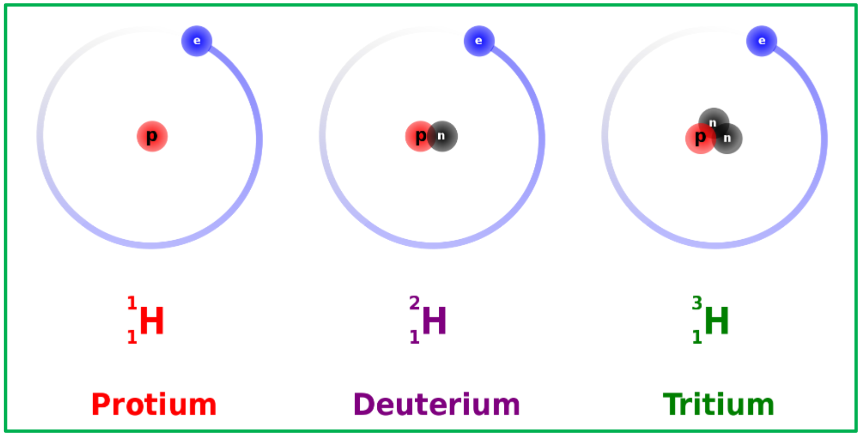
General aspects of stable isotopes and IRMS

definitions, use, measurement principles

Prof. Ivo Leito

Isotopes

- **What are Isotopes?**
  - Atoms of the same element (i.e., same number of protons and electrons) but different numbers of neutrons

