Stable isotopes

in Earth Sciences

Anna Szreter

Content

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- stable isotopes
- fractionation
- notation
- standards

Methods

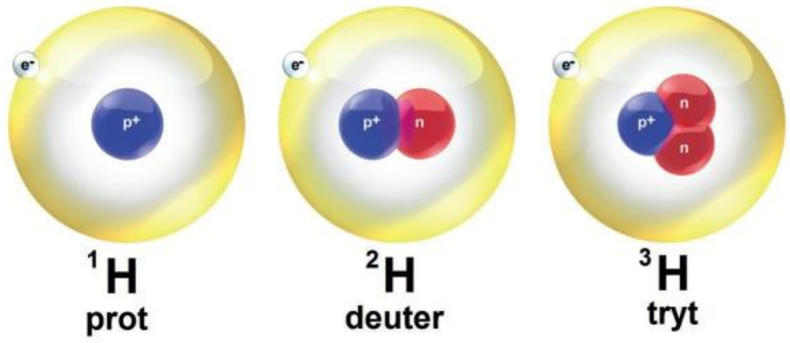
- IRMS
- alternatives
- traps

Applications

- general
- isotopic systems
- examples

Isotopes

”atoms of the same chemical element with the same atomic numer, position in periodic table and chemical properties, but different atomic masses and physical properties (Britannica)



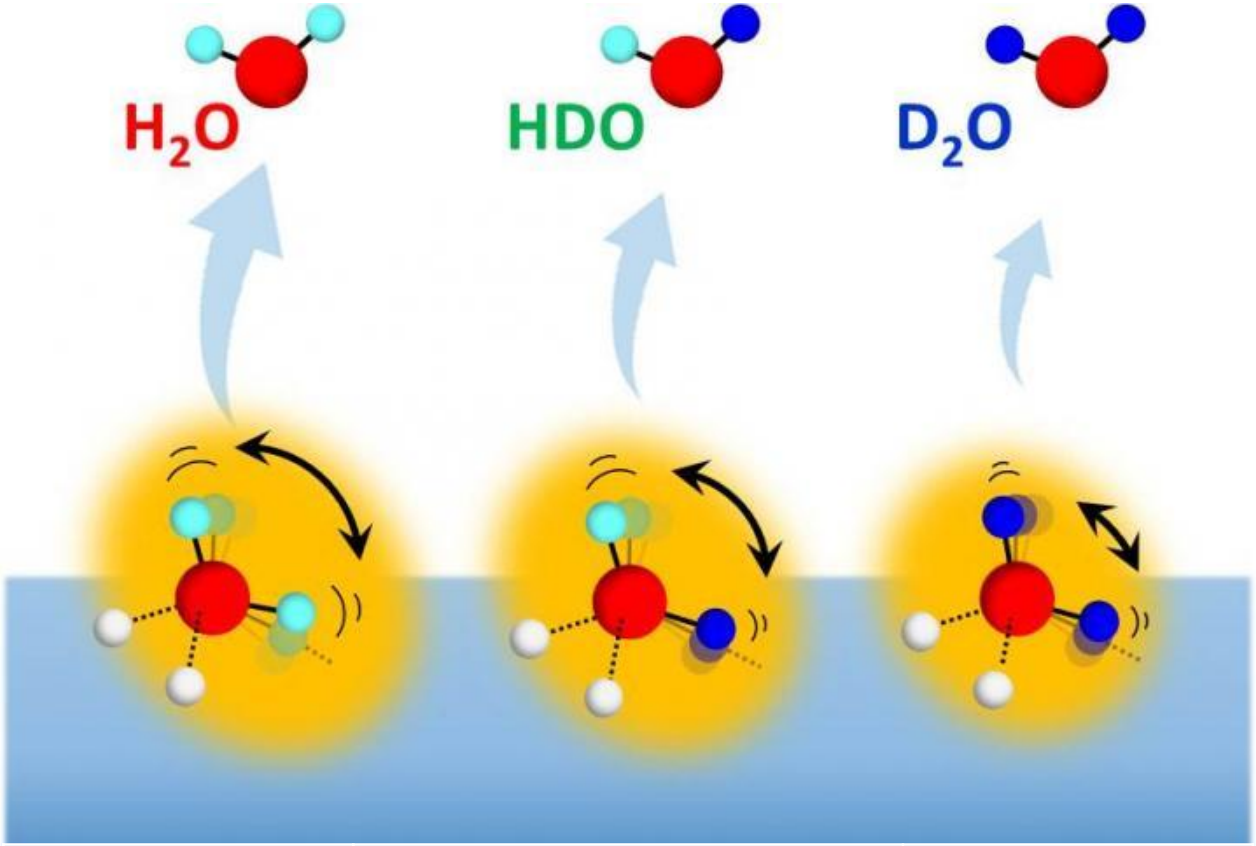
A – mass numer

(protons + neutrons)

Z – atomic number

(numer of protons)

$$^{A}_{Z}X$$

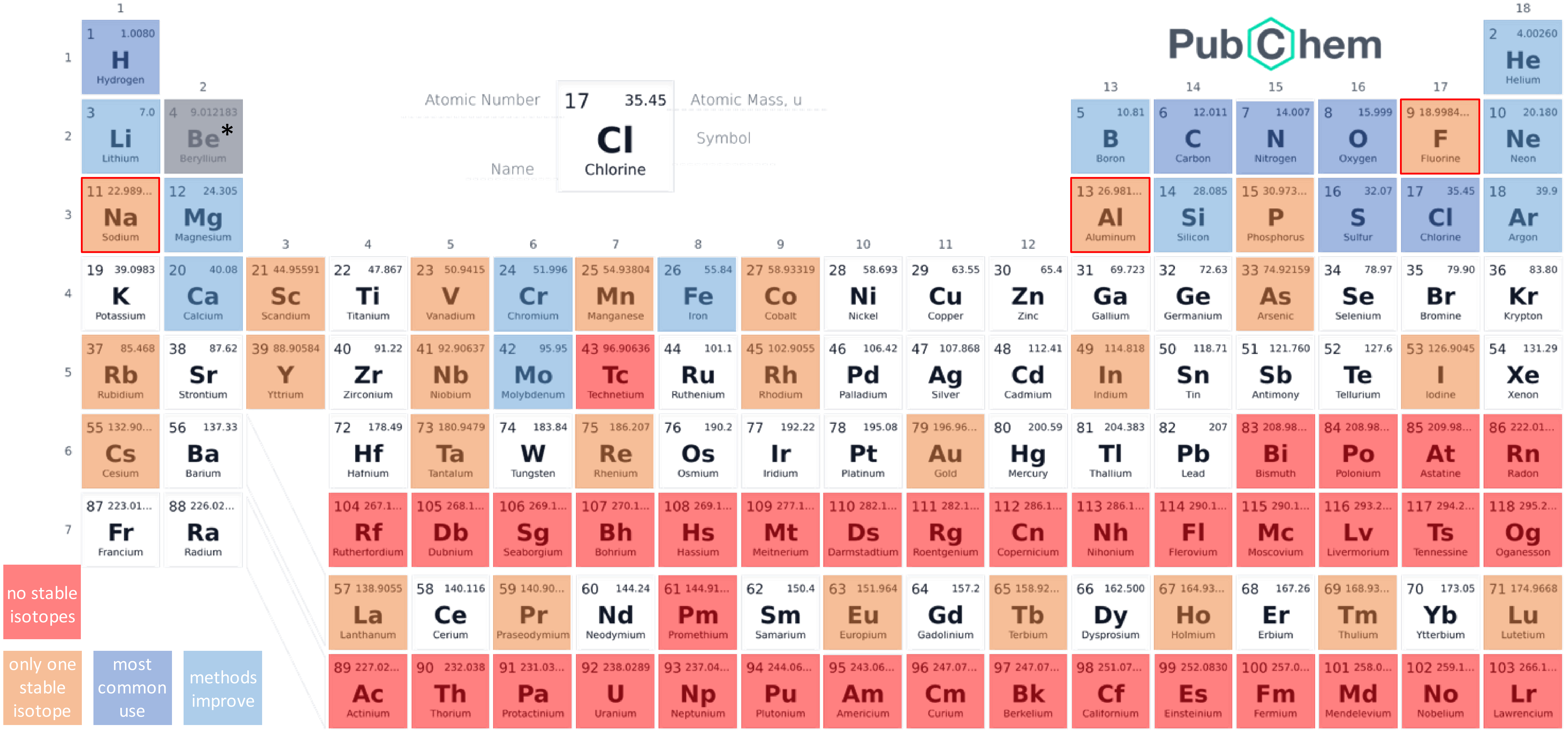


H_2O	Property	D_2O
100.00	Boiling point [°C]	101.42
0.00	Freezing point [°C]	3.82

https://promieniowanie.blogspot.com/

https://www.innovations-report.com/

PERIODIC TABLE OF ELEMENTS



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 1.0080 **H** Hydrogen																	2 4.00260 **He** Helium
2	3 7.0 **Li** Lithium	4 9.012183 **Be*** Beryllium											5 10.81 **B** Boron	6 12.011 **C** Carbon	7 14.007 **N** Nitrogen	8 15.999 **O** Oxygen	9 18.9984... **F** Fluorine	10 20.180 **Ne** Neon
3	11 22.989... **Na** Sodium	12 24.305 **Mg** Magnesium											13 26.981... **Al** Aluminum	14 28.085 **Si** Silicon	15 30.973... **P** Phosphorus	16 32.07 **S** Sulfur	17 35.45 **Cl** Chlorine	18 39.9 **Ar** Argon
4	19 39.0983 **K** Potassium	20 40.08 **Ca** Calcium	21 44.95591 **Sc** Scandium	22 47.867 **Ti** Titanium	23 50.9415 **V** Vanadium	24 51.996 **Cr** Chromium	25 54.93804 **Mn** Manganese	26 55.84 **Fe** Iron	27 58.93319 **Co** Cobalt	28 58.693 **Ni** Nickel	29 63.55 **Cu** Copper	30 65.4 **Zn** Zinc	31 69.723 **Ga** Gallium	32 72.63 **Ge** Germanium	33 74.92159 **As** Arsenic	34 78.97 **Se** Selenium	35 79.90 **Br** Bromine	36 83.80 **Kr** Krypton
5	37 85.468 **Rb** Rubidium	38 87.62 **Sr** Strontium	39 88.90584 **Y** Yttrium	40 91.22 **Zr** Zirconium	41 92.90637 **Nb** Niobium	42 95.95 **Mo** Molybdenum	43 96.90636 **Tc** Technetium	44 101.1 **Ru** Ruthenium	45 102.9055 **Rh** Rhodium	46 106.42 **Pd** Palladium	47 107.868 **Ag** Silver	48 112.41 **Cd** Cadmium	49 114.818 **In** Indium	50 118.71 **Sn** Tin	51 121.760 **Sb** Antimony	52 127.6 **Te** Tellurium	53 126.9045 **I** Iodine	54 131.29 **Xe** Xenon
6	55 132.90... **Cs** Cesium	56 137.33 **Ba** Barium		72 178.49 **Hf** Hafnium	73 180.9479 **Ta** Tantalum	74 183.84 **W** Tungsten	75 186.207 **Re** Rhenium	76 190.2 **Os** Osmium	77 192.22 **Ir** Iridium	78 195.08 **Pt** Platinum	79 196.96... **Au** Gold	80 200.59 **Hg** Mercury	81 204.383 **Tl** Thallium	82 207 **Pb** Lead	83 208.98... **Bi** Bismuth	84 208.98... **Po** Polonium	85 209.98... **At** Astatine	86 222.01... **Rn** Radon
7	87 223.01... **Fr** Francium	88 226.02... **Ra** Radium		104 267.1... **Rf** Rutherfordium	105 268.1... **Db** Dubnium	106 269.1... **Sg** Seaborgium	107 270.1... **Bh** Bohrium	108 269.1... **Hs** Hassium	109 277.1... **Mt** Meitnerium	110 282.1... **Ds** Darmstadtium	111 282.1... **Rg** Roentgenium	112 286.1... **Cn** Copernicium	113 286.1... **Nh** Nihonium	114 290.1... **Fl** Flerovium	115 290.1... **Mc** Moscovium	116 293.2... **Lv** Livermorium	117 294.2... **Ts** Tennessine	118 295.2... **Og** Oganesson
				57 138.9055 **La** Lanthanum	58 140.116 **Ce** Cerium	59 140.90... **Pr** Praseodymium	60 144.24 **Nd** Neodymium	61 144.91... **Pm** Promethium	62 150.4 **Sm** Samarium	63 151.964 **Eu** Europium	64 157.2 **Gd** Gadolinium	65 158.92... **Tb** Terbium	66 162.500 **Dy** Dysprosium	67 164.93... **Ho** Holmium	68 167.26 **Er** Erbium	69 168.93... **Tm** Thulium	70 173.05 **Yb** Ytterbium	71 174.9668 **Lu** Lutetium
				89 227.02... **Ac** Actinium	90 232.038 **Th** Thorium	91 231.03... **Pa** Protactinium	92 238.0289 **U** Uranium	93 237.04... **Np** Neptunium	94 244.06... **Pu** Plutonium	95 243.06... **Am** Americium	96 247.07... **Cm** Curium	97 247.07... **Bk** Berkelium	98 251.07... **Cf** Californium	99 252.0830 **Es** Einsteinium	100 257.0... **Fm** Fermium	101 258.0... **Md** Mendelevium	102 259.1... **No** Nobelium	103 266.1... **Lr** Lawrencium

