0.0006	0.01
Ce	0.0001	0.00014	0.02	0.0858	0.0006	0.018
Nd	0.00042	0.00052	0.02	0.1873	0.0006	0.059
Hf	0.0011	0.0044	0.05	0.256	0.0045	0.35
Sm	0.0011	0.0016	0.067	0.33	0.0006	0.214
Dy	0.0014	0.0084	0.1247	0.442	0.0015	1.06
Er	0.03	0.017	0.1437	0.43	0.003	2.54
Yb	0.03	0.03	0.1437	0.43	0.0045	6.01
Lu	0.02	0.04	0.149	0.433	0.0045	7

Stochiometry of melt reactions					
	Olivine	Orthopyroxene	Clinopyroxene	Spinel	Garnet
>75km	0.05	-0.49	1.31	0	0.13
75-60km	0.375	-0.5	1.125	0	0
60-48km	-0.25	-0.25	1.5	0	0
48-33km	-0.45	0.403	1.047	0	0
<33km	-0.375	0.625	0.875	0	0

Initial composition					
>75km	0.53	0.04	0.38	0	0.05
<75km	0.53	0.15	0.3	0.02	0

Example for melting reaction at > 75 km:

1.31 cpx + 0.13 gt + 0.05 ol ----> 1.0 melt + 0.49 opx

Quantitative relations during melting:

I - BATCH MELTING

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

MODAL BATCH MELTING

$$C_L^i = \frac{C_0^i}{\overline{D}_0^i + F(1 - \overline{P}^i)}$$

NON-MODAL and INCONGRUENT BATCH MELTING

Quantitative relations during melting:

II - FRACTIONAL MELTING

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

MODAL FRACTIONAL MELTING

$$C_L^i = \frac{C_0^i}{\overline{D}_0^i}\left(1-\frac{F\,P}{\overline{D}_0^i}\right)^{\left(\frac{1}{P}-1\right)}$$

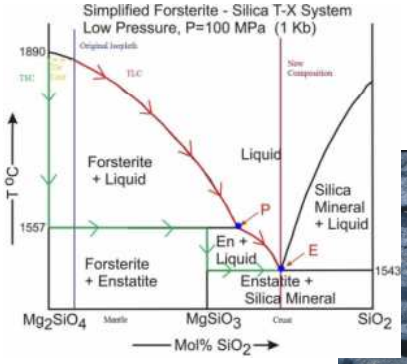
NON-MODAL and INCONGRUENT FRACTIONAL MELTING

$$C_L^i = \frac{C_0^i}{F}\left[1-\left(1-\frac{F\,P}{\overline{D}_o^i}\right)^{\frac{1}{P}}\right]$$

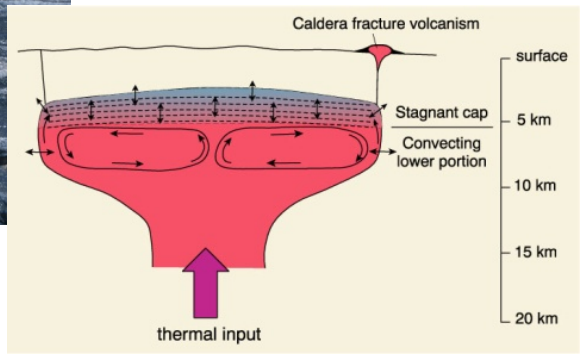
NON-MODAL and INCONGRUENT **AGGREGATE** FRACTIONAL MELTING

Chapter 3

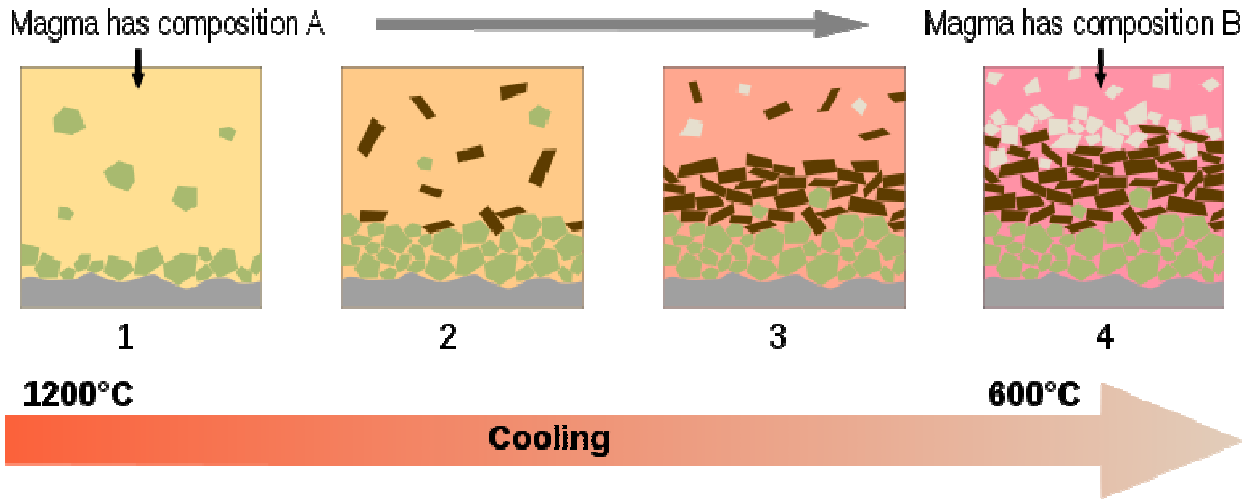
FRACTIONAL CRYSTALLISATION



Layered gabbros, Oman

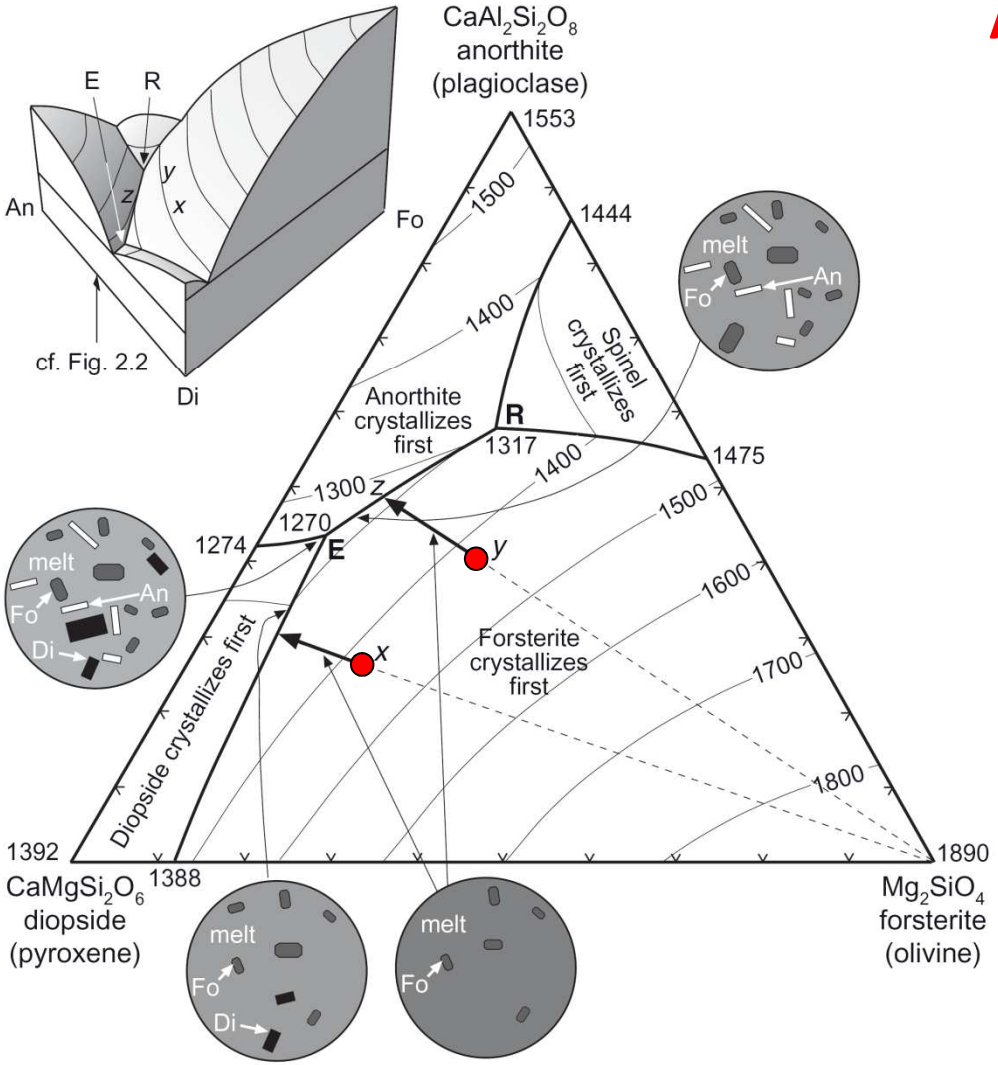


During fractional crystallisation, basically the same principles as for partial melting control the distribution of trace elements between the crystallising solid and the remaining melt!



Note, however, that during fractional crystallisation the **major element** composition (i.e. the „modal composition“) of a magma **changes** continuously !!!!

Crystallisation of a basaltic melt:

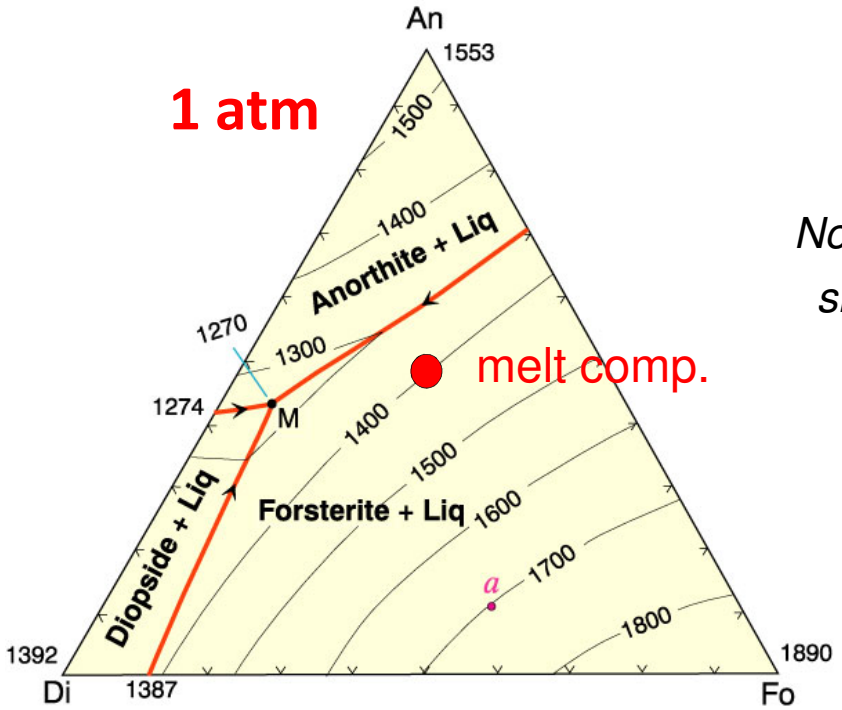


An – Di – Fo at 1 bar

Effect of melt composition on the order of crystallisation

x and y denote two different melt compositions, starting crystallisation at ~1450°C

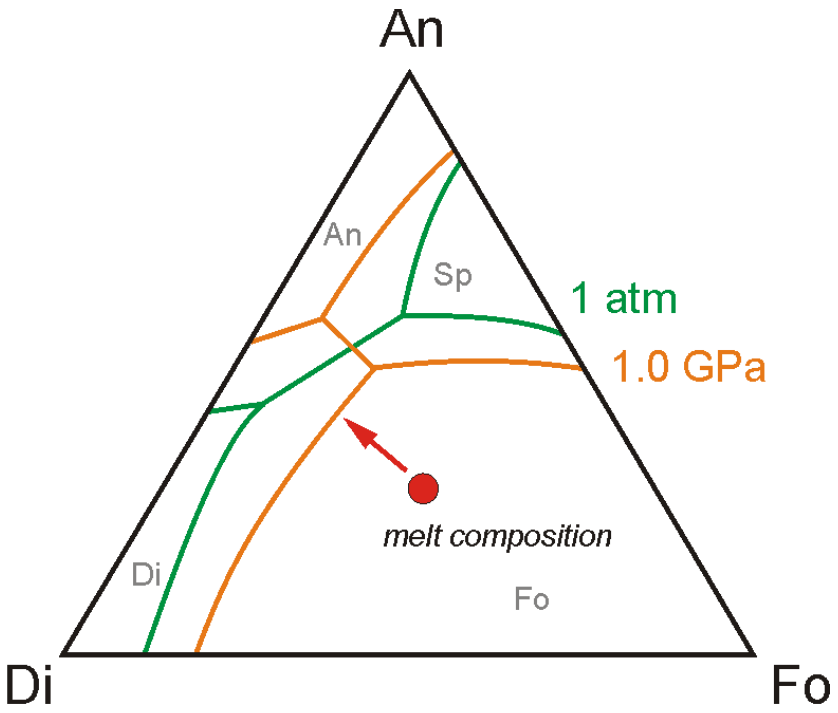
Crystallisation of a basaltic melt:



Taken from John D. Winter's petrology lecture (after Bowen,1915, Am. J. Sci., and Morse, 1994, Basalts and Phase Diagrams. Krieger Publishers)

Effect of pressure on the order of crystallisation

Note that the location of the phase boundaries, i.e. the sizes of the liquidus areas, is a function of pressure!



Crystallisation models

- equilibrium crystallisation

  (melt and crystallising solid are in **chemical** and **thermodynamic** **equilibrium** during the whole crystallisation process)

- fractional crystallisation (Rayleigh fractionation)

  (crystallising minerals do **NOT** re-equilibrate with the remaining melt, i.e. were „instantaneously“ removed from the melt *(for orientation: sinking velocity of olivin **~4 mm/h**, rising velocity of plagioclase **~0.7 mm/h**!)*)

*Zonation in minerals indicates **disequilibrium**, e.g. near fractional crystallisation!*

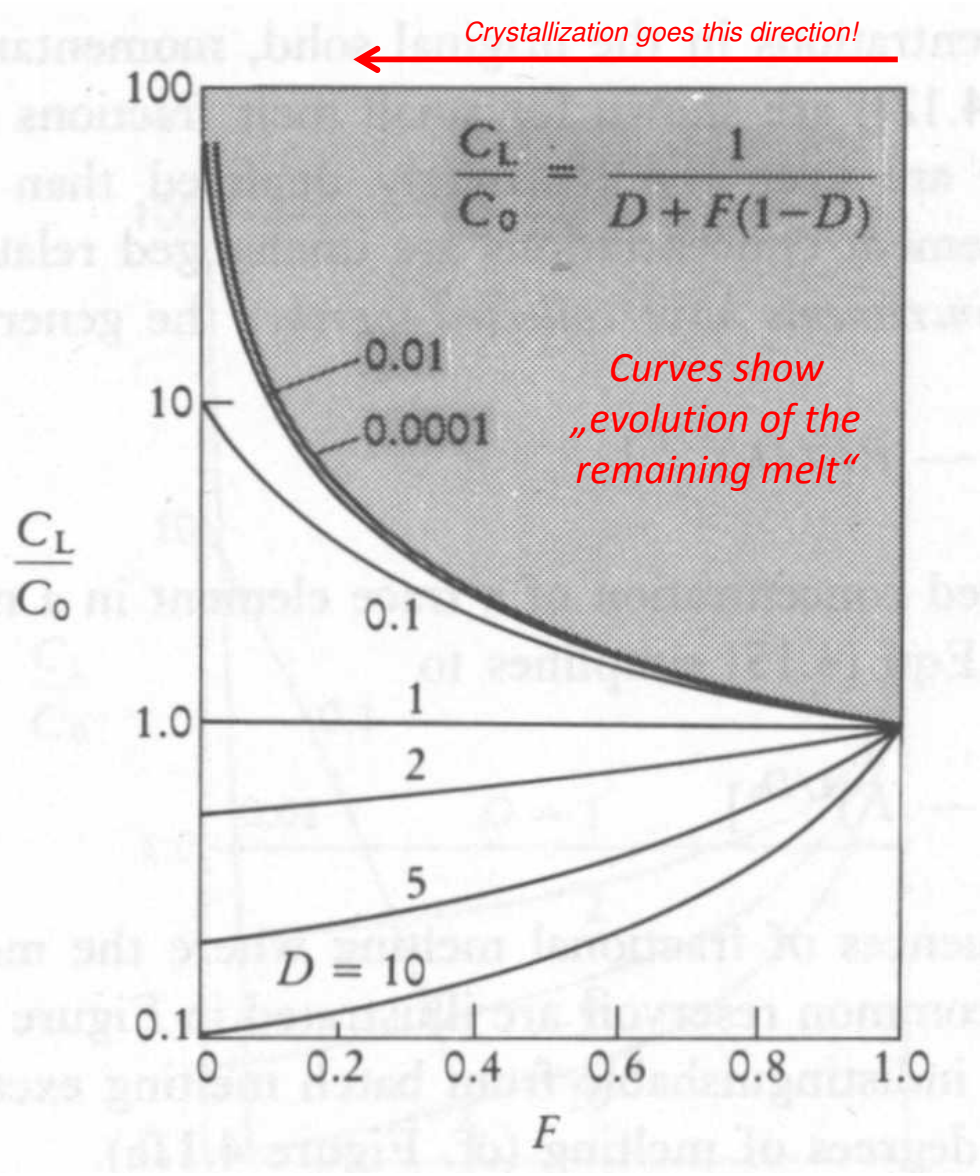
Or magma replenishment, mixing, convection, heterogeneity, ...

Quantitative relations during crystallisation:

Composition of remaining melt during **equilibrium crystallisation** (identical to batch melting!)

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

$\overline{D}^i$ = *bulk partition coefficient of element* **i** *between* ***crystallizing solid*** *and melt*



Quantitative relations during crystallisation:

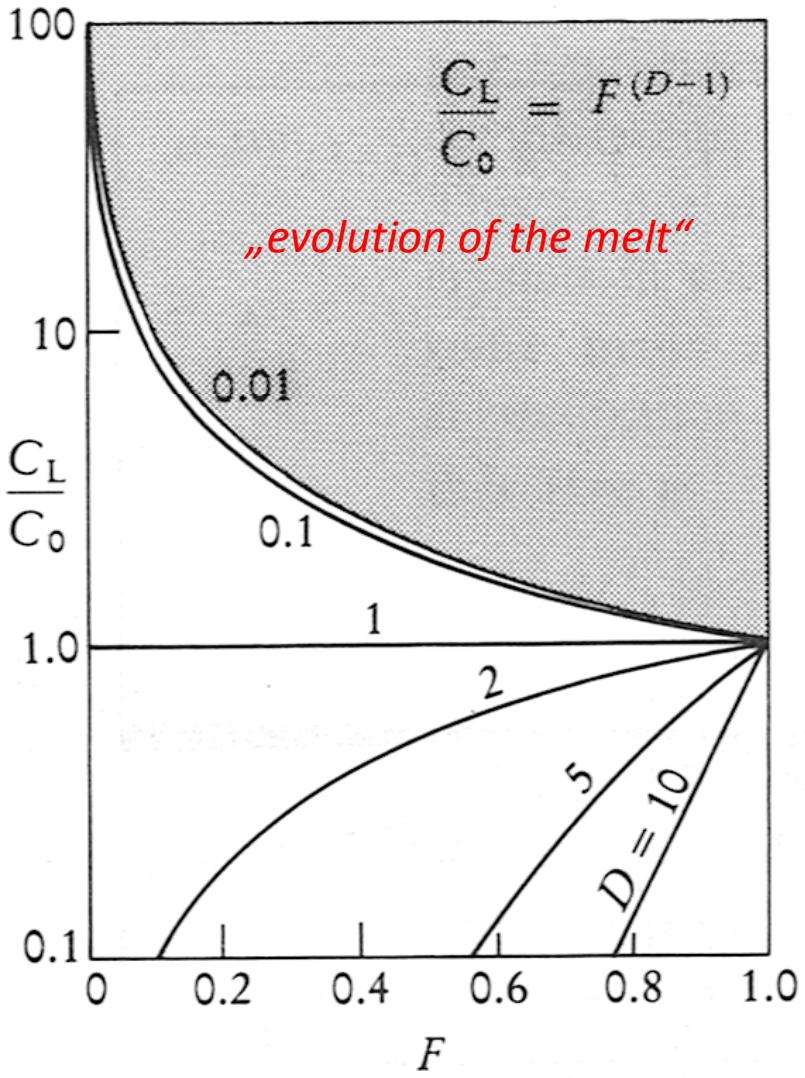
Composition of <u>remaining melt</u> during **fractional crystallisation** (**Rayleigh fractionation**)

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

$\overline{D}^i$ = *bulk partition coefficient of element* **i** *between* ***crystallizing solid*** *and melt*

Note the extreme depletion of <u>compatible</u> trace elements in the melt!

And the extreme enrichement of only weakly incompatible elements at the end of the process!!

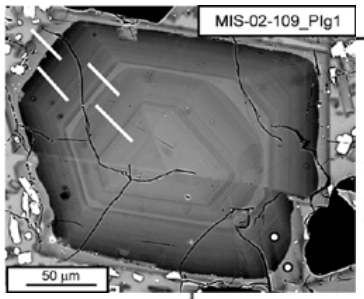


Quantitative relations during crystallisation:

Composition of *instantaneous* solid during **fractional crystallisation (Rayleigh fractionation)**

$$\frac{C_S^i}{C_0^i} = \overline{D}^i F^{(1-\overline{D}^i)}$$

$\overline{D}^i$ = *bulk partition coefficient of element* ***i*** *between* ***crystallizing solid*** *and melt*

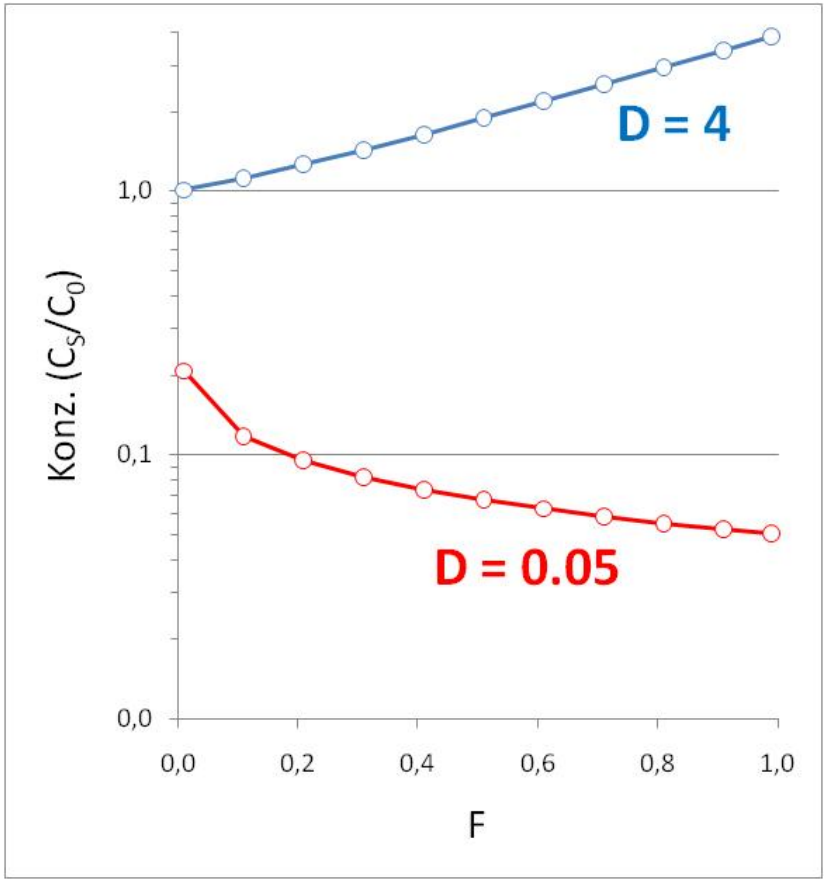


Quantitative relations during crystallisation:

Composition of *averaged* solid during fractional crystallisation **(Rayleigh fractionation)**

$$\frac{C_S^i}{C_0^i} = \frac{1 - F^{\overline{D}^i}}{1 - F}$$

$\overline{D}^i$ = *bulk partition coefficient of element* **i** *between* ***crystallizing solid*** *and melt*



Problem:

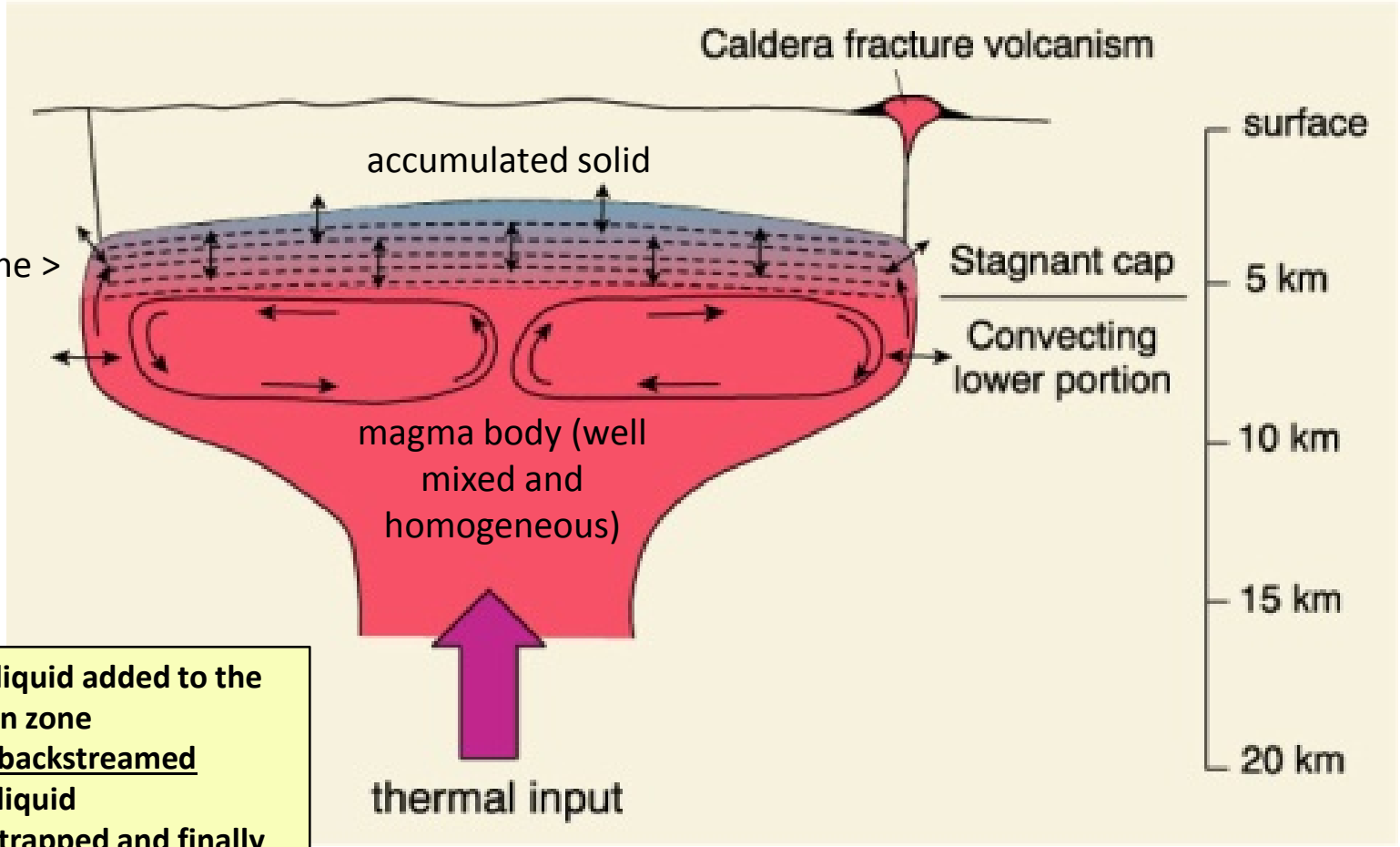
Magma crystallisation typically does **not** occur in a *closed system*! Instead, magmatic differentiation is usually an **open-system process**, better described by:

- **in situ crystallisation**
  (crystallisation in a ***transition zone*** between solidus and liquidus, i.e. within a thermal boundary)

- **magma replenishment**
  (periodic injection and eruption of magma in an open system magma chamber)

