GERMAN FEDERAL INSTITUTE FOR RISK ASSESSMENT

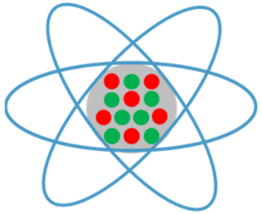
Bundesinstitut für Risikobewertung

IRMS – Stable Isotopes – Part 1

Dr. Melanie Gimpel

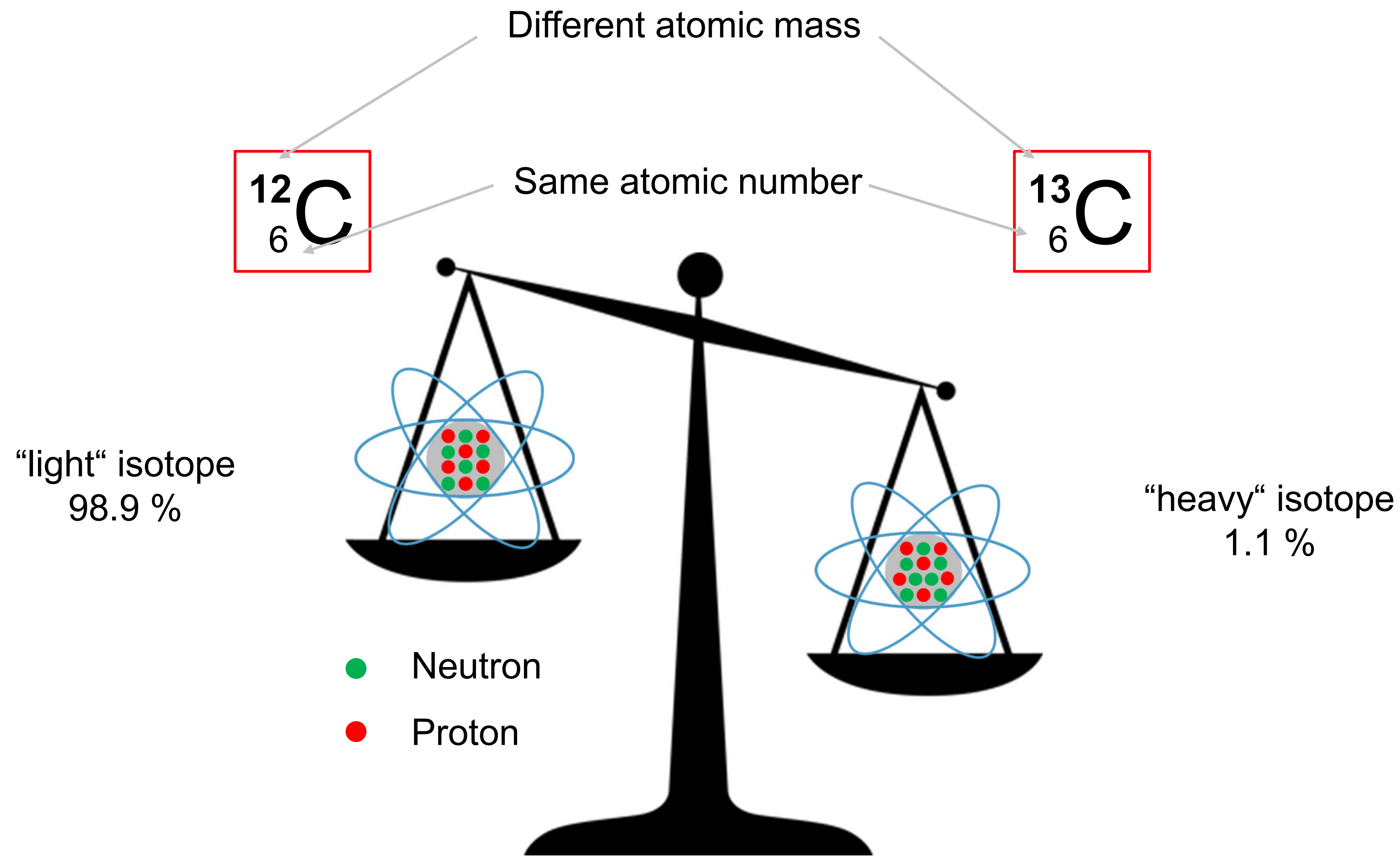
Overview

- What is an isotope?
- Isotopic fractionation
- Geographical origin
- Botanical origin
- Isotopic methods in the food area
- Delta notation






What is an isotope?