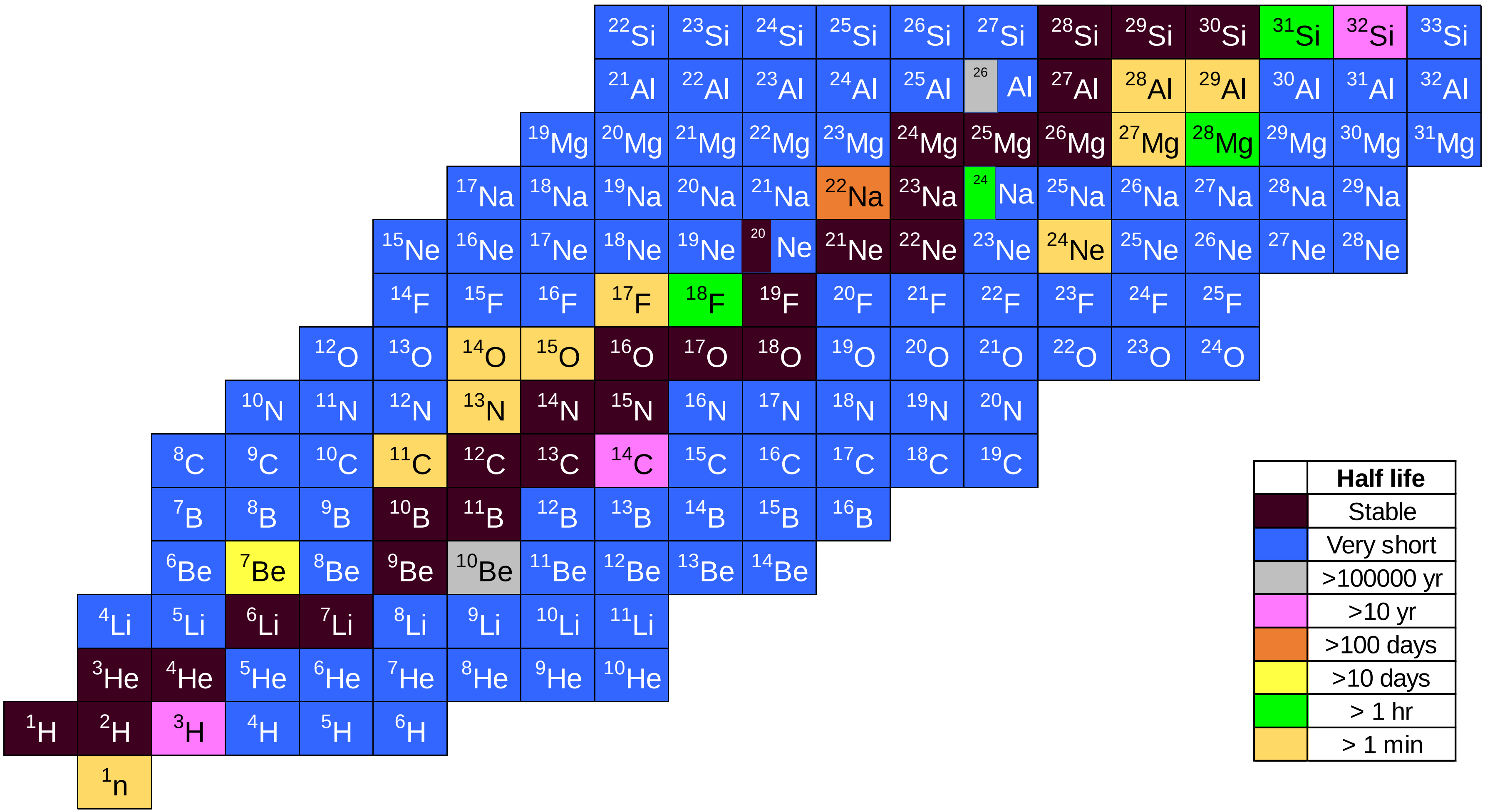


Stable | Stable | Not stable

The three naturally-occurring isotopes of hydrogen.

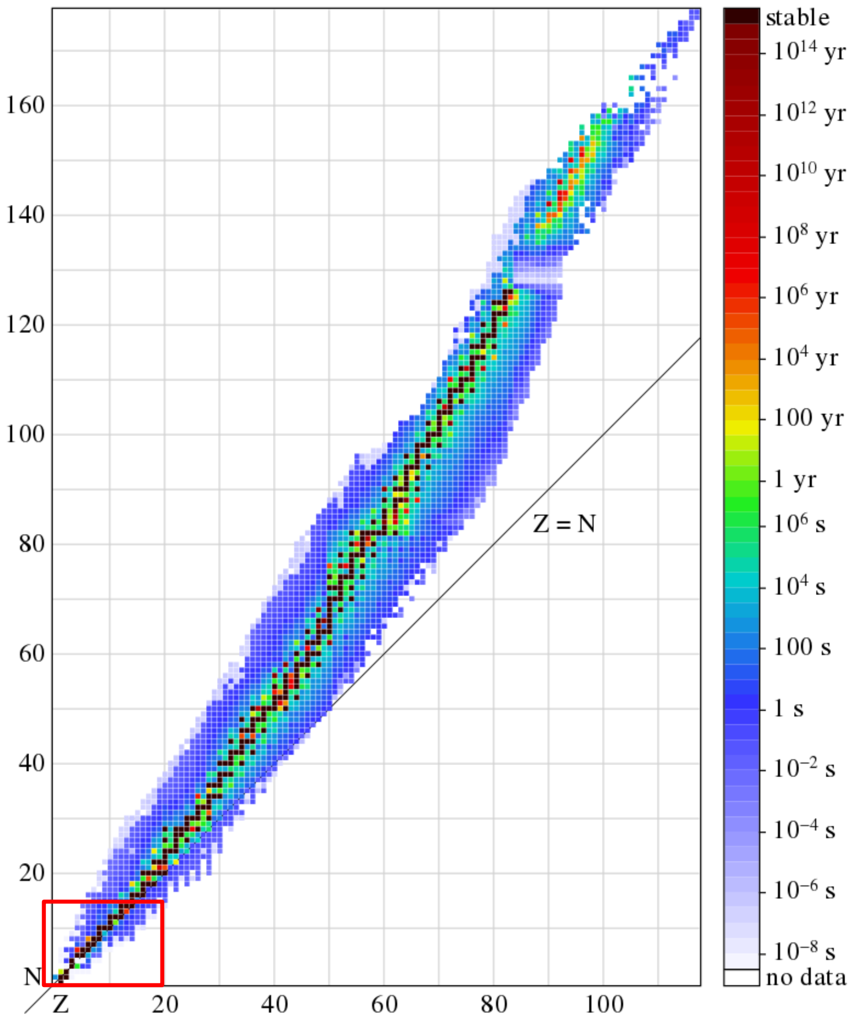
- **What is a Stable Isotope?**
  - isotope(s) of an element that do not undergo radioactive decay, but they may be radiogenic (i.e., produced by radioactive decay)

