STABLE ISOTOPE ANALYSIS

EXAMPLE AND PRINCIPLES

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- Typical problem: A positive detection of methane was reported during operation at the so-called "sniffer" - ZS2 Branch B in Jakubov. A chromatographic analysis was performed on the sample.

| November 2022	reservoir gas	sample from the sniffer	97x less Methane
Helium	0,011	0,003	-
Hydrogen	0,001	0,001	-
Oxygen	0	20,034	-
Nitrogen	0,921	78,923	-
Methane	92,583	0,959	0,959
Carbondioxide	0,917	0,079	0,009
Ethane	**4,268**	-	**0,044**
Propane	0,894	-	0,009
Isobutane	0,147	-	0,002
n-Butane	0,148	-	0,002
Neopentane	0,002	-	0,000
Isopentane	0,033	-	0,000
n-Pentane	0,025	-	0,000
n-Hexane/C6+	0,050	-	0,001
KS, C1/(C2+C3)	18	?	18

HOW CAN STABLE ISOTOPE ANALYSIS HELP?

- To eliminate concerns that it could be reservoir gas from a compromised pipeline, a GC-IRMS isotopic analysis was also conducted.

Izotopická analýza	$\delta^{13}C$ [‰]		$\delta^{2}H$ [‰]	
Methane	**-58,8**	+/- 1,3	**-311,7**	+/- 11,2

- By inputting the **$\delta^{13}C$** and **δ^2H** values into the Schoell and Coleman plot, it was determined that the sample from the sniffer (★) contains (sub)surface biogenic methane, not reservoir gas or a mixture with it.
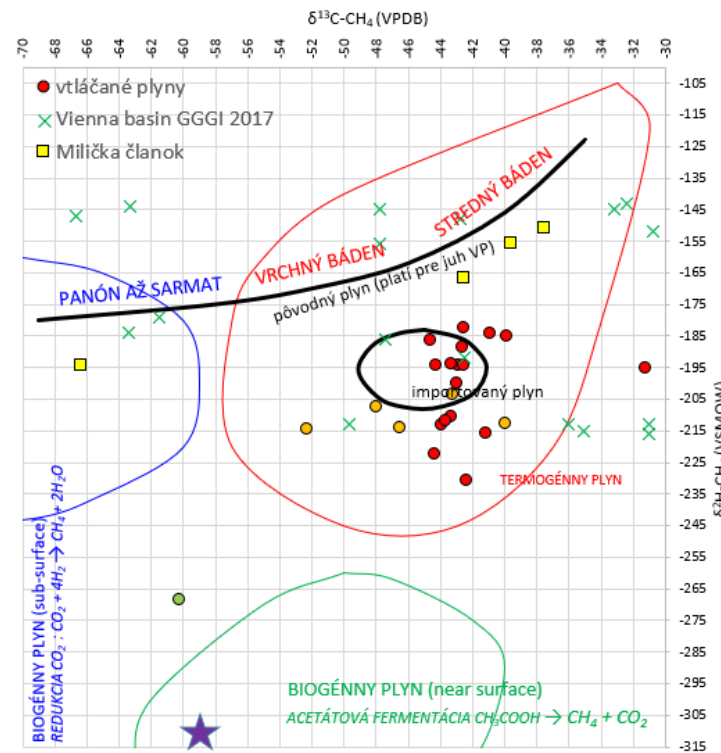
Schoell, M., 1980; Coleman, et. al., 1993
VPDB - