

## Trace element fractionation: Implications for geochronology and isotope geochemistry

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**No Geochronology  
without  
trace element fractionation!**

## What is trace element fractionation?

**To change a concentration  
ratio of two elements by a  
specific process!**

Trace elements are:

Chemical elements that occur in only very low concentrations in natural rocks and minerals (in the ppm range) – e.g. Nb, Th, U, Hf, Ta ...

Other important trace elements: Rare Earth Elements, REE: La, Ce, Nd, Sm, Eu, .... Lu

But there are exceptions: e.g. Zircon, Monazite

Periodic table of the elements

The periodic table shows elements from Hydrogen (H) to Oganesson (Og). Several elements are circled in red, including Potassium (K), Calcium (Ca), Rubidium (Rb), Strontium (Sr), Yttrium (Y), Zirconium (Zr), Niobium (Nb), Molybdenum (Mo), Technetium (Tc), Ruthenium (Ru), Rhodium (Rh), Palladium (Pd), Silver (Ag), Cadmium (Cd), Indium (In), Tin (Sn), Antimony (Sb), Tellurium (Te), Iodine (I), Xenon (Xe), Cesium (Cs), Barium (Ba), Lanthanum (La) through Lutetium (Lu), Hafnium (Hf), Tantalum (Ta), Tungsten (W), Rhenium (Re), Osmium (Os), Iridium (Ir), Platinum (Pt), Gold (Au), Mercury (Hg), Thallium (Tl), Lead (Pb), Bismuth (Bi), Polonium (Po), Astatine (At), and Radon (Rn). The bottom row includes Actinides (Ac) through Lawrencium (Lr).

## Compatibility - Incompatibility

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

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



Fractionation of trace element ratios:

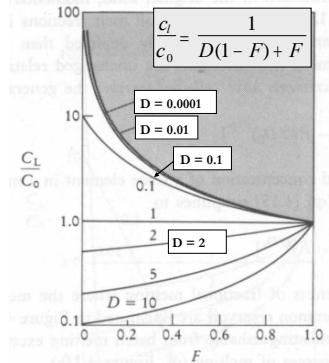
The concentration of a trace element in a melt is a function of D and the degree of melting (F):

$$c_l = \frac{c_0}{D(1-F) + F} \quad \text{equilibrium melting}$$

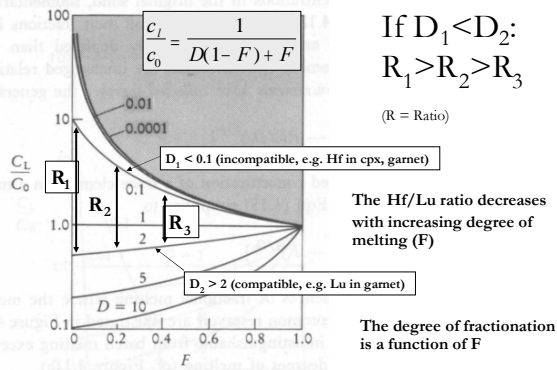
c = concentration (l=liquid, 0=in the solid before (!) melting)  
 D = partition coefficient  
 F = degree of melting (between 0 and 1)

Concentration of a trace element in a melt as f(F):

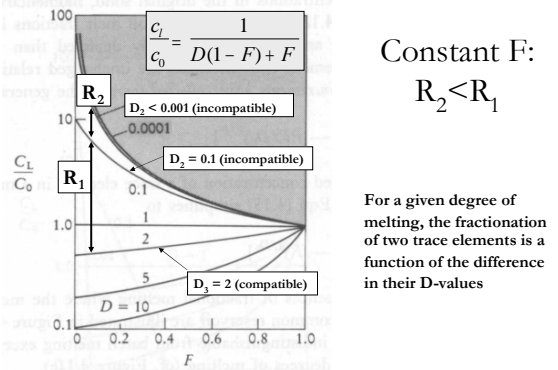
Valid for equilibrium melting and equilibrium crystallisation only!



Fractionation of trace element ratios:

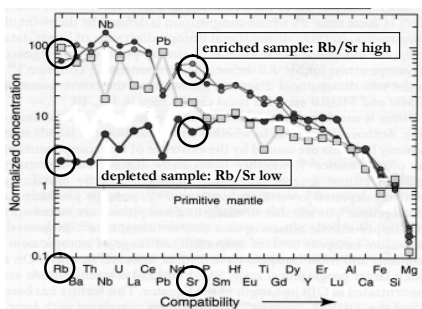


Fractionation of trace element ratios:



Fractionation of trace element ratios:

The larger the distance between parent-daughter elements in a Spidergram, the stronger the fractionation:



Fractionation of trace element ratios:

Using the equation shown before, the concentration ratio of two trace elements can be calculated as a function of F (here, for example, for Rb/Sr), assuming equilibrium melting:

$$\frac{Rb}{Sr} = \frac{c_{Rb}}{c_{Sr}} = \frac{D_{Sr}(1-F) + F}{D_{Rb}(1-F) + F} \cdot \frac{c_{Rb}^0}{c_{Sr}^0}$$