Layered gabbros, Oman

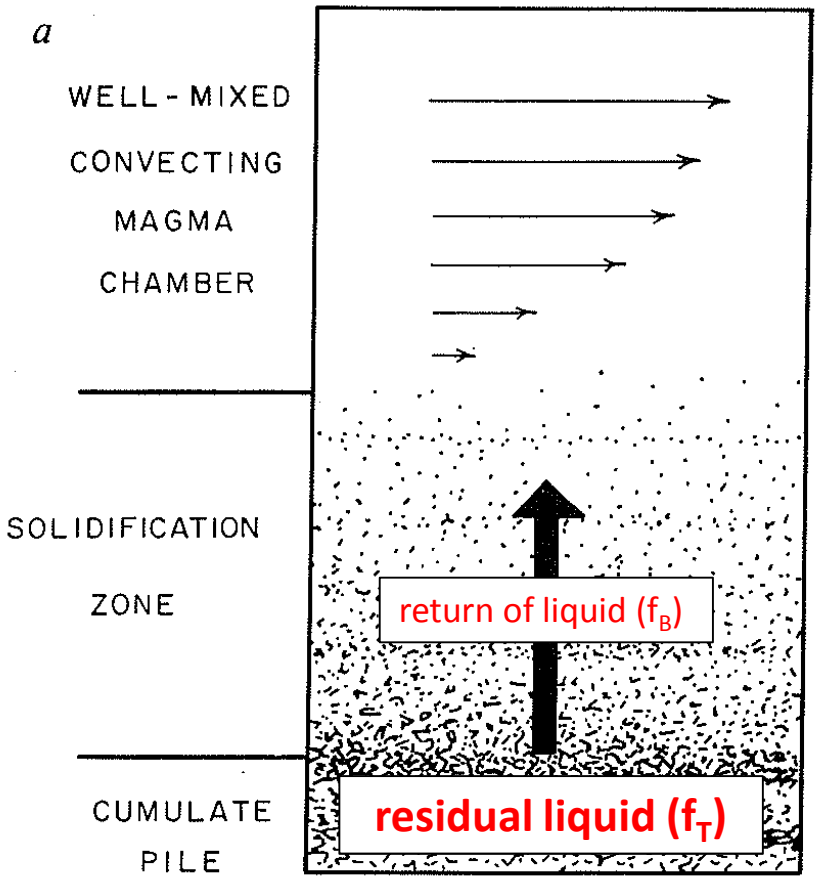
In situ crystallisation: Model

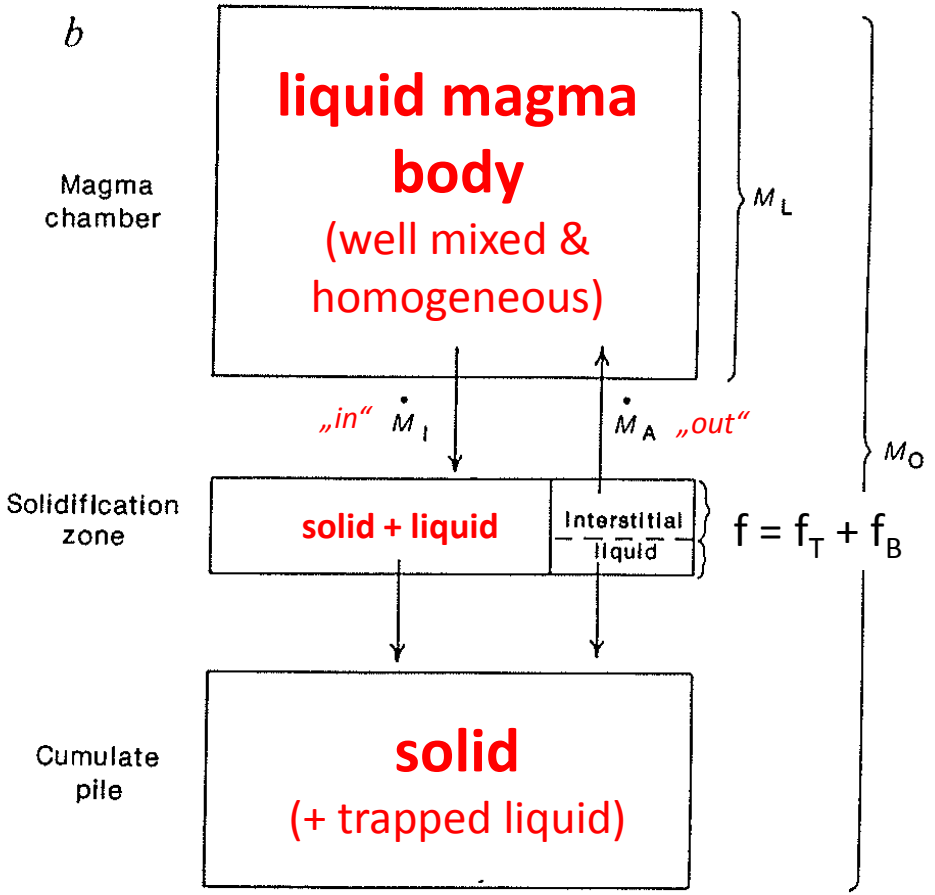


f = fraction of liquid added to the solidification zone
f_B = fraction of <u>backstreamed</u> interstitial liquid
f_T = fraction of <u>trapped</u> and finally solidified liquid

In situ crystallisation: Model

f = fraction of liquid added to the solidification zone
f_B = fraction of backstreamed interstitial liquid
f_T = fraction of trapped and finally solidified liquid





From: Langmuir, 1989, Nature

In situ crystallisation: Equation:

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

Rayleigh fract.

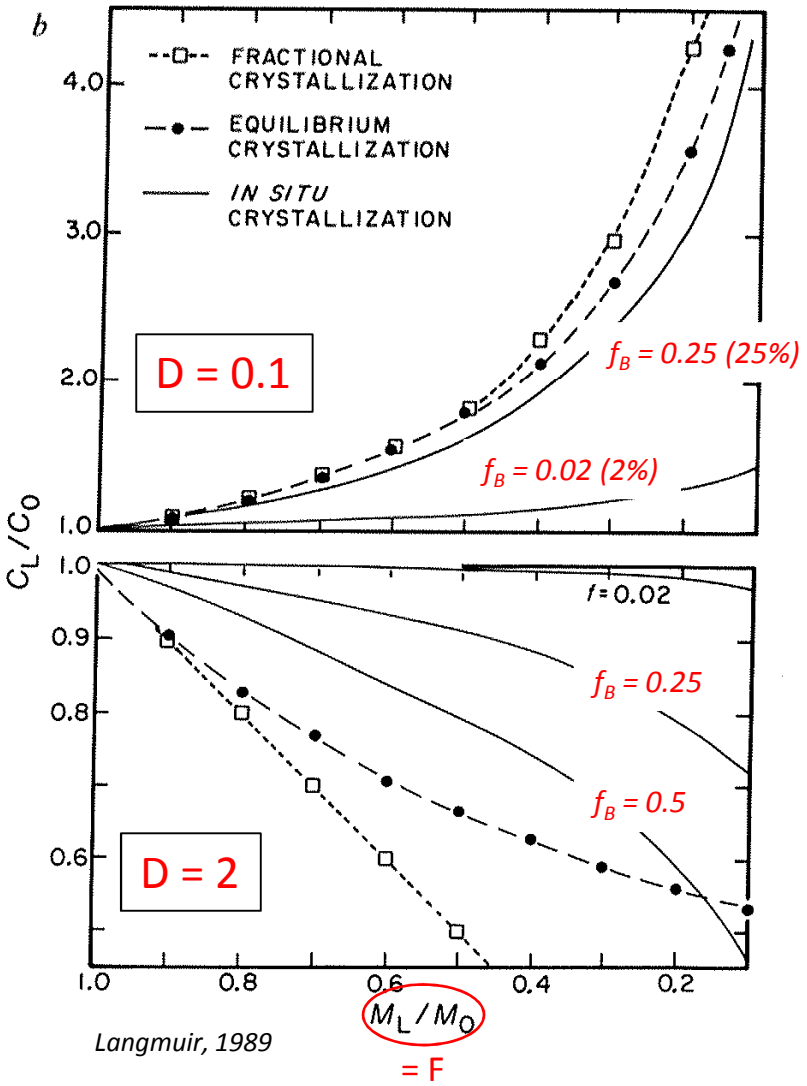
$$\frac{C_L^i}{C_0^i} = \left(\frac{M_L}{M_0}\right)^{f_B(E-1)/(f_B-1)} = F^{f_B(E-1)/(f_B-1)}$$

For $f_B = 0$ we get $C_L/C_0 = 1$
For $f_B \rightarrow 1$ we get perfect fractional crystallisation

with: $E = \frac{C_B^i}{C_L^i}$ and: $E \approx \frac{1}{D(1-f_B)+f_B}$

f_B = *fraction of melt that **returns to the magma chamber** out of the **solidification zone** (backstreaming liquid)*
C_B = *concentration of a trace element in the **returning liquid** (i.e. in the fractionated, **backstreaming** liquid)*
C_L = *concentration of a trace element in the magma chamber*
E = ***„enrichment (or depletion) factor“**, i.e. concentration ratio between the liquid **returning** to the convecting magma chamber and the liquid **added** to the solidification zone (E contains D-value, crystallisation model (batch or fractional), ...)*

In situ vs. fractional and equilibrium crystallisation



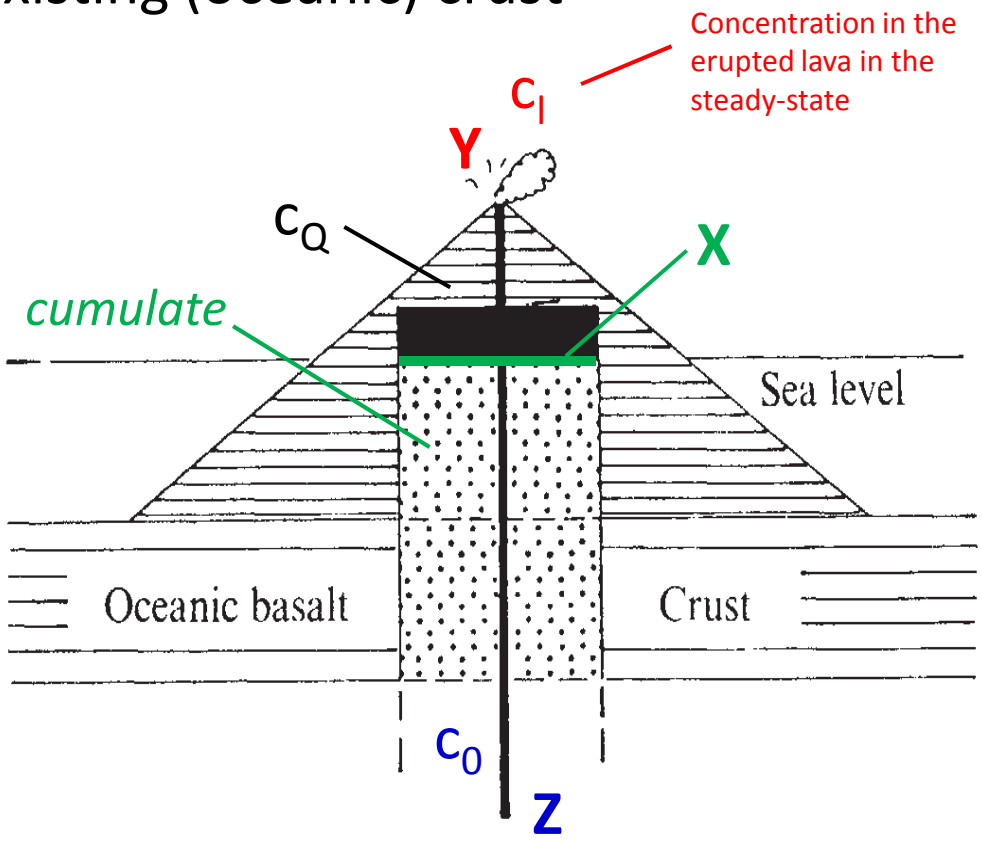
Enrichment of <u>incompatible</u> elements in the magma (chamber) <u>decreases</u> with decreasing $\mathbf{f_B}$

Depletion of <u>compatible</u> elements in the magma (chamber) is <u>less</u> if $\mathbf{f_B}$ decreases

f_B = fraction of melt that returns to the convecting magma out of the solidification zone (backstream)

Open system fractional crystallisation: Model

A periodically refilled magma chamber piling up through pre-existing (oceanic) crust



O'Hara, 1977, Nature

X *= mass fraction of cumulate formed during a cycle*

Y *= mass fraction erupted at the end of a cycle*

Z *= mass fraction of added parental magma per cycle*

C_Q *= concentration in the assimilated material (zone refining)*

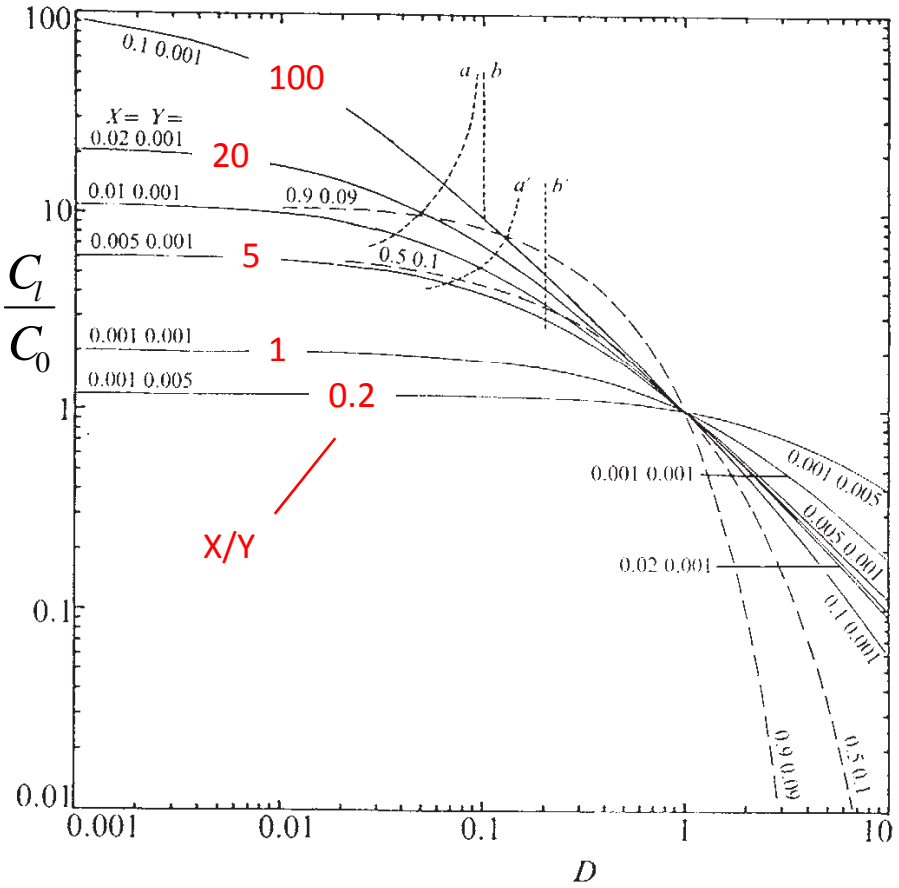
All expressed relative to the initial size of the magma chamber

Open system fractional crystallisation: Melt evolution

Enrichment of a trace element in the erupted lava in the **steady-state** relative to the concentration of this element in the parental magma added to the magma chamber

$$\frac{C_l}{C_0} = \frac{(X+Y)(1-X)^{D-1}}{1-(1-X-Y)(1-X)^{D-1}}$$

Red numbers denote the ratio **X/Y** (**fractionation** to **eruption** rate)

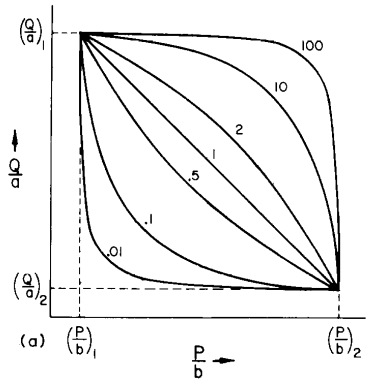


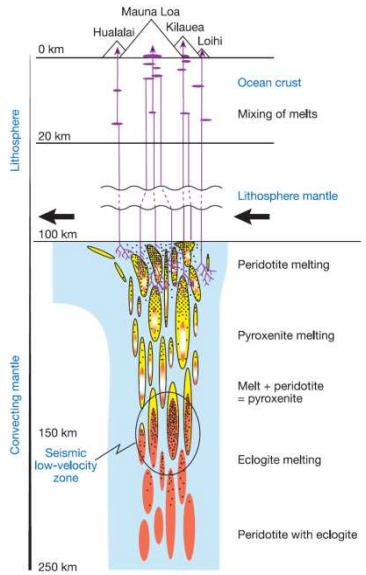
O'Hara, 1977, Nature

Chapter 4

(Magma)