Isotopes of light elements

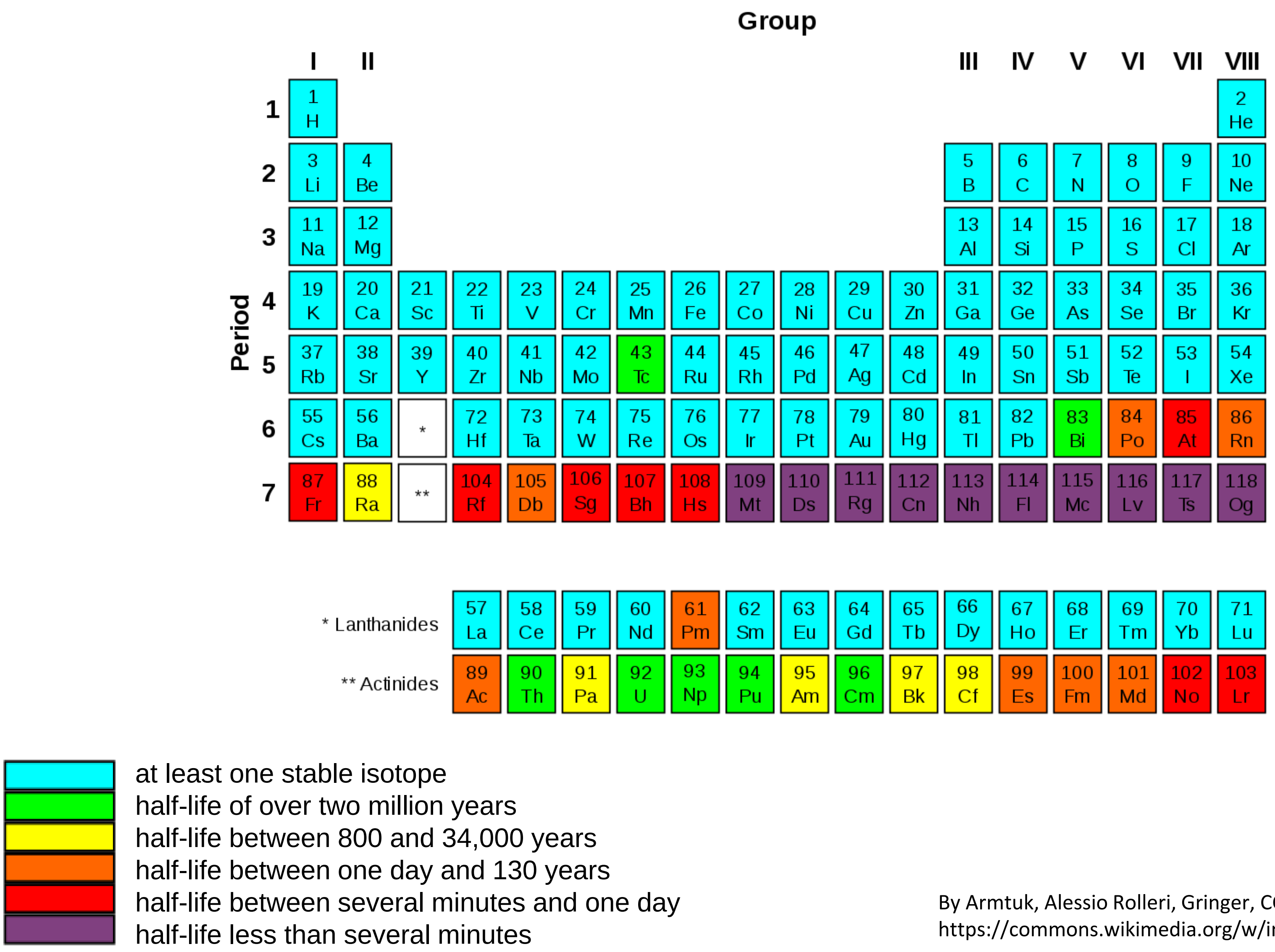


Isotopes of elements

- **Symmetry rule:** neutron-to-proton ratio (N/Z) of stable isotopes in light elements equals approximately to unity
- In elements with **Z or N > 20** the N/Z ratio is always greater than unity, **up to 1.5** for the heaviest stable nuclei
- To maintain the stability in the nuclei more neutrons than protons are required in progressively heavier elements



Elements according to the half-life of their most stable isotope



Isotopic abundances

- Natural elements are mostly **mixtures of isotopes**
- Example: **standard** natural stable **C**
  - Abundances: 98.89 % is ^{12}C; 1.11 % is ^{13}C
  - **Depending on origin** the ^{13}C content can vary markedly: ca 1.00 .. 1.12 %