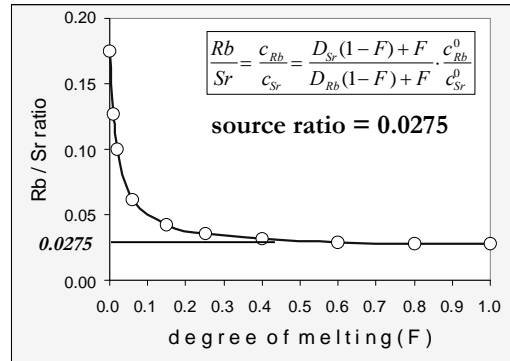
Fractionation of trace element ratios:

$$\frac{Rb}{Sr} = \frac{c_{Rb}}{c_{Sr}} = \frac{D_{Sr}(1-F) + F \cdot c_{Rb}^0}{D_{Rb}(1-F) + F \cdot c_{Sr}^0}$$

Example:

Source composition:  
 Initial Rb concentration ( $c_0 = 0.5$  ppm)  
 Initial Sr concentration ( $c_0 = 18.2$  ppm)  
 this yields an initial Rb/Sr ratio = 0.027  
 $D_{Sr} = 0.12$   
 $D_{Rb} = 0.018$

Fractionation of trace element ratios:



To summarise:

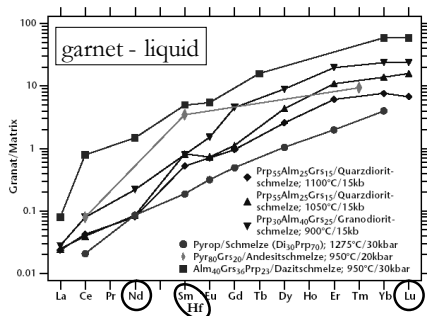
- 1) The lower the degree of melting, the stronger is the fractionation between two trace elements (e.g. between Sm and Nd, Lu and Hf, Rb and Sr, U and Pb, ....).
- 2) The larger the difference in the D-values between two trace elements, the stronger is the fractionation between them (only, if the D-values are not too far away from 1!)

However:

Not only melting fractionates trace element ratios relevant for Geochronology!

Crystallisation of mineral phases with extreme D-values for specific trace elements also strongly fractionate trace element ratios!

Trace element fractionation by different mineral phases: Example 1: Garnet



This means:

Garnet strongly fractionates the REE.

Therefore, garnet bearing systems (e.g. garnet schists, garnet bearing gneises, amphibolites) can be dated by the Lu-Hf and Sm-Nd method!

Trace element fractionation by different mineral phases: Example 2: Mica

$D_{Sr}$  in Biotite  $\sim 0.4$  (i.e. incompatible)

$D_{Rb}$  in Biotite  $\sim 3.2$  (i.e. compatible)

Rb/Sr in mica in equilibrium with a „rhyolitic whole rock “ with Rb/Sr = 1:

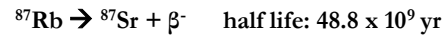
$$\frac{Rb}{Sr} = \frac{D_{Rb} \times c_l^{Rb}}{D_{Sr} \times c_l^{Sr}} = \frac{3.2 \times 1}{0.4 \times 1} = 8$$

Rb/Sr in mica significantly higher than in whole rock!

Application to isotope evolution:

Example: The Rb-Sr Geochronometer:

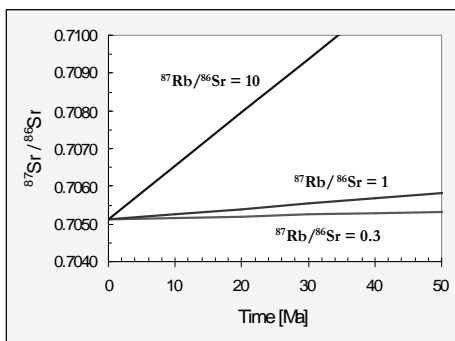
Decay of  $^{87}Rb$  to  $^{87}Sr$ :



Increase in radiogenic  $^{87}Sr$  relative to constant  $^{86}Sr$  over time is proportional to the initial Rb/Sr ratio

Application to isotope evolution:

Rb-Sr fractionation:  $^{87}Rb$  decays to  $^{87}Sr$ ,  $^{86}Sr$  is constant



Application to isotope evolution:

For age determination by the Rb-Sr method, at least two mineral fractions with different Rb/Sr (and thus  $^{87}Sr/^{86}Sr$ ) ratios are required from a single piece of rock.

Most important:  
The stronger the difference in Rb/Sr, the more precise is the age determination.

This is, of course, also valid for other dating systems!

More generally:

1) The stronger the fractionation between a parent and daughter trace element, the stronger will be the isotopic deviation over time compared to an "unfractionated" reference system (e.g. a meteorite)

2) The longer a fractionation event lies in the past, the stronger is the isotopic deviation compared to an "unfractionated" reference system

Summary I:

- 1) Fractionation of parent-daughter trace element ratios (e.g. Sm/Nd, Lu/Hf, Rb/Sr, U/Pb, Re/Os,....) during geological processes is the basic condition of all geochronological methods
- 2) The stronger the parent-daughter fractionation in a specific mineral phase with respect to the whole rock, the better to obtain precise radiometric ages
- 3) Strong parent-daughter fractionation is obtained for low-degree melting and by crystallisation or growth of specific mineral phases (garnet, mica, zircon, apatite, monazite)

## Summary II:

- 4) Mica (biotite, muscovite, phengite) strongly fractionates Rb/Sr ratios (Rb is compatible, Sr is incompatible), thus mica bearing rocks can be well dated using the Rb-Sr system
- 5) Lu is highly compatible in garnet, Hf is incompatible: Garnet bearing systems can be dated using the Lu-Hf (or the Sm-Nd) system
- 6) Zircon incorporates lots of U, but virtually no Pb: Zircons are ideally suited for U-Pb dating