# Stable isotope geochemistry

Franck Poitrasson
CNRS – Toulouse

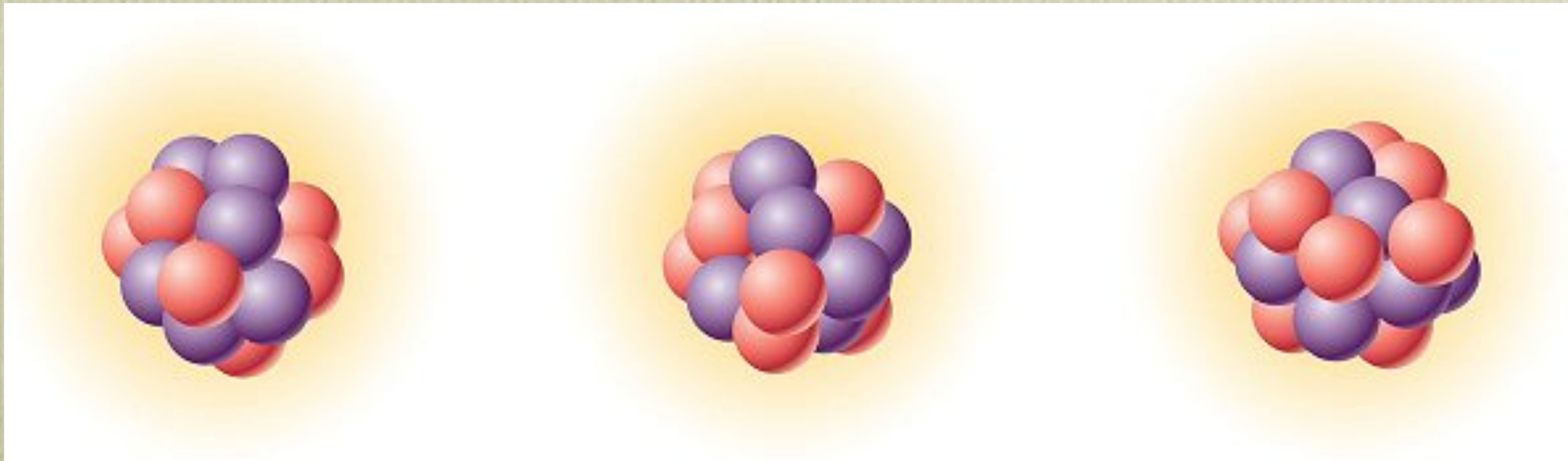
# Suggested readings:

- Allègre, C.J., 2008. Isotope geology. Cambridge University Press, Cambridge, 512 pp.
- Hoefs, J., 2004. Stable isotope geochemistry. Springer-Verlag, Berlin, 244 pp.
- Criss, R.E., 1999. Principles of stable isotope distribution. Oxford University Press, Oxford, 254 pp.
- Reviews in Mineralogy (and Geochemistry) on Stable Isotopes (vol. 16, 1986 & vol. 43, 2001)

# Isotopes

- Atoms with the same number of protons, but a different number of neutrons:

→ **relate to composition of the nucleus of atoms**



Carbon-12
6 protons
6 neutrons
6 electrons

Carbon-13
6 protons
7 neutrons
6 electrons

Carbon-14
6 protons
8 neutrons
6 electrons

- The number of stable isotopes may vary depending on the chemical element:
- From one: ${}^{23}_{11}Na$, ${}^{93}_{41}Nb$, ${}^{165}_{67}Ho$, ${}^{197}_{79}Au$ (21 naturally occurring)
- To several: ${}^{63}_{29}Cu$, ${}^{65}_{29}Cu$

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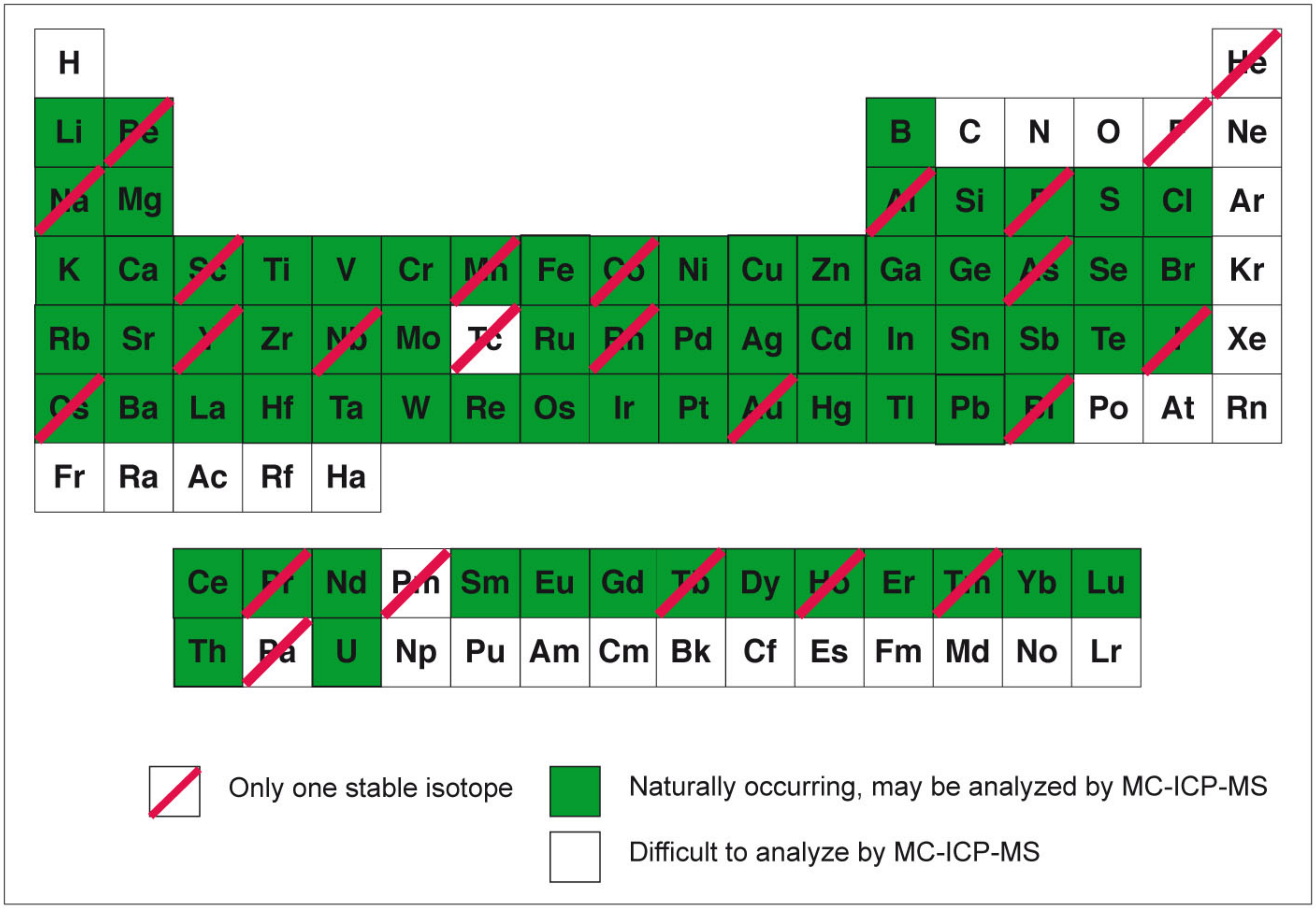
$${}^{112}_{50}Sn, {}^{114}_{50}Sn, {}^{115}_{50}Sn, {}^{116}_{50}Sn, {}^{117}_{50}Sn, {}^{118}_{50}Sn, {}^{119}_{50}Sn, {}^{120}_{50}Sn, {}^{122}_{50}Sn, {}^{124}_{50}Sn$$

→ **Isotope geochemistry requires at least two isotopes!**

# Periodic chart of elements



| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | ~~He~~ |
| Li | ~~Be~~ | | | | | | | | | | | B | C | N | O | ~~F~~ | Ne |
| ~~Na~~ | Mg | | | | | | | | | | | ~~Al~~ | Si | ~~P~~ | S | Cl | Ar |
| K | Ca | ~~Sc~~ | Ti | V | Cr | ~~Mn~~ | Fe | ~~Co~~ | Ni | Cu | Zn | Ga | Ge | ~~As~~ | Se | Br | Kr |
| Rb | Sr | ~~Y~~ | Zr | ~~Nb~~ | Mo | ~~Tc~~ | Ru | ~~Rh~~ | Pd | Ag | Cd | In | Sn | Sb | Te | ~~I~~ | Xe |
| ~~Cs~~ | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | ~~Au~~ | Hg | Tl | Pb | ~~Bi~~ | Po | At | Rn |
| Fr | Ra | Ac | Rf | Ha | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | |
| | | Ce | ~~Pr~~ | Nd | ~~Pm~~ | Sm | Eu | Gd | ~~Tb~~ | Dy | ~~Ho~~ | Er | ~~Tm~~ | Yb | Lu | | |
| | | Th | ~~Pa~~ | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr | | |

⧄ Only one stable isotope

🟩 Naturally occurring, may be analyzed by MC-ICP-MS

☐ Difficult to analyze by MC-ICP-MS

→ Over 60 elements suitable for stable isotope studies

# The “XVIII$^{e}$ century view”:

- Atoms with different number of protons have different names because they have different chemical and physical properties

# The “XVIIIe century view”:

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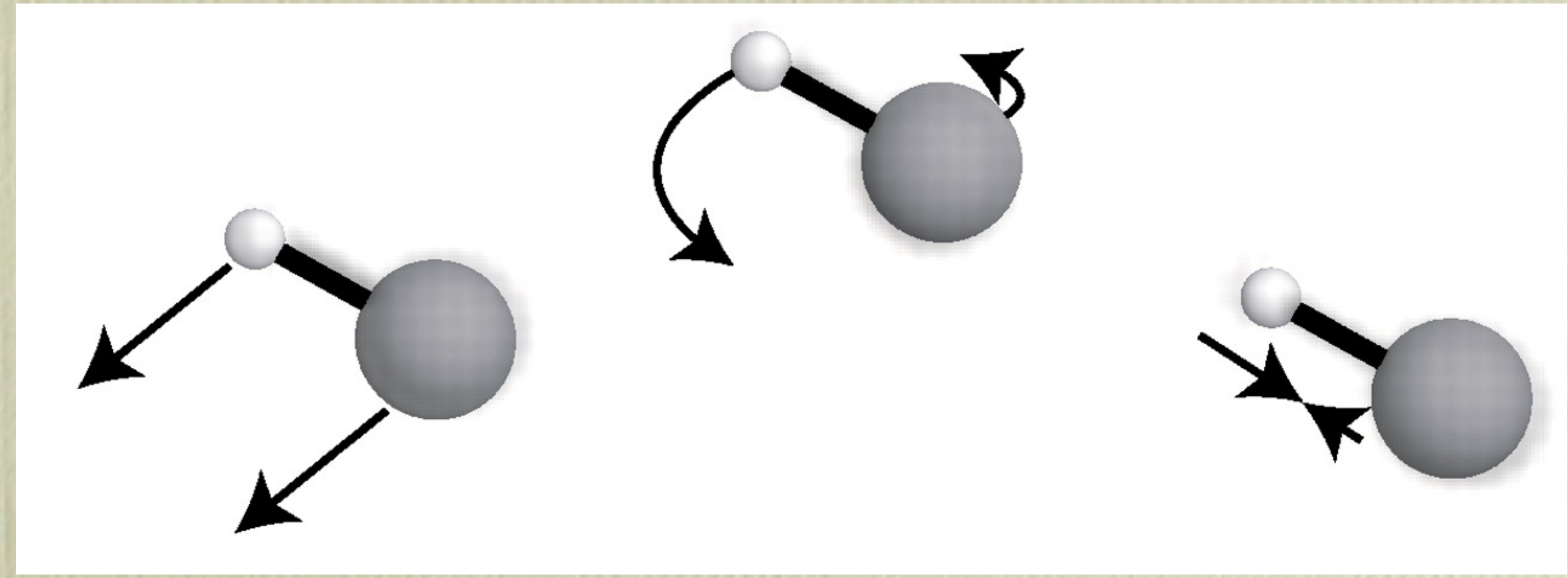
# The XXe century view:

- In detail, atoms with the same number of protons but different number of neutrons (isotopes) have slightly different chemical and physical properties due to slight mass difference of their host molecules...

# How is it possible?

- Gaseous, aqueous molecules and mineral lattices are vibrating continuously, and the vibration frequencies will depend on the isotopic composition (weight) of the molecule

- They are three vibrating modes:



Schauble., 2004, RiMG

**translational** **rotational** **vibrational**

- The effect of these different levels of energy on isotopic signatures may be observed when exchanges between two reservoirs occur, i.e., through an exchange reaction.

$$1/3 MgSi^{16}O_3 + 1/4 Mg_2Si^{18}O_4 \Leftrightarrow 1/3 MgSi^{18}O_3 + 1/4 Mg_2Si^{16}O_4$$

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The equilibrium constant is (assuming ideal mixing):

$$K = \frac{\left({}^{18}O^3_{opx}\right)^{1/3}\cdot\left({}^{16}O^4_{ol}\right)^{1/4}}{\left({}^{16}O^3_{opx}\right)^{1/3}\cdot\left({}^{18}O^4_{ol}\right)^{1/4}} = \frac{\left[\left({}^{18}O/{}^{16}O\right)^3_{opx}\right]^{1/3}}{\left[\left({}^{18}O/{}^{16}O\right)^4_{ol}\right]^{1/4}} = \frac{\left({}^{18}O/{}^{16}O\right)_{opx}}{\left({}^{18}O/{}^{16}O\right)_{ol}} = \alpha_{opx-ol}$$

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Each molar quantity above may be calculated through partition functions that describes all possible energy states of the substance:

$$Q = Q_{tr} \cdot Q_{rot} \cdot Q_{vib}$$

# Notations and conventions:

- So far, we only used the isotopic fractionation factor α between two substances A and B, defined as:

$$\alpha_{A-B} = \frac{\left(N^{*}/N\right)_{A}}{\left(N^{*}/N\right)_{B}}$$

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- An other useful quantity for analytical reasons is the delta value $\delta_A$ of a substance A, relative to a standard, defined as:

$$\delta_A = 1000 \cdot \left[ \frac{\left(N^*/N\right)_A}{\left(N^*/N\right)_{std}} - 1 \right]$$

**expressed in *‰***

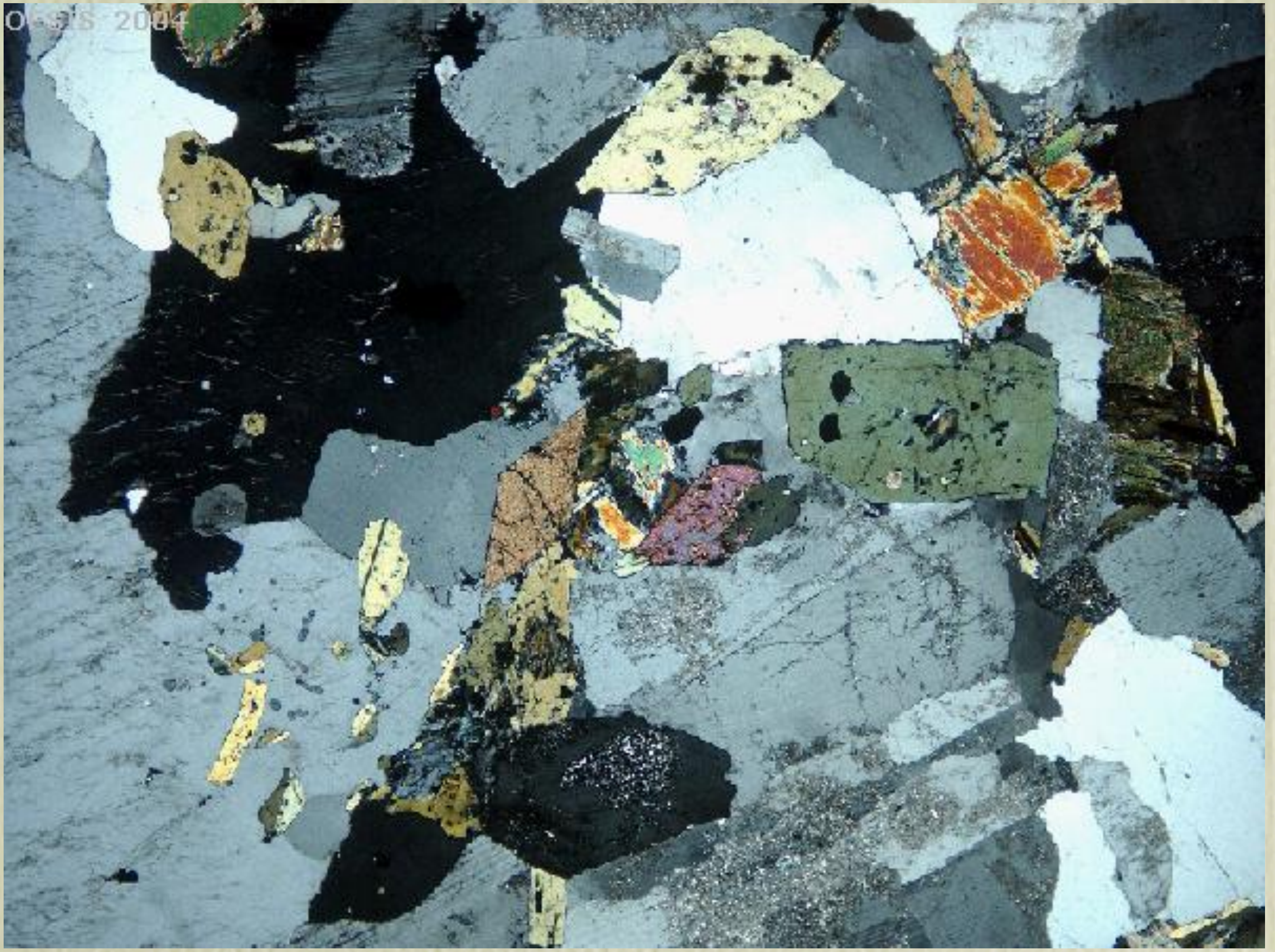
- It may be shown that $\alpha$ and $\delta$ are linked:

$$\alpha_{A-B} = \frac{\left(N^*/N\right)_A}{\left(N^*/N\right)_B} = \frac{1000 + \delta_A}{1000 + \delta_B}$$