δ scale

- Isotope abundance ratios in real samples, e.g. $^{13}C/^{12}C$ ratio in charcoal, are expressed relative to international standard in the **$\delta^{13}C$ scale**:

$$\%^{13}C = 1.11\% \rightarrow \delta^{13}C = 0$$

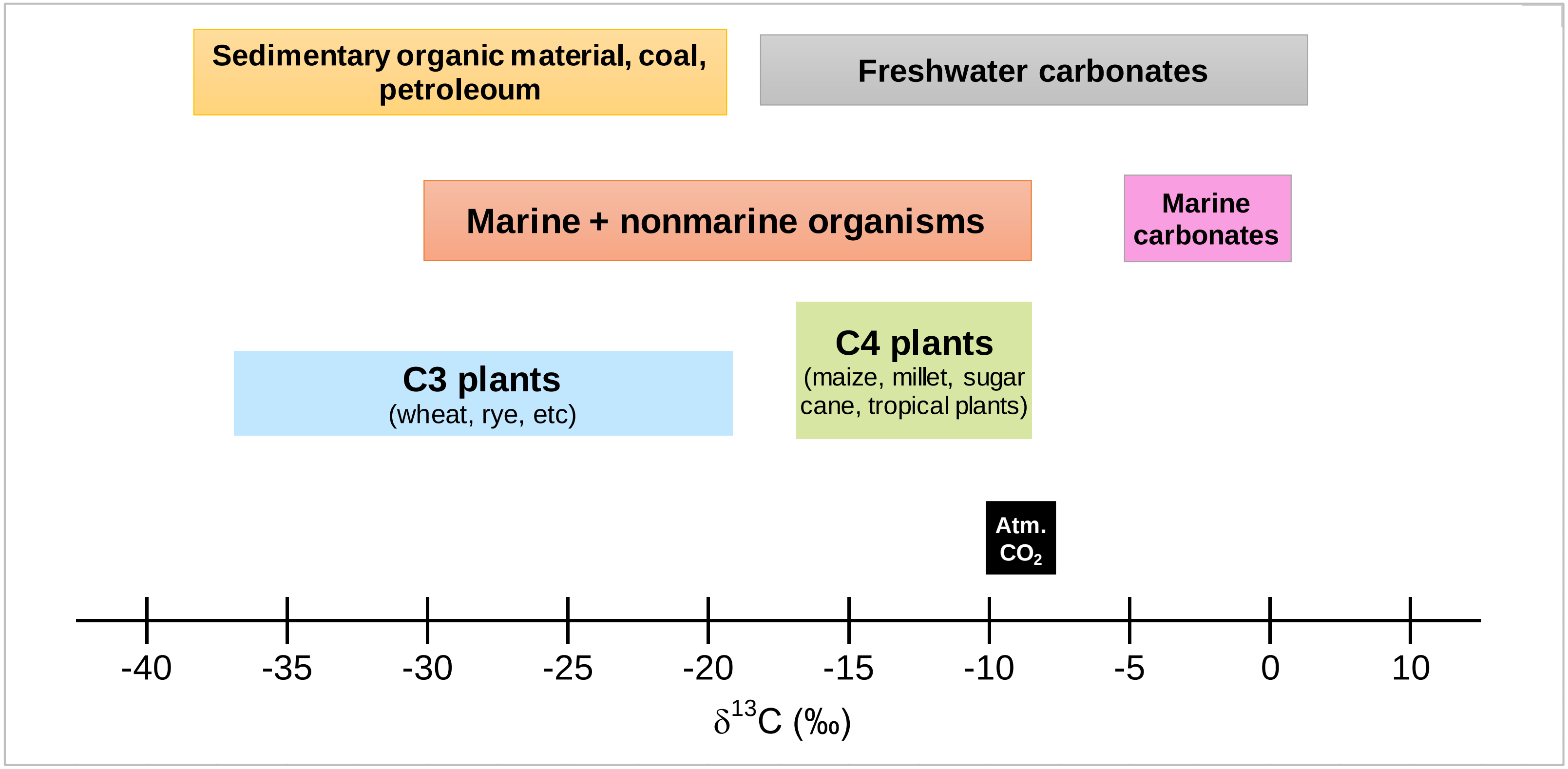
$$\%^{13}C = 1.06\% \rightarrow \delta^{13}C = -44$$

$$\delta = \left(\frac{R_x}{R_{std}} - 1 \right) \times 1000$$

Isotope Fractionation

- Isotopes of an element undergo the same chemical reactions and physical processes
- **Differences in mass** can influence the **rate** or extent of
  - **physical** processes (e.g. evaporation)
  - **chemical** reactions (e.g. photosynthesis)
  - **partitioning** of isotopes differentially among phases
- Isotopic separation during chemical, physical, or biological processes is called **Isotope fractionation**