*Be has only one stable isotope, but cosmogenic ^{10}Be with half live of 1.5 mln years is generated in upper atmosphere and so ^{10}Be/^{9}Be ratio can be measured in waters or soils

https://pubchem.ncbi.nlm.nih.gov/periodic-table/, modified

Isotopic fractionation

”enrichment of one isotope relative to another in a chemical or physical proces (Britannica)

”relative partitioning of the heavier and lighter isotopes between two coexisting phases in a natural system (Tiwari 2015)

Fractionation

Kinetic isotope effects

kinetic energy [$E_k=(mv^2)/2$] per molecule is the same in all ideal gases

higher mass = lower velocity

heavy molecules more stable

operates mostly on the surface

irreversible

Equilibrium isotope effects

equilibrium exchange reactions

effect of atomic mass on bond energy

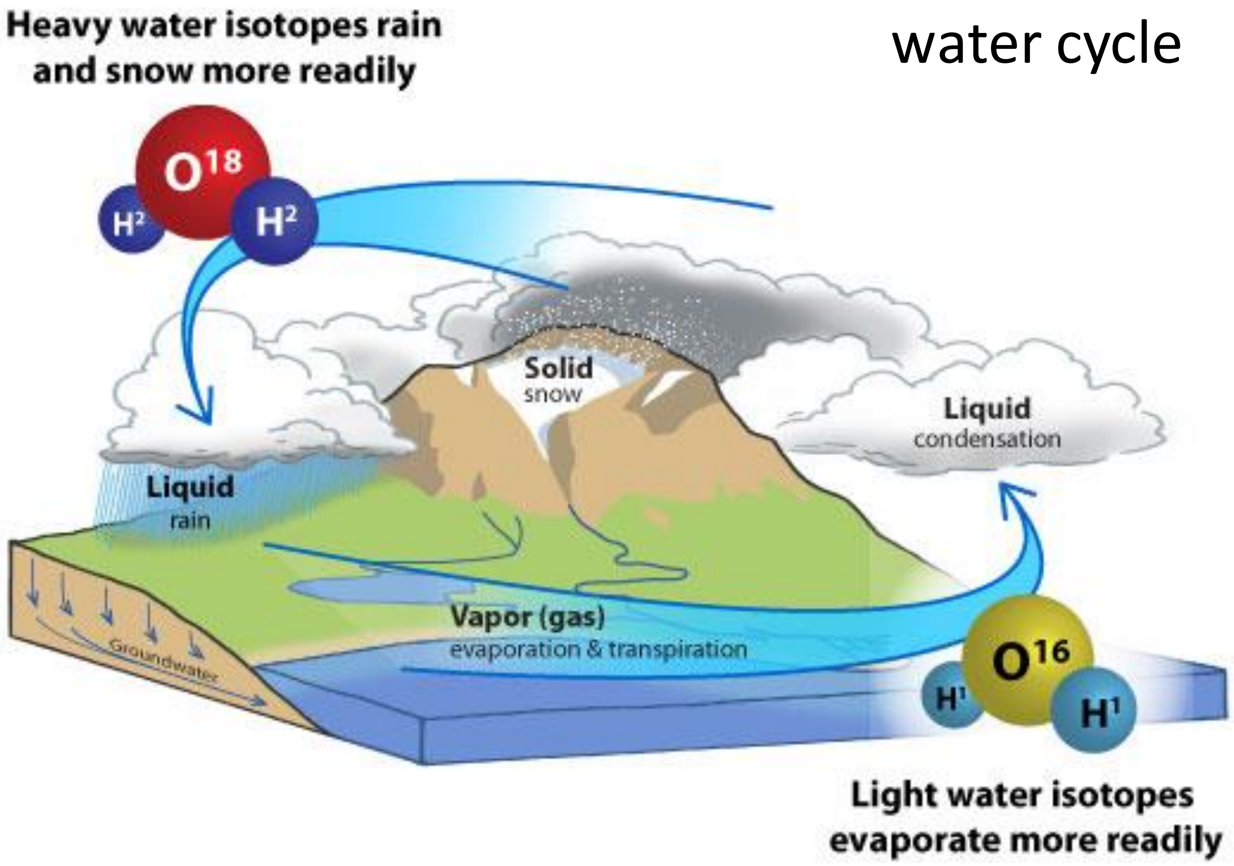
varies as a function of temperature

expressed by fractionation factor

reversible

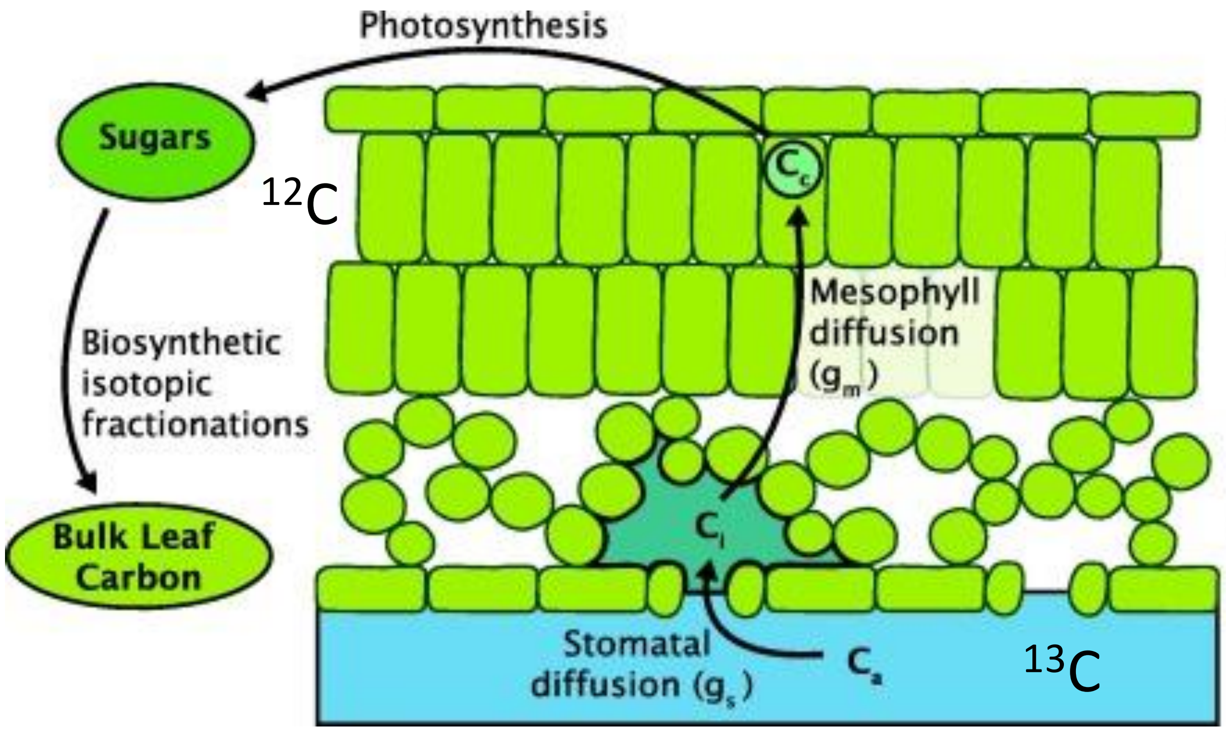
Kinetic isotope fractionation

water cycle



https://www.usgs.gov/media/images/water-cycle-and-water-isotopes

photosynthesis



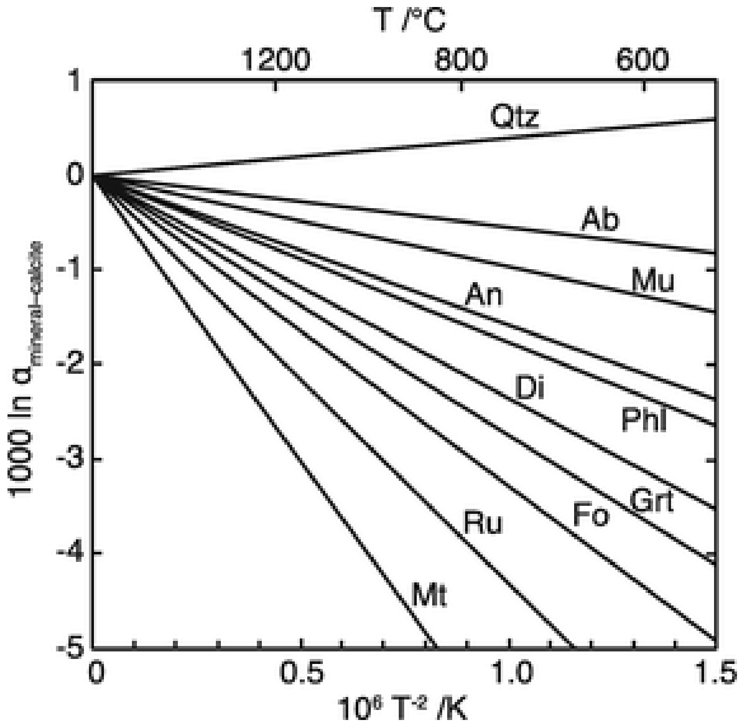
Scher, M. A. *et al.* (2022). The effect of CO2 concentration on carbon isotope discrimination during photosynthesis in Ginkgo biloba: implications for reconstructing atmospheric CO2 levels in the geologic past. *Geochimica et Cosmochimica Acta*, *337*, 82-94.

Equilibrium isotope fractionation

Rules of equilibrium isotope fractionation (Schauble 2004):

1. fractionation decreases with increasing temperature, proportional to $1/T^2$
2. degree of fractionation is larger for the elements whose mass ratio is larger
3. heavy isotope is preferentially partitioned into the site with stiffest bond (stiff = strong & short), that is with:
   - higher oxidation state
   - lighter elements
   - more covalent bonds
   - lower coordination number

oxygen isotope geothermometer



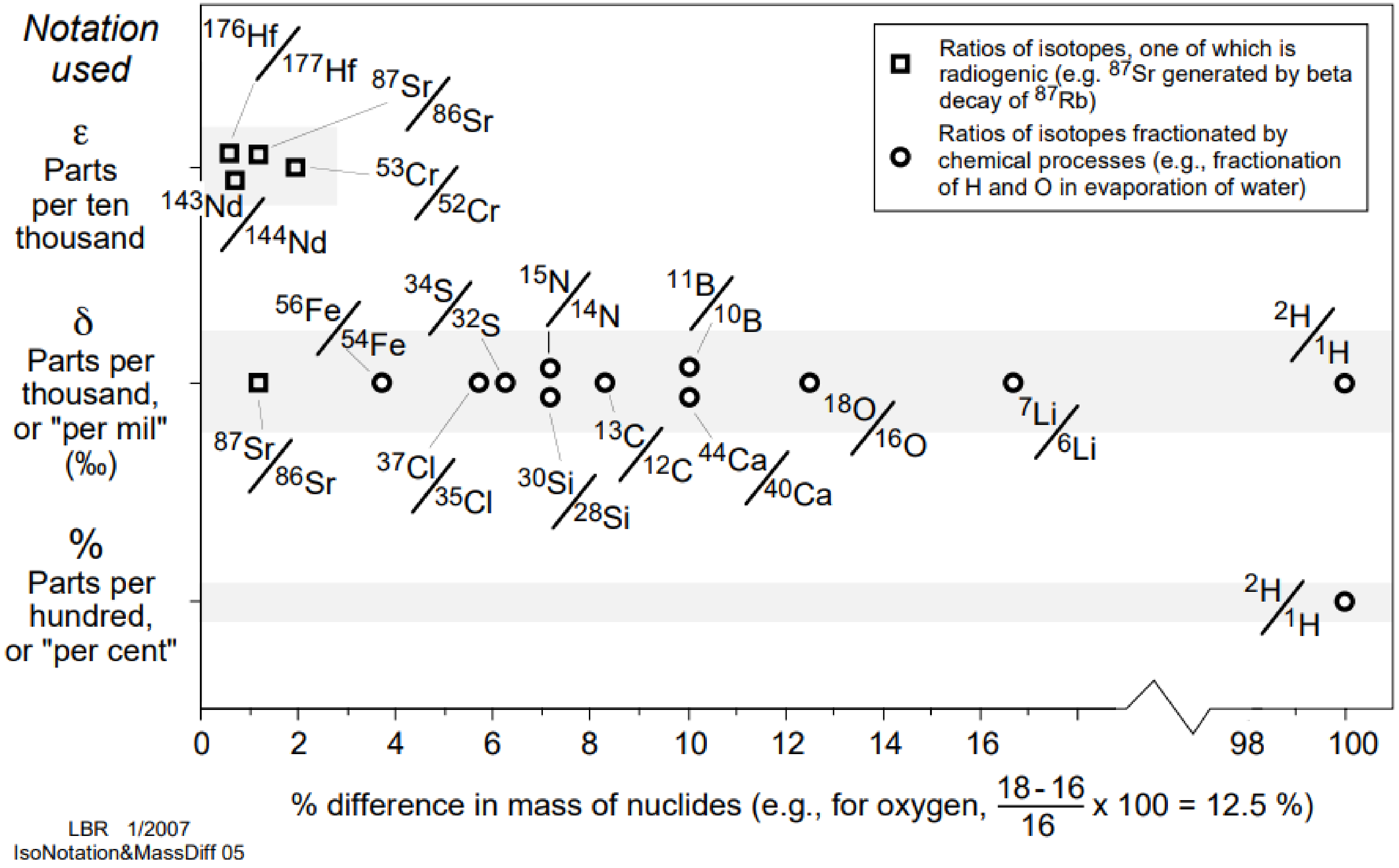
Yurimoto, H. (2018). Oxygen Isotopes. In: White, W. (eds) Encyclopedia of Geochemistry. Encyclopedia of Earth Sciences Series. Springer, Cham.

Notation

- mass of heavy and light isotope is measured
- mass ratio (R) is calculated
- this is referred to the isotope ratio of a standard material

”for most of the elements, δ (delta) notation is used, but in some cases, ε (epsilon) or percentage works better

Notations



https://railsback.org/Fundamentals/

mass ratio

$$R = \frac{m_{heavy} - m_{light}}{m_{heavy} \times m_{light}}$$

isotopic ratios

$$\%s = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 100$$

$$\delta = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000$$

$$\varepsilon = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 10\,000$$

Standards

”stable isotope standards, or isotope reference materials, are compounds (solids, liquids or gases) with precisely defined isotopic compositions

”international standards are used to enable data comparability between labs

Isotopic reference materials

- perfectly voluminous, homogeneous and available
- standards were originally defined, stored and distributed by IAEA – International Atomic Energy Agency in Vienna; now more units does it
- N – atmospheric air (no standards stored or distributed)
- O, H – ocean water
- O, C – fossil belemnite
- S – meteorite

standard	full name	substance	for
vSMOW	Vienna Standard Mean Ocean Water	water	H,O
vPDB	Pee-Dee Belemnite	calcite*	C
vCDT	Canyon Diablo Troilite	Troilite*	S
AIR	atmospheric air	gas	N

*supply exhausted, current standard is not a physical material, but mathematical construct

Analytical methods

universal & unconventional

An embarrassment of reaches

- **IRMS – Isotope Ratio Mass Spectrometry**
  - **CF-IRMS – Continuoun Flow IRMS**
  - **DI-IRMS – Double Inlet IRMS**
  - **GC-IRMS – Gas Chromatography IRMS**
- **TIMS – Thermal Ionisation Mass Spectrometry**
- **Electronic Bombardment**
- **ICP-MS – Inductively Coupled Plasma Mass Spectrometry**
  - **LA-ICP-MS – Laser Ablation ICP-MS**
  - **MC-ICP-MS – Multi-Collector ICP-MS**
- **SIMS – Secondary Ion Mass Spectrometry (also called Ion Microprobe)**
  - **SHRIMP – Sensitive High-Resolution Ion Microprobe**
- **AMS – Accelerator Mass Spectrometry**

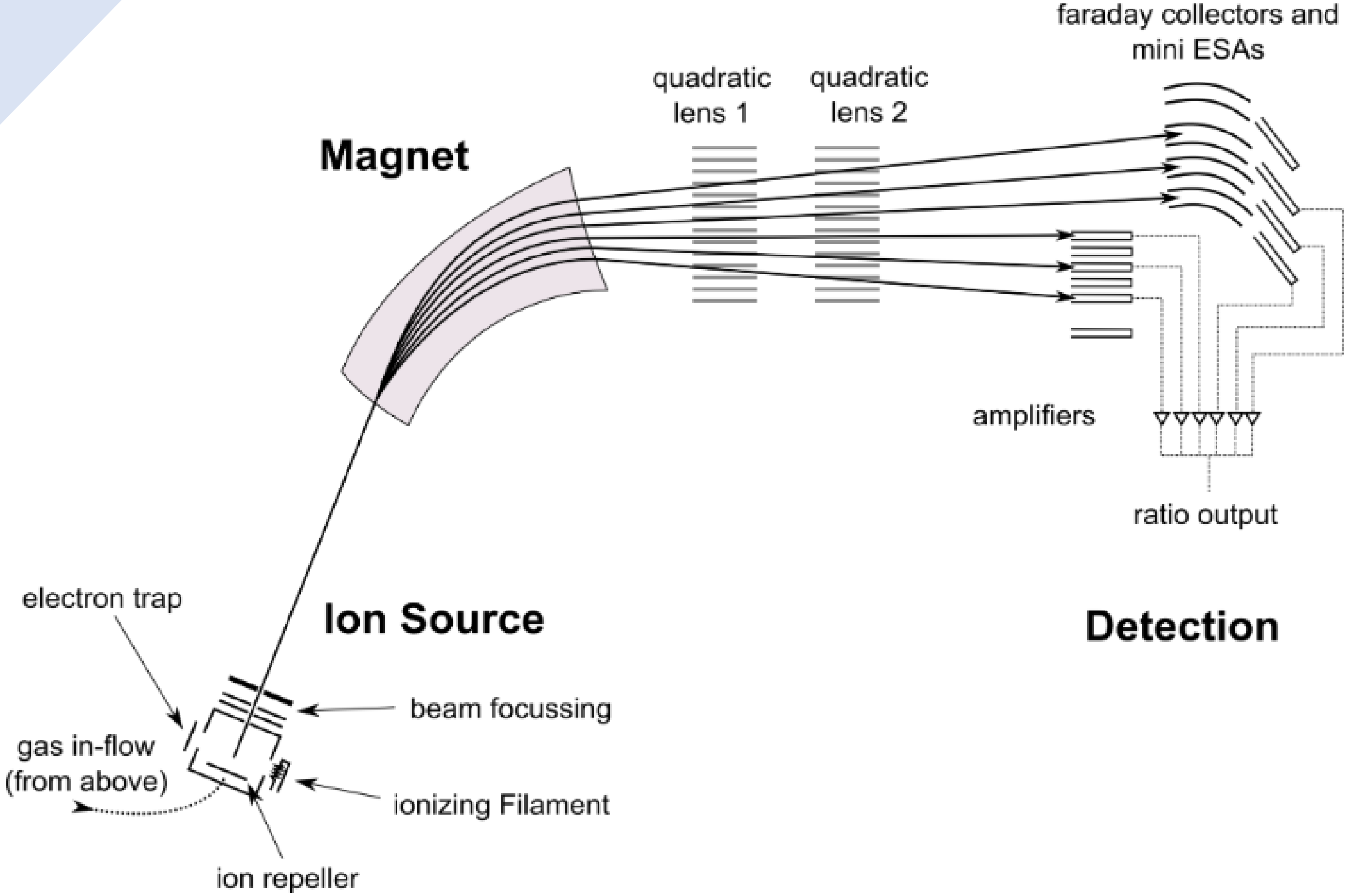
separate
atomise
ionise
accelerate
separate
detect

separation

- in clean labs
- overlapping elements (e.g. ^{87}Rb - ^{87}Sr)
- the limiting stage now

atomisation
ionisation

- various methods
- sample type (solid, liquid, gas)
- element to measure



https://www.nu-ins.com/products/irms/introductiontoirms

Which method to choose?

- solid samples, heavy elements (Rb, Sr, Pb)
  - TIMS
- gas samples, light elements & noble gases (H, C, He, Ne)
  - Electronic bombardment
- heavy elements reluctant to thermal emission (Hf, Th)
  - ICP-MS
- very small samples (e.g. interstellar dust)
  - SIMS