# But how do we measure these stable isotope ratio?

# Sample preparation: some basic principles

- For bulk solid samples, the starting material should be large enough to average local heterogeneity



**Granodiorite: cm-scale minerals are common**

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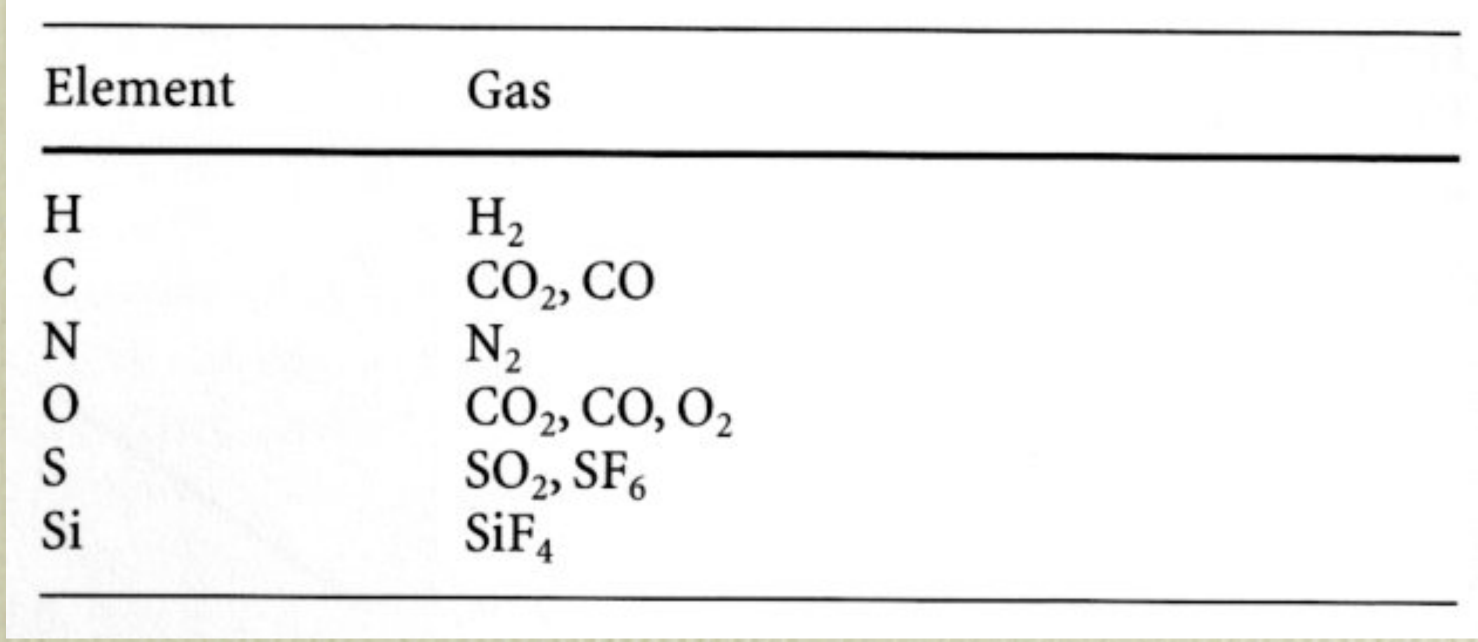

| Element | Gas |
|---|---|
| H | $H_2$ |
| C | $CO_2$, CO |
| N | $N_2$ |
| O | $CO_2$, CO, $O_2$ |
| S | $SO_2$, $SF_6$ |
| Si | $SiF_4$ |

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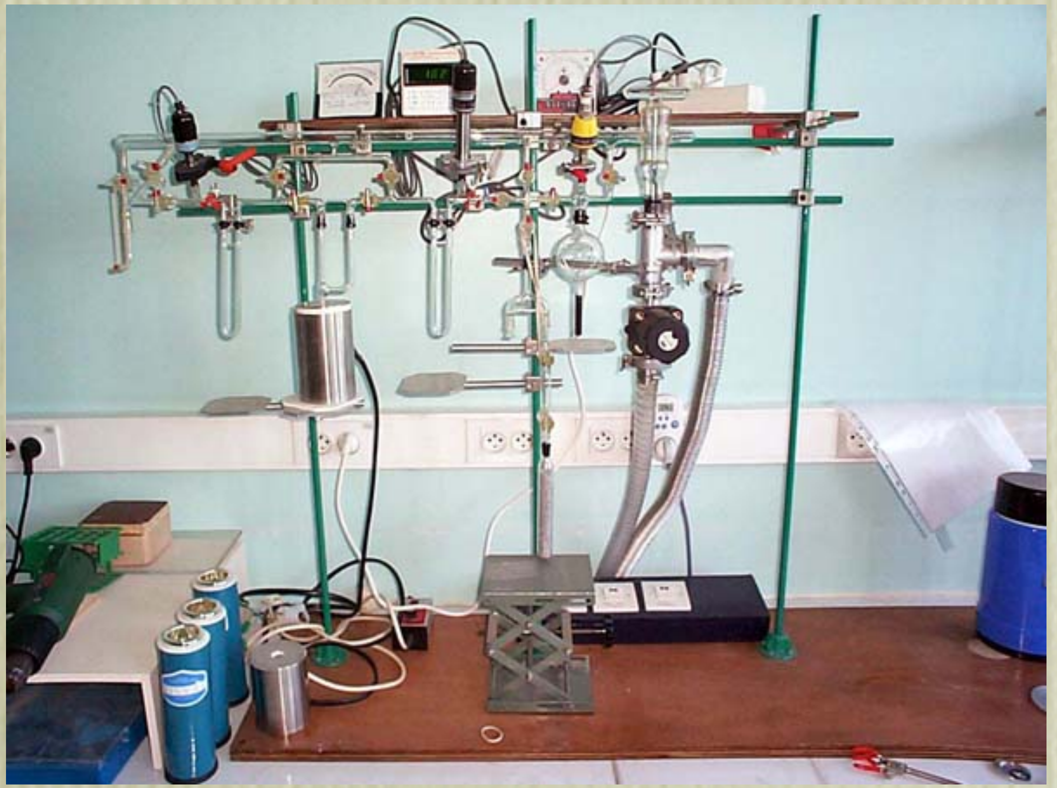
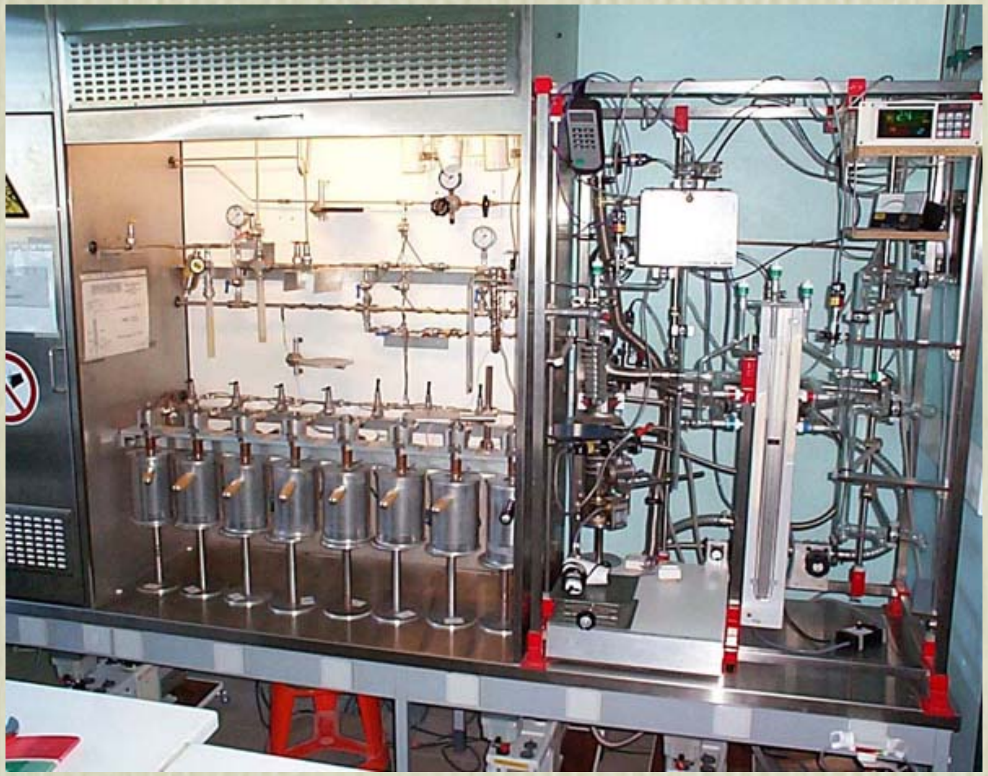
- The element of interest should be purified, i.e., separated from its matrix



H extraction line



O extraction line from silicates

University of St Etienne-CNRS LMV laboratory photos

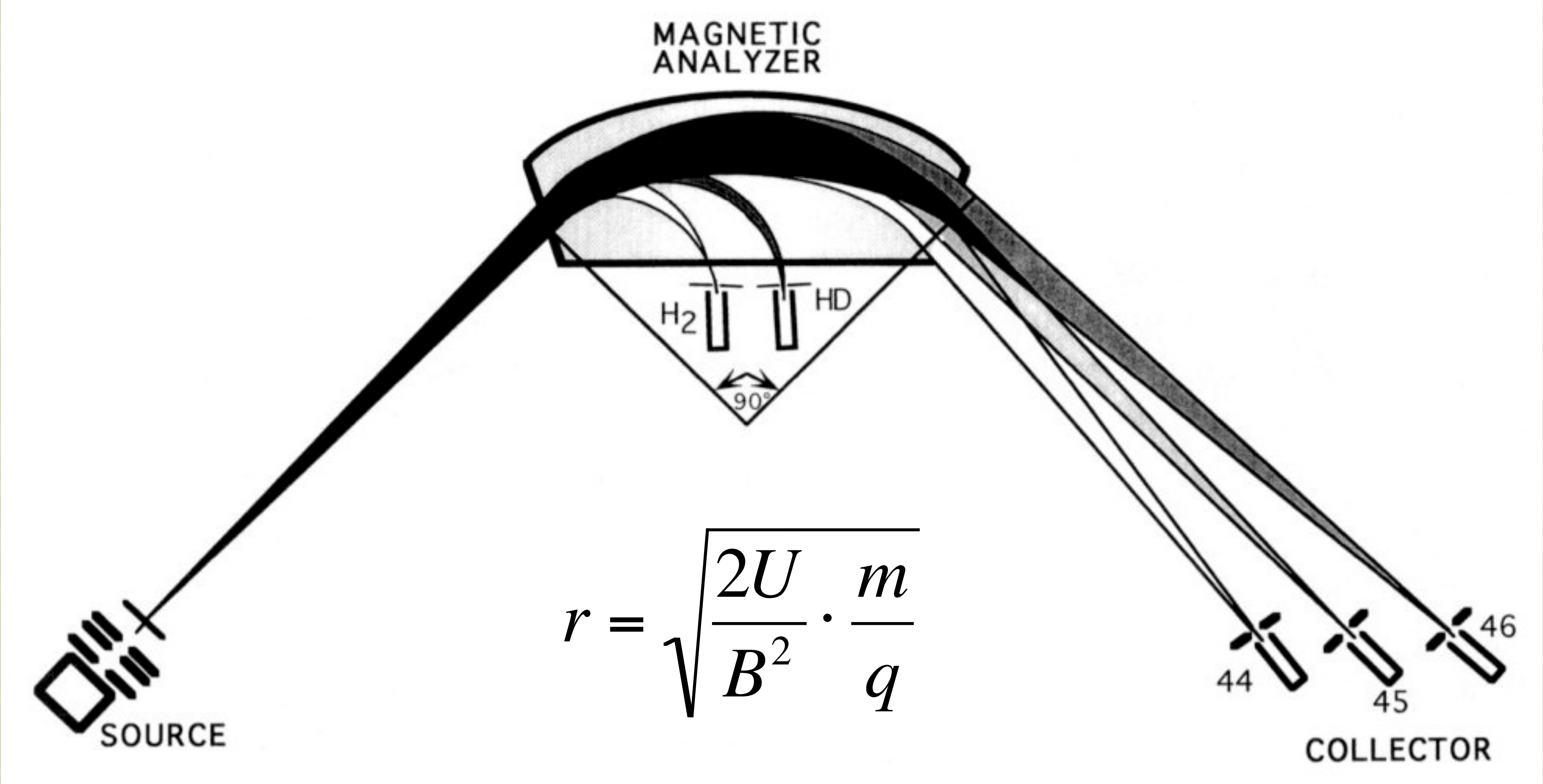
# Sample preparation: some basic principles

- For bulk solid samples, the starting material should be large enough to average local heterogeneity
- Isotope ratio are frequently measured on gases
- The element of interest should be purified, i.e., separated from its matrix
- Methods should be clean to avoid contamination. The mg level is the typical sample size.
- 100% yield during purification is required