Usefulness of Stable Isotopes

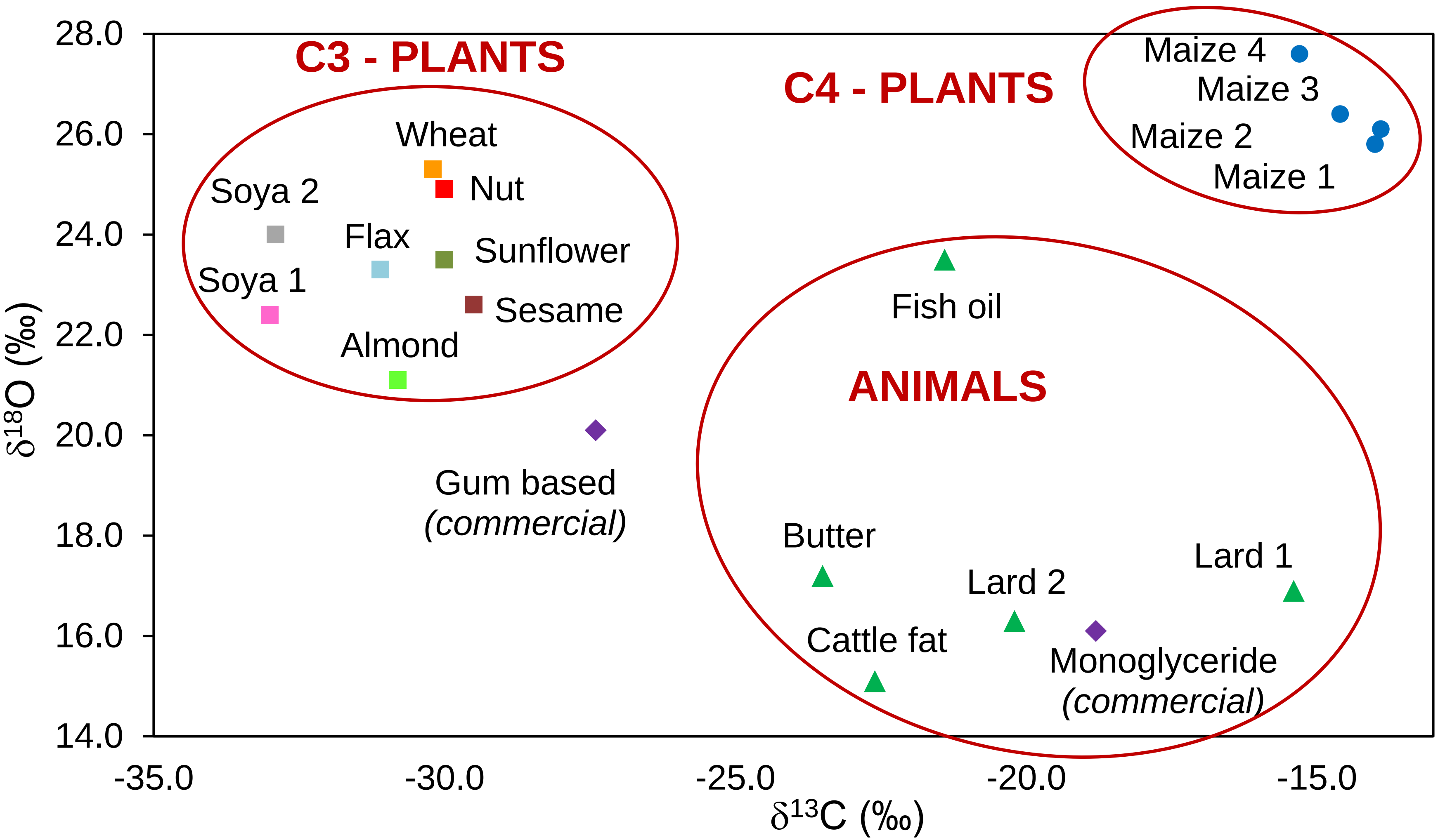


Stable Isotopes are useful as:

- **indicators** of physical or chemical (incl. biological) processes and geochemical cycles
- conservative **tracers** to identify, for example, food sources, nutrient cycling etc.

