General aspects of stable isotopes and IRMS

definitions, use, measurement principles

Prof. Ivo Leito



What are Isotopes?

 Atoms of the same element (i.e., same number of protons and electrons) but different numbers of neutrons



• 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

								²² Si	²³ Si	²⁴ Si	²⁵ Si	²⁶ Si	²⁷ Si	²⁸ Si	²⁹ Si	³⁰ Si	³¹ Si	³² Si	³³ Si
								²¹ AI	²² AI	²³ AI	²⁴ AI	²⁵ AI	²⁶ Al	²⁷ AI	²⁸ AI	²⁹ AI	³⁰ AI	³¹ AI	³² AI
							¹⁹ Mg	²⁰ Mg	²¹ Mg	²² Mg	²³ Mg	²⁴ Mg	²⁵ Mg	²⁶ Mg	²⁷ Mg	²⁸ Mg	²⁹ Mg	³⁰ Mg	³¹ Mg
						¹⁷ Na	¹⁸ Na	¹⁹ Na	²⁰ Na	²¹ Na	²² Na	²³ Na	²⁴ Na	²⁵ Na	²⁶ Na	²⁷ Na	²⁸ Na	²⁹ Na	
					¹⁵ Ne	¹⁶ Ne	¹⁷ Ne	¹⁸ Ne	¹⁹ Ne	²⁰ Ne	²¹ Ne	²² Ne	²³ Ne	²⁴ Ne	²⁵ Ne	²⁶ Ne	²⁷ Ne	²⁸ Ne	
					¹⁴ F	¹⁵ F	¹⁶ F	¹⁷ F	¹⁸ F	¹⁹ F	²⁰ F	²¹ F	²² F	²³ F	²⁴ F	²⁵ F			
				¹² O	¹³ O	¹⁴ O	¹⁵ O	¹⁶ O	¹⁷ O	¹⁸ O	¹⁹ O	²⁰ O	²¹ O	²² O	²³ O	²⁴ O			
			¹⁰ N	¹¹ N	¹² N	¹³ N	¹⁴ N	¹⁵ N	¹⁶ N	¹⁷ N	¹⁸ N	¹⁹ N	²⁰ N						
		⁸ C	⁹ C	¹⁰ C	¹¹ C	¹² C	¹³ C	¹⁴ C	¹⁵ C	¹⁶ C	¹⁷ C	¹⁸ C	¹⁹ C			Γ		Half lif	e
		⁷ B	⁸ B	⁹ B	¹⁰ B	¹¹ B	¹² B	¹³ B	¹⁴ B	¹⁵ B	¹⁶ B			•				Stable	<u> </u>
		⁶ Be	⁷ Be	⁸ Be	⁹ Be	¹⁰ Be	¹¹ Be	¹² Be	¹³ Be	¹⁴ Be							>	/ery sh 100000	ort) yr
	⁴ Li	⁵ Li	⁶ Li	⁷ Li	⁸ Li	⁹ Li	¹⁰ Li	¹¹ Li										>10 y	r
	³ He	⁴He	⁵ He	⁶ He	⁷ He	⁸ He	⁹ He	¹⁰ He										>100 da	ys ys
Н	² H	³ H	⁴ H	⁵ H	⁶ H				1									> 1 h	
	¹ n					Į										L		>	

Isotopes of elements

- Symmetry rule: neutron-toproton 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





at least one stable isotope half-life of over two million years half-life between 800 and 34,000 years half-life between one day and 130 years half-life between several minutes and one day half-life less than several minutes

By Armtuk, Alessio Rolleri, Gringer, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=4281027

Isotopic abundances

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

δ scale

 Isotope abundance ratios in real samples, e.g. ¹³C/¹²C ratio in charcoal, are expressed relative to international standard in the δ¹³C scale:

%¹³C = 1.11% →
$$\delta^{13}$$
C = 0
%¹³C = 1.06% → δ^{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 (¹³C/¹²C)
- N (¹⁵N/¹⁴N)
- O (¹⁸O/¹⁶O)
- H (²H/¹H)

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				



- 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