# Gas source mass spectrometer

Thermo Scientific photo

# Gas source mass spectrometer

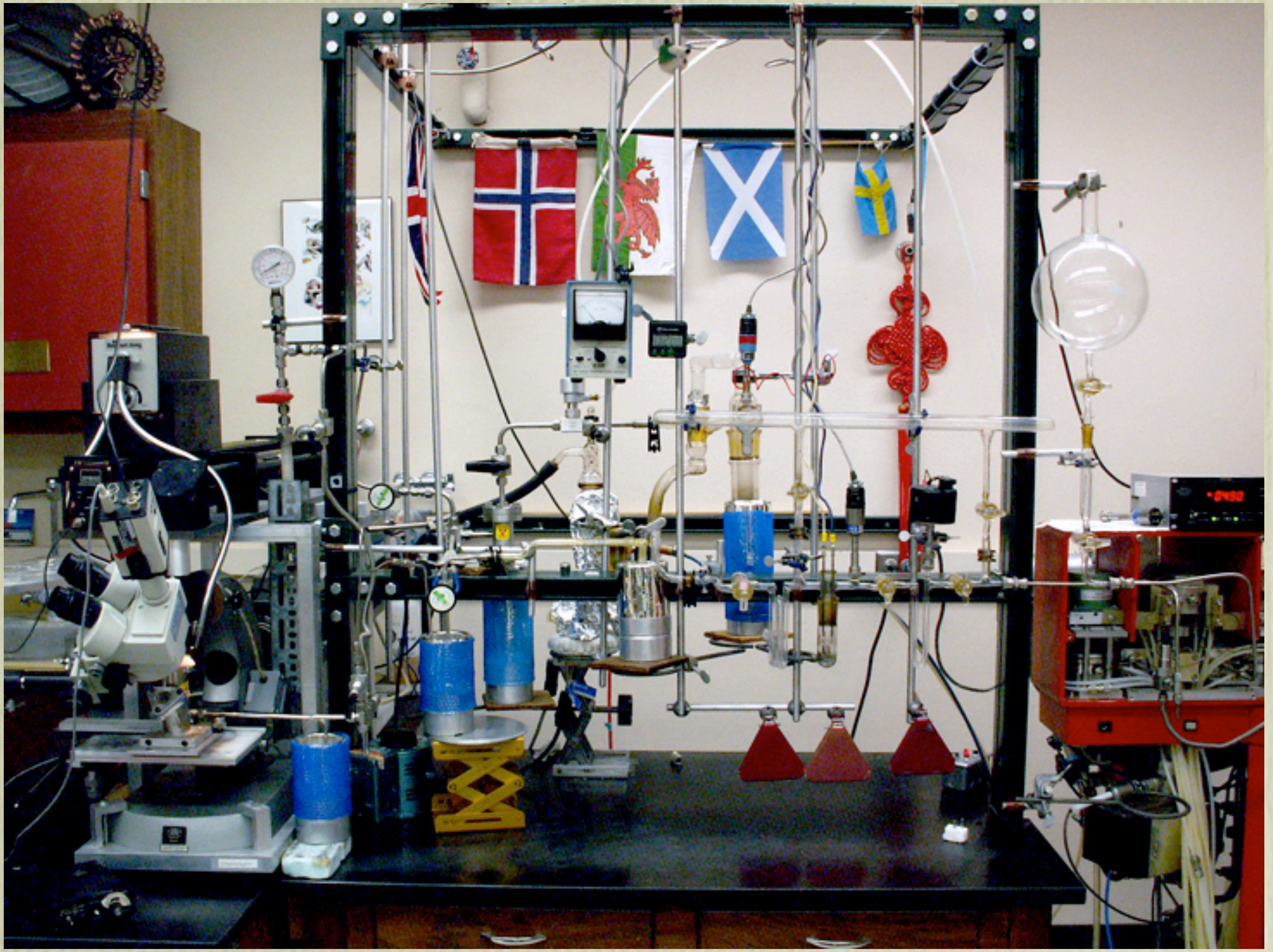


$$r = \sqrt{\frac{2U}{B^2} \cdot \frac{m}{q}}$$

where: U is the accelerating voltage, B the magnetic field, m/q the mass/charge ratio of the ion and r the radius of its circular path in the magnetic field

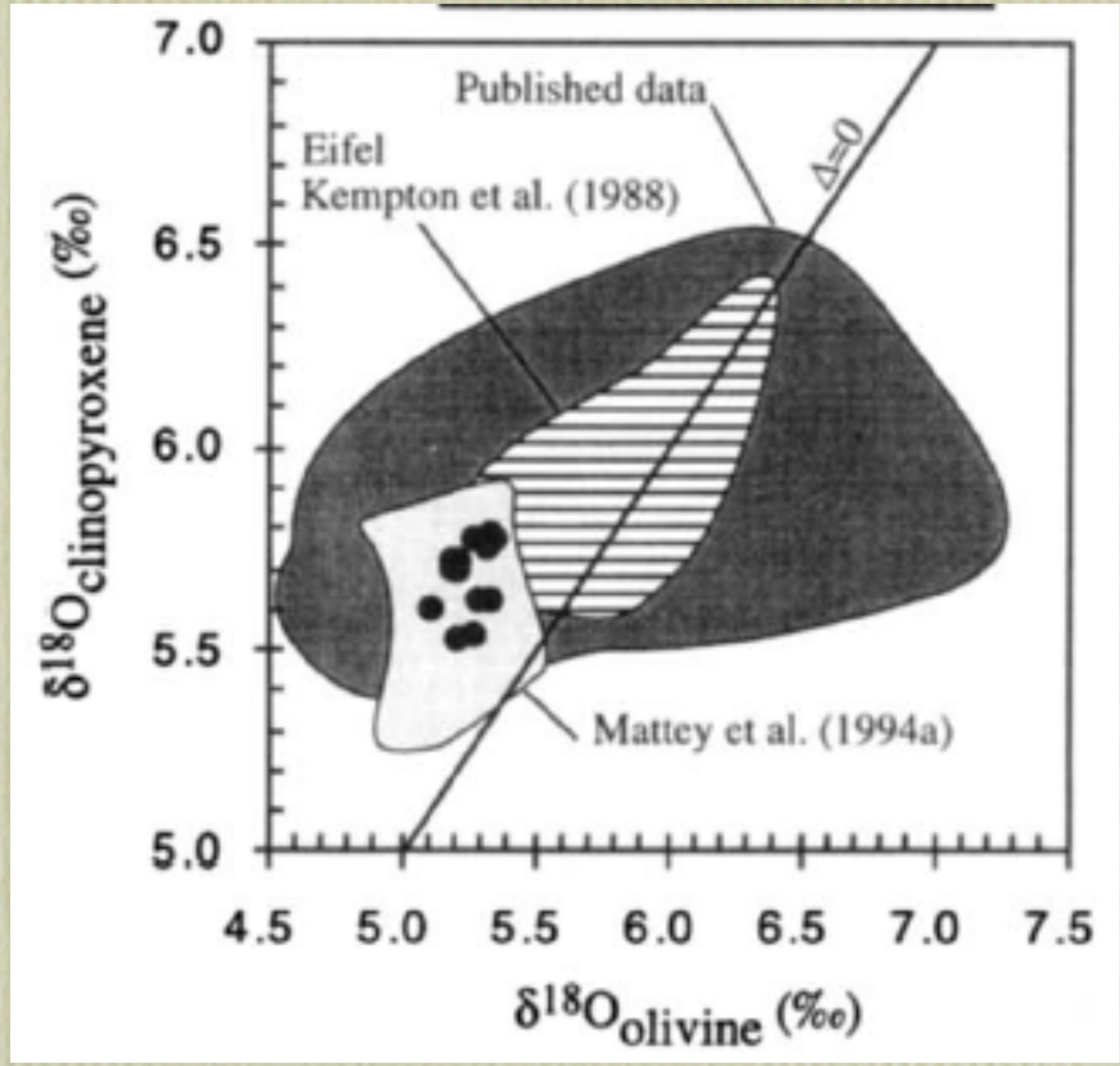
→ The lighter ions will turn faster!

# Laser fluorination for mineral analysis



University of Madison-Wisconsin laboratory photo

# Benefit of laser fluorination for mineral analysis:



Mattey et al., 1994: Laser fluorination data
Others: conventional data

Chazot et al., 1997, GCA

➡ The range in O isotope composition previously reported was an analytical artifact!

# In situ light (H, C, O...) stable isotope measurements: ion microprobe

CNRS-CRPG Nancy Laboratory photo

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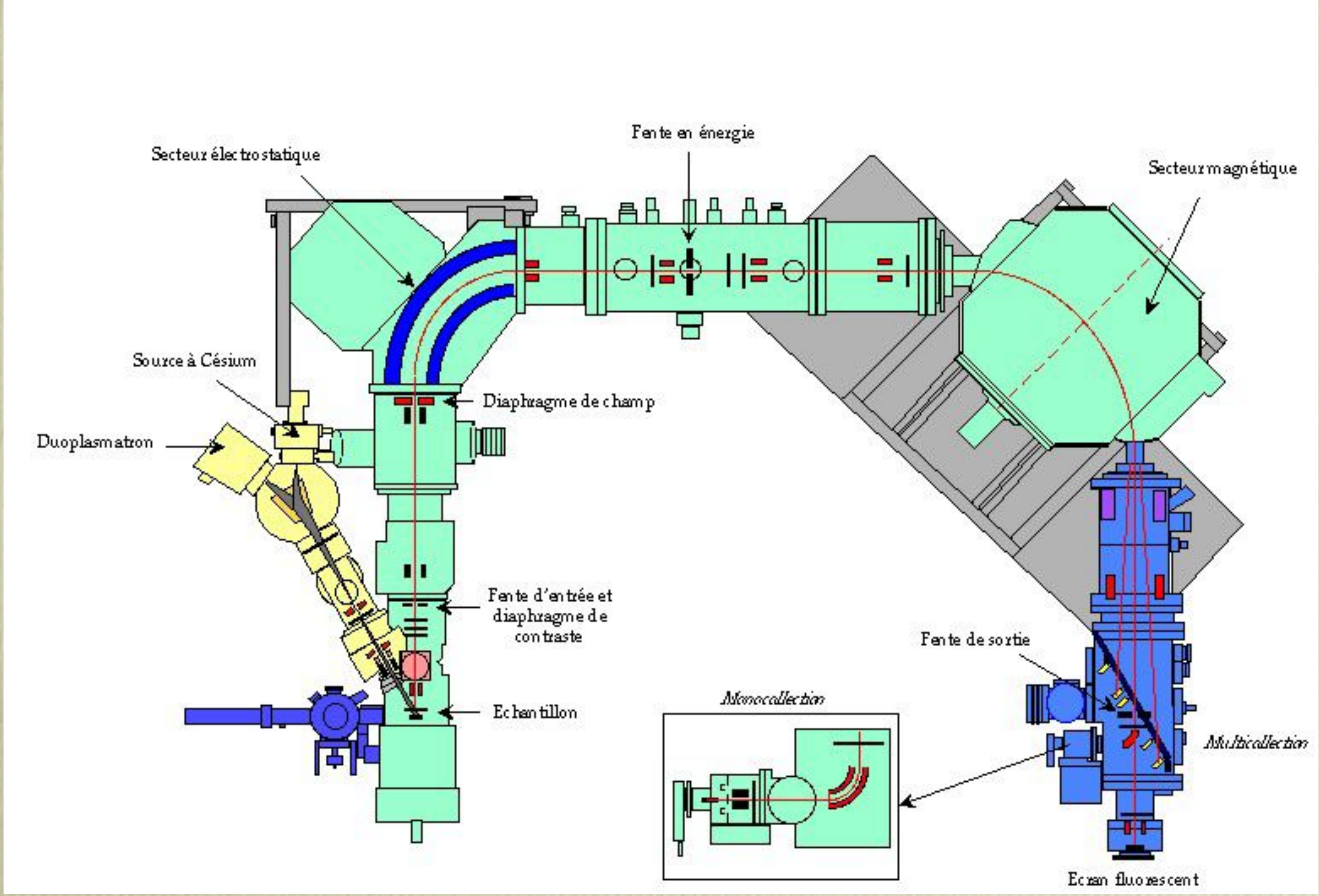
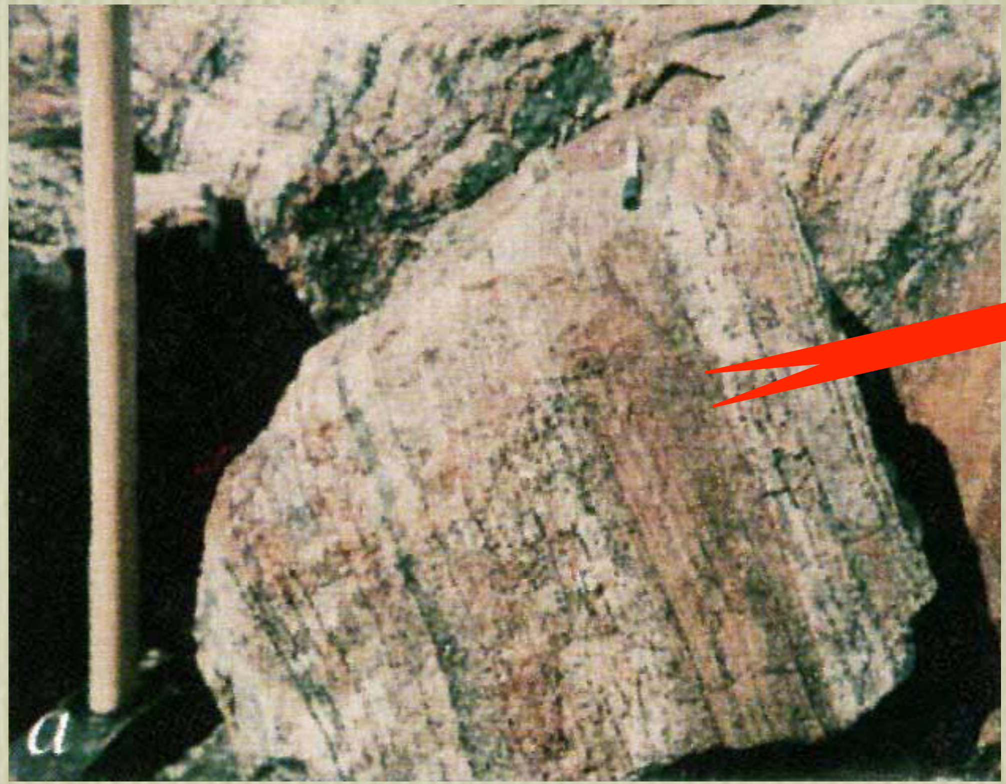
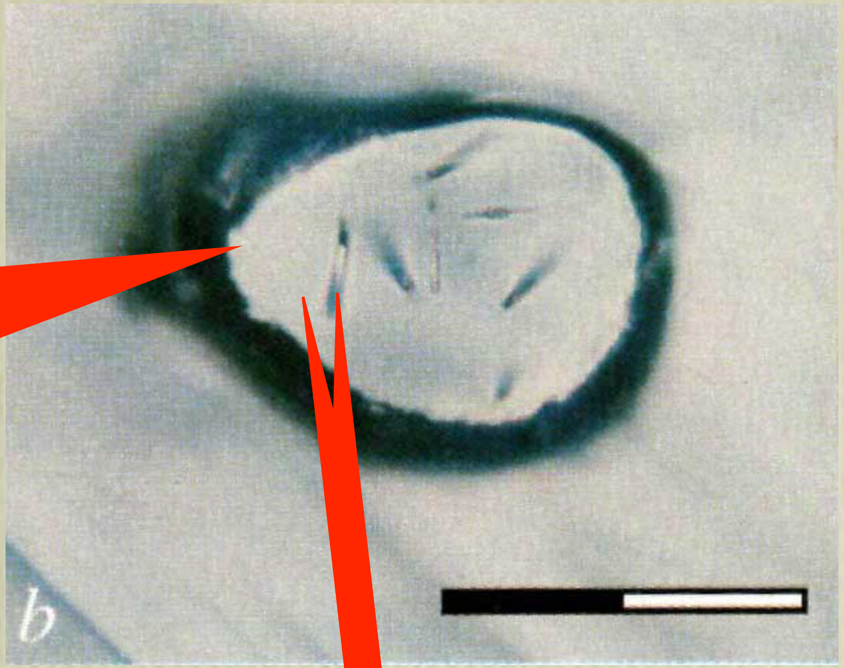


CAMECA IMS 1270 ion probe

# Ion microprobe: very useful for very small samples



3,8 Ga Akilia gneiss, Greenland



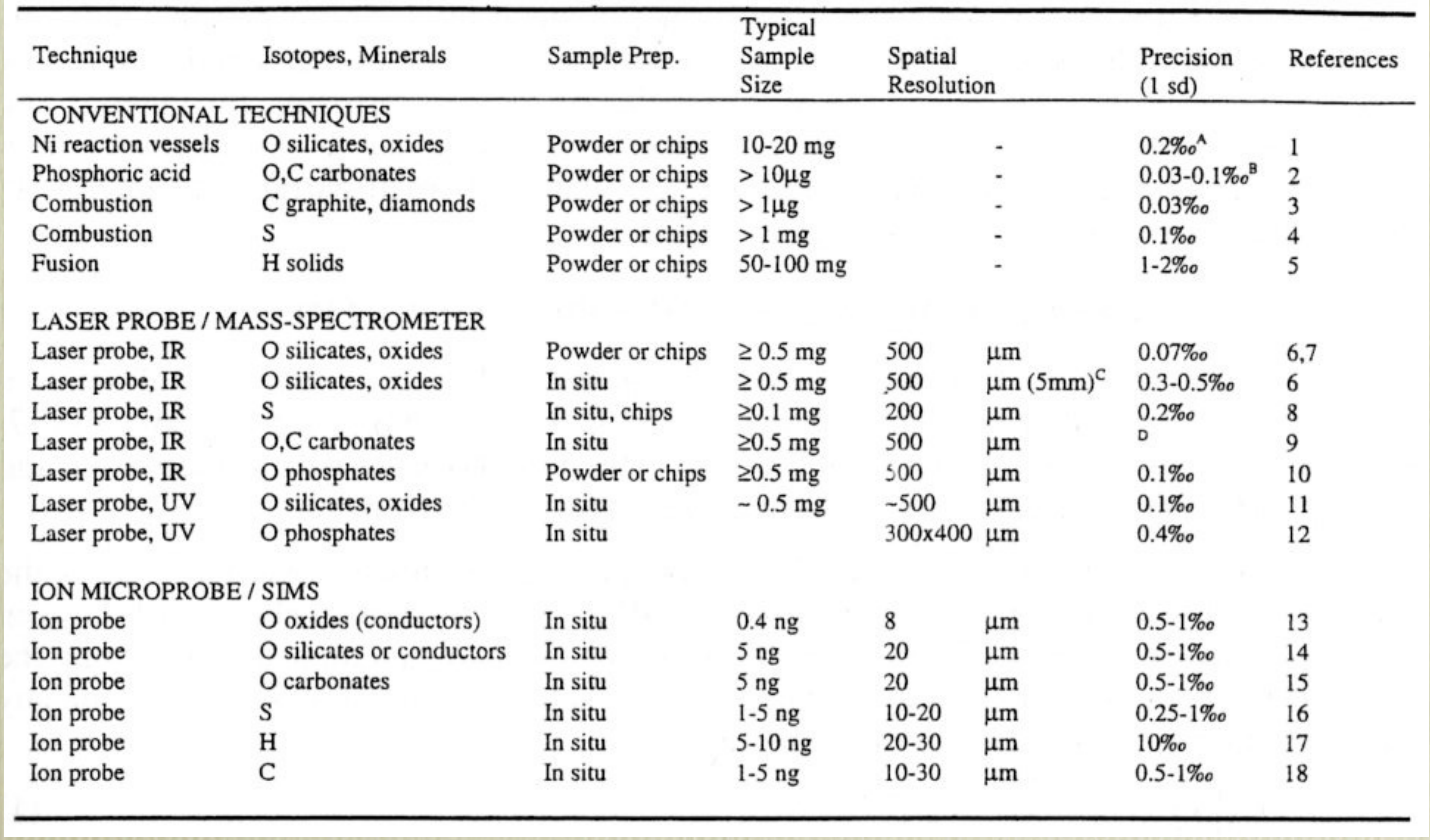
Apatite
(scale: 20 µm)