Several elements: better differentiation

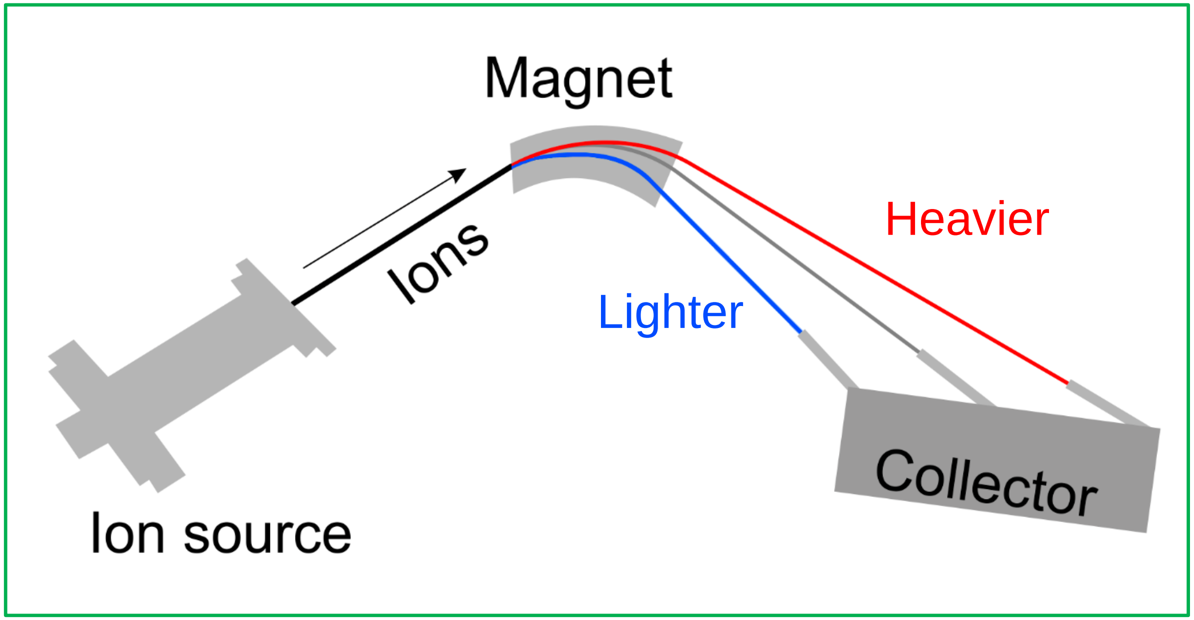
Glycerol samples from fats of plant and animal origin



Data from: Fronza, G.; et al. *Rapid Commun. Mass Spectrom*. 2001; 15: 763-766. http://dx.doi.org/10.1002/rcm.296

Isotope Ratio Mass Spectrometry (IRMS)

- **Ratios** of isotope abundances of an element in a sample are extremely small and are measured with **very high accuracy**
  - Typically light elements (traditional stable isotoope systems) are used: H, C, N, O or S, but also non-traditional isotopes (Li, B, Mg, Ca, Fe, Mo, etc) can be useful in some applications



Stable isotope ratios in organic compounds:

- C ($^{13}C/^{12}C$)
- N ($^{15}N/^{14}N$)
- O ($^{18}O/^{16}O$)
- H ($^{2}H/^{1}H$)

EA-IRMS and GC-C-IRMS

(on the example of C)

Aspect	Elemental analysis isotope ratio mass spectrometry (EA-IRMS)	Gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS)
Overall vs selective	A bulk measurement technique Measures average isotope ratios for the **entire sample**	Isotope ratios can be measured for **specific compounds**
Sample type	Non-volatile samples, gases, liquids, powders	Suitable for GC: volatile and thermally stable
Sample preparation	Relatively easy (homogenization, weighing and packing)	Can be work-intensive, possibly involves derivatization
Required sample amount (very approximate)	0.1 mg to hundreds of mg	Depends on the amount of organic compounds in the sample

Summary

- Natural elements are mostly **mixtures of isotopes**
- Isotope abundances of elements can vary depending on the **origin** of the material
  - Ratios of stable isotope abundances of H, C, O, N and S are the most typically used
- IRMS allows **measurements** of isotope abundances with **very high accuracy**
  - IRMS can be realised in several configurations of which two versions are most commonly used: EA-IRMS, GC-C-IRMS