„**Isotope**" (old greek) = *ísos*, „**equal**" + *topós*, „**place**": same place in the periodic table

Natural abundance of the heavy isotopes

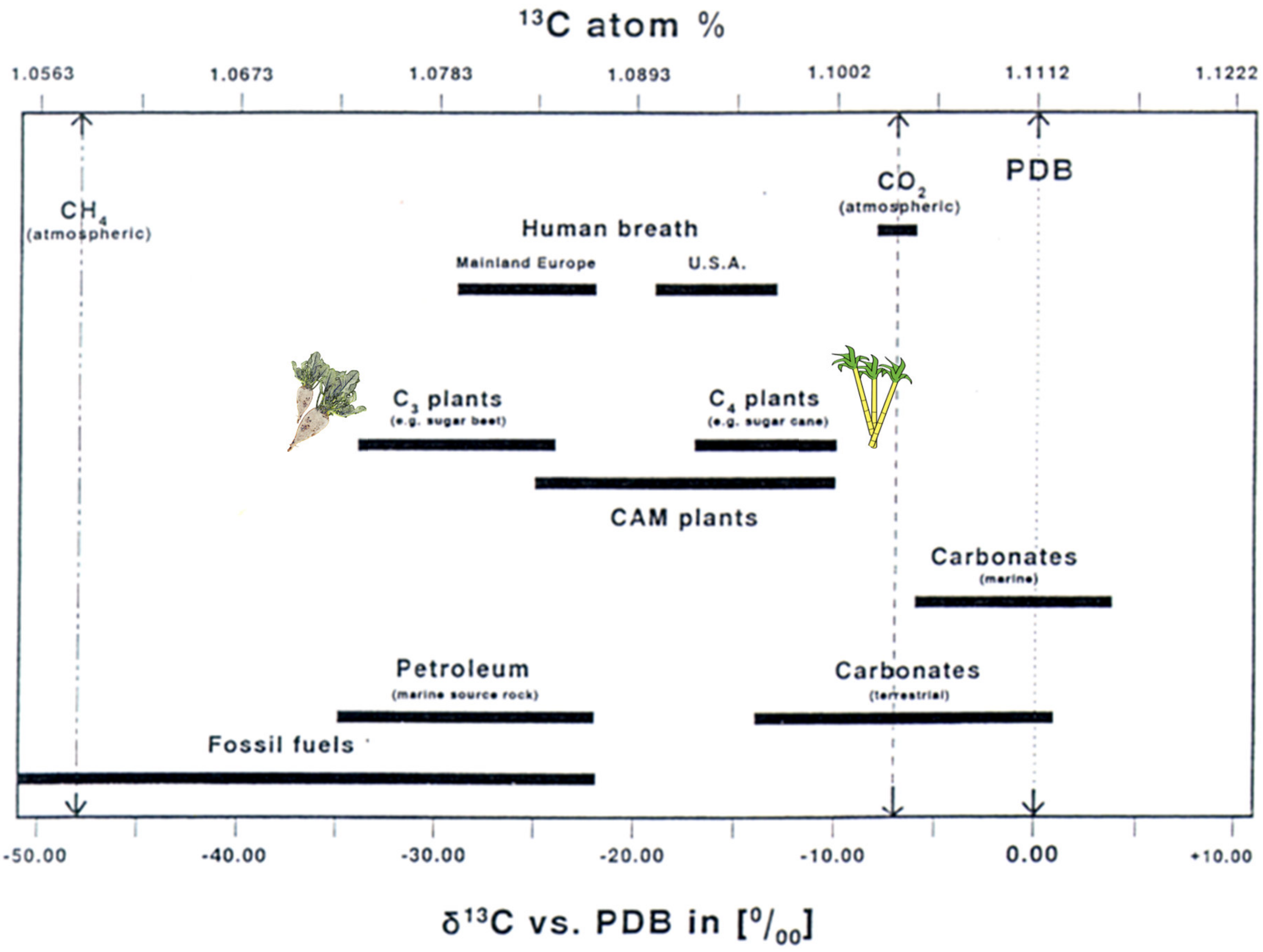
- Precise Isotope Ratios

Element	Minor Isotope	Natural Abundance [%]
Hydrogen	^{2}H (D)	0.015**57**
Carbon	^{13}C	1,111**40**
Nitrogen	^{15}N	0.366**30**
Oxygen	^{18}O	0.200**04**
Sulfur	^{34}S	4.215**00**