Carbon-rich inclusion with
a life-like $\delta^{13}C$ signature

After Mosjzsis et al., 1996, Nature

# Characteristics of various techniques for light isotope analysis

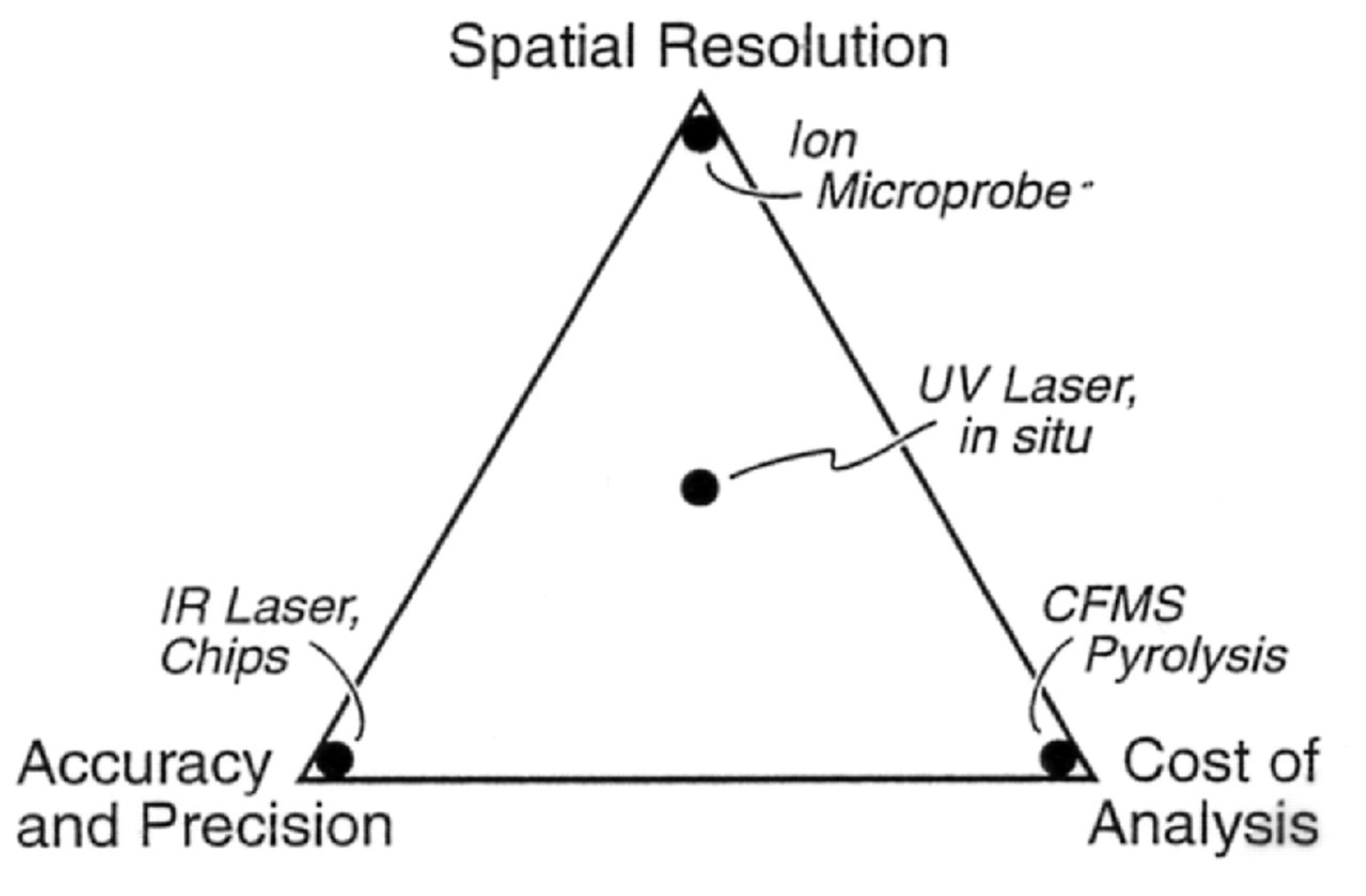
(Valley et al., 1998, RiMG)



| Technique | Isotopes, Minerals | Sample Prep. | Typical Sample Size | Spatial Resolution | Precision (1 sd) | References |
|---|---|---|---|---|---|---|
| CONVENTIONAL TECHNIQUES | | | | | | |
| Ni reaction vessels | O silicates, oxides | Powder or chips | 10-20 mg | - | 0.2‰[A] | 1 |
| Phosphoric acid | O,C carbonates | Powder or chips | > 10μg | - | 0.03-0.1‰[B] | 2 |
| Combustion | C graphite, diamonds | Powder or chips | > 1μg | - | 0.03‰ | 3 |
| Combustion | S | Powder or chips | > 1 mg | - | 0.1‰ | 4 |
| Fusion | H solids | Powder or chips | 50-100 mg | - | 1-2‰ | 5 |
| LASER PROBE / MASS-SPECTROMETER | | | | | | |
| Laser probe, IR | O silicates, oxides | Powder or chips | ≥ 0.5 mg | 500 μm | 0.07‰ | 6,7 |
| Laser probe, IR | O silicates, oxides | In situ | ≥ 0.5 mg | 500 μm (5mm)[C] | 0.3-0.5‰ | 6 |
| Laser probe, IR | S | In situ, chips | ≥0.1 mg | 200 μm | 0.2‰ | 8 |
| Laser probe, IR | O,C carbonates | In situ | ≥0.5 mg | 500 μm | [D] | 9 |
| Laser probe, IR | O phosphates | Powder or chips | ≥0.5 mg | 500 μm | 0.1‰ | 10 |
| Laser probe, UV | O silicates, oxides | In situ | ~ 0.5 mg | ~500 μm | 0.1‰ | 11 |
| Laser probe, UV | O phosphates | In situ | | 300x400 μm | 0.4‰ | 12 |
| ION MICROPROBE / SIMS | | | | | | |
| Ion probe | O oxides (conductors) | In situ | 0.4 ng | 8 μm | 0.5-1‰ | 13 |
| Ion probe | O silicates or conductors | In situ | 5 ng | 20 μm | 0.5-1‰ | 14 |
| Ion probe | O carbonates | In situ | 5 ng | 20 μm | 0.5-1‰ | 15 |
| Ion probe | S | In situ | 1-5 ng | 10-20 μm | 0.25-1‰ | 16 |
| Ion probe | H | In situ | 5-10 ng | 20-30 μm | 10‰ | 17 |
| Ion probe | C | In situ | 1-5 ng | 10-30 μm | 0.5-1‰ | 18 |

# Characteristics of various techniques for light isotope analysis

(Valley et al., 1998, RiMG)



# Factors affecting equilibrium stable isotope fractionation:

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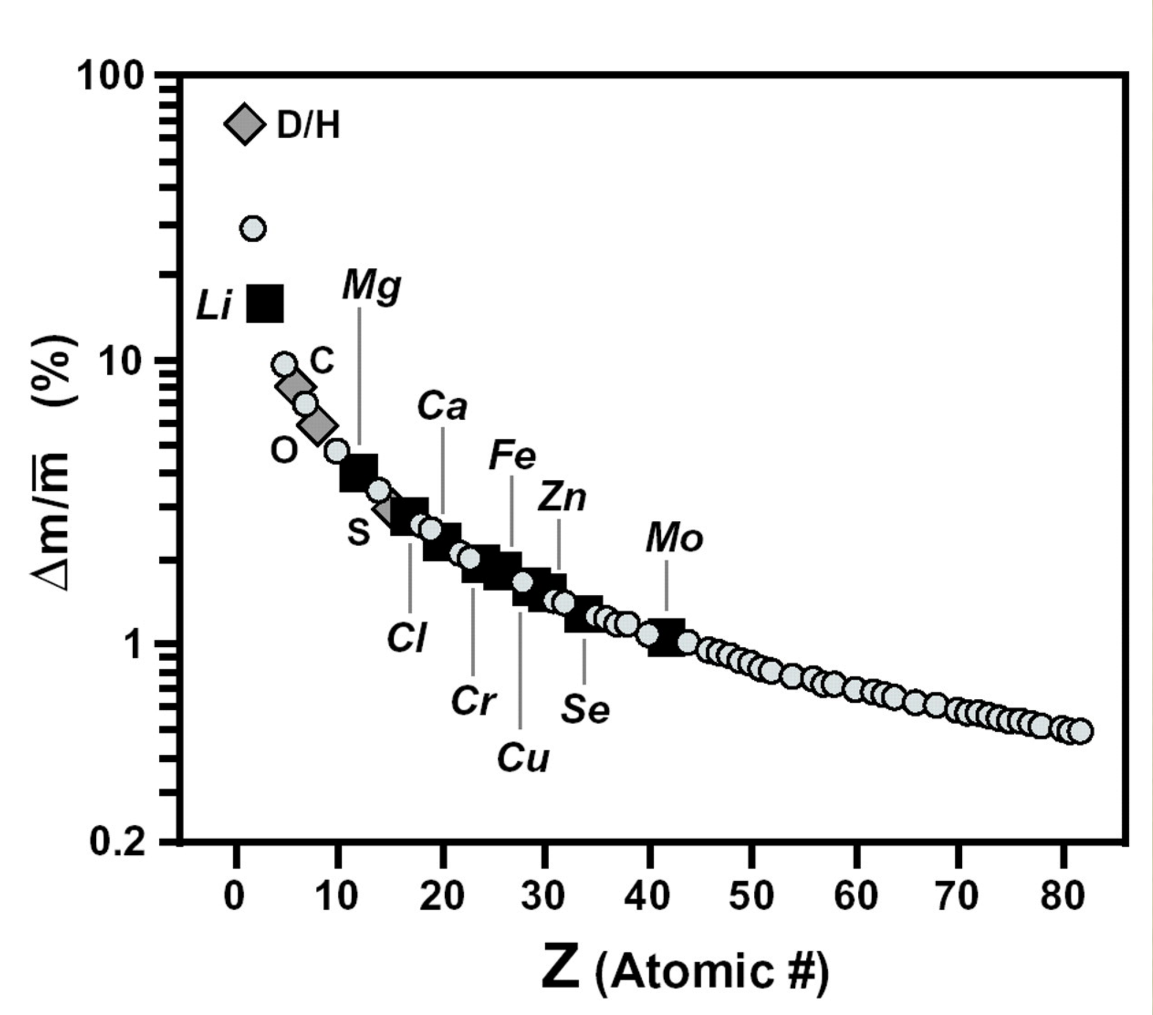


**In general, the larger the relative mass difference between isotopes of a given element, the larger the stable isotope fractionation in nature ... but they are many exceptions...**

# Factors affecting equilibrium stable isotope fractionation:

- Mass difference between isotopes
- Nature of the interatomic bonds

**C-C bonds in diamond are more covalent than in graphite, and therefore of higher energy. Thus:**

$$\alpha_{dia-gra} = \frac{\left({}^{13}C/{}^{12}C\right)_{dia}}{\left({}^{13}C/{}^{12}C\right)_{gra}} > 1$$

# Factors affecting equilibrium stable isotope fractionation:

- Mass difference between isotopes
- Nature of the interatomic bonds
- Coordination chemistry

$$B(OH)_3 + OH^- \Leftrightarrow B(OH)_4^-$$

**Triangular** **tetrahedral coordination**
**Higher energy** **Lower energy**

$$\alpha_{B(OH)_4^- - B(OH)_3} = \frac{\left({}^{11}B/{}^{10}B\right)_{B(OH)_4^-}}{\left({}^{11}B/{}^{10}B\right)_{B(OH)_3}} < 1$$

→ **A possible approach to measure ocean's paleo-pH?**

# Factors affecting equilibrium stable isotope fractionation:

- Mass difference between isotopes
- Nature of the interatomic bonds
- Coordination chemistry
- Redox state of elements

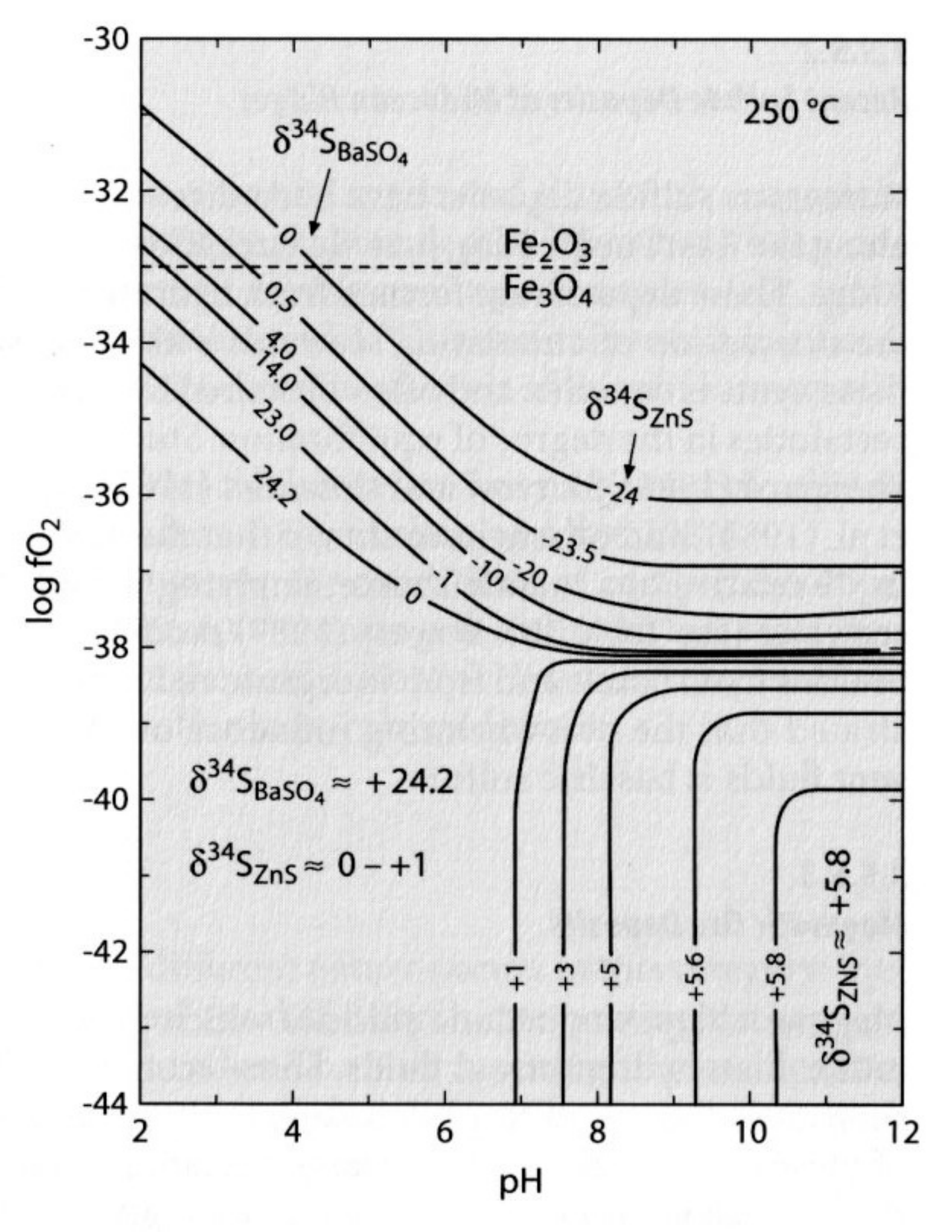
**$S^{2-}$ in sulfide species, $S^{\circ}$ in native sulfur, $S^{4+}$ in $SO_2$ and $S^{6+}$ in sulfate**

**and:**

$$\alpha_{sulfates-sulfides} = \frac{\left({}^{34}S/{}^{32}S\right)_{sulfates}}{\left({}^{34}S/{}^{32}S\right)_{sulfides}} > \alpha_{SO_2-sulfides} = \frac{\left({}^{34}S/{}^{32}S\right)_{SO_2}}{\left({}^{34}S/{}^{32}S\right)_{sulfides}} > 1$$

# Application to estimate the formation conditions of ore deposits

Madan, Bulgaria



After Ohmoto, 1972, Econ. Geol.