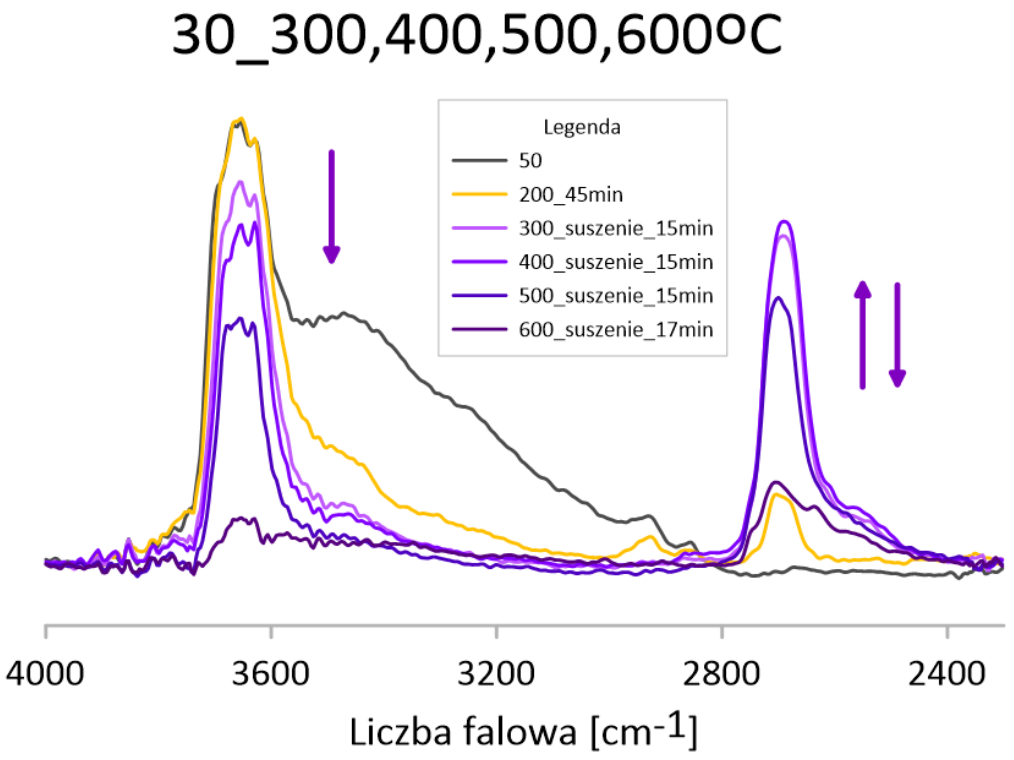
Other approaches

IR case study

OH and OD vibrations have different wavelengths

on FTIR spectra they appear on different wavenumbers

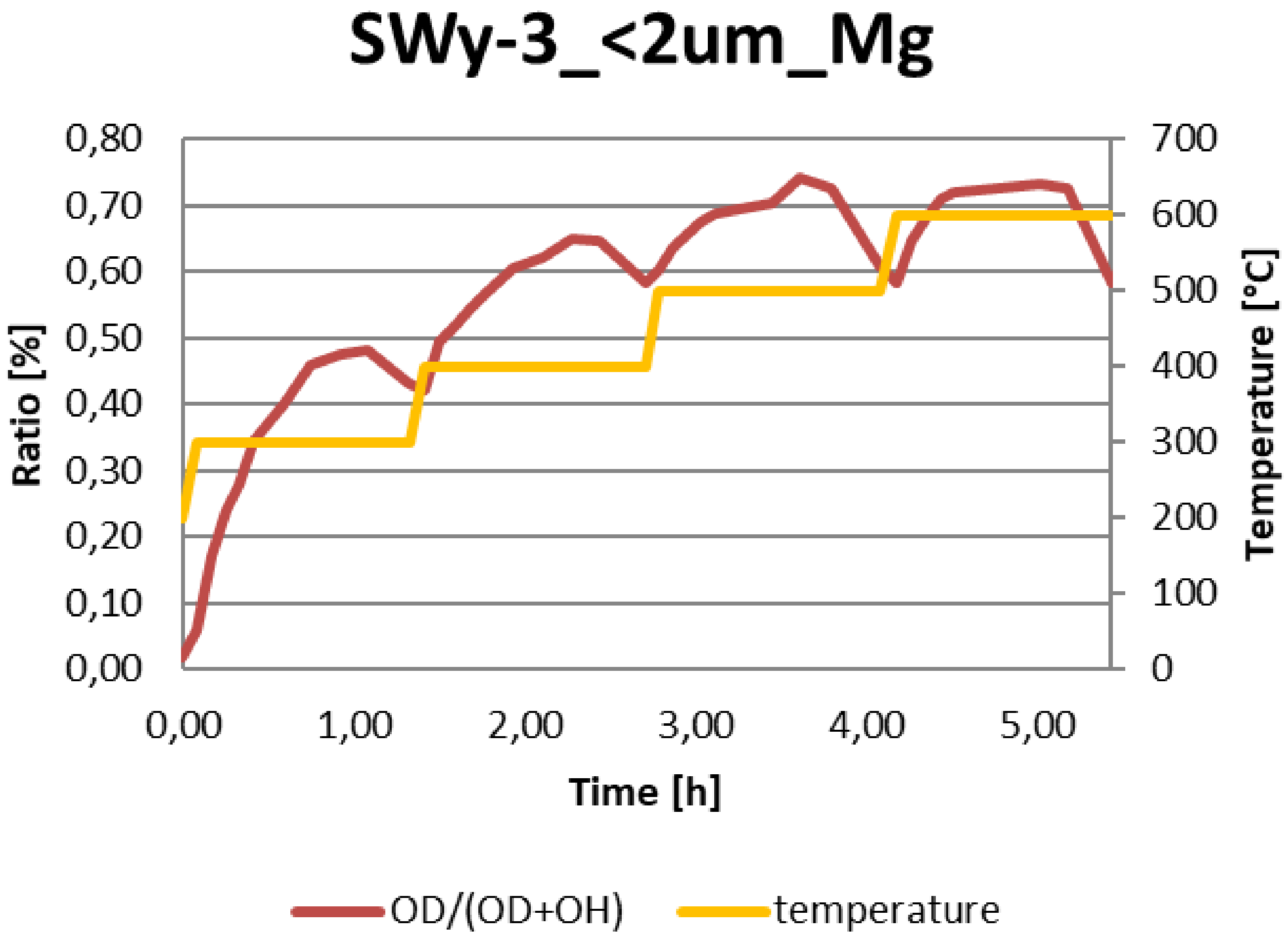
it is possible to observe the OH-OD exchange *in situ* in clay minerals



30_300,400,500,600ºC

beidellite (smectite)

Other approaches – infrared spectroscopy



montmorillonite (smectite)

Applications

litosphere and astenosphere

Applications in Earth Sciences

- geochemistry
- climatology
- hydrology
- plant physiology
- ecology
- archaeology

thermometry

- formation temperatures of rocks or minerals can be determined based on fractionation of cogenetic phases

tracers

- large reservoirs like oceans, mantle or organic matter have distinct isotope signatures -> can be used to trace the origin of rocks, fluids, contaminants etc.

reaction mechanisms

- e.g. differentiation between diffusion and recrystallization, bacterial and thermogenic processes

palaeoclimatology

- isotope ratios of minerals, gas inclusions, bones, shells, ice etc. preserve information about past conditions

- forensic medicine
- meteorology
- atmospheric science
- meteoritics
- palaeobiology
- bacteriology

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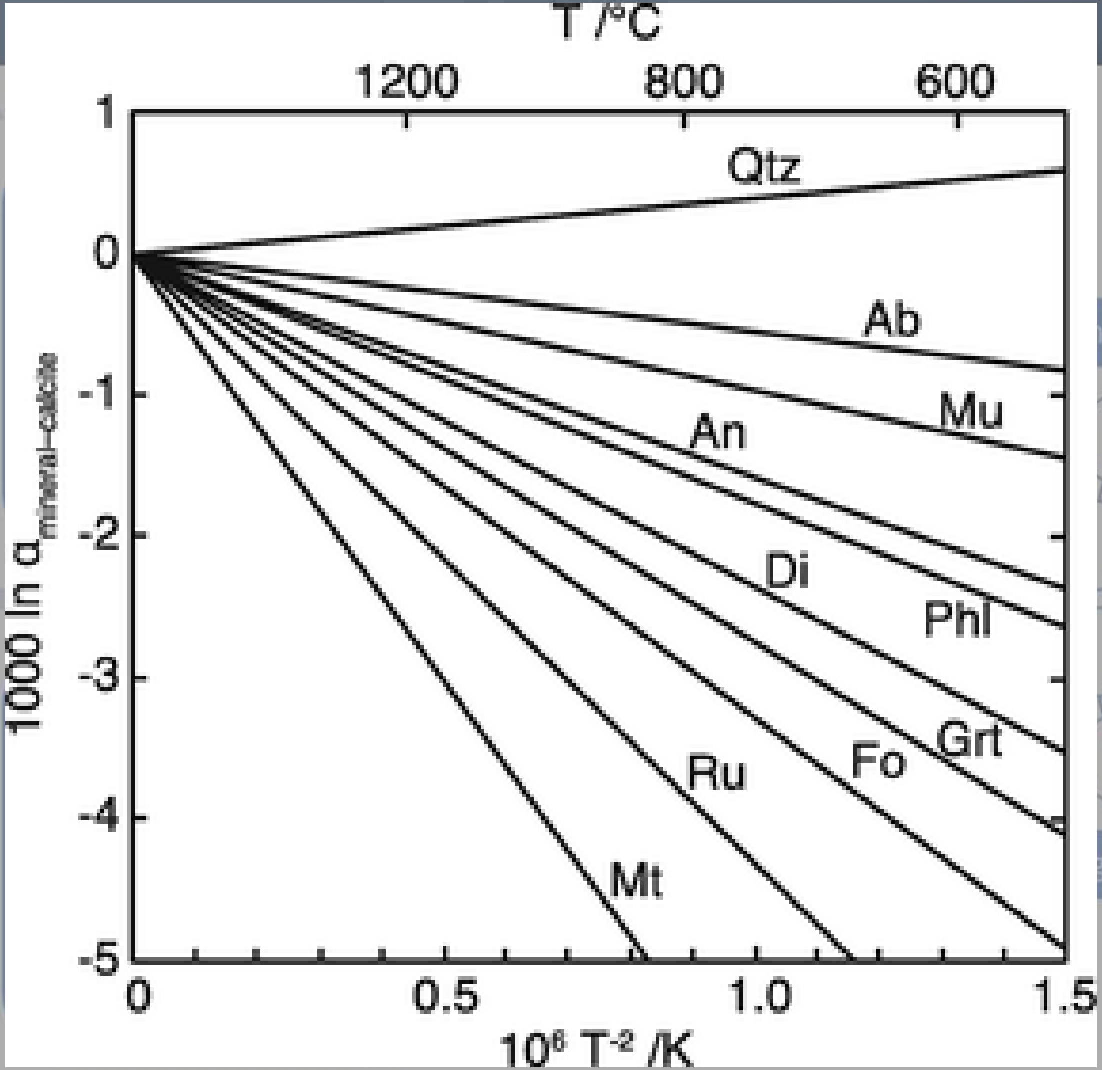
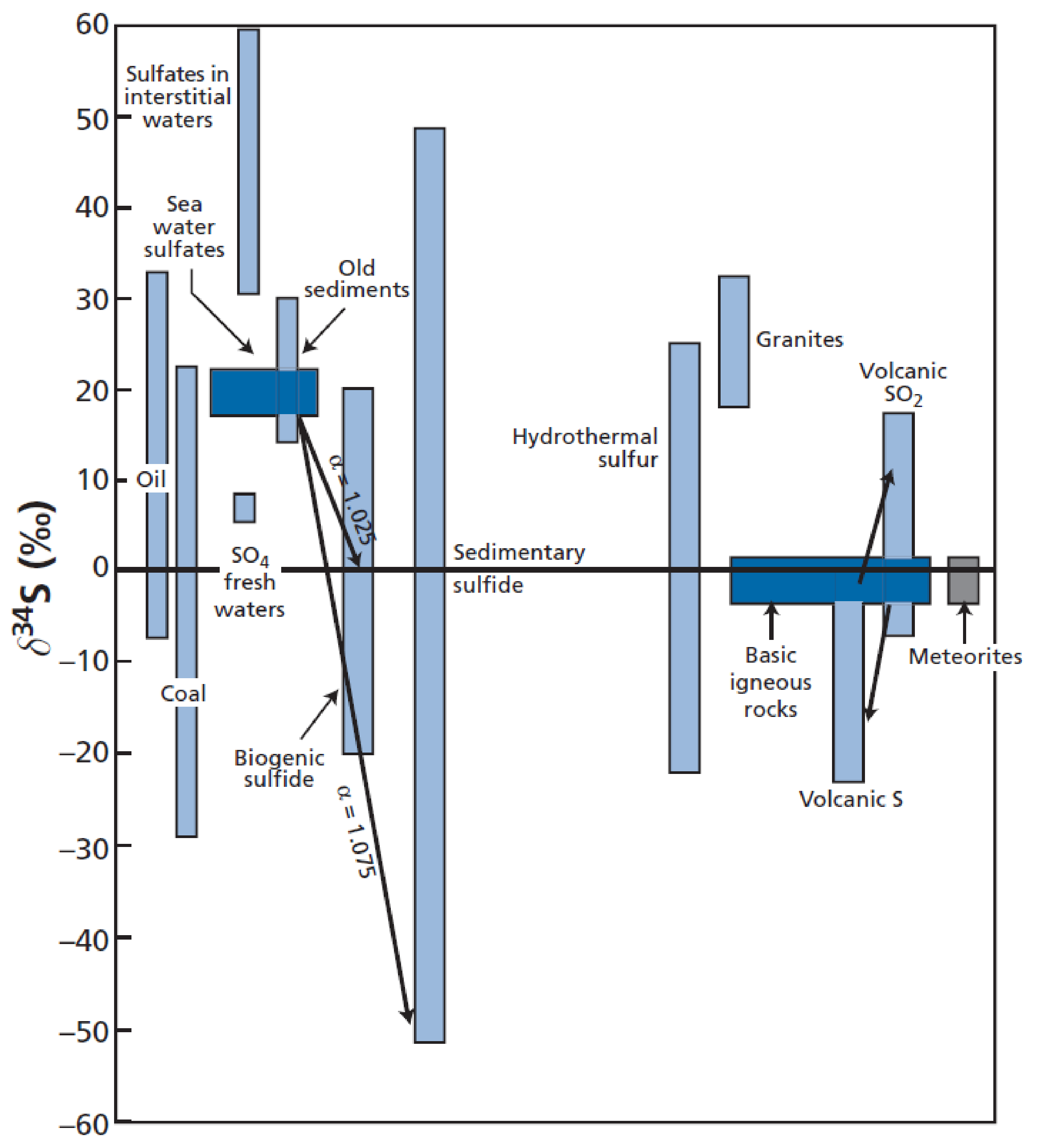