MIXING AND ASSIMILATION



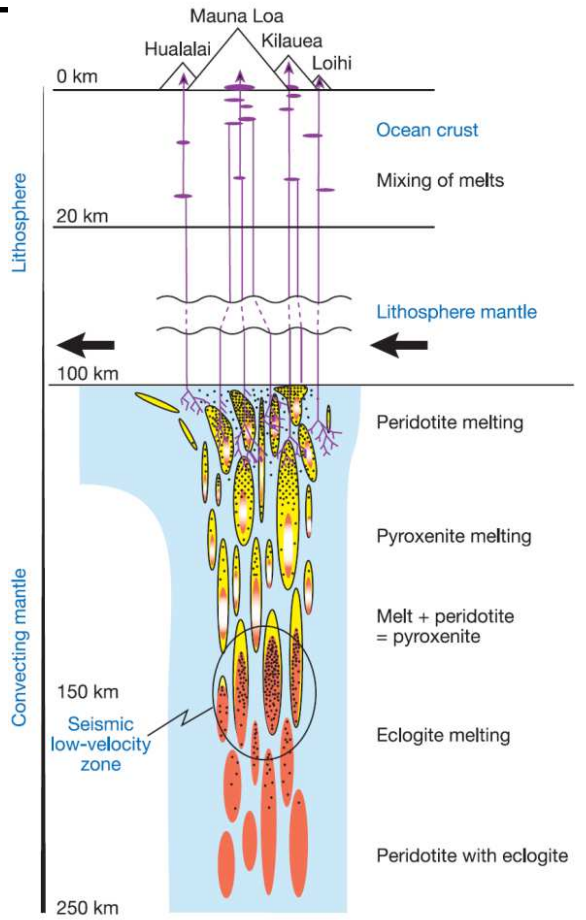


Mixing processes occur, for example :

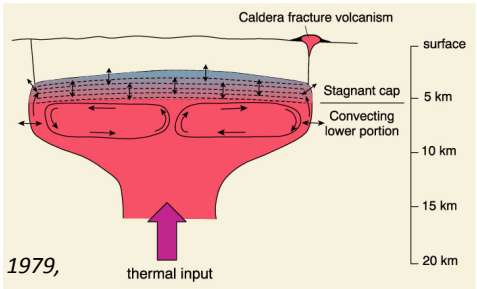
- If different **melt fractions** from different mantle **source regions** rise to the surface
- During magma chamber **replenishment**

Assimilation processes occur:

- If magma passes the **lithosphere** (lithospheric mantle & crust)
- During and after magma emplacement in a **magma chamber**



From Sobolev et al. 2005, Nature



From J. D. Winter; after Hildreth 1979, Geol. Soc. Amer. Special Paper

Olivine crystals and melt inclusions within them

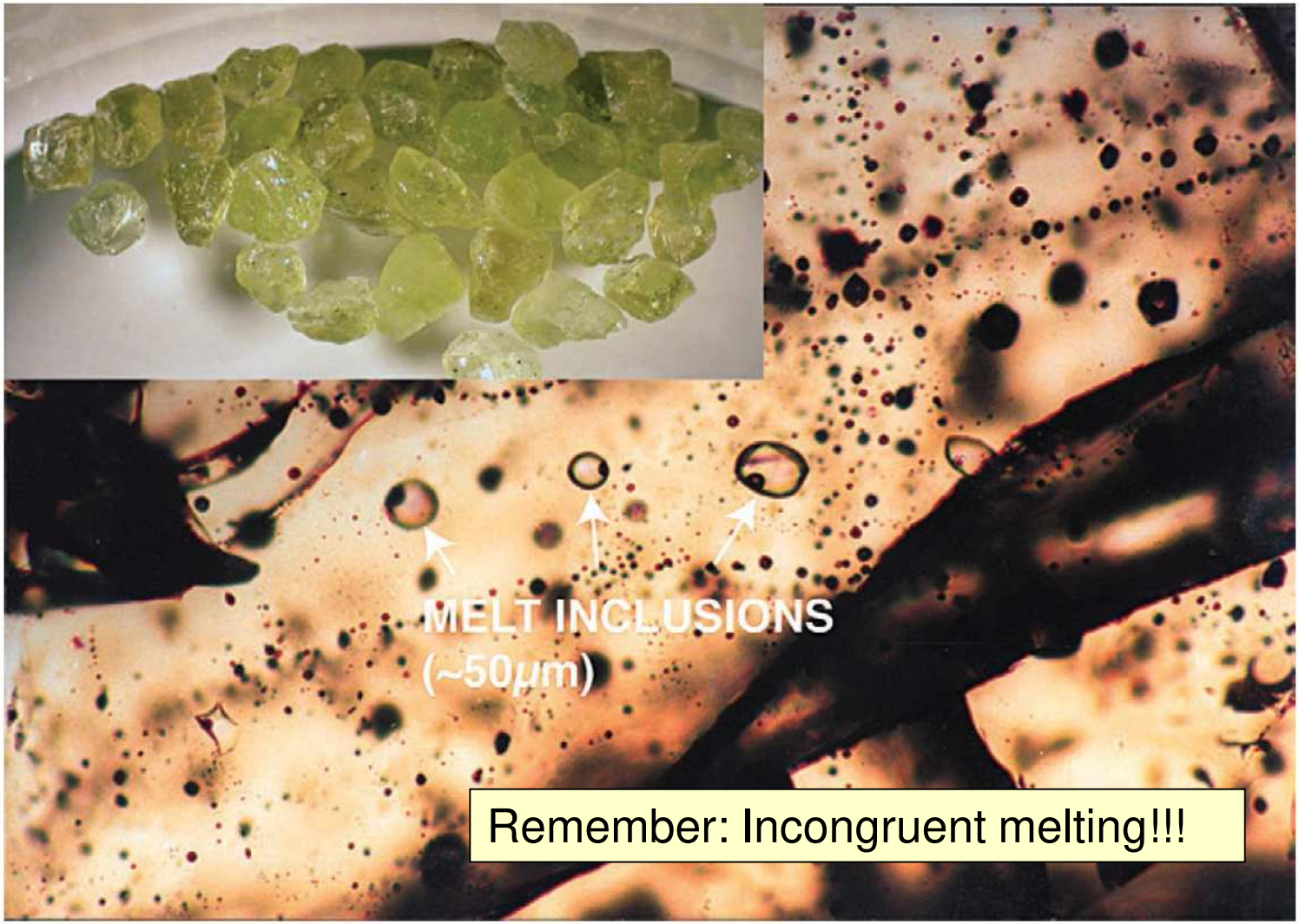
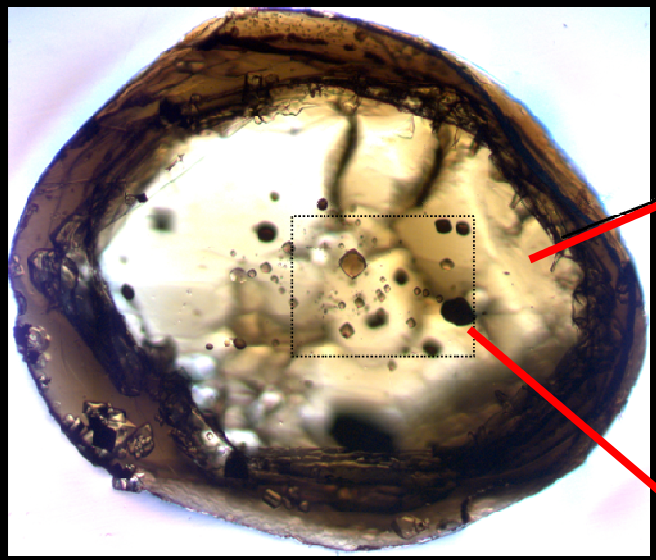
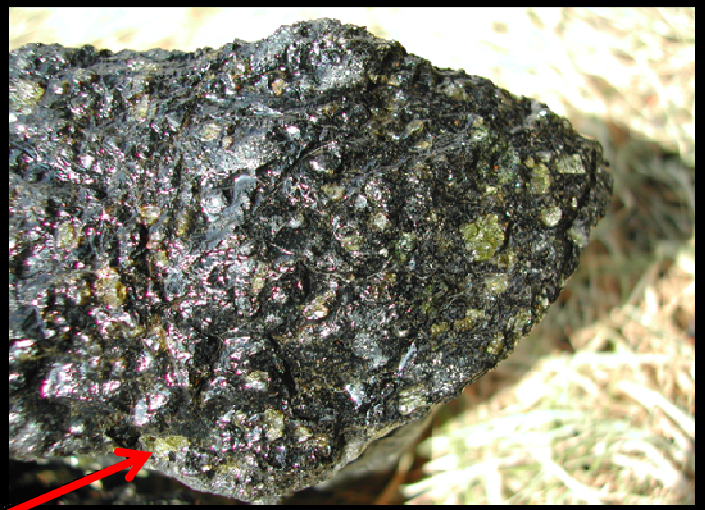


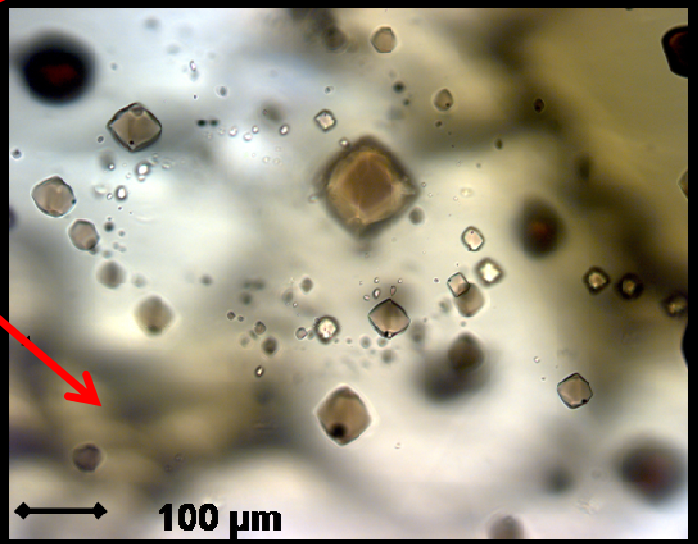
Photo credit: Manuel Moreira.

From Moreira, 2013, Noble gas constraints on the origin and evolution of Earth's volatiles

olivine with melt inclusions from Icelandic picrite





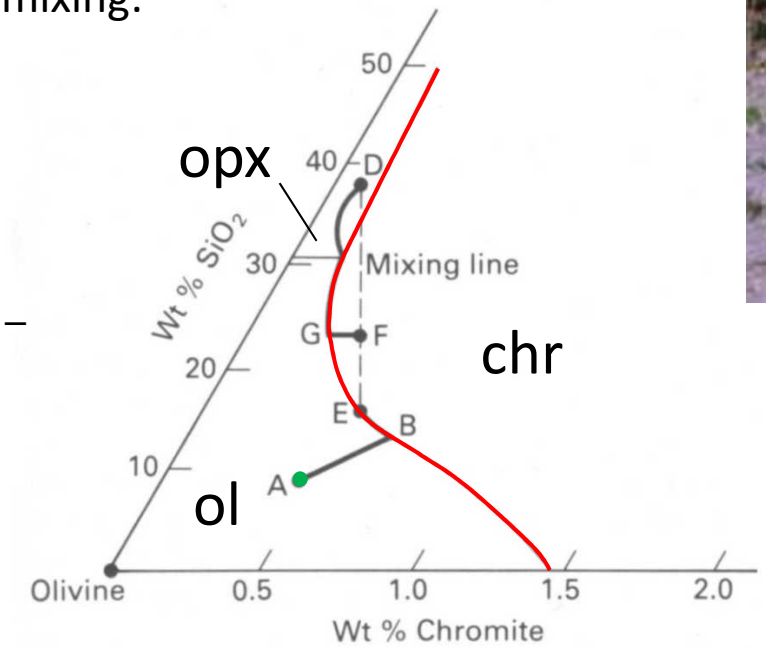


(Petrological) Consequences of mixing (and assimilation):

- Change in *chemical composition* can produce a change in *phase equilibria* relations

Example: Formation of massive chromite layers by pure chromite crystallisation from a melt produced by mixing:

Ternary phase diagram ol – opx - chr



Modified from Irvine (1977)

*Chromite layers in **anorthosite** (plagioclase layers) in the **Bushveld Complex**, South Africa (from: www.mineralsocal.org/bulletin/images/2006_s10.jpg)*

Element mixing:

Conservation of mass: **Two-component** mixing equation:

$$C_M^i M_M = C_A^i M_A + C_B^i M_B$$

Defining: $M = M_A + M_B = 1$

and: $f = \frac{M_A}{M_A + M_B} = \frac{M_A}{M_M}$

C^i_M = *Concentration of element* ***i*** *in the* ***mixture***
C^i_A = *Concentration of element* ***i*** *in* ***component A***
C^i_B = *Concentration of element* ***i*** *in* ***component B***
M_M = *Mass of the* ***mixture***
M_A = *Mass of component A*
M_B = *Mass of component B*

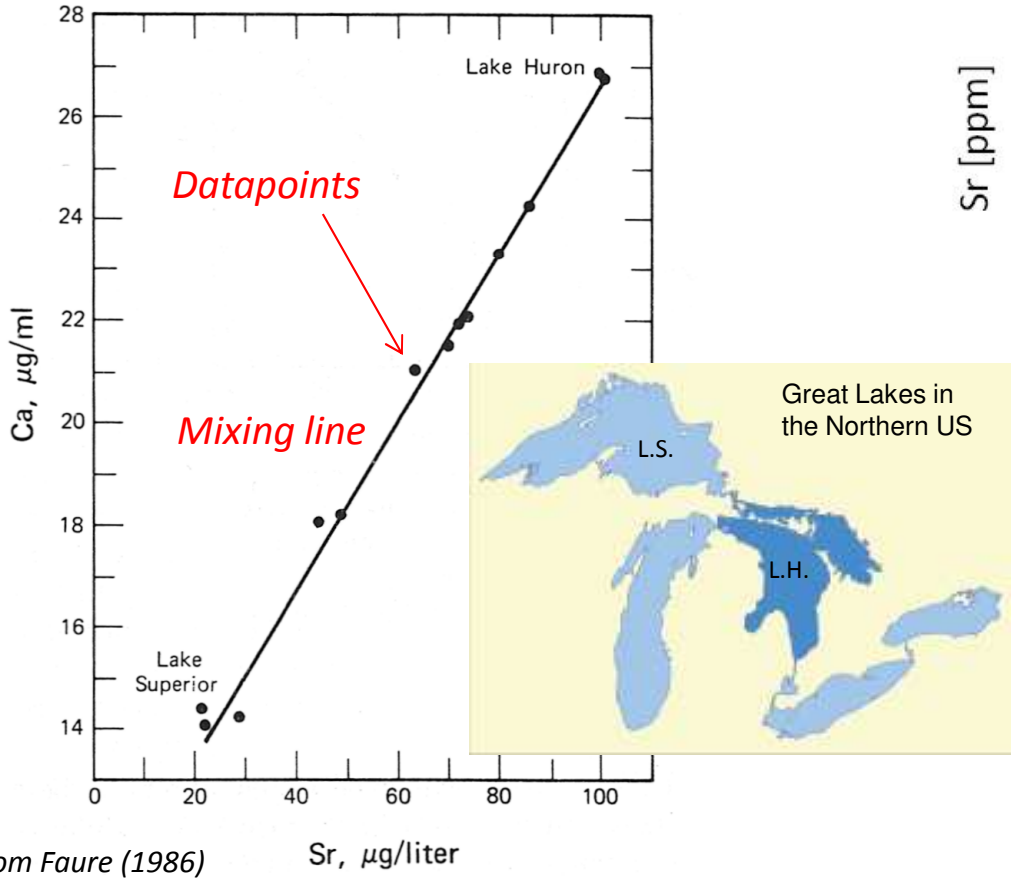
f = *Portion of component* ***A*** *in the mixture (0-1)*