# Factors affecting equilibrium stable isotope fractionation:

- Mass difference between isotopes
- Nature of the interatomic bonds
- Coordination chemistry
- Redox state of elements
- Temperature

**We have seen that for a reaction like:**

$$1/3MgSi^{16}O_3 + 1/4Mg_2Si^{18}O_4 \Leftrightarrow 1/3MgSi^{18}O_3 + 1/4Mg_2Si^{16}O_4$$

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**$\alpha$ = K, if the stoechiometric coefficients of the reaction are well chosen. A more generic relationship is:** $\alpha = K^{1/n}$

**where n is the number of atoms exchanged.**

The equilibrium constant K is linked to T by:

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

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For isotope exchanges, temperature dependence is more precisely described using statistical mechanics that allows to compute partition functions (Q):

$$(Q^*/Q) = \left(\frac{m^*}{m}\right)^{3n/2} \frac{\sigma}{\sigma^*} \prod_i \frac{\nu_i^* e^{-U_i^*/2}}{\nu_i e^{-U_i/2}} \frac{1-e^{-U_i}}{1-e^{-U_i^*}}$$

where * stands for the heavy isotope, m for mass, σ for symmetry number, ν for vibration frequency and:

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$$U_i = h\nu_i / kT$$

where h is the Planck’s constant, k is the Bolzmann’s constant, i is a running index of vibrational modes and T is the temperature in °K.

Use of these equations and experimental work show that:

$$1000 \ln \alpha = A/T^2 + B$$

at T ≥ 500-600°C for minerals and ≥ 100°C for gases, and

$$1000 \ln \alpha = A/T + B$$

at lower temperatures

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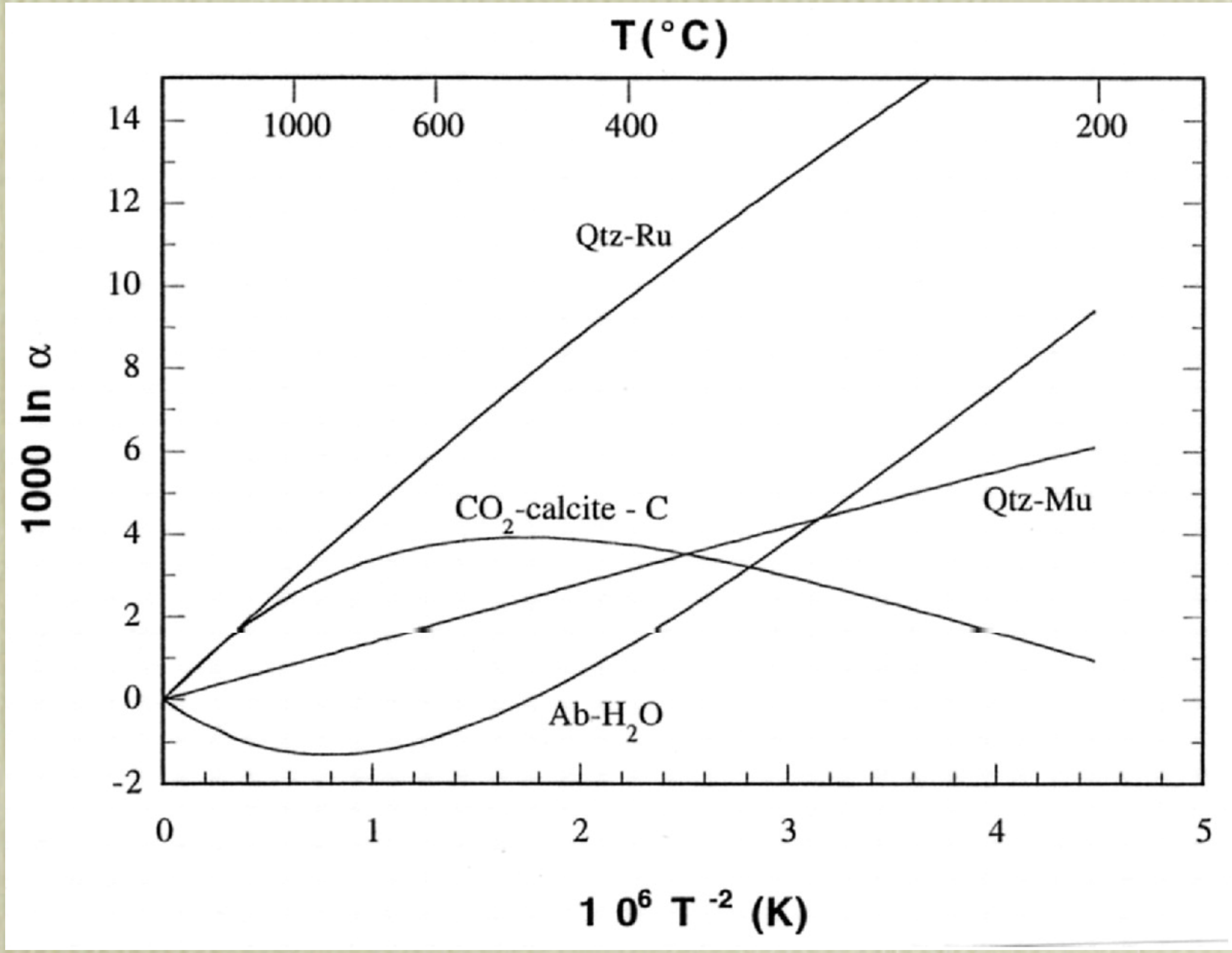
$$1000 \ln\alpha = A/T + B$$

at lower temperatures, but other relationships and exceptions exist:



Oxygen and carbon (- C) fractionation factors as a function of T

Chacko et al., 2001, RiMG

➡ **Thermometry possible in simple and well constrained cases**

# Kinetic stable isotope fractionation

- Occurs when not enough time is given for exchange reactions to reach completion (e.g., at low T, in biological processes, if diffusion in solids is required), or
- When products and reactants are rapidly separated (e.g., through a phase change interface, through a biological cell)

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- When products and reactants are rapidly separated (e.g., through a phase change interface, through a biological cell)

**In those situations, lightest isotopes are enriched in the reaction products because of their fastest velocity and their lower activation energy required for reactions to proceed**

# Kinetic stable isotope fractionation for diffusing gases:

**For ideal gases:** $E_c = E_c^*$ **and** $E_c = 1/2mV^2(= 3/2kT)$

**where * stands for the heavy gaseous species. As a result:**

$\frac{V}{V^*} = \sqrt{\frac{m*}{m}} = \alpha_1 > 1$ **where α is the isotopic fractionation factor**

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**On Earth, where gas collisions occur, or in solutions or solids, diffusion (D) should be considered:**

$$\frac{D}{D^*} = \sqrt{\frac{1/m + 1/m_{dm}}{1/m^* + 1/m_{dm}}} = \alpha_2$$

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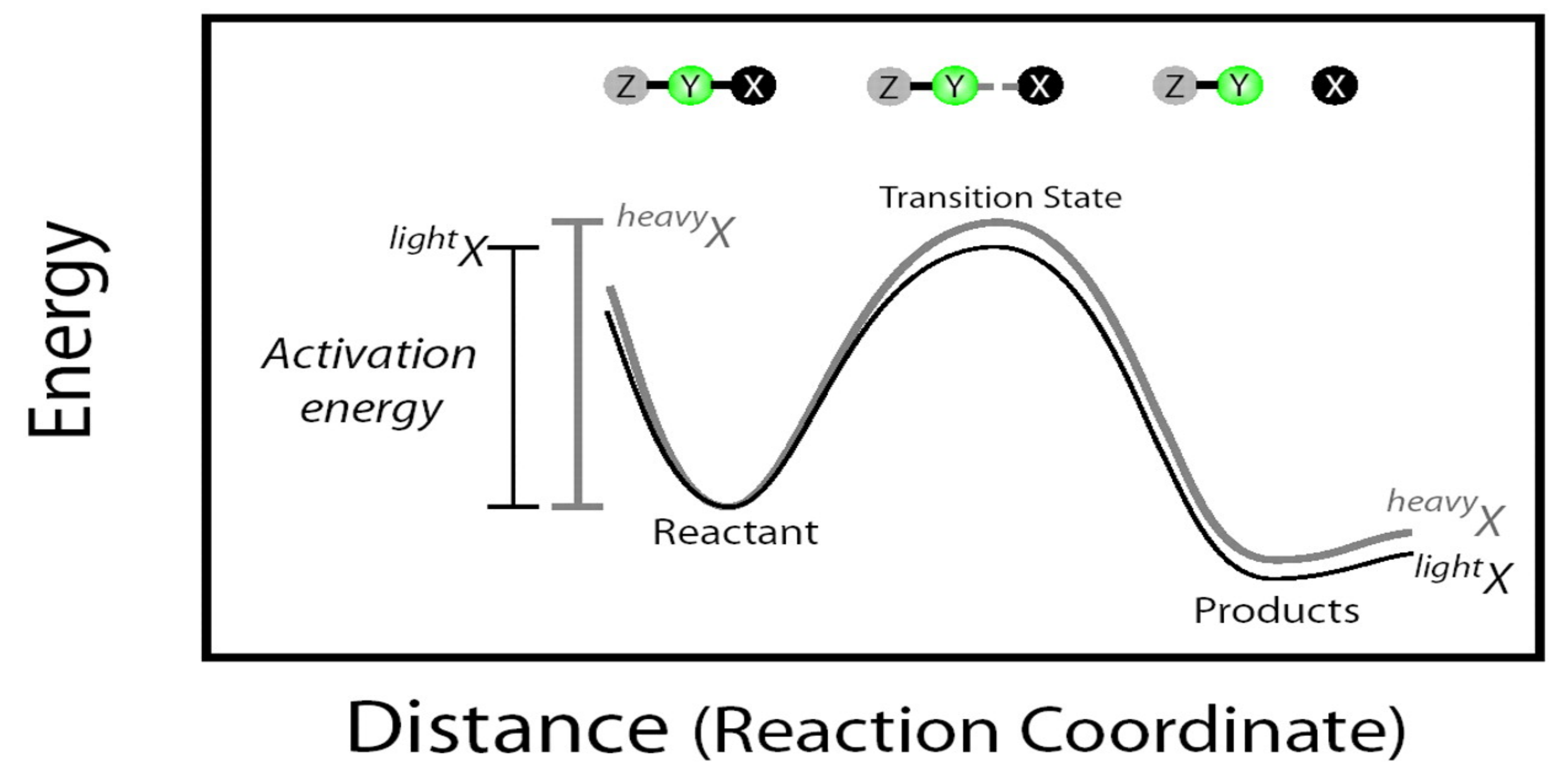
We will have: $\alpha_1 > \alpha_2 > 1$ → Medium-limited diffusion will minimize kinetic isotope fractionation factors

# Kinetic stable isotope fractionation during a chemical reaction:

In simple cases where only one molecule dissociates, a simplified approach to calculate isotopic effects on reaction rates is used, in which only the energy barrier between the reactants and a single rate-limiting transition-state is considered:

$$p(E_A) = \exp(-E_A/kT)$$

where $p(E_A)$ is the probability of a molecule having enough energy to reach the transition-state of activation energy $E_A$.



Schauble., 2004, RiMG

# Notations and conventions:

- We saw that the isotopic fractionation factor $\alpha$ between two substances A and B, is defined as:

$$\alpha_{A-B} = \frac{\left(N^*/N\right)_A}{\left(N^*/N\right)_B}$$

**where N* and N are the number of atoms of the heavy and light isotopes, respectively**

- An other useful quantity for analytical reasons is the delta value $\delta_A$ of a substance A, relative to a standard, defined as:

$$\delta_A = 1000 \cdot \left[\frac{\left(N^*/N\right)_A}{\left(N^*/N\right)_{std}} - 1\right]$$

**expressed in *‰***

- It may be shown that $\alpha$ and $\delta$ are linked:

$$\alpha_{A-B} = \frac{\left(N^*/N\right)_A}{\left(N^*/N\right)_B} = \frac{1000 + \delta_A}{1000 + \delta_B}$$

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- An other useful approximation, possible for most stable isotope fractionation observed in nature:

$$\Delta_{A-B} = \delta_A - \delta_B \approx 1000 \cdot \ln\alpha_{A-B}$$

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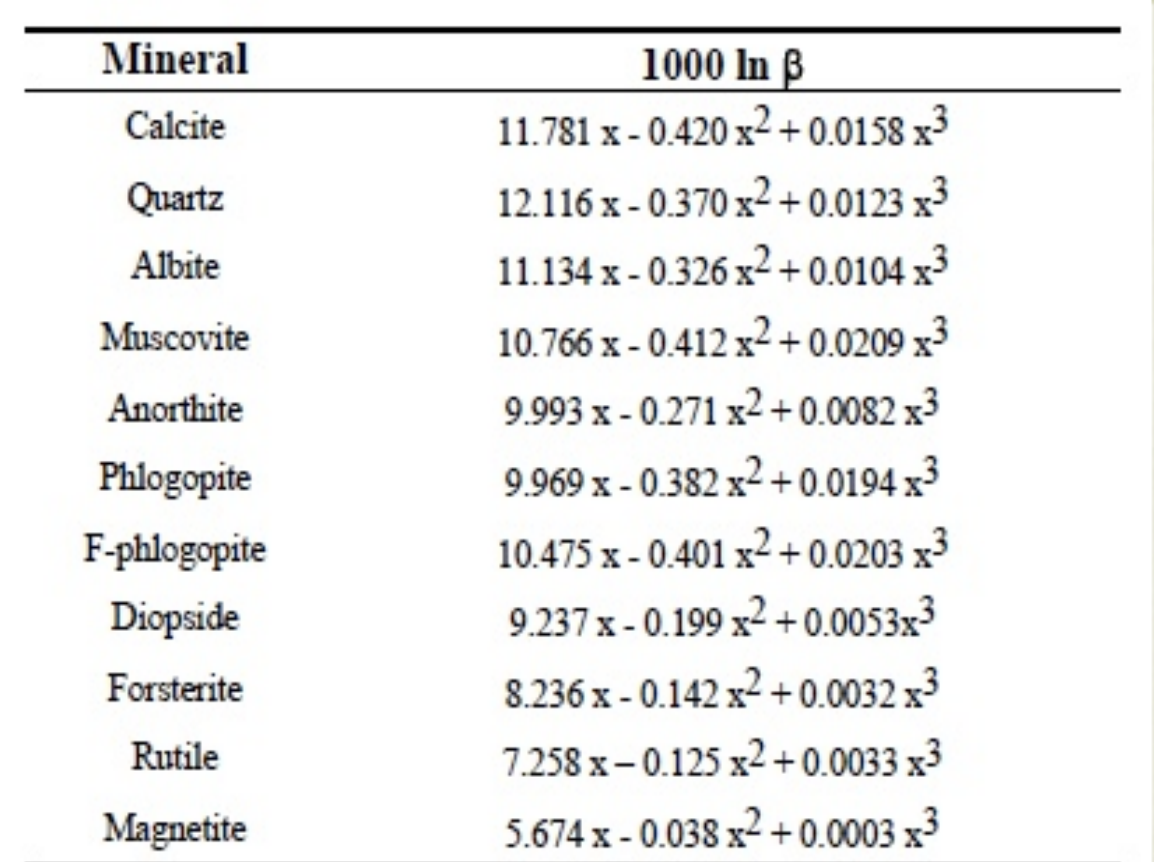
- These reduced partition function computed from statistical mechanics methods are commonly in the form:

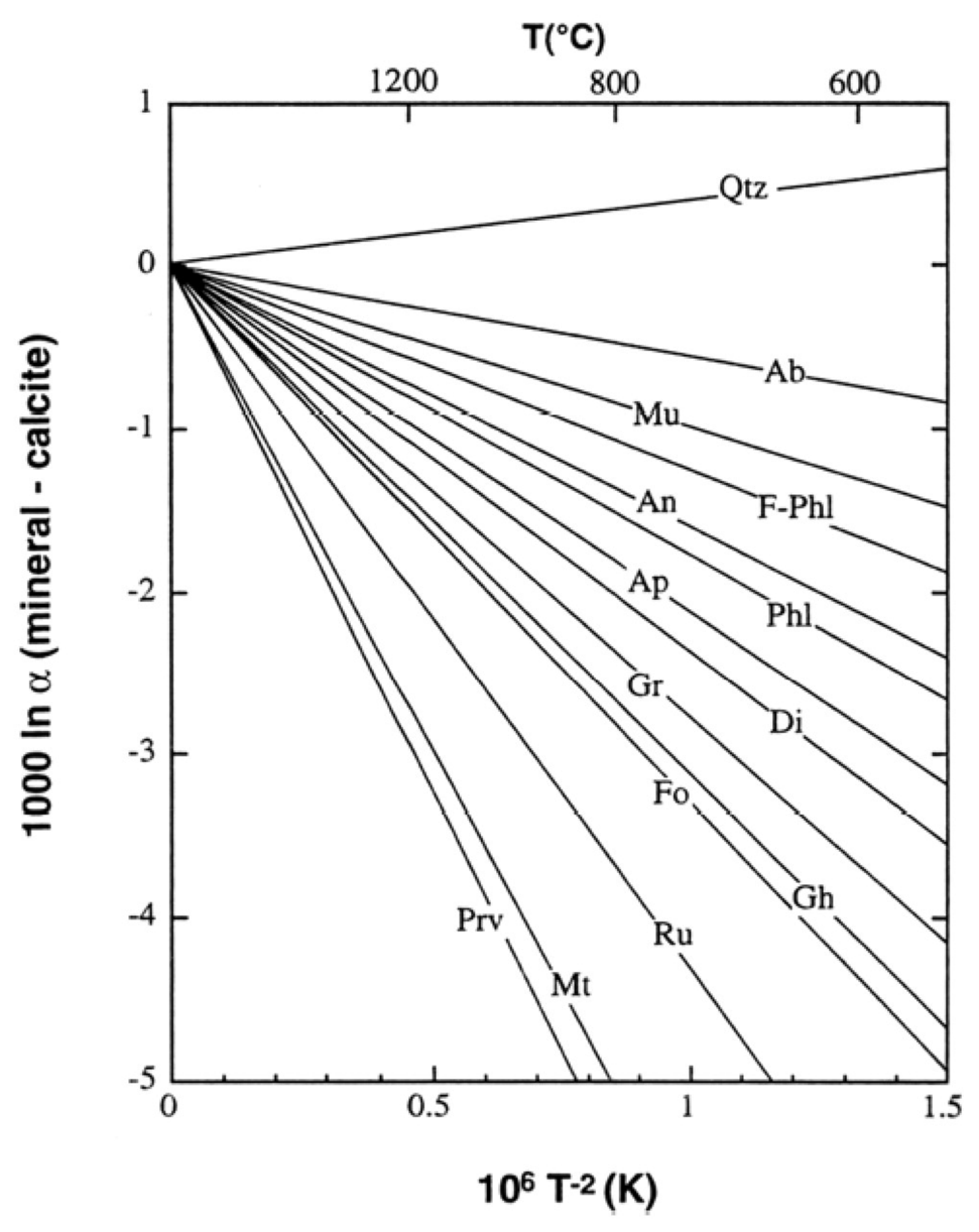
$$1000 \cdot \ln \beta_A = a \cdot x + b \cdot x^2 + c \cdot x^3$$

**where** $x = 10^6 / T^2$ **with T in K and a, b and c are tabulated factors**

# Example of reduced partition function for oxygen isotopes in minerals



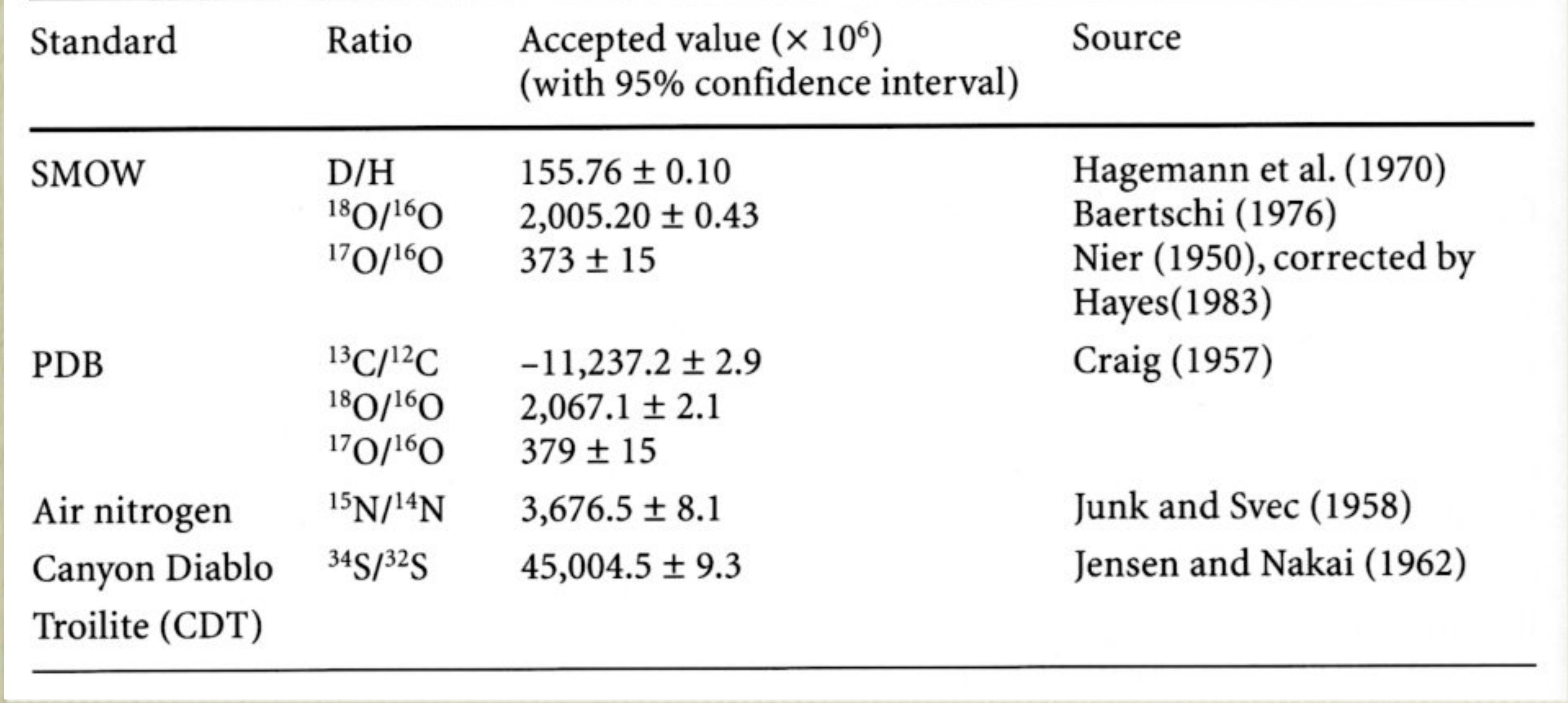
| Mineral | 1000 ln β |
|---|---|
| Calcite | $11.781\,x - 0.420\,x^2 + 0.0158\,x^3$ |
| Quartz | $12.116\,x - 0.370\,x^2 + 0.0123\,x^3$ |
| Albite | $11.134\,x - 0.326\,x^2 + 0.0104\,x^3$ |
| Muscovite | $10.766\,x - 0.412\,x^2 + 0.0209\,x^3$ |
| Anorthite | $9.993\,x - 0.271\,x^2 + 0.0082\,x^3$ |
| Phlogopite | $9.969\,x - 0.382\,x^2 + 0.0194\,x^3$ |
| F-phlogopite | $10.475\,x - 0.401\,x^2 + 0.0203\,x^3$ |
| Diopside | $9.237\,x - 0.199\,x^2 + 0.0053x^3$ |
| Forsterite | $8.236\,x - 0.142\,x^2 + 0.0032\,x^3$ |
| Rutile | $7.258\,x – 0.125\,x^2 + 0.0033\,x^3$ |
| Magnetite | $5.674\,x - 0.038\,x^2 + 0.0003\,x^3$ |



Chacko et al., 2001, RiMG

# Notations and standards used as reference for delta values

$$\delta_A = 1000 \cdot \left[ \frac{\left(N^* / N\right)_A}{\left(N^* / N\right)_{std}} - 1 \right]$$ **in ‰**



| Standard | Ratio | Accepted value (× $10^6$) (with 95% confidence interval) | Source |
|---|---|---|---|
| SMOW | D/H | 155.76 ± 0.10 | Hagemann et al. (1970) |
| | $^{18}O/^{16}O$ | 2,005.20 ± 0.43 | Baertschi (1976) |
| | $^{17}O/^{16}O$ | 373 ± 15 | Nier (1950), corrected by Hayes(1983) |
| PDB | $^{13}C/^{12}C$ | –11,237.2 ± 2.9 | Craig (1957) |
| | $^{18}O/^{16}O$ | 2,067.1 ± 2.1 | |
| | $^{17}O/^{16}O$ | 379 ± 15 | |
| Air nitrogen | $^{15}N/^{14}N$ | 3,676.5 ± 8.1 | Junk and Svec (1958) |
| Canyon Diablo Troilite (CDT) | $^{34}S/^{32}S$ | 45,004.5 ± 9.3 | Jensen and Nakai (1962) |

Franck Poitrasson, CNRS

# Mixing relationships

**we take:** $R = N^{*}/N$

- Closed system (e.g., minerals in a rock):

$R_M = X_A \cdot R_A + (1 - X_A) \cdot R_B$ **in delta:** $\delta_M = X_A \cdot \delta_A + (1 - X_A) \cdot \delta_B$

**where $\delta_M$ stands for the isotopic composition of a mixture of components A and B and $X_A$ is the molar fraction of component A.**

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- Open system (e.g., a mineral in the ocean):

$R = \alpha \cdot R_0$ **and since:** $\dfrac{R}{R_0} = \dfrac{1 + \dfrac{\delta}{1000}}{1 + \dfrac{\delta_0}{1000}} \approx 1 + \dfrac{(\delta - \delta_0)}{1000}$

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**In the "open system" situation, there is no need to consider mass balance constraints, only the isotopic fractionation factor and the isotopic composition of the big reservoir will determine de isotopic composition of the small reservoir.**

# A useful specific open-system case: the Rayleigh isotopic fractionation

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$$R = R_i \cdot f^{(\alpha - 1)}$$

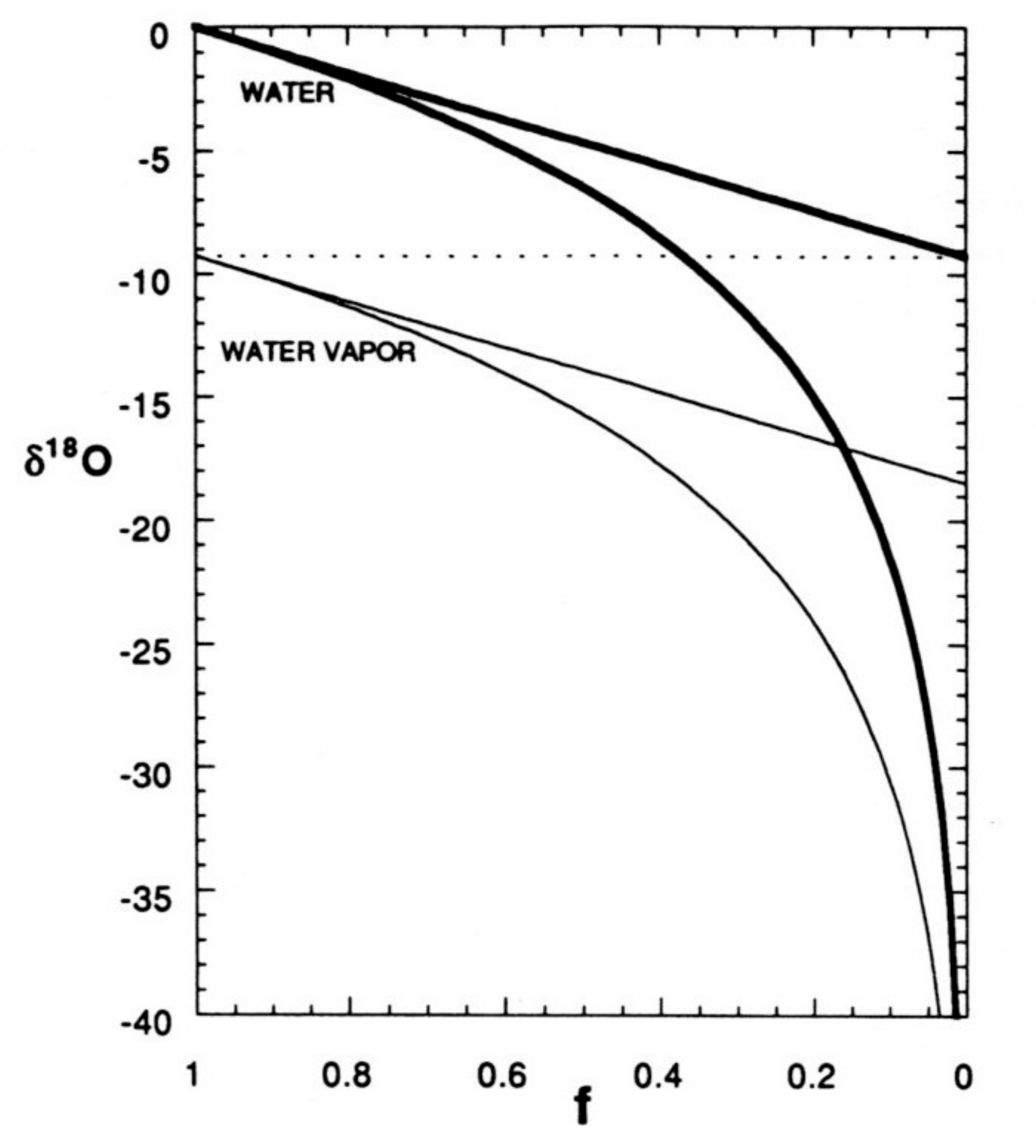
where $R_i$ is the isotopic ratio of the reservoir at the beginning of the process, when the fraction remaining, f =1.

α is the fractionation factor.