ciences



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forensic medicine

meteorology

atmospheric science

meteoritics

palaeobiology

bacteriology

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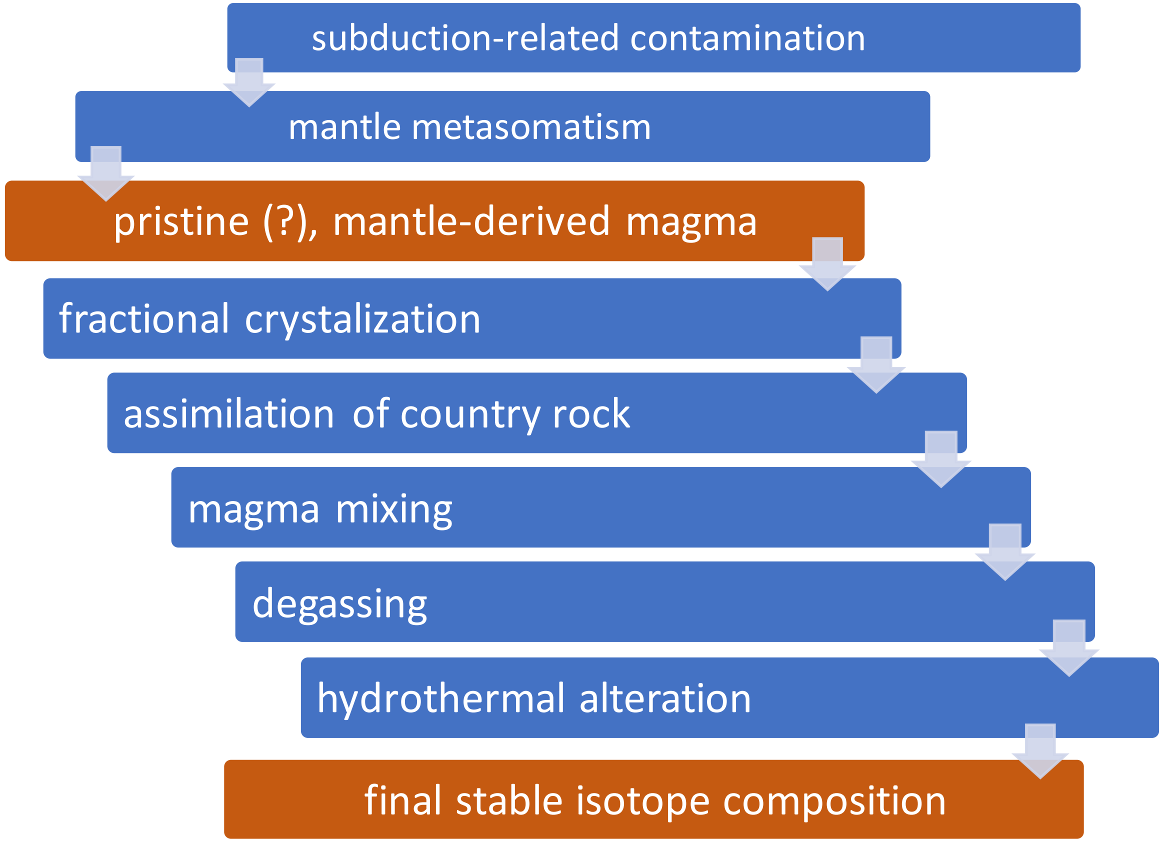
- bacteriology

Principles – igneous rocks

Provided that no subsolidus isotope exchange or hydrothermal alteration occured, the isotope composition of an igneous rock is determined by:

- isotope composition of the source region where magma was generated
- temperature of magma generation and crystallization
- mineralogical composition of the rock
- evolutionary history of the magma, including isotope exchange, assimilation of country rock and magma mixing



subduction-related contamination

mantle metasomatism

pristine (?), mantle-derived magma

fractional crystallization

assimilation of country rock

magma mixing

degassing

hydrothermal alteration

final stable isotope composition

$^{2}He^{*}$, ^{3}He, ^{4}He

Helium

- information about **mantle environment** and **crustal contamination**

- second lightest element
- noble gas
- light isotope (^{3}He) is less abundant than heavy (^{4}He)

- required material which is not porous for ions
- some **sulphides** bear He in fluid inclusions

^{14}N, ^{15}N

Nitrogen

- strong fingerprint of **surface processes**
- identifies **subduction/meteoric waters**
- **various mantle environments**

- small number of minerals
- standard – atmosphere

- possible **substitutions of NH_4^+ for K^+** in **silicate minerals** of igneous rocks
- present e.g. in feldspars and micas

^{6}Li, ^{7}Li

Lithium

- powerful tracer of **water-rock interactions**
- impact of meteoric waters or seawater (e.g. from dehydration or subducting slab)

- third lightest element
- low concentrations
- light isotope (^{6}Li) is less abundant than heavy (^{7}Li)

- present e.g. in **aluminofluorides**, micas

^{10}B, ^{11}B

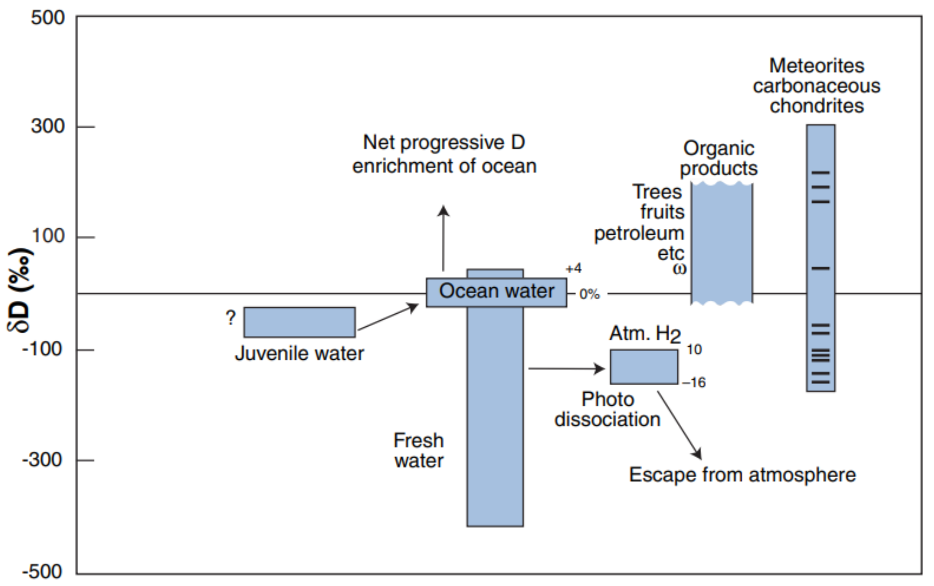
Boron

- tracer of **water-rock interactions**
- impact of meteoric waters or seawater (e.g. from dehydration or subducting slab)

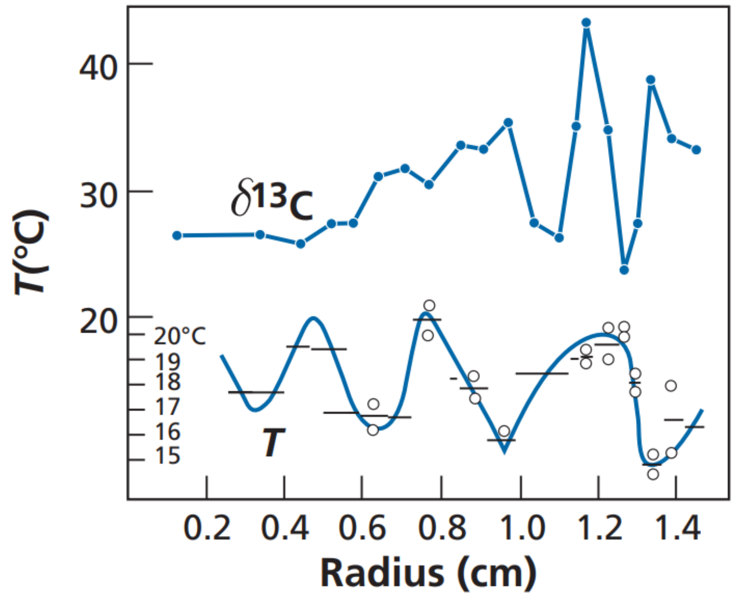
- significant mass difference -> large isotope effect
- high concentrations of the less abundant element – almost 19% of boron is ^{10}B

- can be measured in **carbonates**, but this requires dissolution and is time-consuming
- *in-situ* analysis far easier
- common e.g. in **tourmalines**

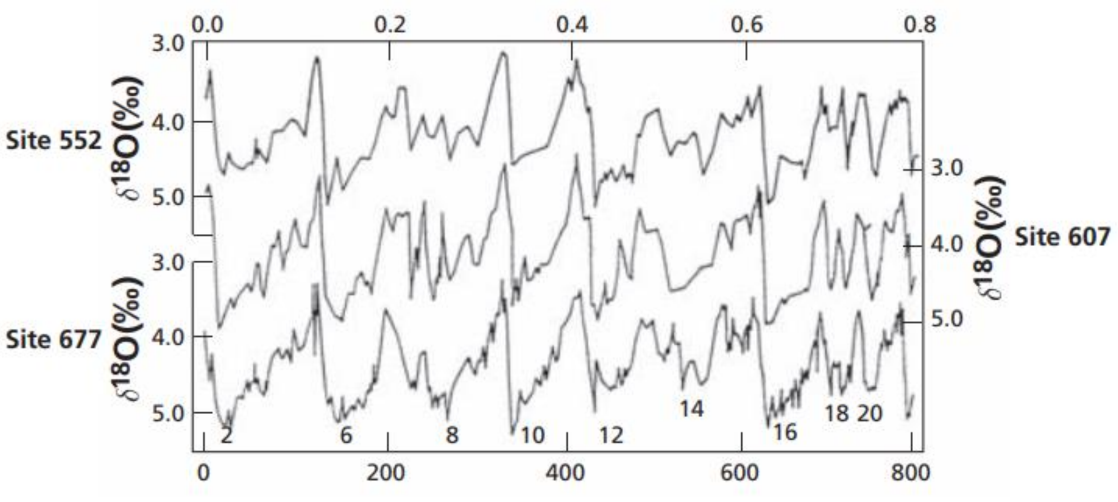
hydrogen in terrestrial reservoirs



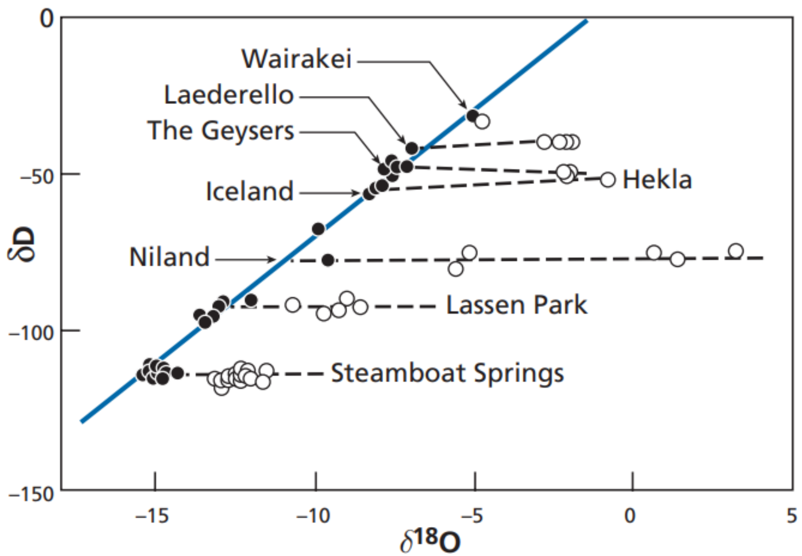
temperature from belemnite shell



foraminifera and Milankovitch cycle



geothermal waters not juvenile

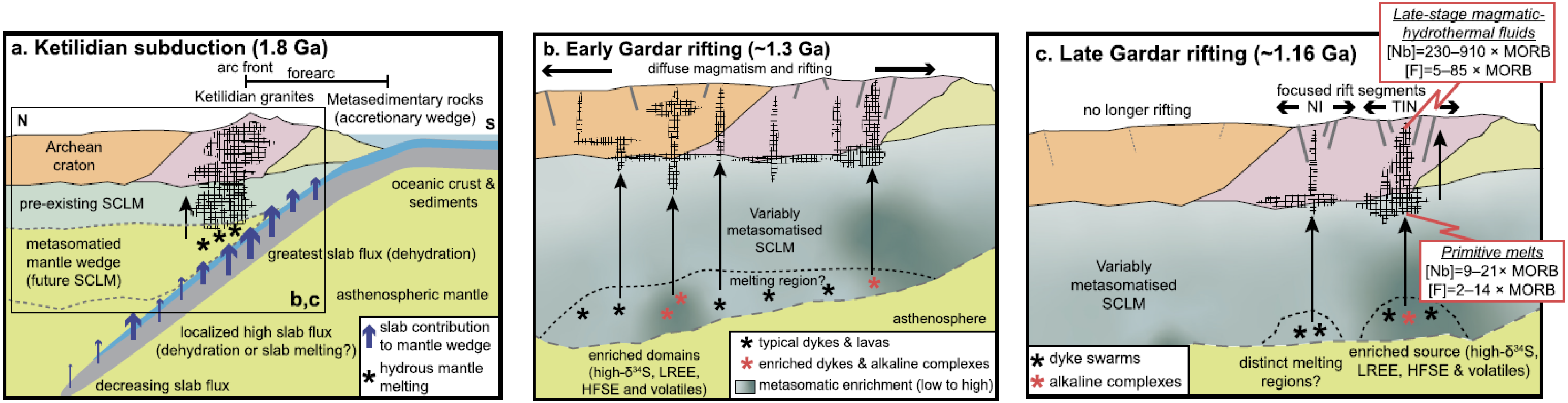


Allègre CJ. Stable isotope geochemistry. In: *Isotope Geology*. Cambridge: Cambridge University Press; 2008:358-435. Based on Craig and Boato (1955), Bradley (1999), Urey *et al*. (1951) and Craig (1963).