Yields: $$C_M^i = C_A^i f + C_B^i (1 - f)$$

Two-component mixing equation

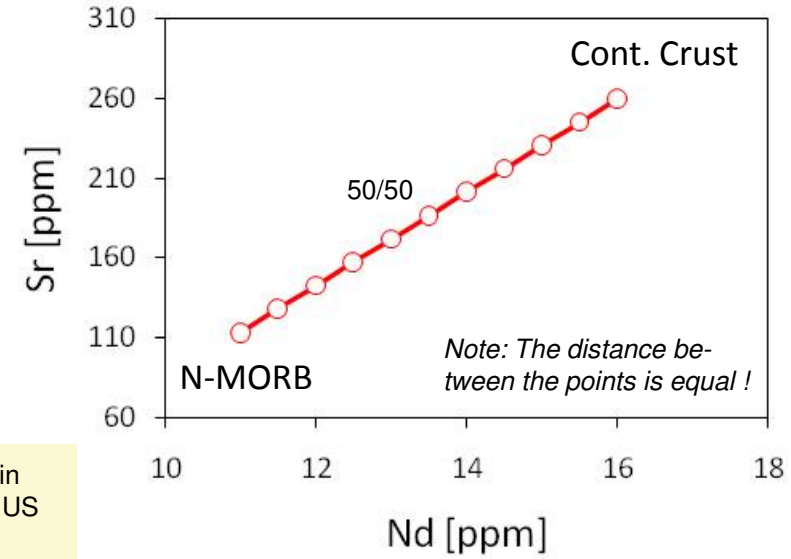
Element mixing - Examples:

Mixing water from Lake Huron & Lake Superior



From Faure (1986)

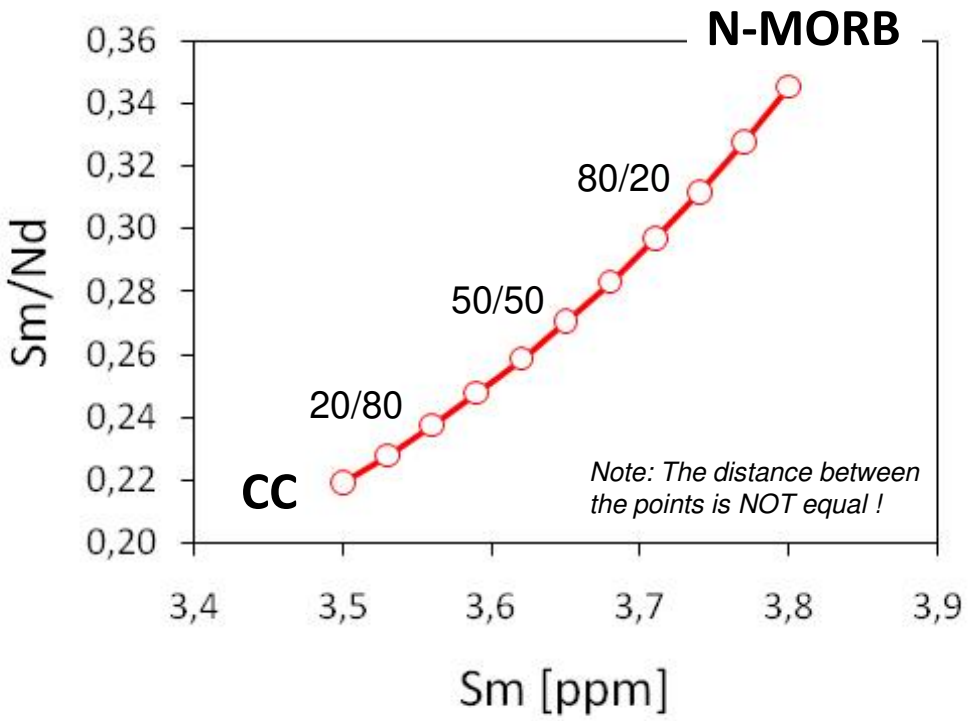
Mixing N-MORB and Continental Crust



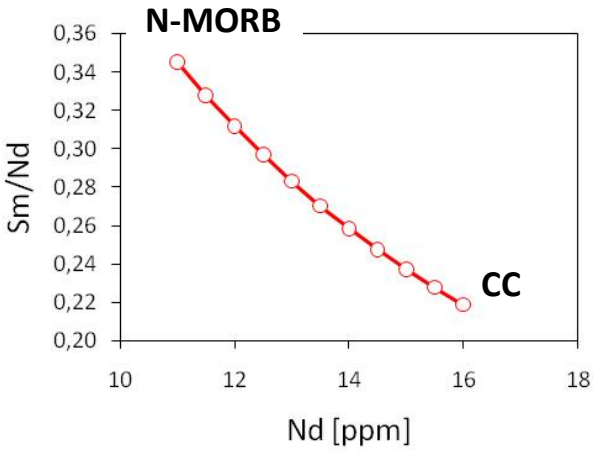
Element – element mixing in a two component system results in a straight mixing line

Element mixing:

Example: Element ratio – element mixing lines



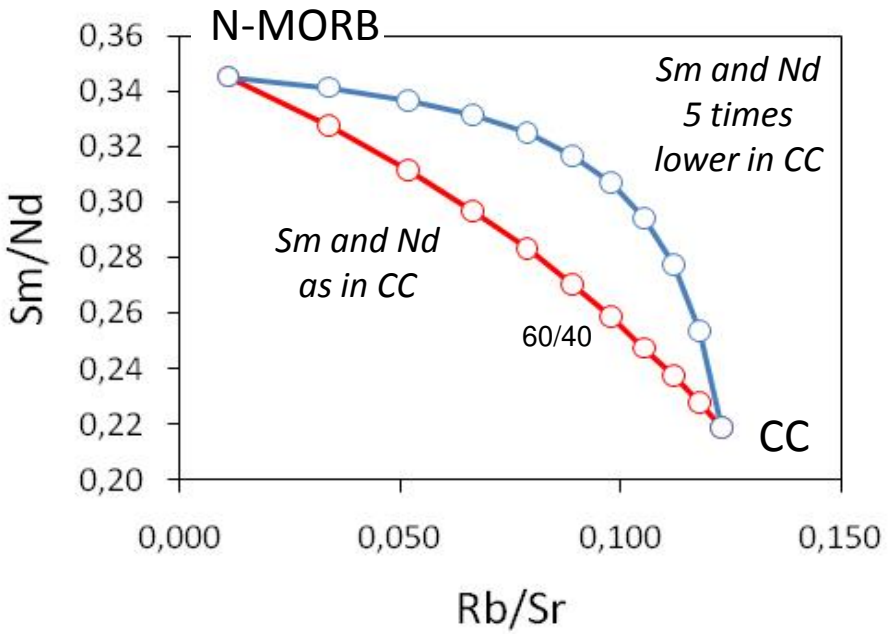
Element ratio – element mixing in a two component system results in a mixing hyperbola



Note that the curvature of the mixing line is a function of the concentration difference between both components!

Element mixing:

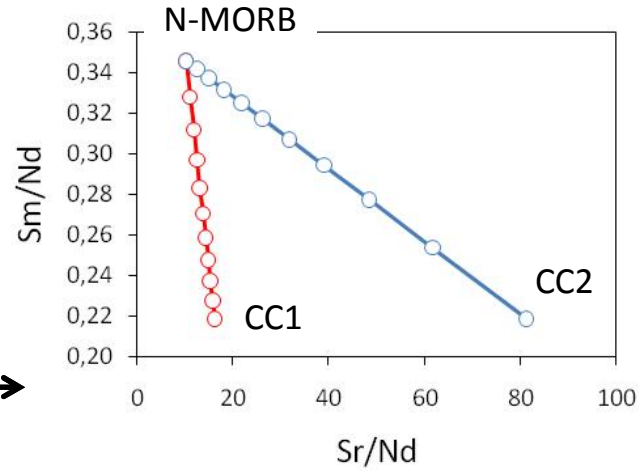
Example: Element ratio – element ratio mixing lines



Element ratio – element ratio mixing in a two component system results also in a mixing hyperbola.

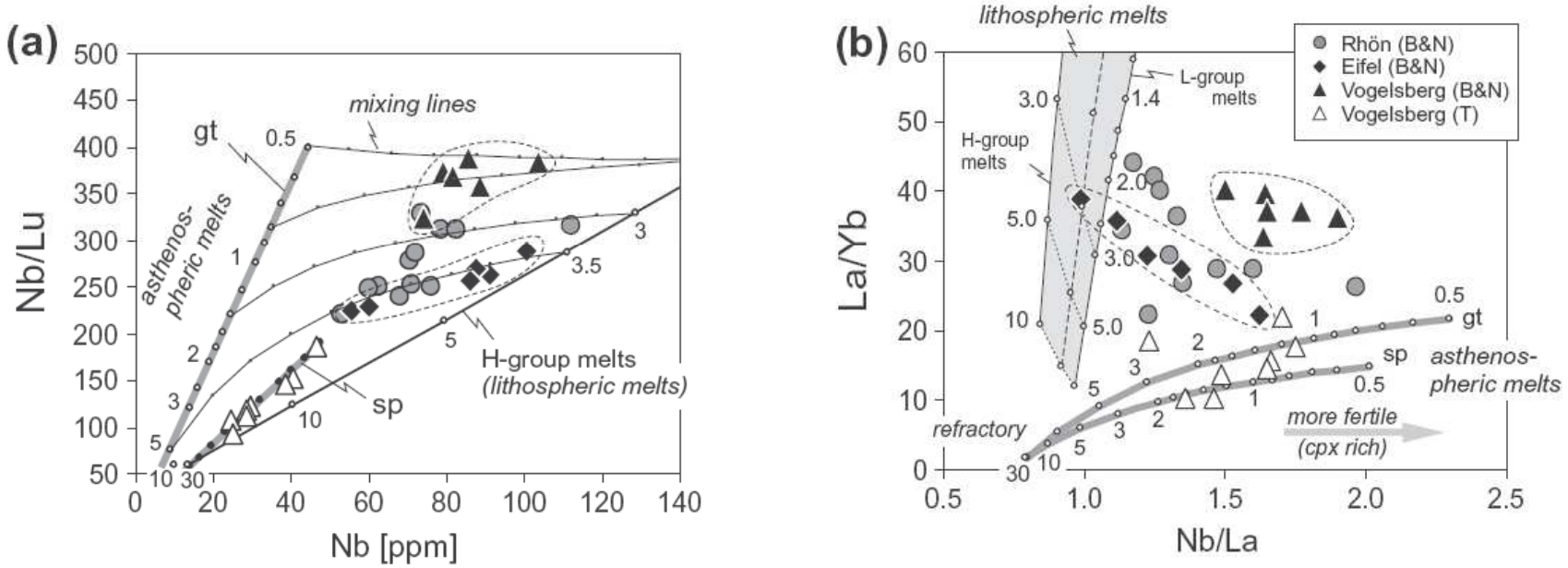
The curvature of the mixing line is a function of the concentration difference between the two components.

NOTE: If the same element is in the denominator of both the X- and Y-axis in such plots, the mixing line becomes a **straight line**!



Mixing processes during magma genesis:

Example: Combined melting and mixing



Composition of **continental basalts** from different regions in Central Germany can be explained by **partial melting** of **garnet** and **spinel** peridotite and **subsequent mixing** of such melts (from *Pfänder et al., 2012, GCA*).

Isotope – element mixing:

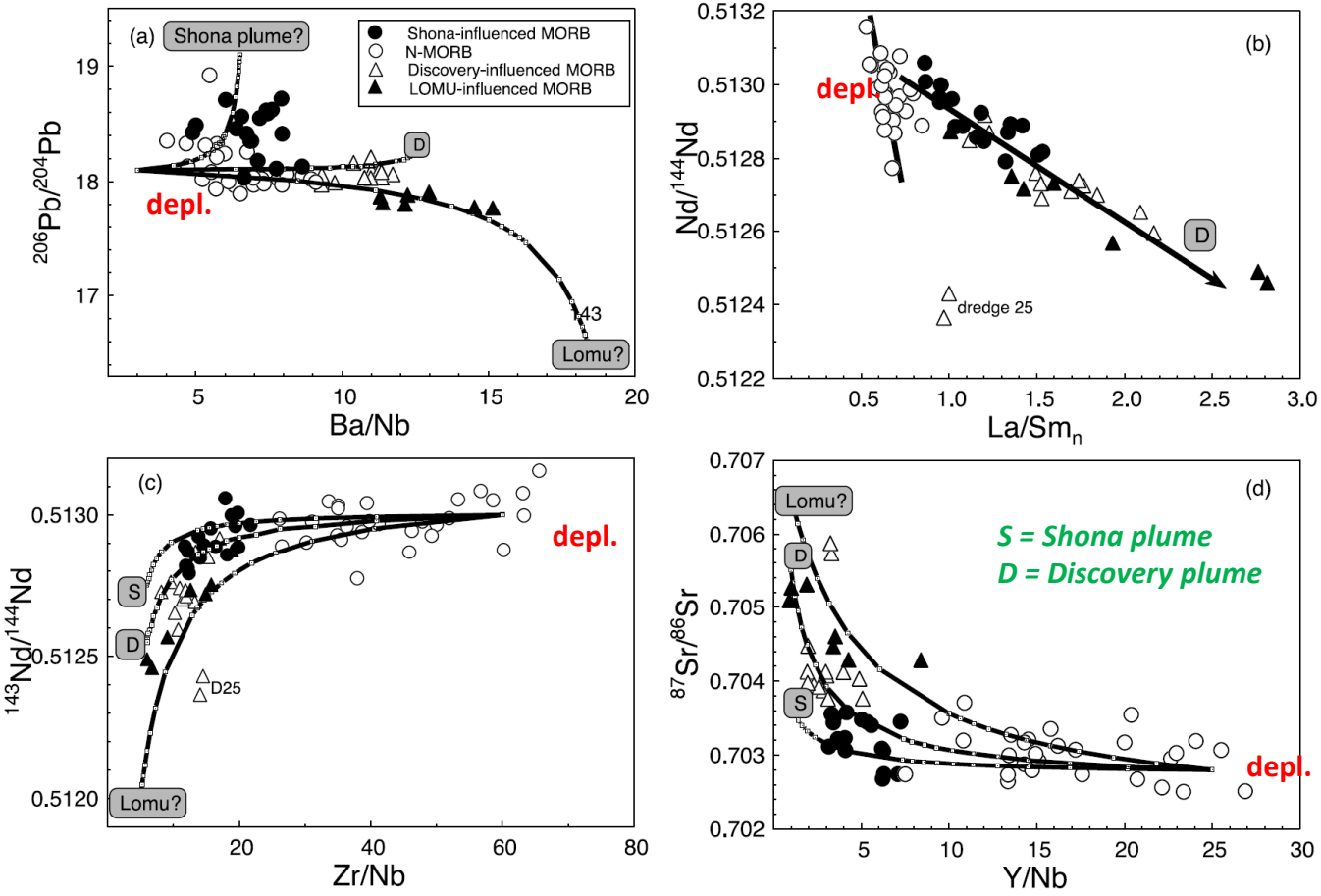
Isotope mixing equation for **two components** (e.g. basaltic magma and continental crust) having different **concentrations** of **element i** and different **isotope ratios** of **element i**:

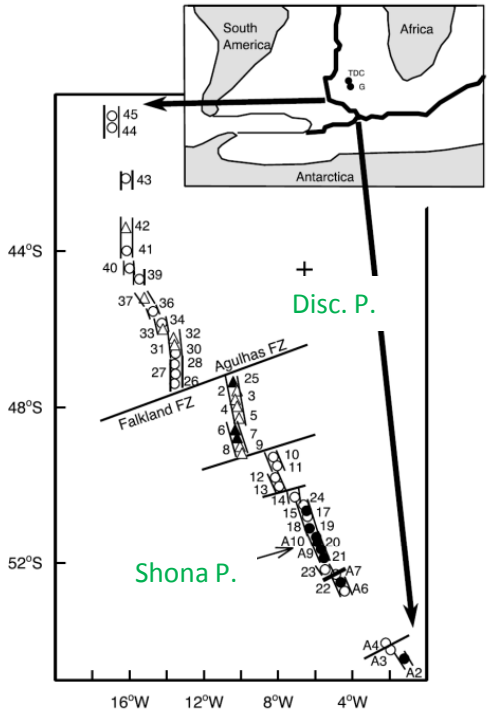
$$R^i_M = \frac{C^i_A}{C^i_M} R^i_A \, f + \frac{C^i_B}{C^i_M} R^i_B \, (1 - f)$$

R^i_M = *Isotope ratio of element i (e.g.* $^{143}Nd/^{144}Nd$*) in the* ***mixture***
R^i_A = *Isotope ratio of element i in* ***component A***
R^i_B = *Isotope ratio of element i in* ***component B***
C^i_M = *Concentration of element* ***i*** *(e.g. Nd) in the* ***mixture***
C^i_A = *Concentration of element* ***i*** *in* ***component A***
C^i_B = *Concentration of element* ***i*** *in* ***component B***
f = *Portion of component A in the mixture (0-1)*

Isotope – element mixing - example:

Mixing trajectories calculated between N-MORB and different „plume“ compositions





sample locations

From: ***Le Roux et al., 2002, EPSL:*** *Mantle heterogeneity beneath the southern Mid-Atlantic Ridge: trace element evidence for contamination of ambient asthenospheric mantle*

Isotope – element mixing:

$$R^i_M = \frac{C^i_A}{C^i_M} R^i_A f + \frac{C^i_B}{C^i_M} R^i_B (1-f)$$

Eliminating **f** by using $C^i_M = C^i_A f + C^i_B (1-f)$

describes $\mathbf{R^i_M}$ solely as a function of $\mathbf{1/C^i_M}$:

$$R^i_M = \underbrace{\frac{C^i_A C^i_B (R^i_B - R^i_A)}{C^i_M (C^i_A - C^i_B)}}_{m} + \underbrace{\frac{(C^i_A R^i_A - C^i_B R^i_B)}{C^i_A - C^i_B}}_{b}$$

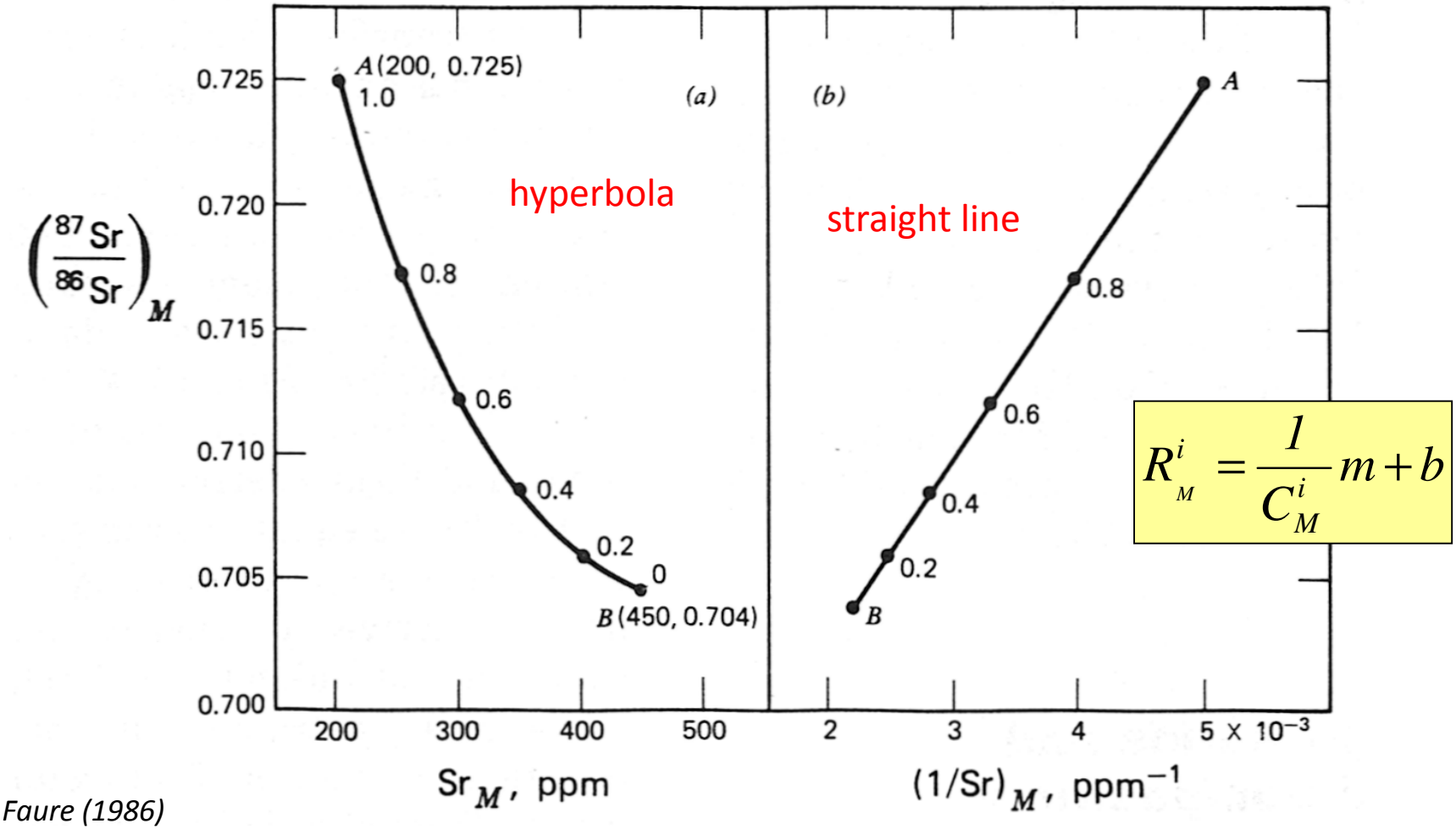
By merging all constants, one yields: $R^i_M = \frac{1}{C^i_M} m + b$

This is a straight line in coordinates of $\mathbf{R^i_M}$ and $\mathbf{1/C^i_M}$!

(Note, that C^i_M itself is a function of f !!!)

Isotope – element mixing:

Example: Isotope ratio – element mixing lines



From Faure (1986)

Isotope – isotope mixing:

If only the **isotope variation in a mixture** is of interest, *(i.e. the concentration of an element in the mixture is not required)*, a more generalized isotope mixing equation can be applied:

$$R^i_M = \frac{R^i_A C^i_A f + R^i_B C^i_B (1-f)}{C^i_A f + C^i_B (1-f)}$$

Note that C^i_M is missing here!

R^i_M = *Isotope ratio of element i (e.g. $^{143}Nd/^{144}Nd$) in the* ***mixture***
R^i_A = *Isotope ratio of element i in* ***component A***
R^i_B = *Isotope ratio of element i in* ***component B***
C^i_A = *Concentration of element* ***i*** *in* ***component A***
C^i_B = *Concentration of element* ***i*** *in* ***component B***
f = *Portion of component A in the mixture (0-1)*

Isotope mixing arrays

Example: Lava samples from Heard Island

South-Africa

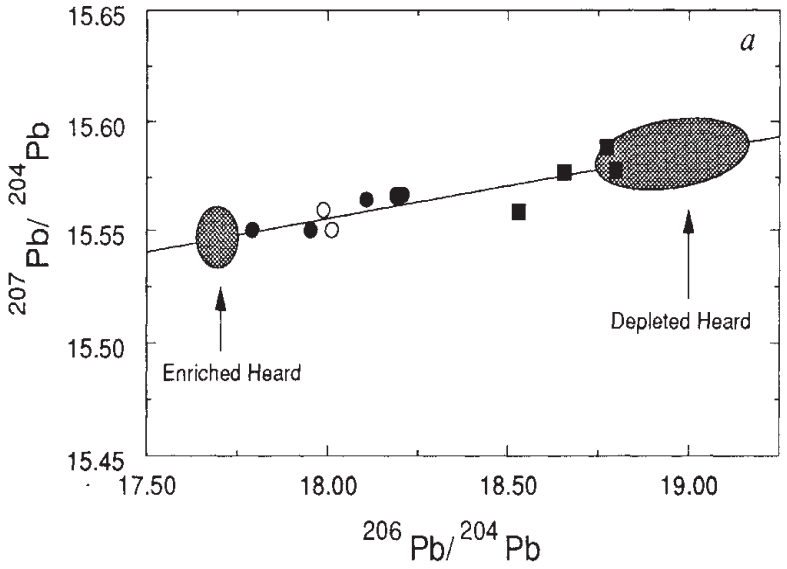
Australia

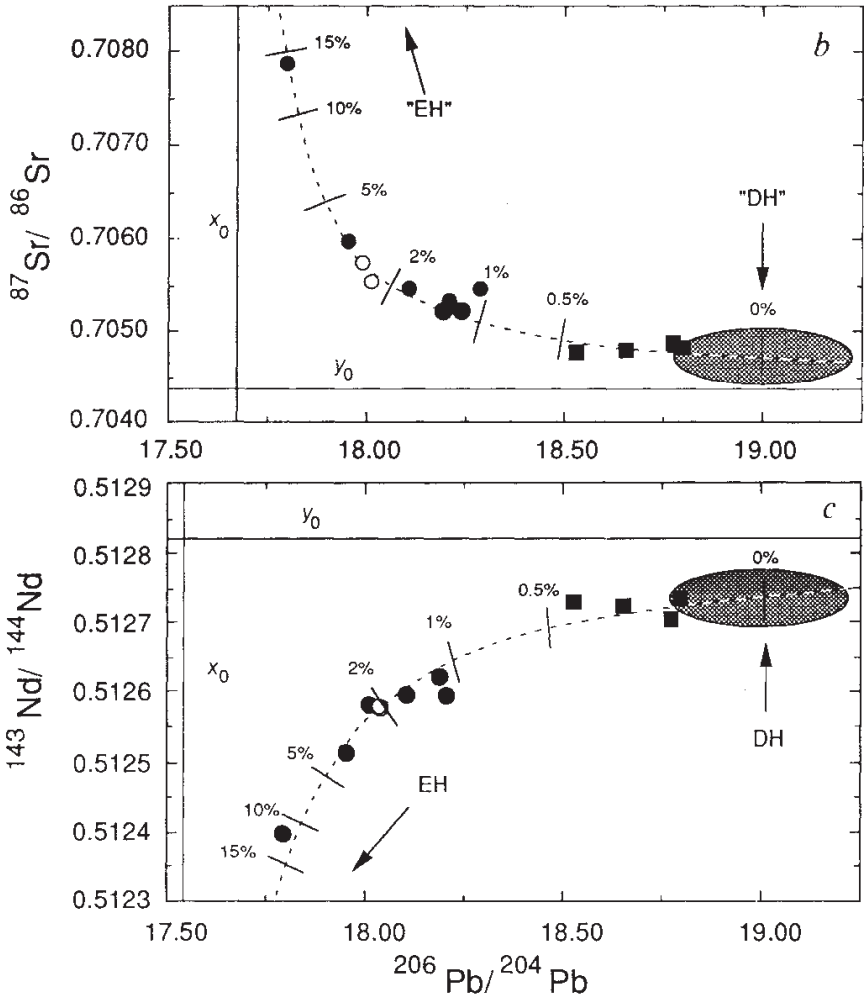
Antarctica

Isotope – isotope mixing:

$$R_M^i = \frac{R_A^i C_A^i f + R_B^i C_B^i (1-f)}{C_A^i f + C_B^i (1-f)}$$

The Lava samples from Heard Island show a strong variation in isotope composition that can be fitted by isotope mixing lines! **This indicates** (only!) **two mantle components,** an enriched and a depleted one!



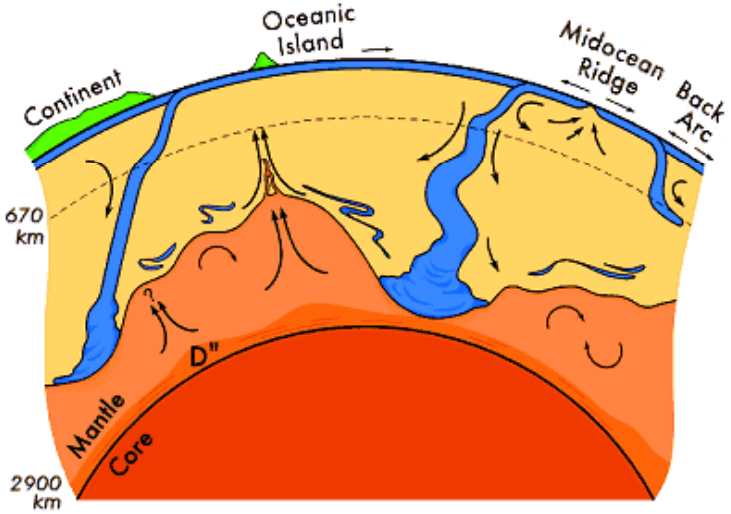


How do these different mantle reservoirs form?

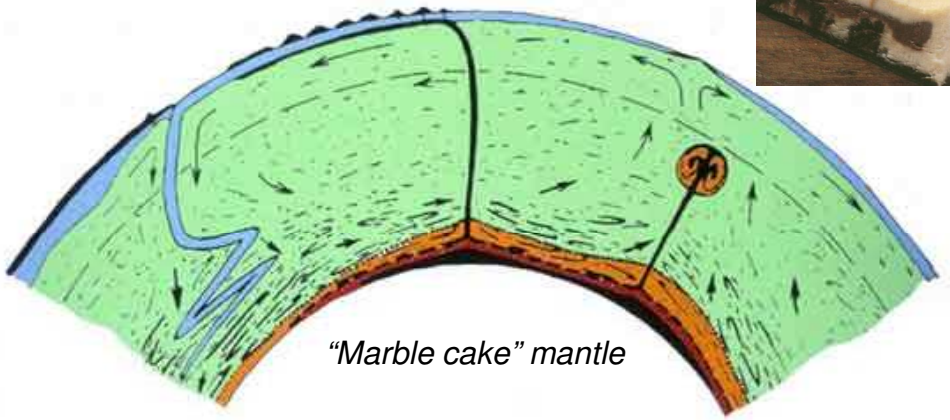
From Barling & Goldstein, 1990, Nature 348, 59-62

How do isotopically distinct reservoirs form?