**Using the delta notation, this expression may be rearranged as:**

$$\delta = \delta_i + 1000 \cdot (\alpha - 1) \cdot \ln f$$

# Example of water condensation effect on oxygen isotopes:



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Franck Poitrasson, CNRS

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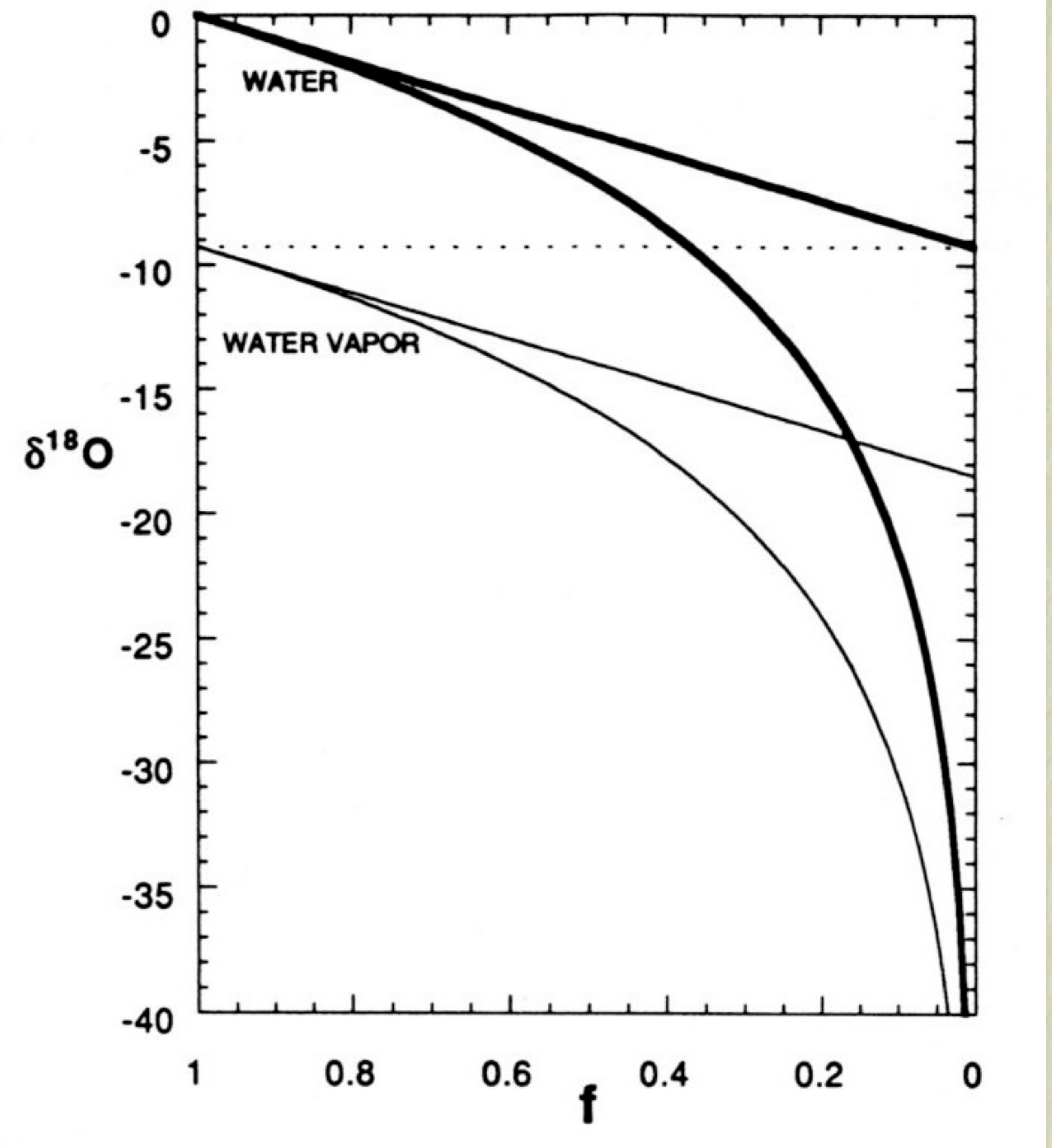
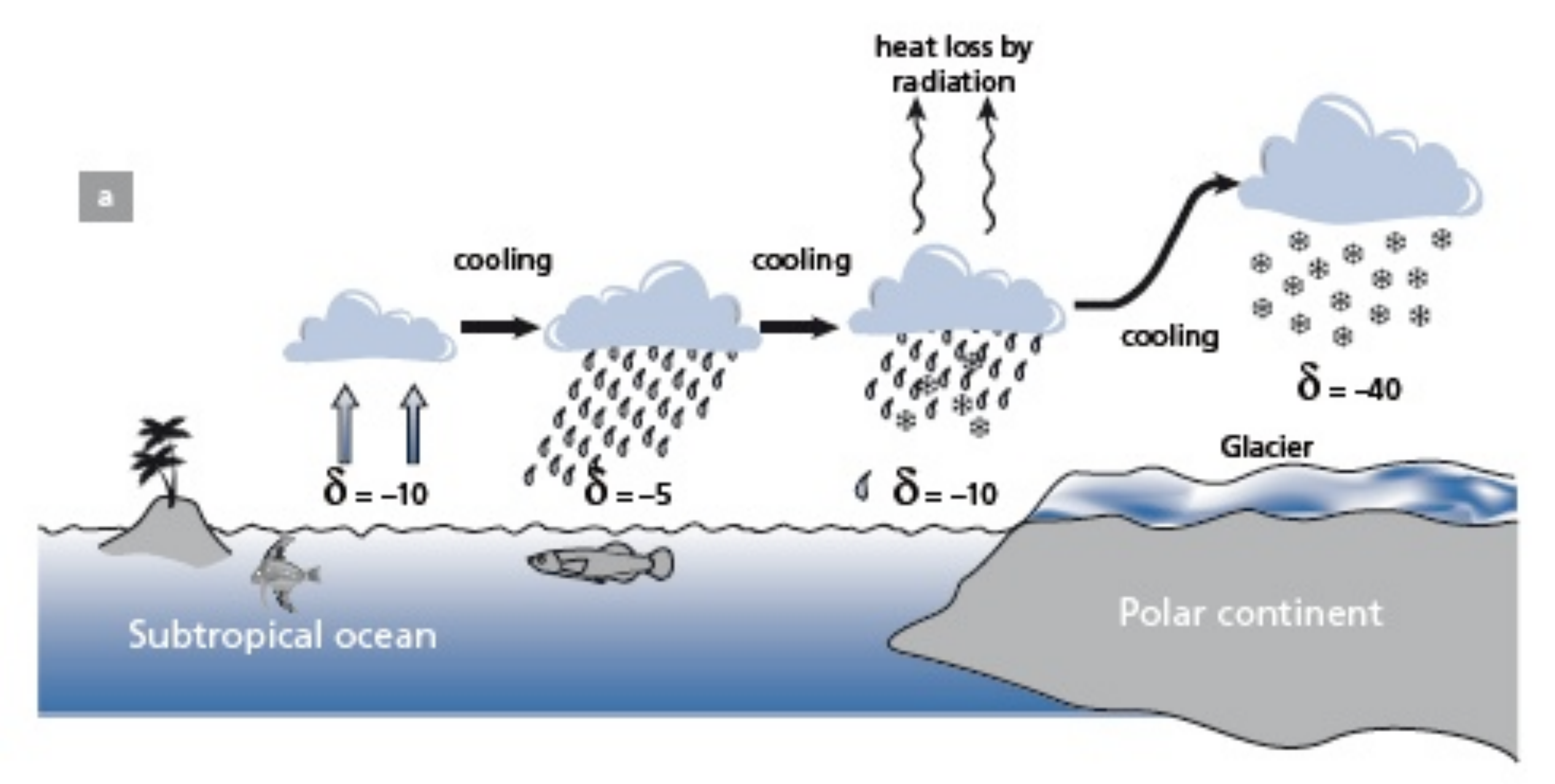


- Closed system (straight lines): the last condensate reach the isotopic composition of the starting vapor

- Open system (Rayleigh distillation, curves): the last condensate reach much lighter oxygen isotope composition

Note: $\alpha$ is constant in both cases

# Application to rainwater $\delta^{18}O$ (‰) from the tropics to the poles



- Precipitations become lighter at higher latitudes

After Dansgaard, 1964, Tellus

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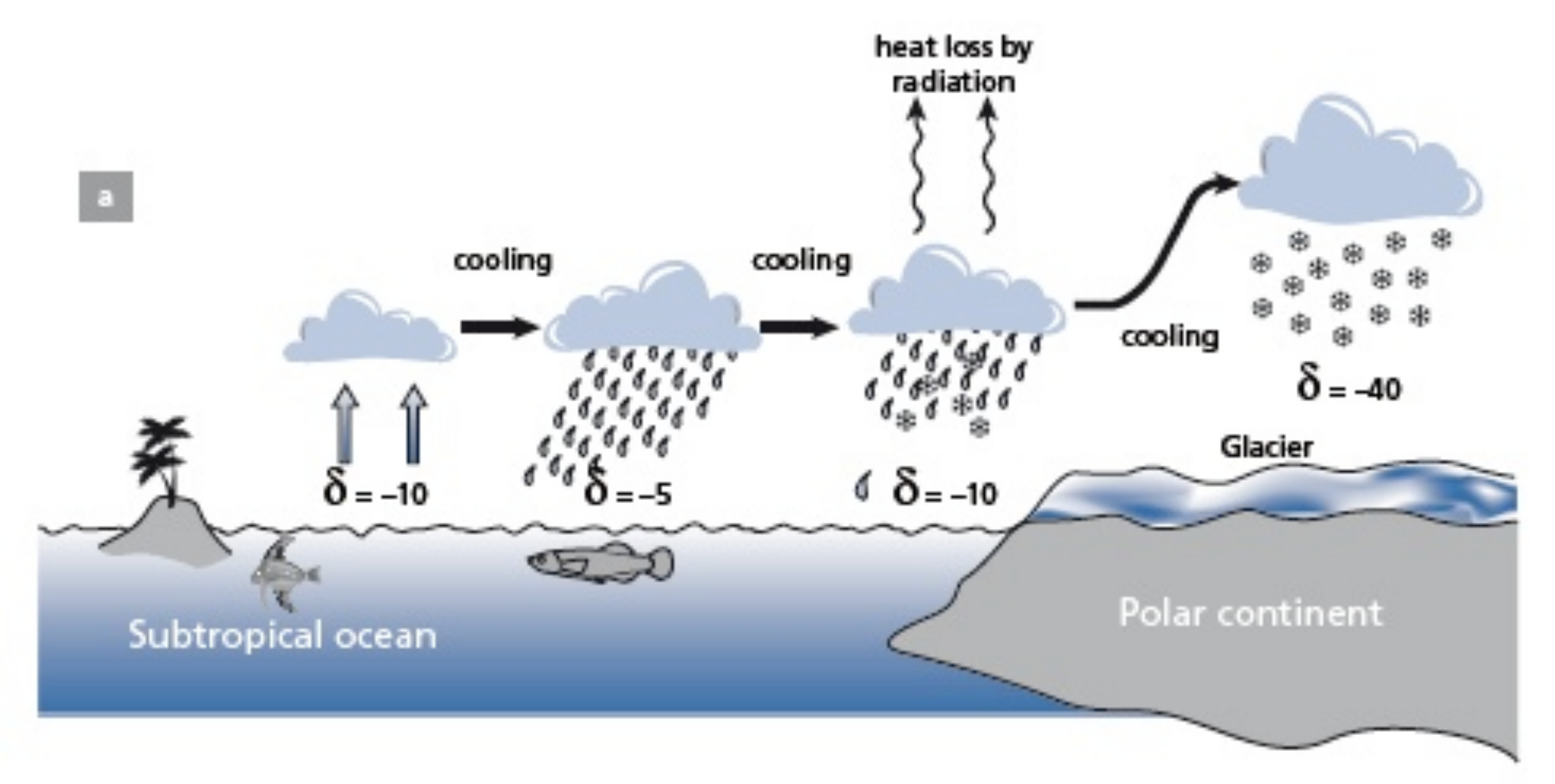