Case study: sulphur

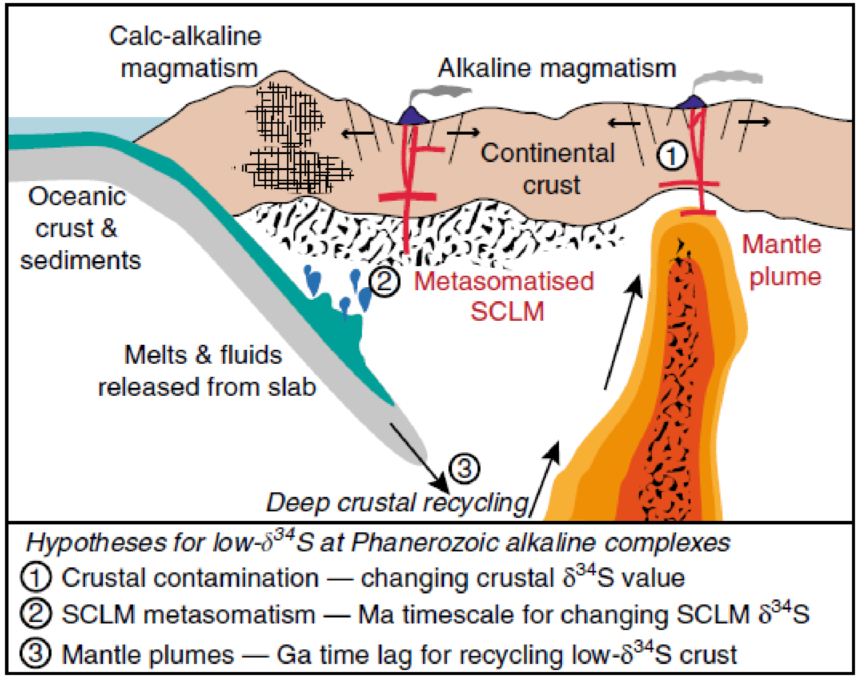
Hutchison *et al.* 2021

Mantle sources and magma evolution in Europe’s largest rare earth element belt (Gardar Province, SW Greenland): New insights from sulfur isotopes



…and PhD project

How fluids make or break Critical Metal Deposits – the Ivittuut cryolite body, SW Greenland



Hypotheses for low-δ^{34}S at Phanerozoic alkaline complexes
① Crustal contamination — changing crustal δ^{34}S value
② SCLM metasomatism — Ma timescale for changing SCLM δ^{34}S
③ Mantle plumes — Ga time lag for recycling low-δ^{34}S crust

Hutchison *et al.* 2019

SULPHIDES

Sample	Mineral	^{4}He	d4	^{3}He/^{4}He	d3/4
HFW-6	galena	18 819,9	2,9	0,040	0,009
HFW-5	galena	27 968,5	4,3	0,081	0,006
AF-92-15	galena	17 182,4	2,9	0,070	0,009
HF-18	galena	13 103,2	2,0	0,073	0,012
HFW-10	pyrite	14 149,3	1,9	1,25	0,02
HFW-11	pyrite	7 070,9	1,0	0,14	0,02
AF-92-15	chalcopyrite	23 966,5	3,1	0,11	0,01
HF-6	chalcopyrite	14 327,7	2,0	0,063	0,011