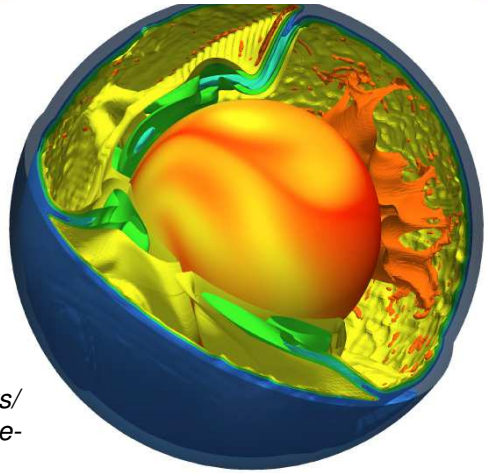
Critical parameters: Parent – daughter fractionation & TIME



Kellog et al., 1999, Science



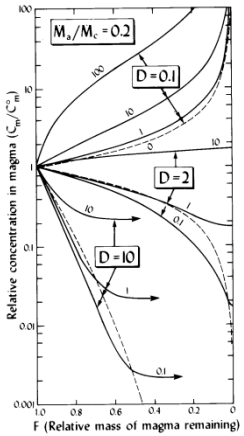
"Marble cake" mantle

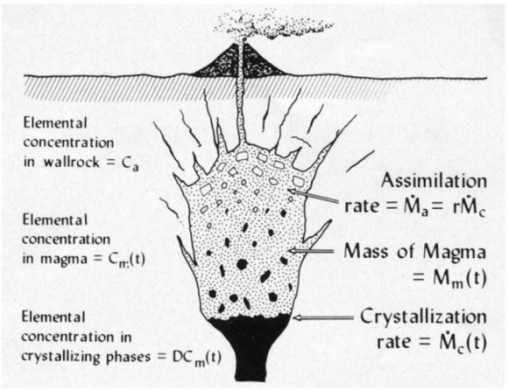


http://www.laboratoryequipment.com/news/2012/02/model-realistically-simulates-plate-tectonics

Chapter 5

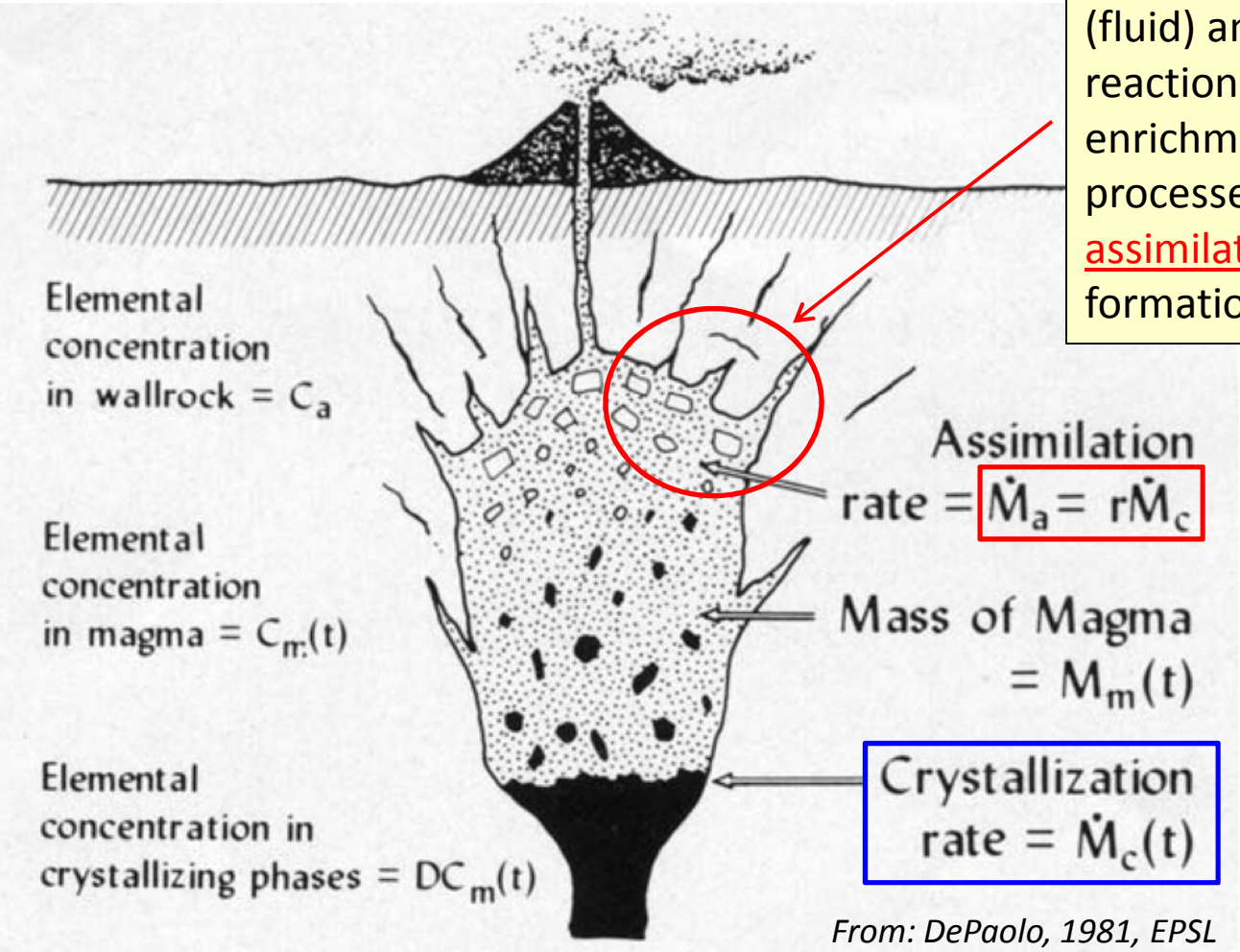
Assimilation and fractional crystallisation (AFC)





AFC processes - model

Contact zone between melt (fluid) and wallrock. Chemical reactions, element exchange, enrichment/depletion processes, wallrock assimilation, crystallisation, formation of deposits, ...



From: DePaolo, 1981, EPSL

Note: we use C_l instead of C_m (l=liquid, m=magma) !!

AFC processes – equation for trace elements

Evolution of **melt composition** for trace element **i**

$$\frac{C_l}{C_l^0} = F^{-z} + \left(\frac{r}{r-1}\right)\frac{C_a}{z\,C_l^0}(1-F^{-z})$$

Where $r = \frac{\dot{M}_a}{\dot{M}_c}$ and $z = \frac{r + \overline{D}^i - 1}{r-1}$

r = *assimilation rate relative to fractional crystallisation rate [mass per time]*
$\dot{M}_a$ = *wall rock assimilation rate [mass per time]*
$\dot{M}_c$ = *fractional crystallisation rate [mass per time]*
F = *portion of remaining melt (at start F=1, i.e. 100% melt)*
C_l = *concentration of the element in the liquid, i.e. the magma*
C_a = *concentration of the element in the assimilated solid, i.e. the wallrock*

From: DePaolo, 1981, EPSL

AFC processes – dependency on the r - Parameter

By varying the **r – Parameter**, the type of the process changes:

$$r = \frac{\dot{M}_a}{\dot{M}_c}$$

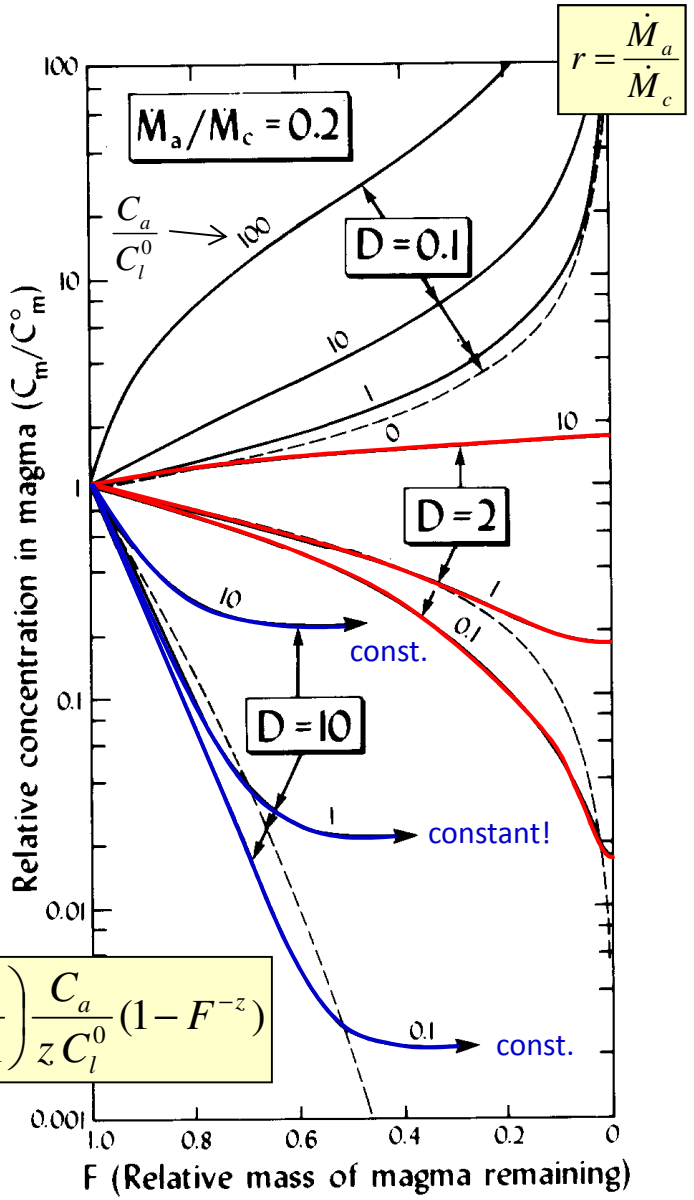
r = 0	Pure **fractional crystallisation**
r = 1	The AFC process is a zone refining process, i.e. the mass of the magma remains constant
< 1	**The AFC process is a combination of zone refining and fractional crystallisation**
r → ∞	The AFC process becomes a simple binary **mixing process** (only assimilation)

AFC processes – melt evolution

(for trace elements)

Evolution of the melt composition as a function of **F** for different **D-values** and different ratios of C_a/C_l^0 for a given **r – value** of **0.2**

- At high C_a/C_l^0, moderately **compatible elements** get enriched in the magma!!
- Compatible elements reach a **constant concentration**, from which no further depletion is observed!!
  The higher C_a/C_l^0, the higher this concentration!



$$\frac{C_l}{C_l^0} = F^{-z} + \left(\frac{r}{r-1}\right)\frac{C_a}{z\,C_l^0}(1-F^{-z})$$

Note: C_l is the same as C_m (the liquid, or melt composition)

From: DePaolo, 1981, EPSL

AFC processes – equation for isotope ratios

Evolution of an isotope ratio R in the melt

(Assumption: No isotope fractionation between solid and liquid phase!)

$$R_l = \frac{\frac{r}{r-1}\frac{C_a}{z}(1-F^{-z})R_a + C_l^0 F^{-z} R_l^0}{\frac{r}{r-1}\frac{C_a}{z}(1-F^{-z}) + C_l^0 F^{-z}}$$

$$z = \frac{r + \overline{D}^i - 1}{r-1}$$

$$r = \frac{\dot{M}_a}{\dot{M}_c}$$

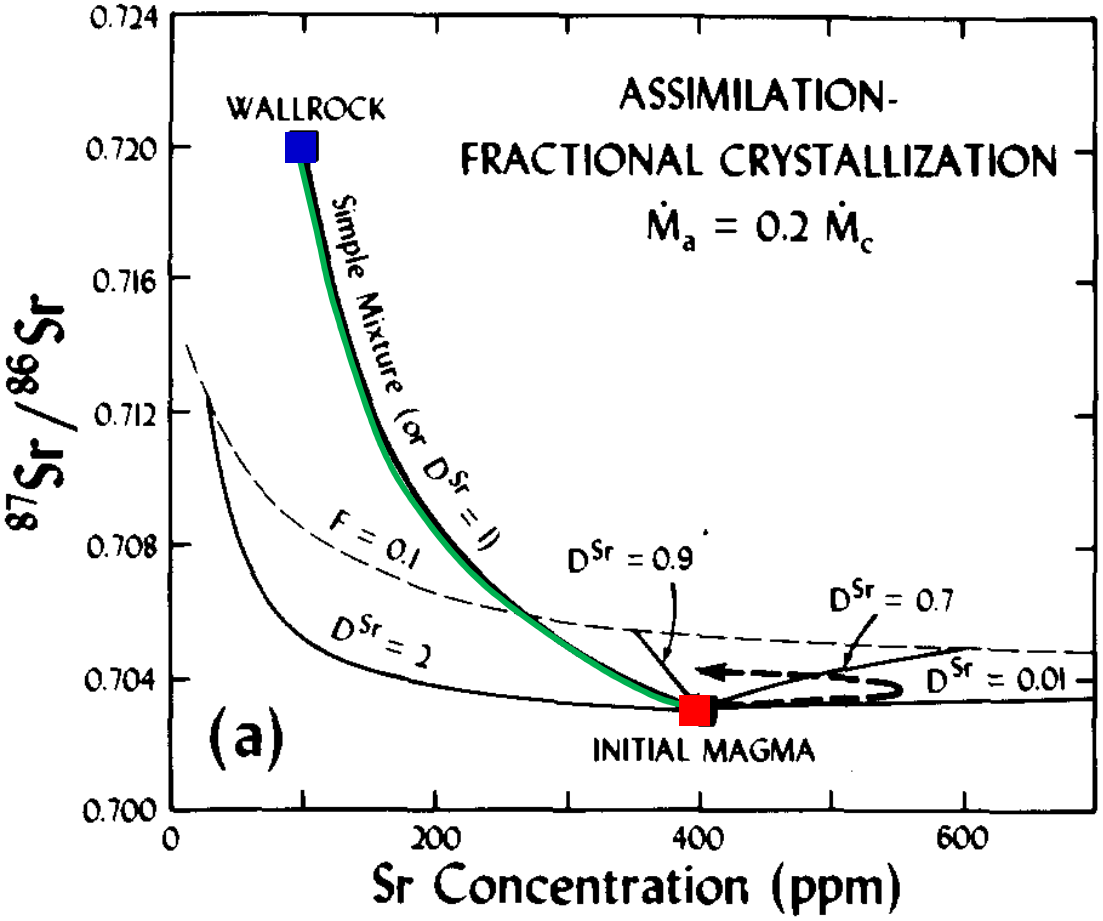
From: DePaolo, 1981, EPSL

R_l = Isotope ratio of an element in the liquid (magma)
R_a = Isotope ratio of this element in the assimilant (wallrock)
R_l^0 = Initial isotope ratio of this element in the liquid (melt), i.e. **before** AFC has started
r = assimilation rate relative to fractional crystallisation rate
F = portion of melt remaining (at start F=1)
C_l^0 = concentration of the element in the liquid, i.e. the **magma**, **before** AFC has started
C_a = concentration of the element in the assimilated solid, i.e. the **wallrock**

Note: This equation can also be used for normalized isotope ratios such as ε_{Nd} !!