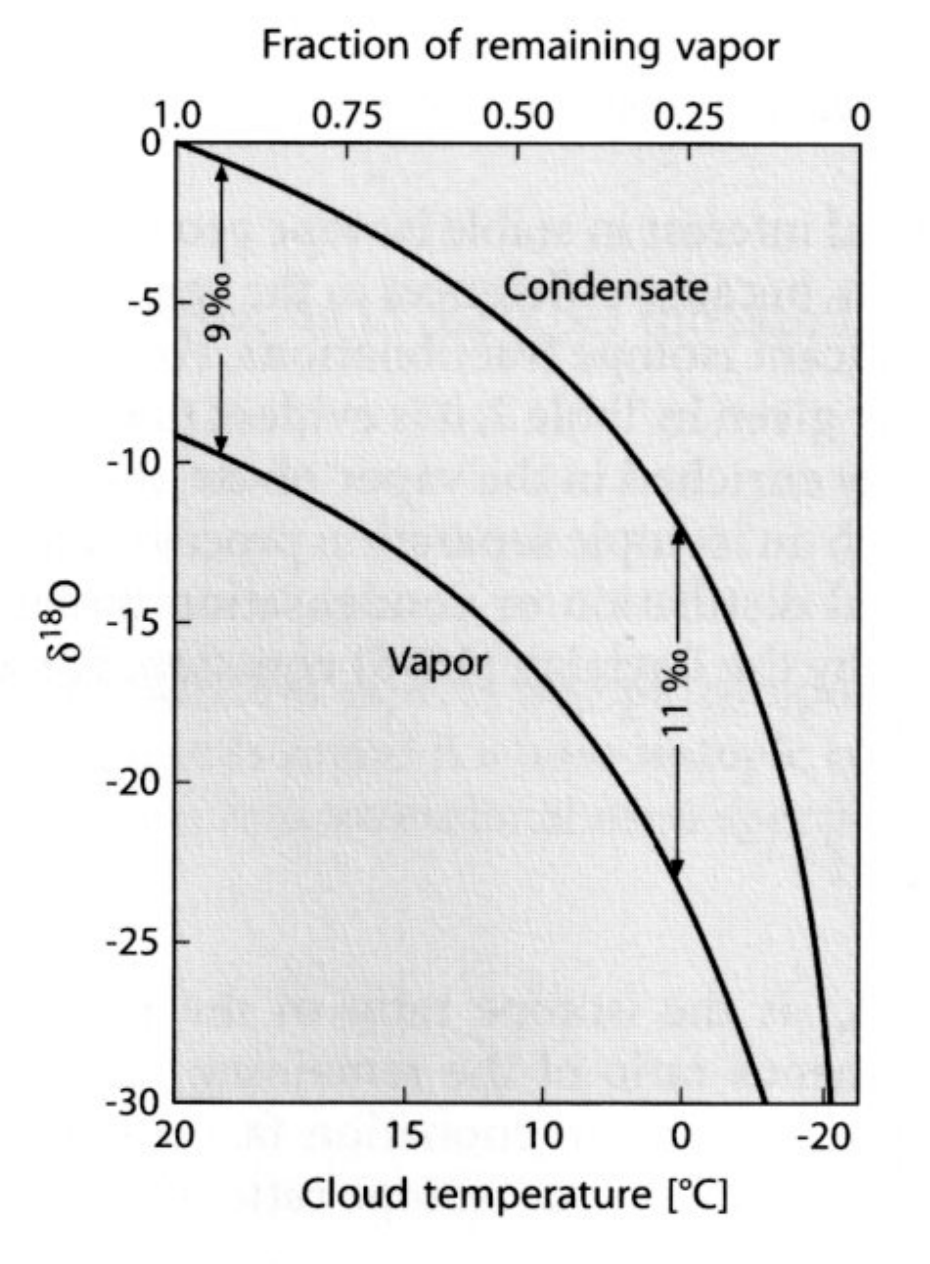

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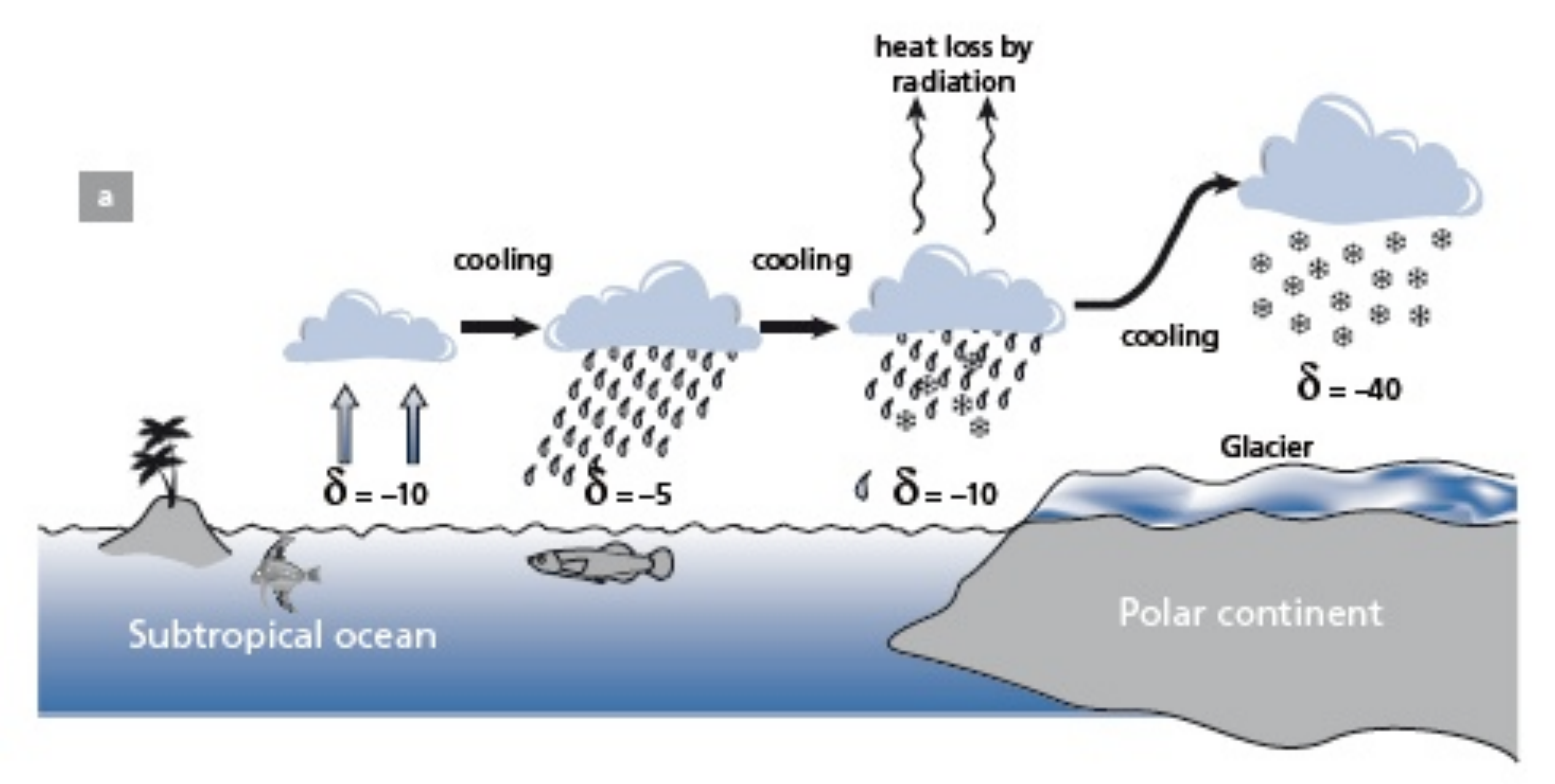
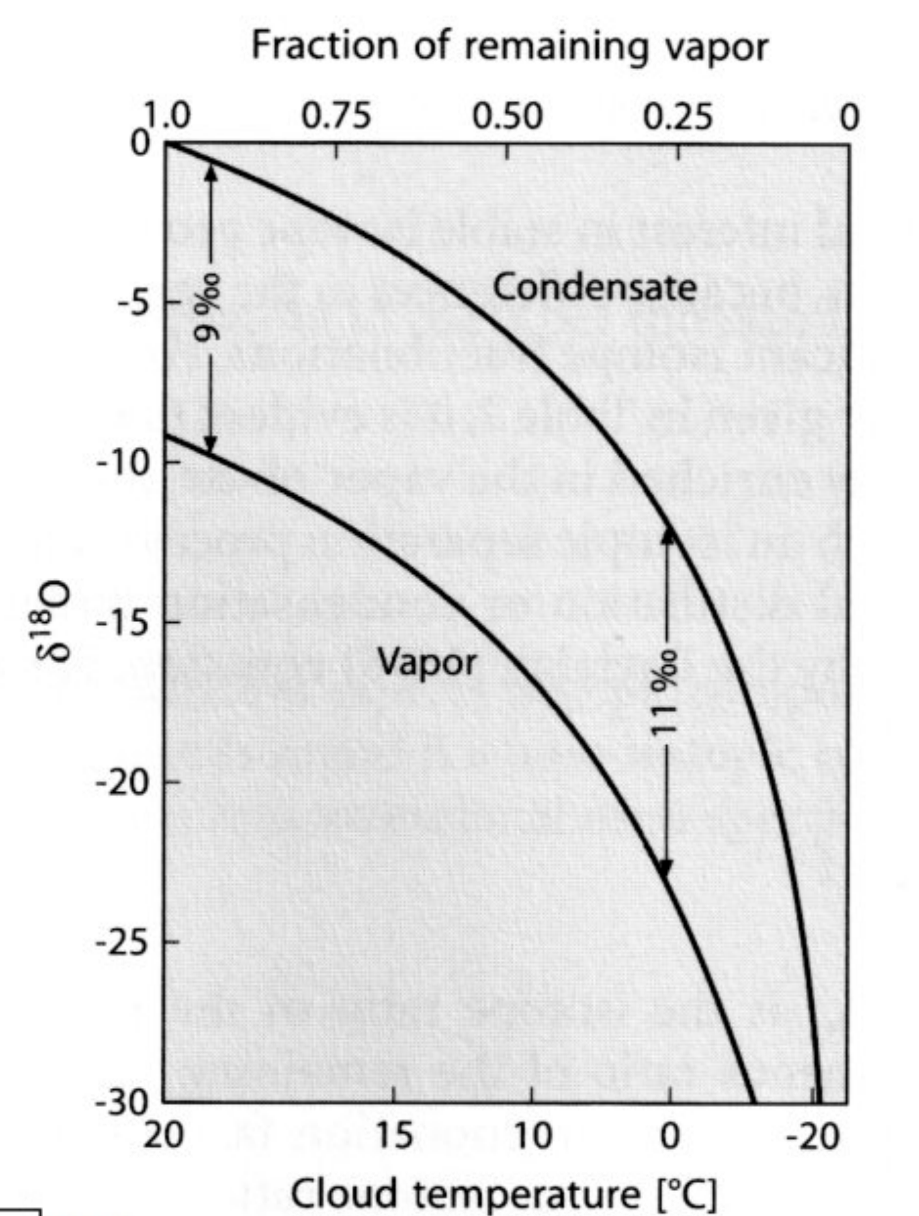
# Application to rainwater δ¹⁸O (‰) from the tropics to the poles

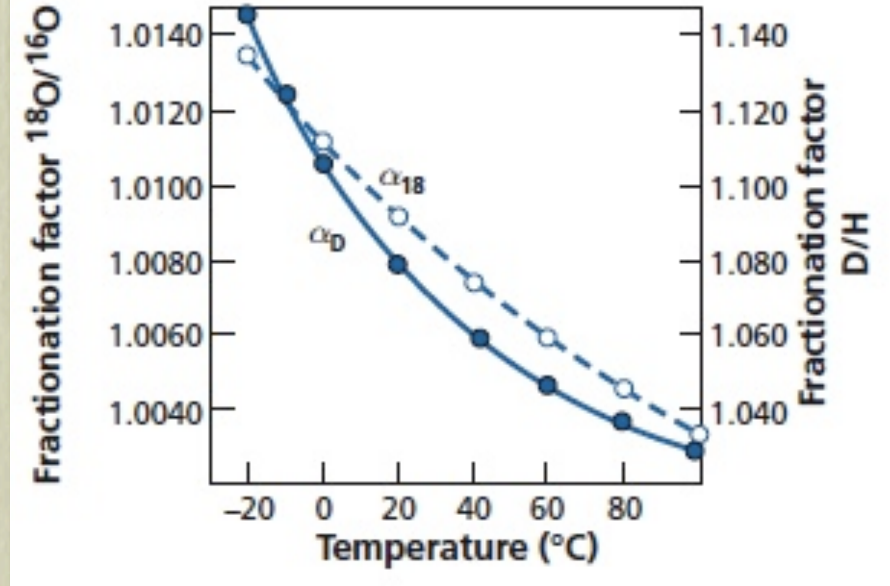




- Precipitations become lighter at higher latitudes

- α varies because there is a temperature effect

- Same story for δD



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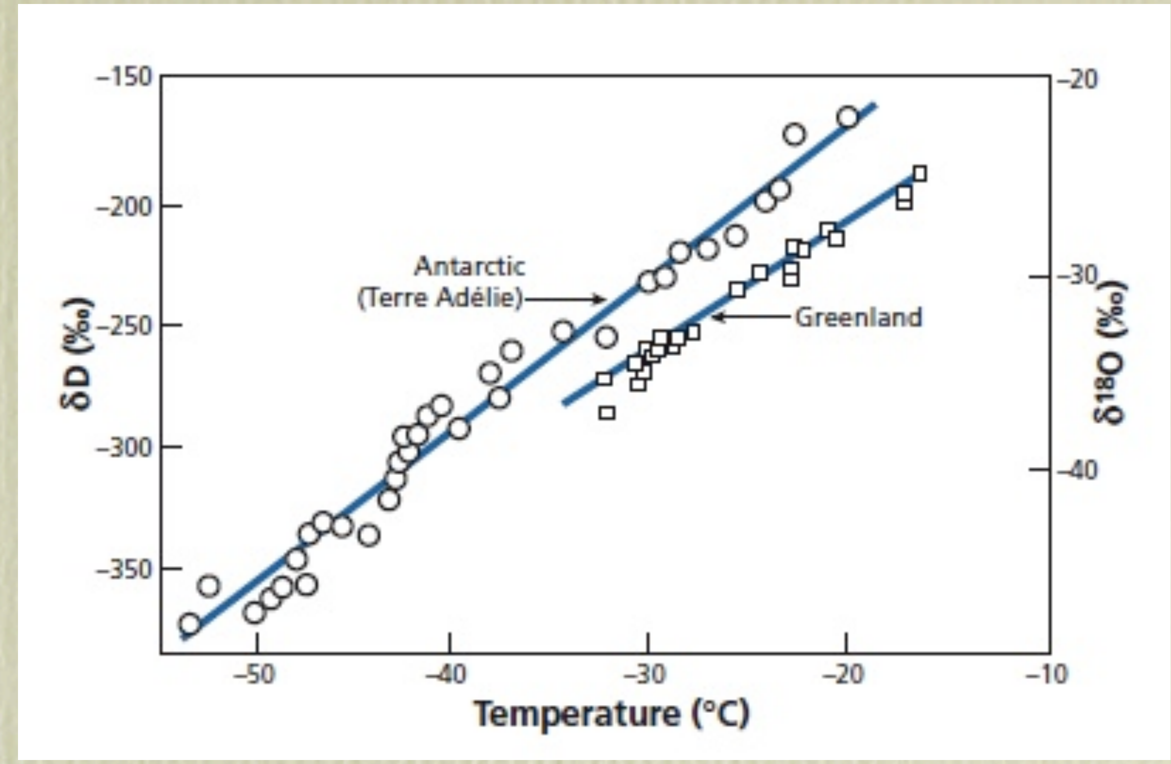
# Application for climate reconstruction using polar ice cores



After Lorius and Merlivat, 1977; Johnsen et al., 1989

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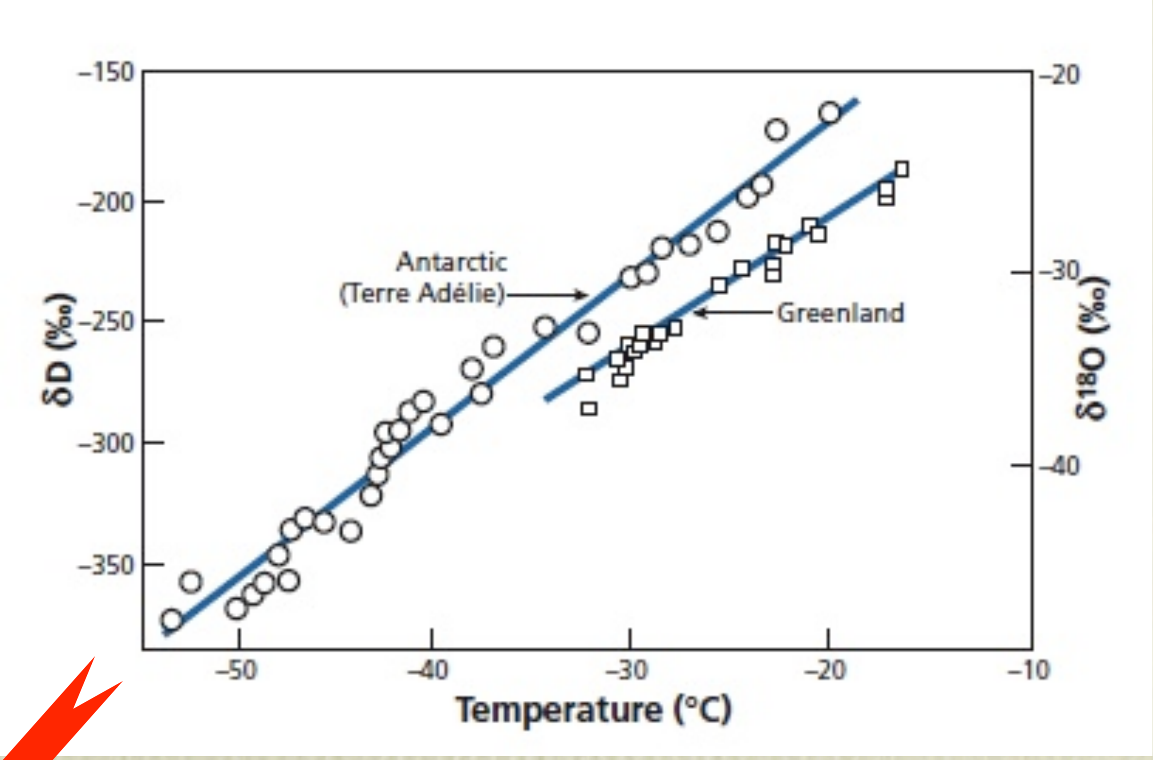

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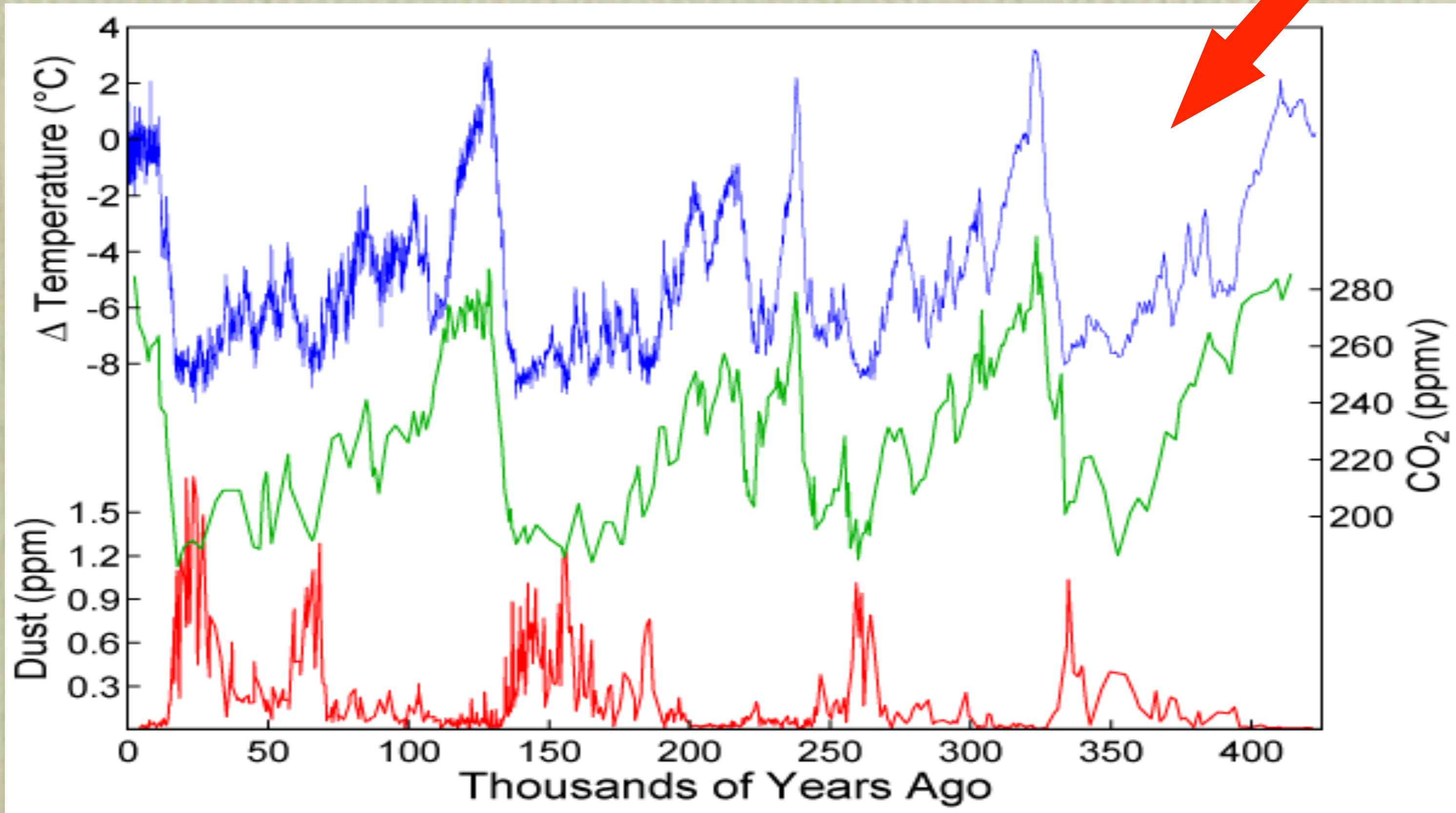

After Petit et al., 1999, Nature

- Temperature in the ice computed from δD
- Allows to show relationships between mean air temperature with other parameters, such as greenhouse gases

# Suggested readings:

- Allègre, C.J., 2008. Isotope geology. Cambridge University Press, Cambridge, 512 pp.
- Hoefs, J., 2004. Stable isotope geochemistry. Springer-Verlag, Berlin, 244 pp.
- Criss, R.E., 1999. Principles of stable isotope distribution. Oxford University Press, Oxford, 254 pp.
- Reviews in Mineralogy (and Geochemistry) on Stable Isotopes (vol. 16, 1986 & vol. 43, 2001)