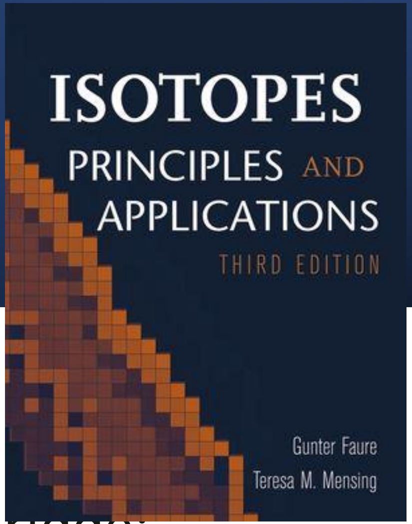
more marerial collected

radiogenic He can be calculated

✓noble gases (He) in fluid inclusions
✓all samples contain some mantle He

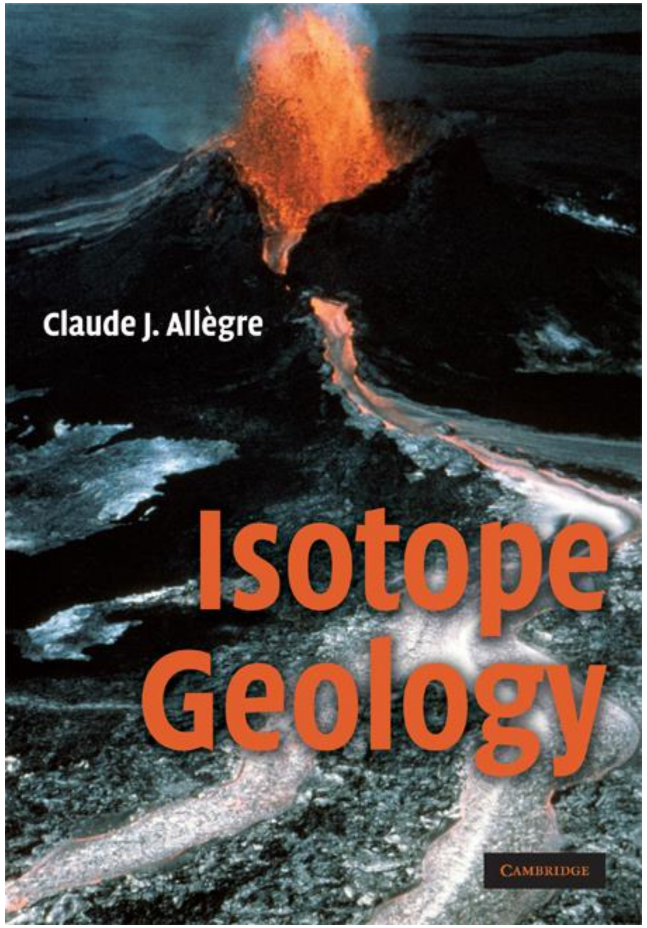
✓radiogenic He dominates

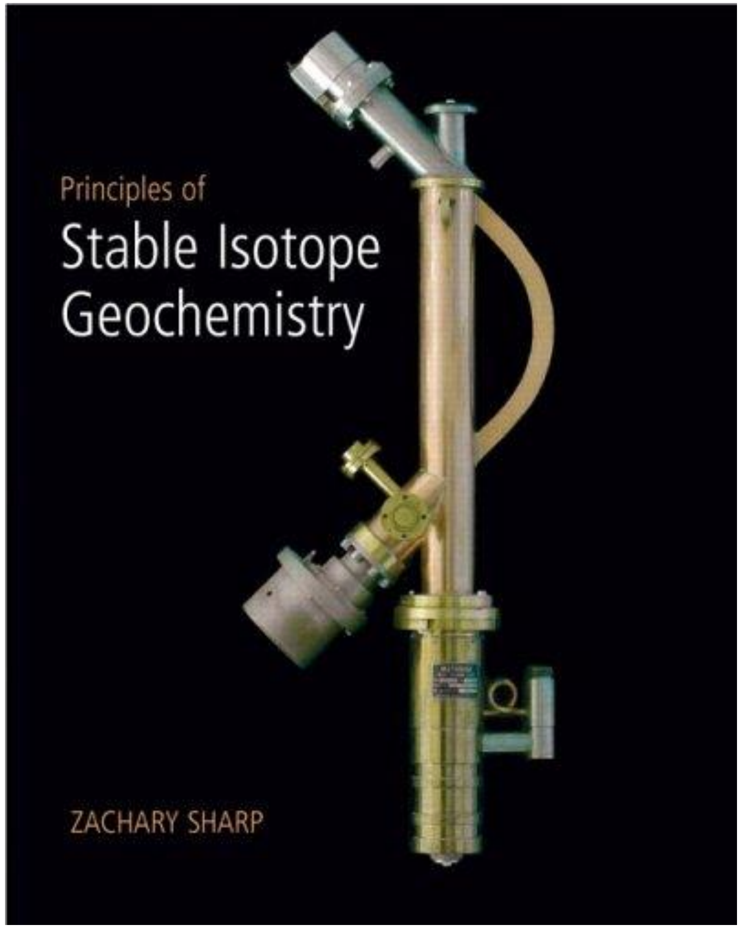
References

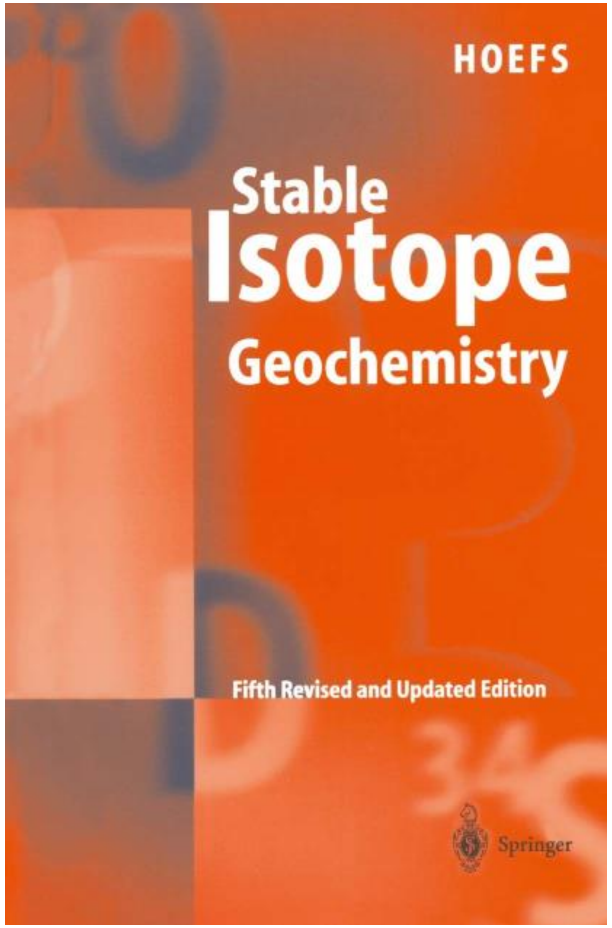


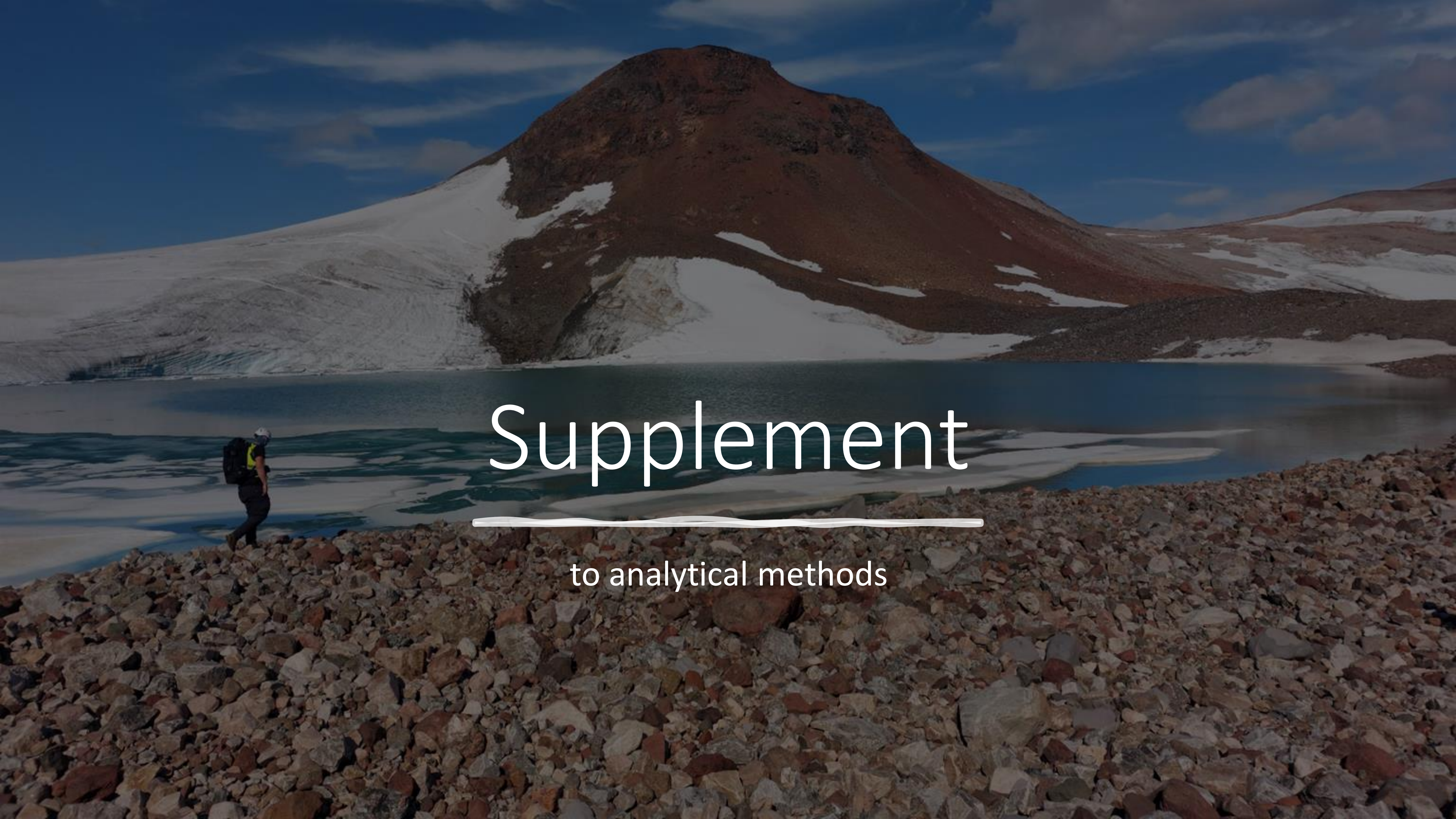
1. Allègre CJ. (2008). Stable isotope geochemistry. In: *Isotope Geology*. Cambridge: Cambridge University Press; 2008:358-435.
2. Hoefs, J., & Hoefs, J. (1997). *Stable isotope geochemistry* (Vol. 201). Berlin: Springer.
3. Sharp, Z. (2007). *Principles of stable isotope geochemistry*. Upper Saddle River: Pearson.
4. Hilton, D. R., & Porcelli, D. (2003). Noble gases as mantle tracers. *Treatise on geochemistry*, *2*, 568.
5. Hutchison, W., Babiel, R. J., Finch, A. A., Marks, M. A., Markl, G., Boyce, A. J., ... & Horsburgh, N. J. (2019). Sulphur isotopes of alkaline magmas unlock long-term records of crustal recycling on Earth. Nature communications, 10(1), 4208.
6. Hutchison, W., Finch, A. A., Borst, A. M., Marks, M. A., Upton, B. G., Zerkle, A. L., ... & Boyce, A. J. (2021). Mantle sources and magma evolution in Europe's largest rare earth element belt (Gardar Province, SW Greenland): New insights from sulfur isotopes. Earth and Planetary Science Letters, 568, 117034.

Suggested readings



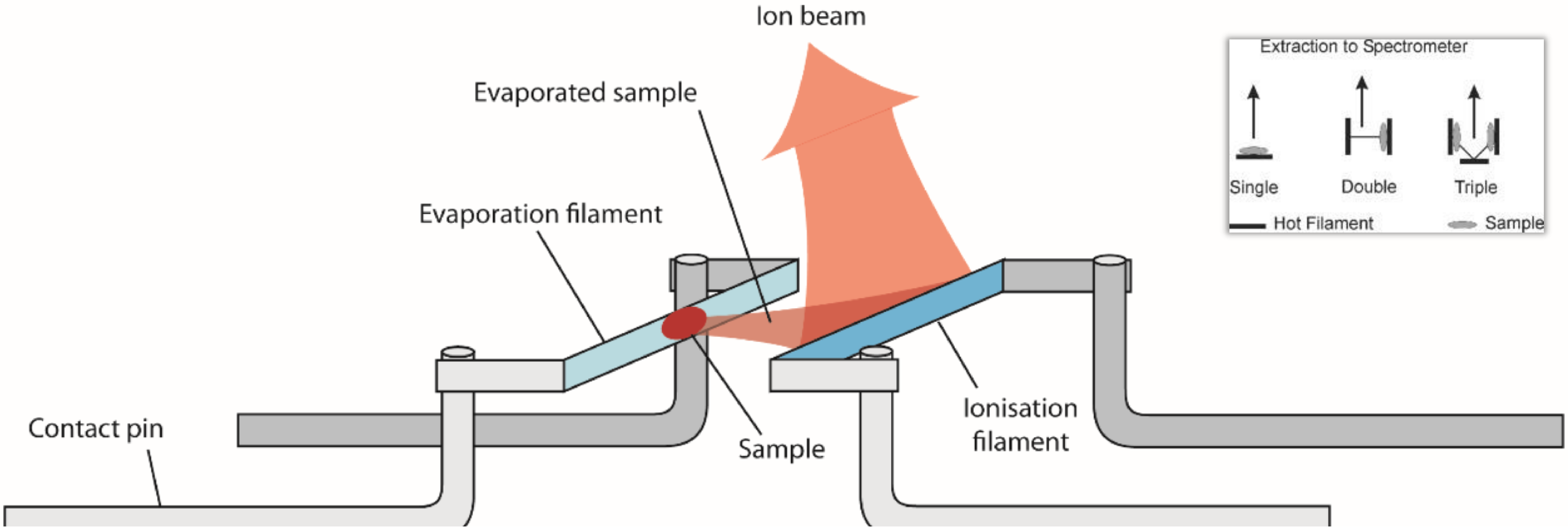






Supplement

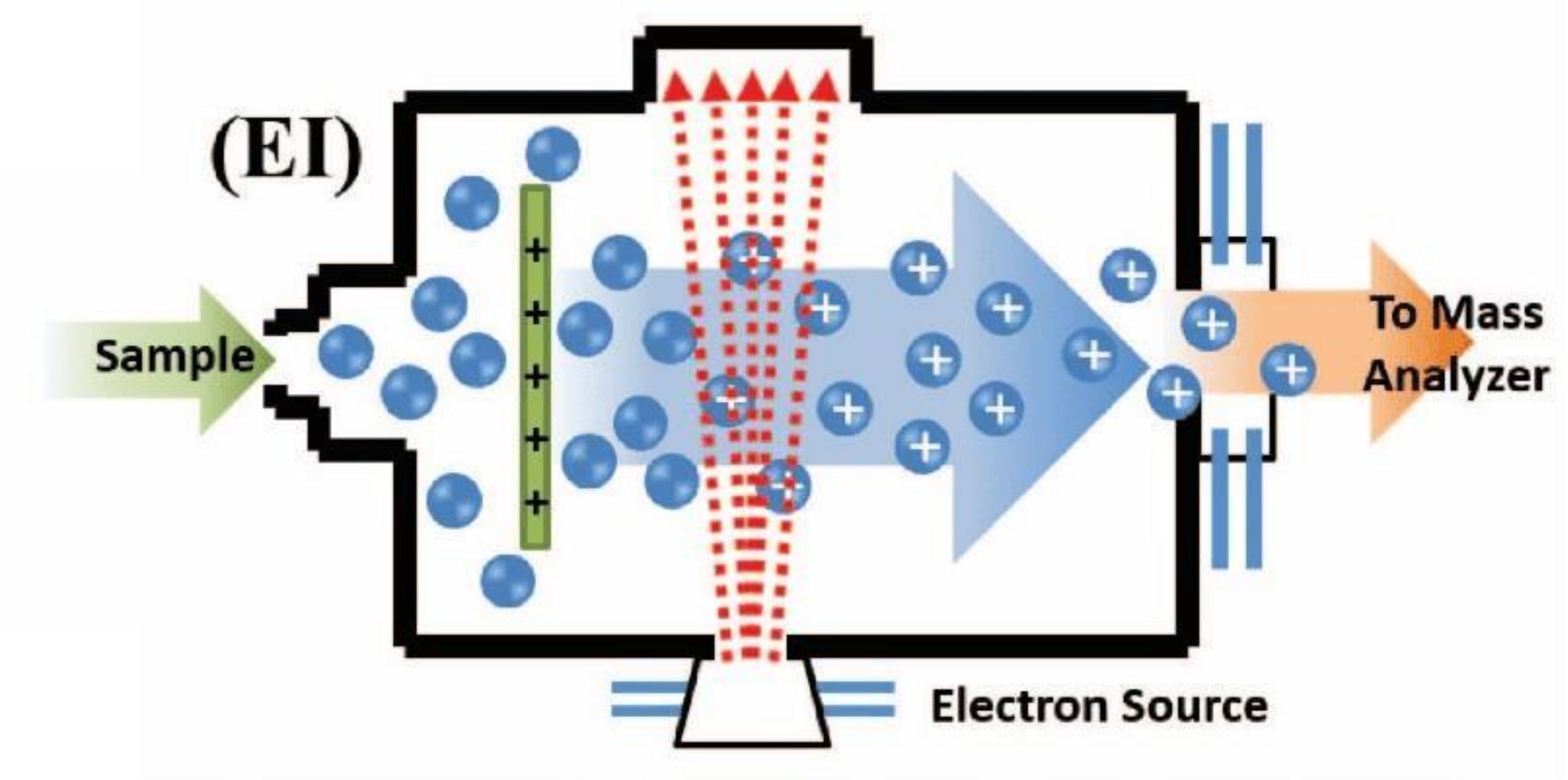
to analytical methods

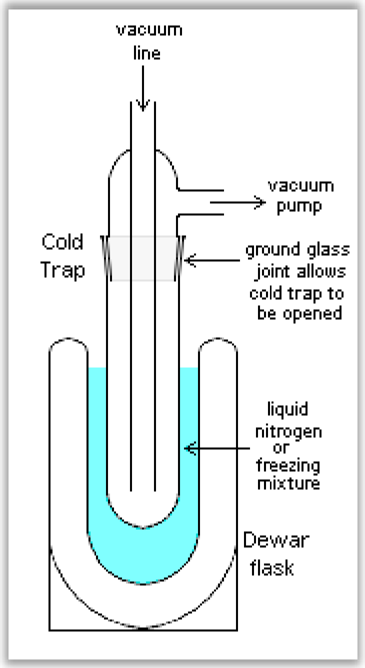


TIMS – Thermal Ionisation Mass Spectrometry

After purification the element to be analysed is deposited on a refractory filament. Heating of the filament ionizes the elements, which become cations (Rb^+, Sr^+) or anions (OsO_3^-, WO_3^-).

https://www.nu-ins.com/products/tims/introductiontotims; HUBER, G., PASSLER, G., WENDT, K., KRATZAND, J. V., & TRAUTMANN, N. (2003). Radioisotope mass spectrometry. In *Handbook of Radioactivity Analysis* (pp. 799-843). Academic Press.