AFC processes – isotope ratio evolution (in a melt)

$^{87}Sr/^{86}Sr$ evolution of a magma during AFC for different **D^{Sr}-values** in the fractionating assemblage at **r = 0.2**



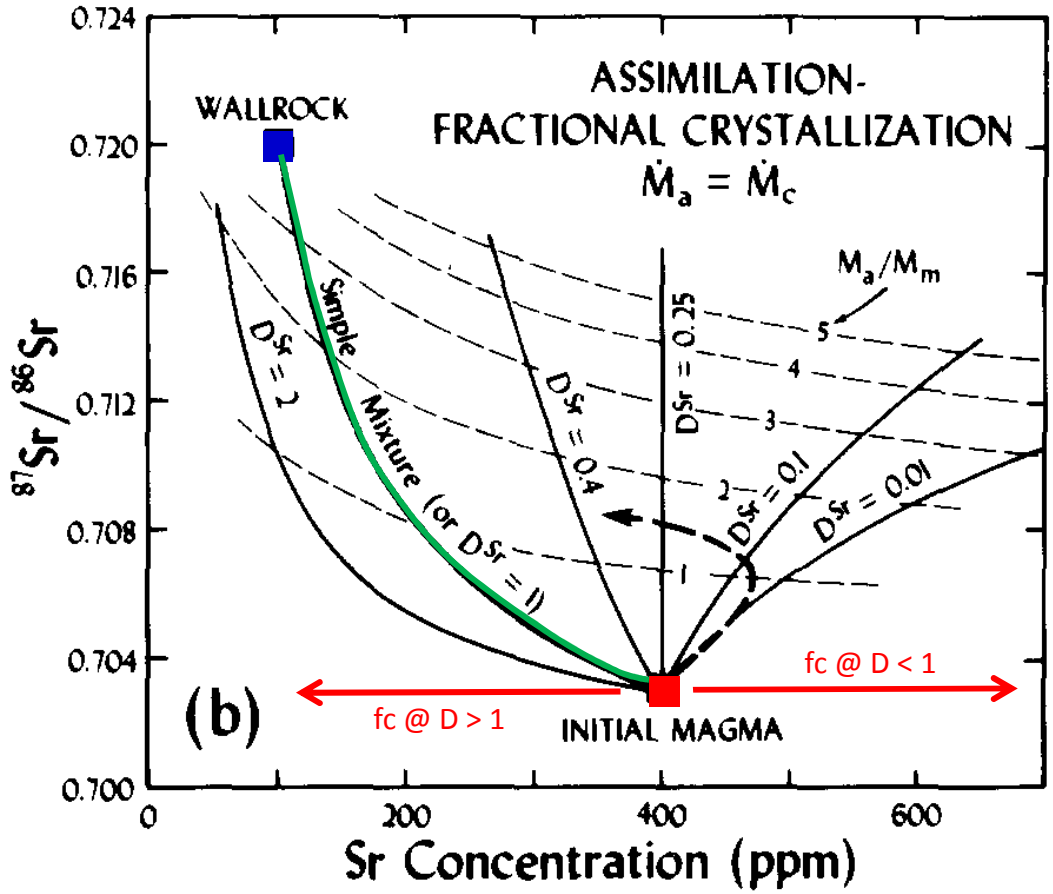
$$r = \frac{\dot{M}_a}{\dot{M}_c} = 0.2 = \frac{1}{5}$$

In this case, **fractional crystallization** dominates the AFC process and the volume of the melt decreases, i.e., F becomes < 1 over time
(realistic scenario...)

From: DePaolo, 1981, EPSL

AFC processes – isotope ratio evolution

$^{87}Sr/^{86}Sr$ evolution of a magma during AFC for different **D^{Sr}-values** in the fractionating assemblage at **r = 1.0** (pure zone refining!)



$$r = \frac{\dot{M}_a}{\dot{M}_c} = 1.0 = \frac{1}{1}$$

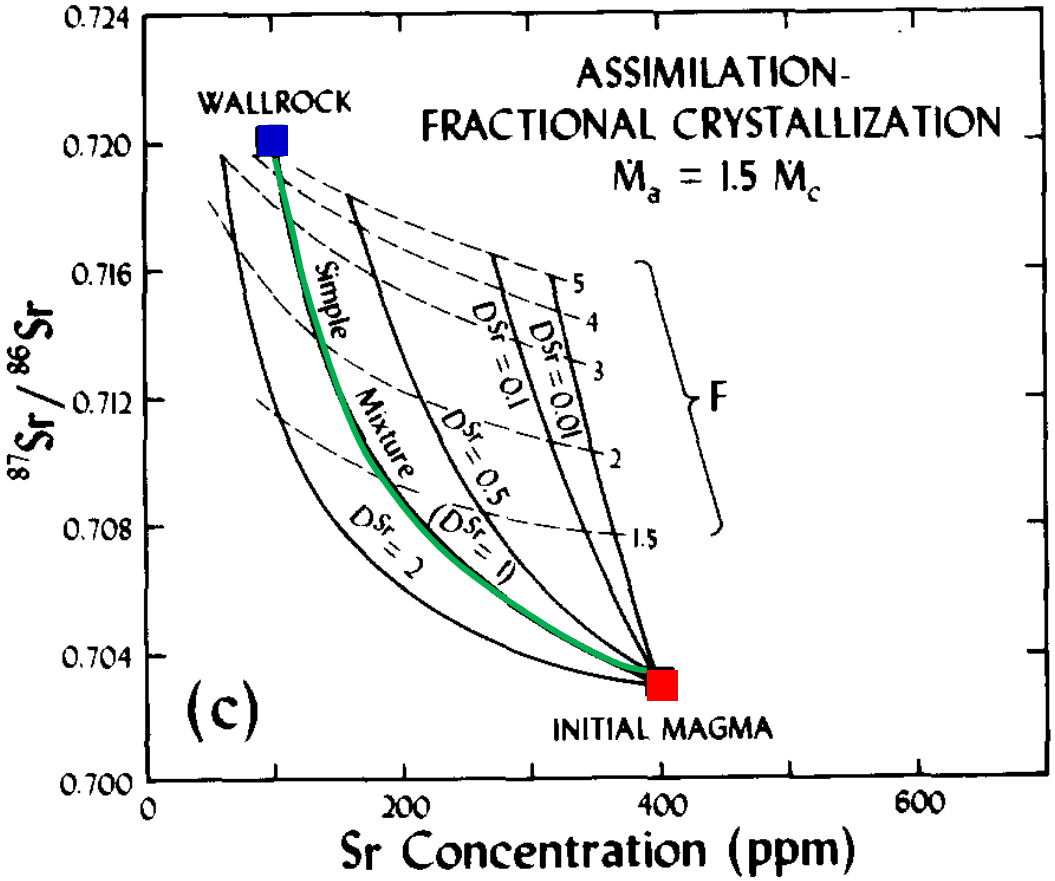
In this special case F remains constant, i.e. is always 1 (zone refining)!

Note that the melt develops AWAY from the wallrock composition for D<1!

From: DePaolo, 1981, EPSL

AFC processes – isotope ratio evolution

$^{87}Sr/^{86}Sr$ evolution of a magma during AFC for different **D^{Sr}-values** in the fractionating assemblage at **r = 1.5**



$$r = \frac{\dot{M}_a}{\dot{M}_c} = 1.5$$

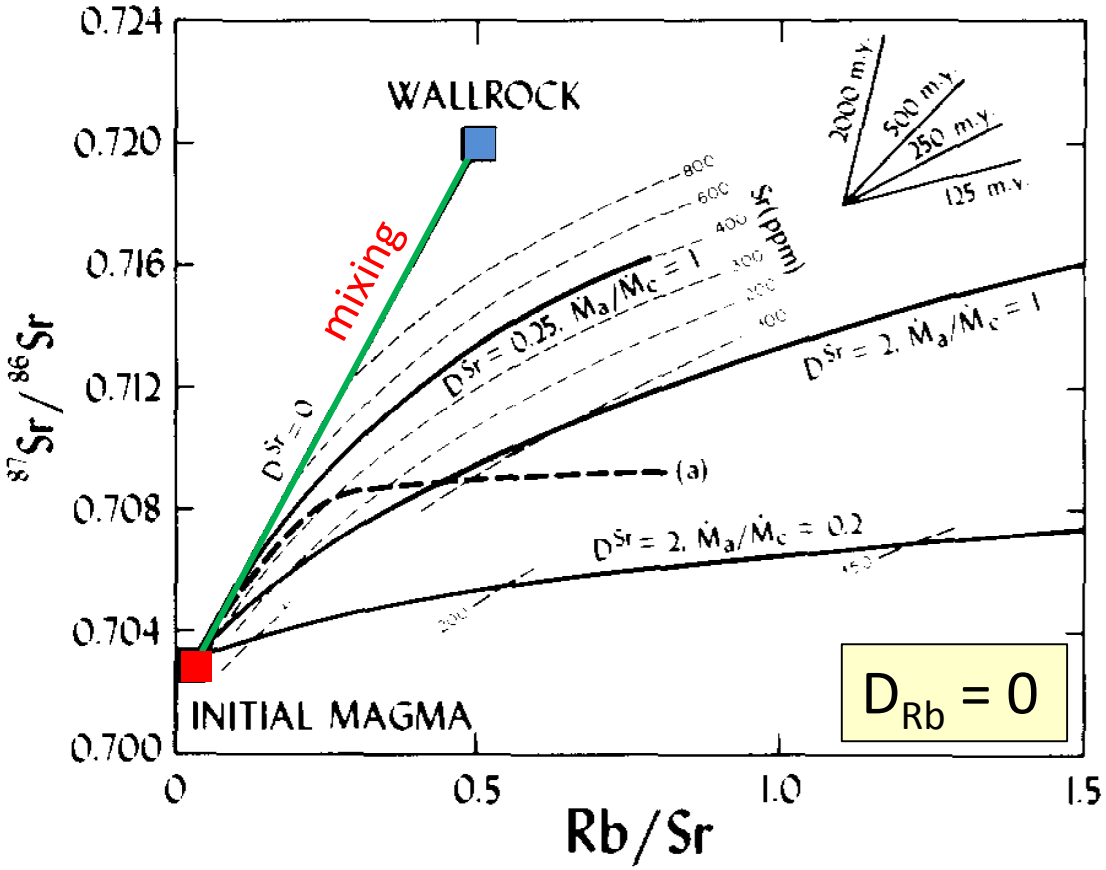
In this case, **wallrock assimilation** dominates the AFC process and the volume of the melt increases, i.e. F becomes > 1
(energetically rather unrealistic...)

Therefore, the duration of the process is limited by energy constraints!

From: DePaolo, 1981, EPSL

AFC processes – isotope evolution

$^{87}Sr/^{86}Sr$ evolution of a magma during AFC for different **D^{Sr}-values** in the fractionating assemblage at **r = 1 and r = 0.2** (D^{Rb} = 0)

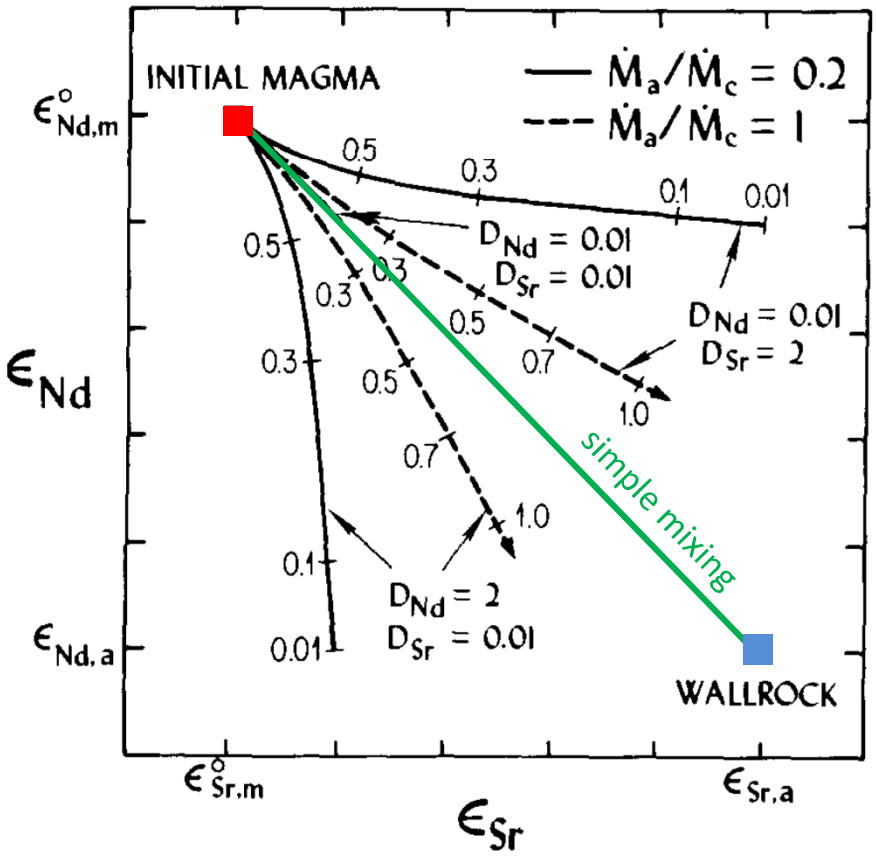


Simple mixing produces a straight line (and thus may pretend an *isochron*!), whereas AFC produces curved lines where the curvature is a function of D^{Sr} and r

From: DePaolo, 1981, EPSL

AFC processes – isotope - isotope evolution

Evolution of a magma during AFC for different D^{Sr}- and D^{Nd}-values in the fractionating assemblage at **r = 1** and **r = 0.2** and assuming equal Nd and Sr concentrations in the magma and wallrock



Simple mixing again produces a straight line, whereas AFC produces curved lines where the curvature is a function of the **D-values** and **r**

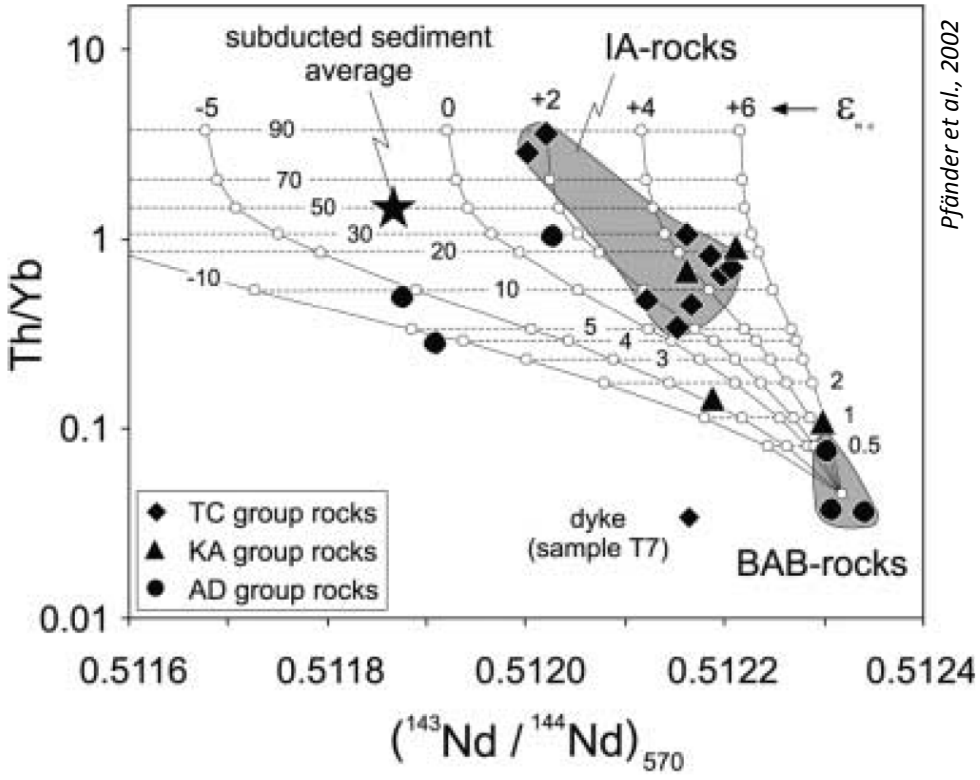
Note that the isotope ratio of the compatible element shifts stronger than that of the incompatible one!

From: DePaolo, 1981, EPSL

AFC process - example

Evolution of a magma during AFC for different ε_{Nd} values at a given Th/Yb ratio in the assimilated material (sediment).

High Th/Yb at a given ε_{Nd} can only be achieved for high assimilation and fractionation rates!



That‘s it!