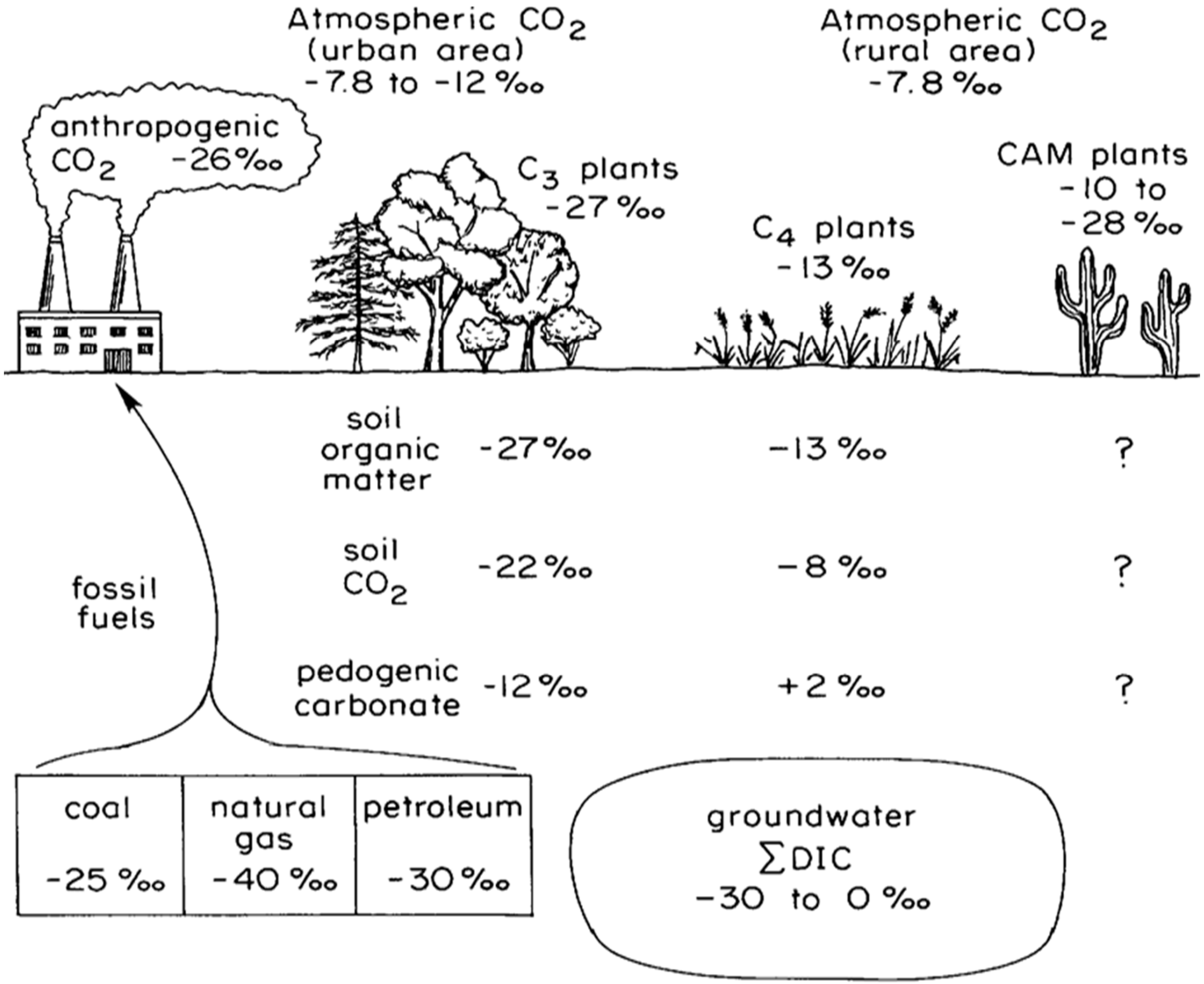
Information from stable isotopes

Stable Isotopes	Information provided
Carbon $^{13}C/^{12}C$	Feed, plant type (photosynthetic pathway)
Hydrogen $^{2}H/^{1}H$ or D/H	Geographical origin
Oxygen $^{18}O/^{16}O$	Geographical origin (sea level and distance from the shore)
Nitrogen $^{15}N/^{14}N$	Agricultural practice
Sulphur $^{34}S/^{32}S$	Geological origin, agricultural practice
Strontium $^{87}Sr/^{86}Sr$	Geological origin

^{13}C abundance in the environment I



^{13}C abundance in the environment II



Isotopic fractionation

- Isotopic fractionation is the shift in the abundance of the isotopes of an element caused by physical or chemical processes.

- The fractionation is thermodynamic and thus temperature-dependent.

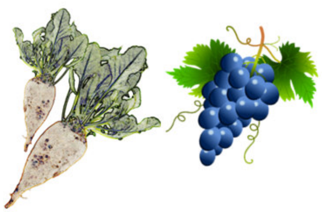
- Isotopic effects are primarily influenced by the relative mass difference of the isotopes.

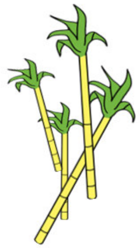
- Isotopic effects and the resulting isotope fractionations therefore lead to particularly significant isotope shifts for elements with relatively low mass (approx. 40 u).

- Examples of isotope fractionating processes:
  - evaporation
  - freezing
  - precipitation
  - chemical reactions

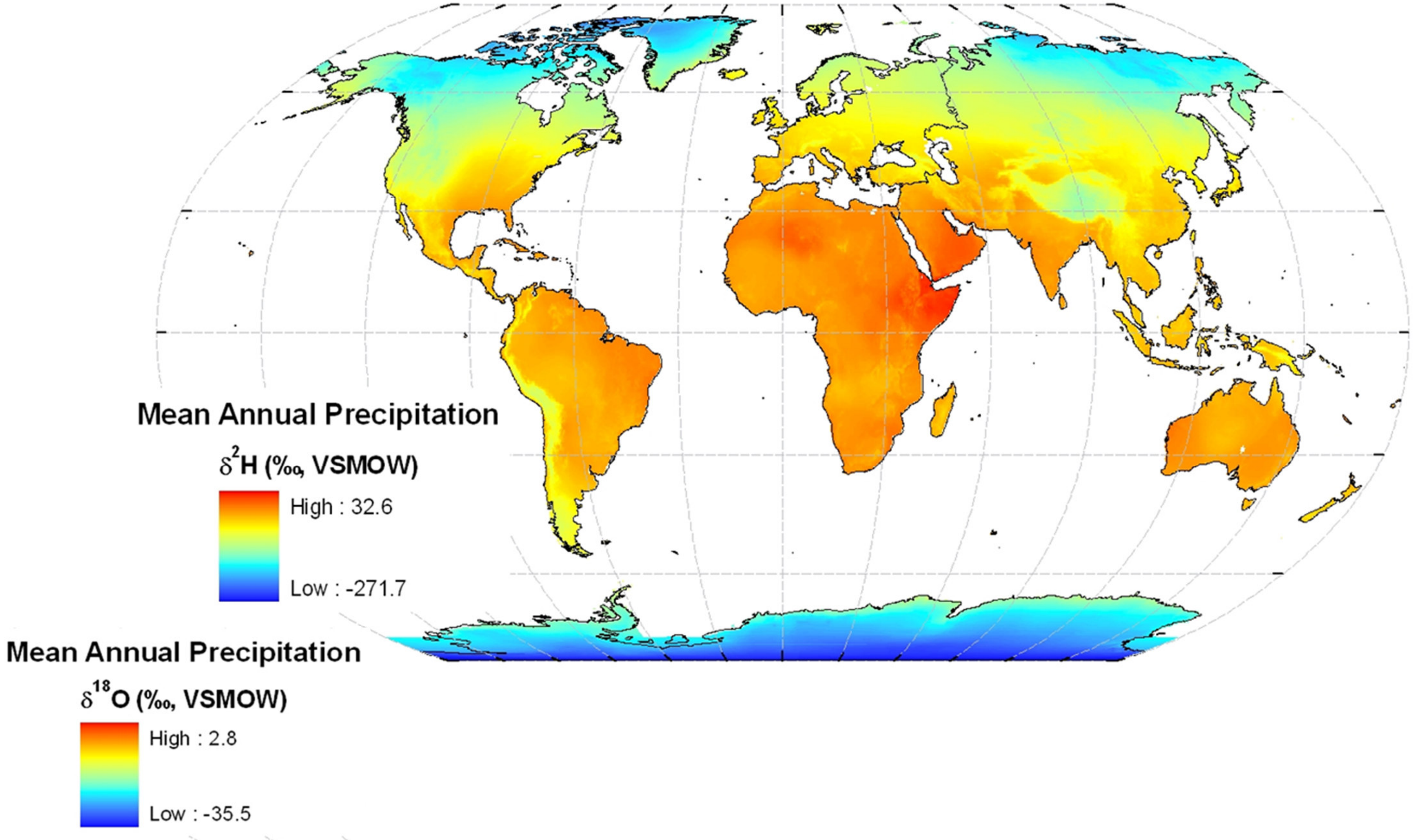
$\delta^{13}C$ - Isotope fractionation by photosynthesis

	C_3 plant	C_4 plant	CAM
CO_2 fixation	Calvin cycle	Hatch-Slack cycle	Crassulacean Acid Metabolism
Primary product	3-Phosphoglyceric acid (C_3)	Oxaloacetic acid (C_4)	C_4 pathway via malate
^{13}C depletion	Relatively strong, „light“ plants	Relatively low, „heavy“ plants	Intermediate position
$\delta^{13}C$ values	-24…-32 [‰]	-10…-16 [‰]	-12…-30 [‰]
Examples of food	Wheat, rye, rice, **sugar beet**, **grapes,** potatoes	Maize, **sugar cane**, millet	Pineapple, vanilla, succulent plants

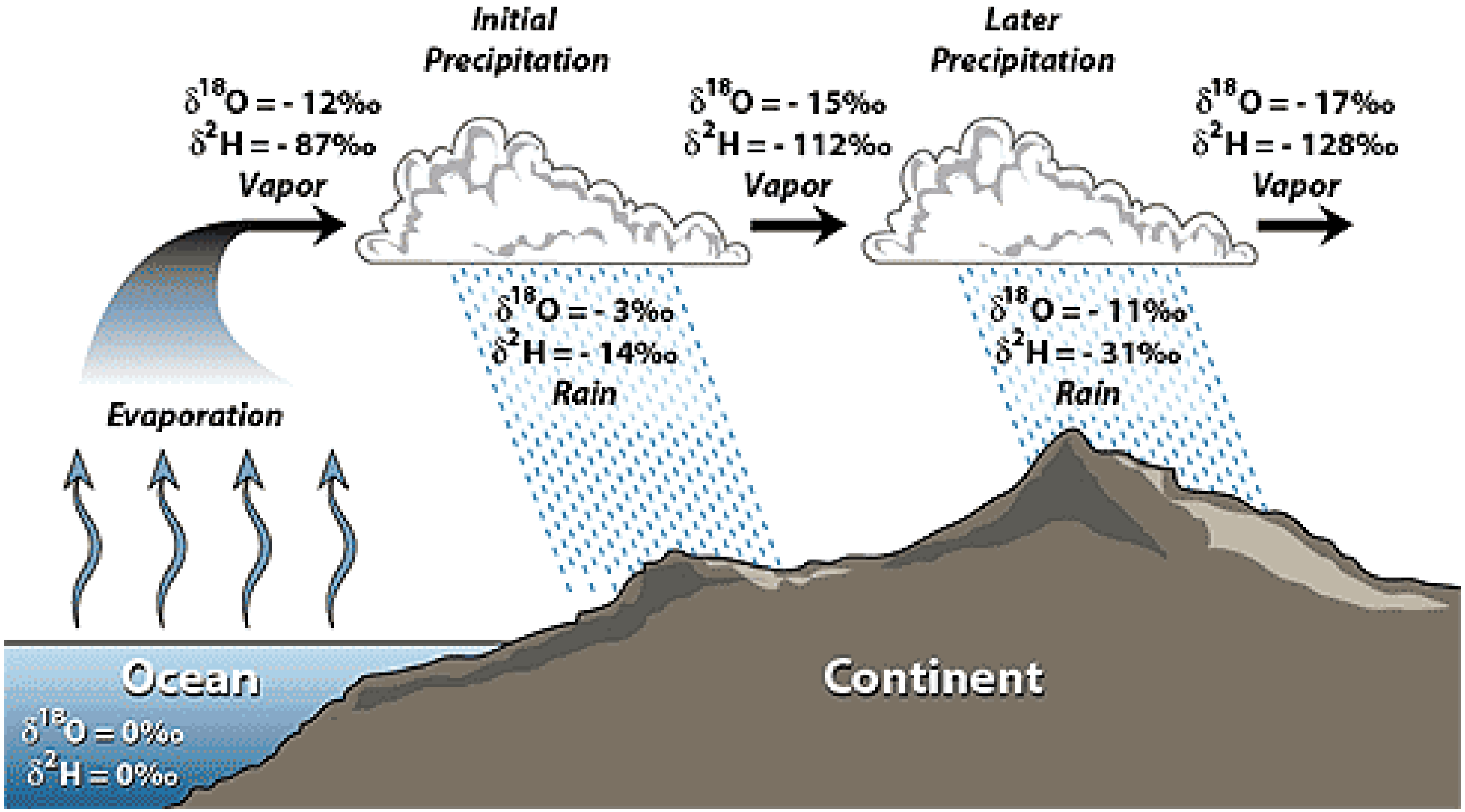




δ^2H and δ18O - Geographical Origin –

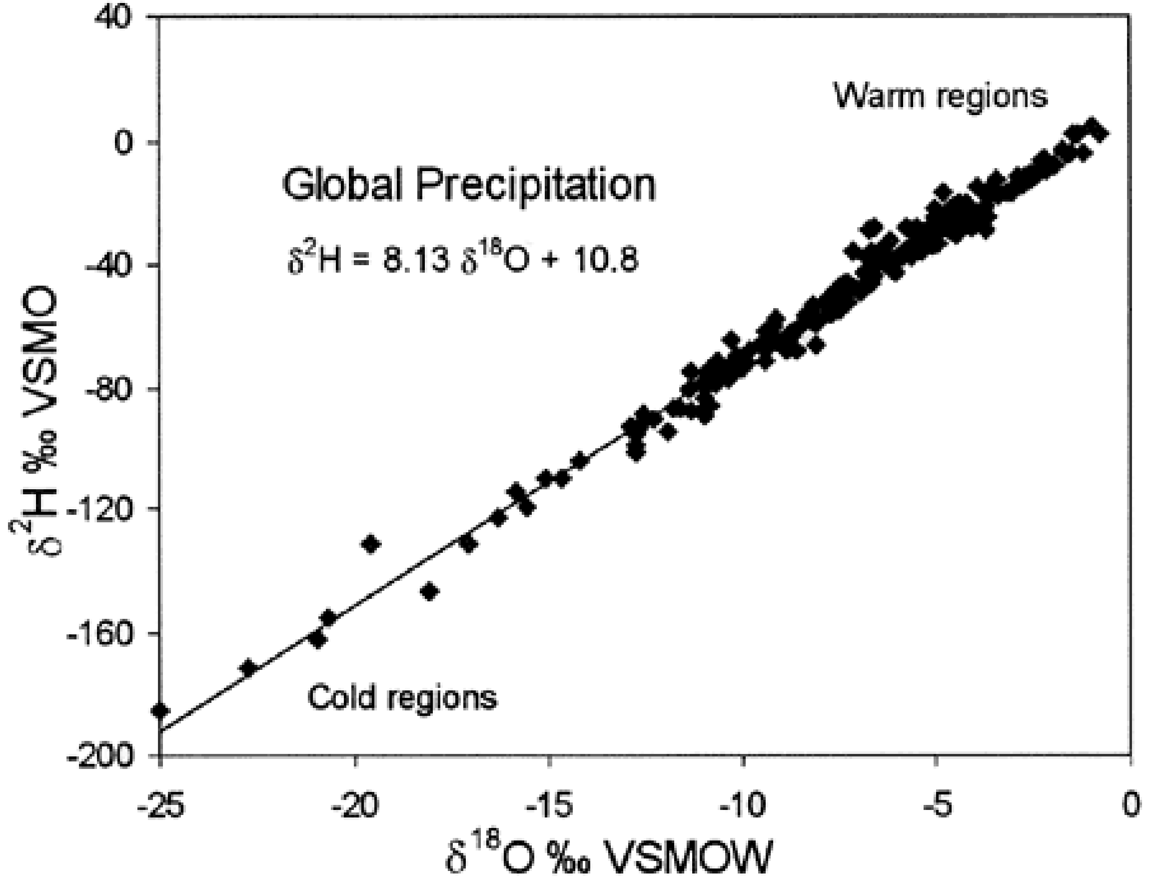


δ^2H and $\delta^{18}O$- Geographical Origin II - Rainout effect



Source: http://web.sahra.arizona.edu/programs/isotopes/oxygen.html

δ^2H and $\delta^{18}O$- Geographical Origin II – Global Meteoric Water Line



Source: http://web.sahra.arizona.edu/programs/isotopes/oxygen.html

Delta (δ) Notation

- Variations in the natural abundance of stable isotopes are expressed using delta (δ) notation.

- **Isotopic ratio R**: $ratio\ (R) = \frac{abundance\ of\ the\ heavy\ Isotope}{abundance\ of\ the\ light\ Isotope}$

$$R = \frac{^{13}C}{^{12}C}$$

$$R = \frac{^{18}O}{^{16}O} \qquad R = \frac{D}{H}$$

- **Delta (δ) in ‰**: $\delta\ [‰] = [\frac{R_{Sample}}{R_{Standard}} - 1] * 1000$

$$\delta^{13}C_{VPDB} = -25{,}5\ ‰$$

- Expression of isotopic ratios as

  ppm, permil ‰ , at% (Atom Percent) and **APE** (Atom Percent Excess)

Primary Calibration Material

- Isotopic ratios are expressed versus these materials that define the δ-scales

Element Ratio	Isotope delta scale
Hydrogen $^{2}H/^{1}H$	**VSMOW** (***S***tandard ***M***ean ***O***cean ***W***ater)
Carbon $^{13}C/^{12}C$	**VPDB** (***P***ee ***D***ee ***B***elemnite)
Nitrogen $^{15}N/^{14}N$	Atmospheric Nitrogen (Air N_2)
Oxygen $^{18}O/^{16}O$	**VSMOW**

- Reference standard materials are available from the International Atomic Energy Agency (IAEA) in Vienna, the NIST (National Institute of Standards and Technology) and the USGS (United States Geological Survey)

International Methods

Year	Method	Product	Fraction	Techniques	Isotope ratios
1987	OIV method OIV-MA-AS311-05	Wine	Ethanol	SNIF-NMR	$(D/H)_I$, $(D/H)_{II}$, R