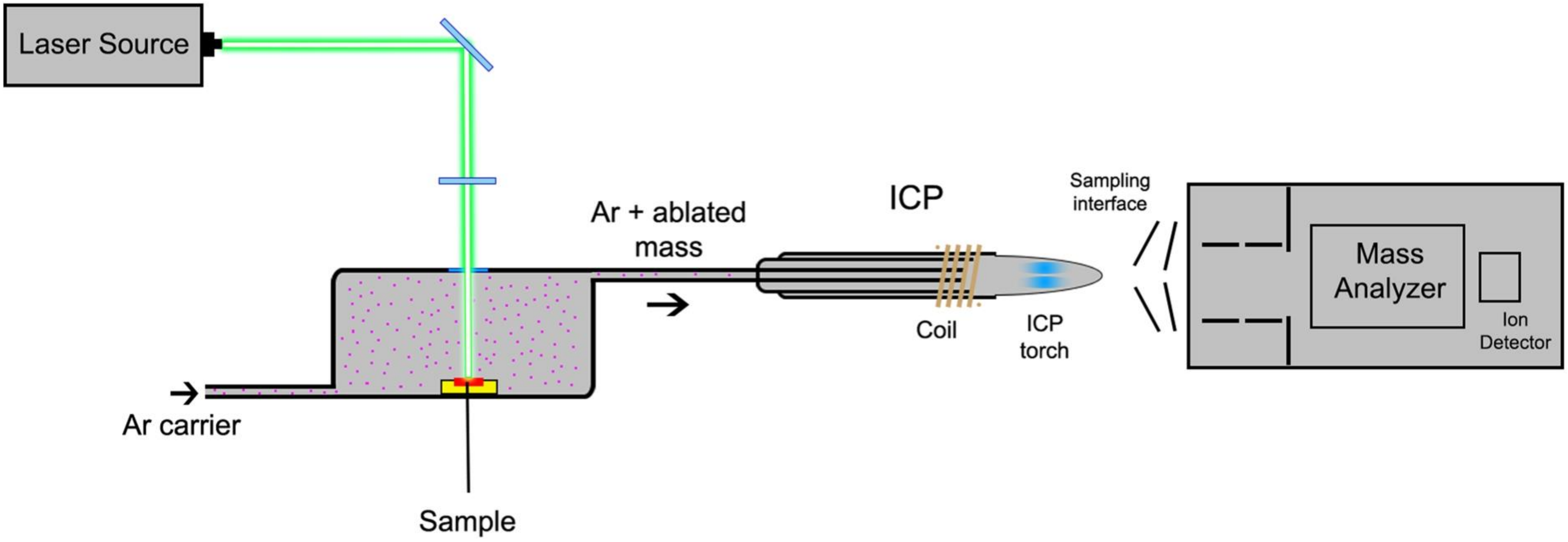


Electronic bombardment

Sample gas in a vacuum is bombarded by an electron beam. Positive ions are formed as electrons are knocked out from the atoms or molecules.

In sample preparation, gas is extracted from the material and purified in a vaccuum line, where other gases are adsorbed or liquified.

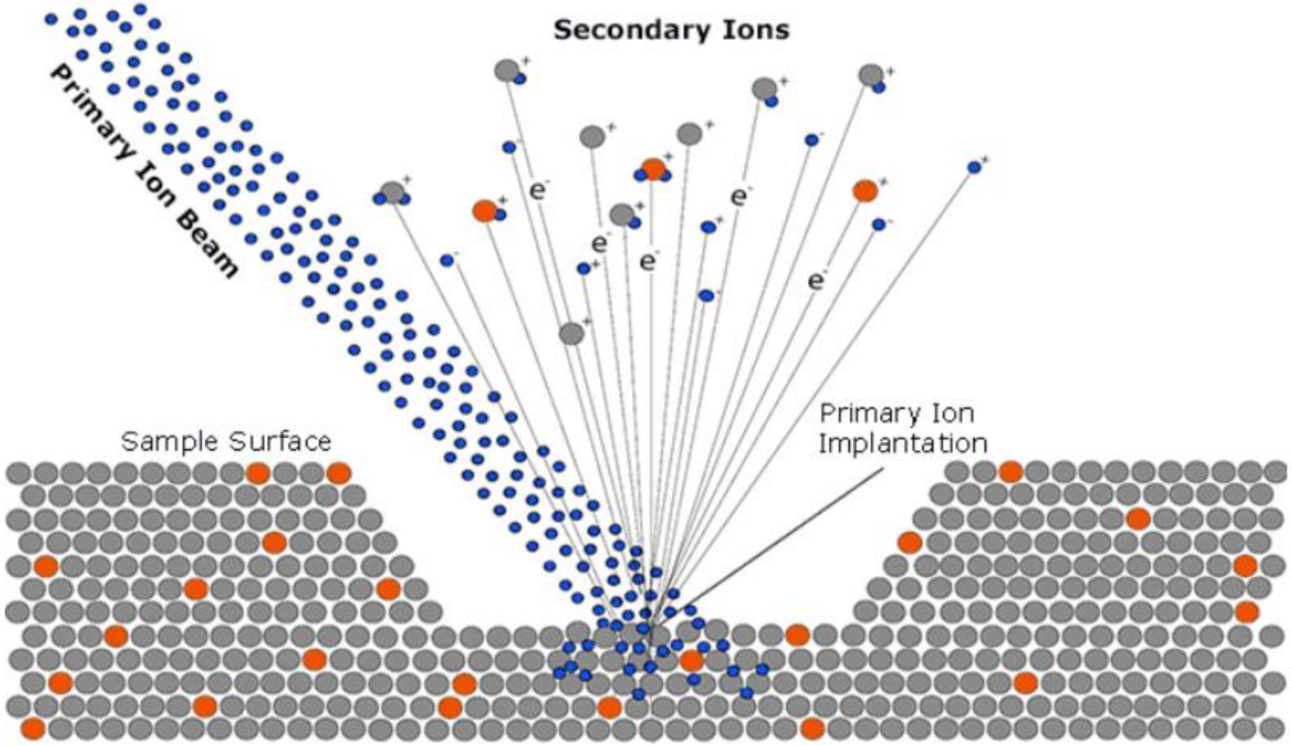
Radauscher, Erich. (2015). Design, Fabrication, and Characterization of Carbon Nanotube Field Emission Devices for Advanced Applications. PhD Thesis. 10.13140/RG.2.2.16376.85767.



LA-ICP-MS – Laser Ablation Inductively Coupled Plasma

Sample is atomised by laser pulses and then ionised in an argon plasma torch. As the plasma temperature is about 10 000 K, this method works for elements difficult to ionise, like Hf or Th.

https://content.iospress.com/articles/biomedical-spectroscopy-and-imaging/bsi200193



SIMS – Secondary Ion Mass Spectrometry

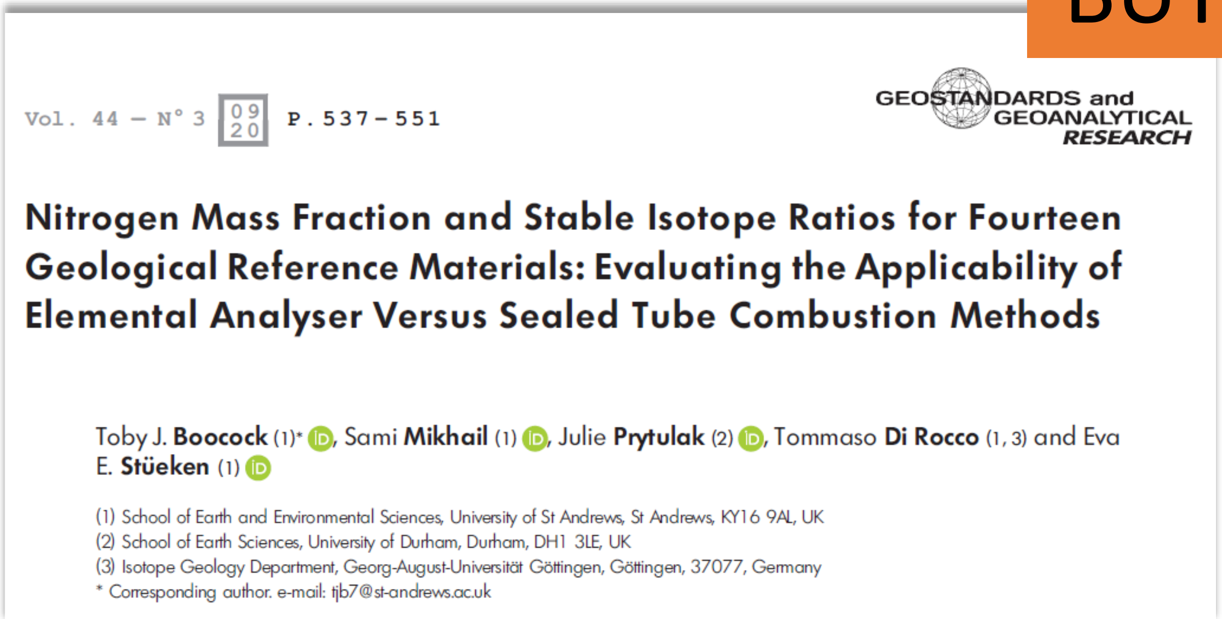
A polished rock sample is placed in a vacuum and bombarded by a primary beam of ions (Ar, O or Cs). This creates a high-temperature plasma (40 000 K) in which the element is atomised and ionised. Its high resolution enables *in-situ* measurements of even tiny grains.

https://www.cameca.com/products/sims/technique

Watch out! N case study

- two methods for N isotope analysis
- both coupled with IRMS
- EA broadly used for organic samples

BUT...



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GEOSTANDARDS and GEOANALYTICAL RESEARCH

Nitrogen Mass Fraction and Stable Isotope Ratios for Fourteen Geological Reference Materials: Evaluating the Applicability of Elemental Analyser Versus Sealed Tube Combustion Methods

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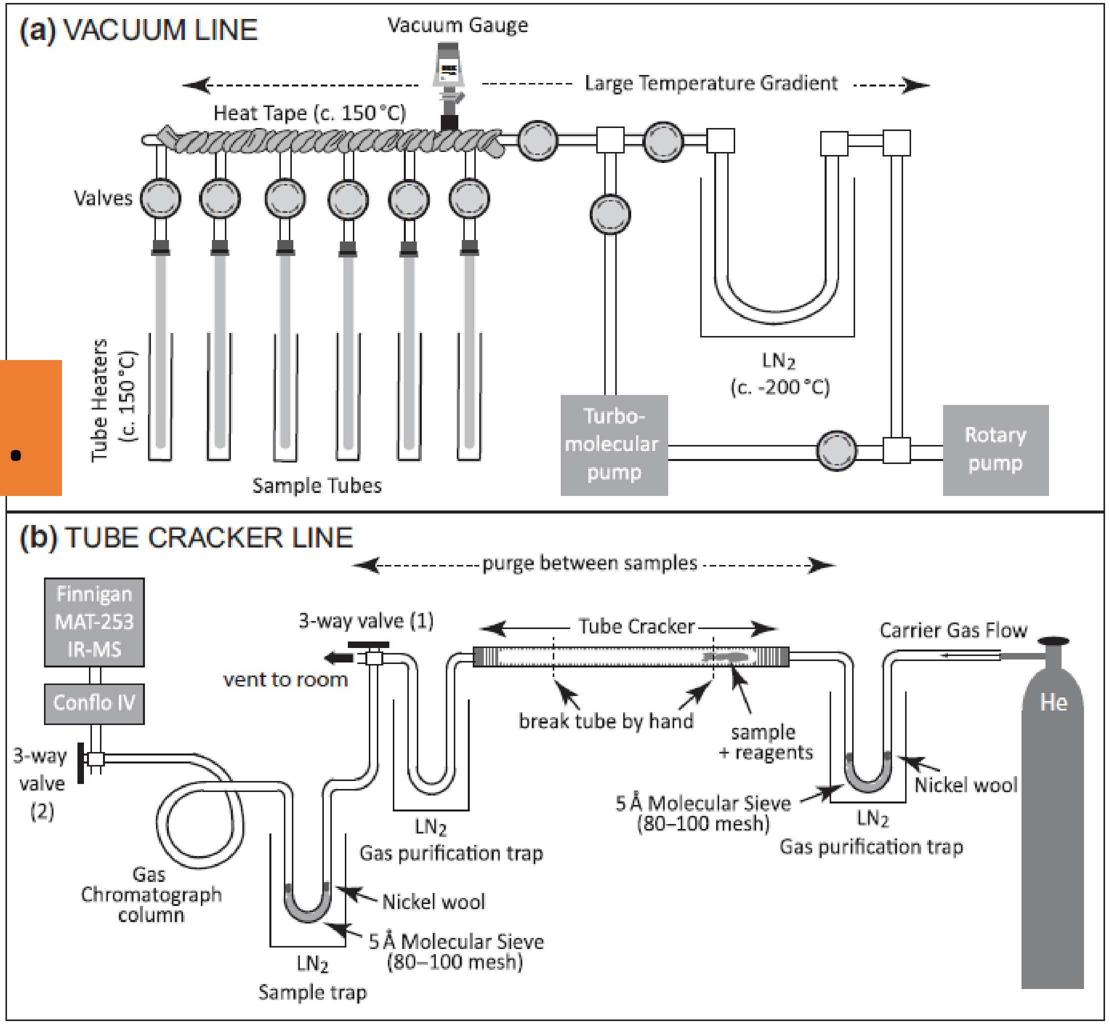

Watch out!

N case study

Sealed Tube Combustion

vs.

Flash Combustion

Sealed Tube Combustion	Flash Combustion
time-consuming	faster, cheaper, less consumables
consumables (glass tubes)	50 mg of sample
350 mg of standard/sample	yields 33-69 % of lattice-bound N
yields lattice-bound N well	better for mafic rocks than felsic