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

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)
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**Quantitative:**

\[ D = \frac{C_s}{C_l} \]

- **D** = partition coefficient
- Incompatible: \( D \)-value < 1
- Compatible: \( D \)-value > 1

**Example:**

\[ D_{\text{Ni}}^{\text{Ol-Liq.}} = \frac{C_s}{C_l} \sim 5 - 30 \]

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

- Ni in olivine = 10.9 \times 150 = 1635 ppm = 0.16%

**Parameters that control D-values**

- The larger the ionic radius, the more incompatible.
- The higher the ionic charge, the more incompatible.
- D-values are also a function of p,T and composition.

**This yields to the „Spidergram“:**

Trace elements ordered by compatibility:

- Enriched samples (e.g. OIBs)
- Depleted sample (e.g. MORB)

**A real „Spidergram“:**

Trace elements ordered by compatibility:

- Enriched samples (e.g. OIBs)
- Depleted sample (e.g. MORB)
Fractionation of trace element ratios:
The concentration of a trace element in a melt is a function of \(D\) and the degree of melting (\(F\)):

\[
c_l = \frac{c_0}{D(1-F) + F}
\]

\(\text{equilibrium melting}\)

\(c\) = concentration \((l=\text{liquid}, 0=\text{in the solid before (!) melting})\)

\(D\) = partition coefficient

\(F\) = degree of melting (between 0 and 1)

The concentration of a trace element in a melt as \(f(F)\):

\[
c = c_0 \left(1 + \frac{D-1}{1-(D-1)F} \right)^{-1}
\]

\(\text{equilibrium melting and crystallisation only!}\)

\(D = 0.0001\)

\(D = 0.01\)

\(D = 0.1\)

\(D = 2\)

Valid for equilibrium melting and crystallisation only!

Fractionation of trace element ratios:

If \(D_1 < D_2\):

\(R_1 > R_2 > R_3\)

\((R = \text{Ratio})\)

The \(\text{Hf/Lu}\) ratio decreases with increasing degree of melting (\(F\))

The degree of fractionation is a function of \(F\)

Fractionation of trace element ratios:

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

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

\[
\frac{\text{Rb}}{\text{Sr}} = \frac{c_{\text{Rb}}}{c_{\text{Sr}}} = \frac{D_{\text{Rb}}(1-F) + F}{D_{\text{Sr}}(1-F) + F} \frac{c_{\text{Rb}}^0}{c_{\text{Sr}}^0}
\]
Fractionation of trace element ratios:

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
$D_{Rb} = 0.12$
$D_{Sr} = 0.018$

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

$D_{\text{Sr}}$ in Biotite $\approx 0.4$ (i.e. incompatible)
$D_{\text{Rb}}$ in Biotite $\approx 3.2$ (i.e. compatible)

$\text{Rb}/\text{Sr}$ in mica in equilibrium with a "rhyolitic whole rock" with $\text{Rb}/\text{Sr} = 1$:

\[
\frac{\text{Rb}}{\text{Sr}} = \frac{D_{\text{Rb}} \times c_{\text{Rb}}^l}{D_{\text{Sr}} \times c_{\text{Sr}}^l} = \frac{3.2 \times 1}{0.4 \times 1} = 8
\]

$\text{Rb}/\text{Sr}$ in mica significantly higher than in whole rock!

Application to isotope evolution:

Example: The Rb-Sr Geochronometer:

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

$^{87}\text{Rb} \rightarrow ^{87}\text{Sr} + \beta^-$ \quad half life: $48.8 \times 10^9$ yr

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

Application to isotope evolution:

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

![Graph showing $\text{Sr}/\text{Sr}$ ratio over time for different Rb/Sr ratios.]

For age determination by the Rb-Sr method, at least two mineral fractions with different Rb/Sr (and thus $^{87}\text{Sr}/^{86}\text{Sr}$) 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.