1991	AOAC method 998.12	Honey	Honey, proteins	IRMS	$^{13}C/^{12}C$
1993	CEN (TC174 N108, ENV 12140)	Fruit juice	Sugar	IRMS	$^{13}C/^{12}C$
1995	AOAC method 995.17	Fruit juice	Ethanol (from fermentation)	SNIF-NMR	$(D/H)_I$, $(D/H)_{II}$, R
1996	OIV method OIV-MA-AS2-12	Wine	Water	IRMS	$^{18}O/^{16}O$
1997	CEN (TC174 N109, ENV 12141)	Fruit Juice	Water	IRMS	$^{18}O/^{16}O$
2000	AOAC Official method 2000.19	Maple syrup	Ethanol (from fermentation)	SNIF-NMR	$(D/H)_I$, $(D/H)_{II}$, R
2001	OIV method OIV-MA-AS312-06	Wine	Ethanol	IRMS	$^{13}C/^{12}C$
2004	AOAC method 2004.01	Fruit juice & maple syrup	Ethanol (from fermentation)	IRMS	$^{13}C/^{12}C$
2006	AOAC method 2006.05	Vanillin	Vanillin	SNIF-NMR	$(D/H)_I$
2010	OIV method OIV-AS312-07	Wine	Glycerol	GC-C-IRMS, HPLC-IRMS	$^{13}C/^{12}C$
2014	OIV method OIV-MA-AS314-03	Sparkling Wine	CO_2	IRMS	$^{13}C/^{12}C$
2017	OIV method RESOLUTION OIV-OENO 479-2017	Wine	Glucose, Fructose, Glycerol, Ethanol	HPLC-IRMS	$^{13}C/^{12}C$

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Thank you for your attention

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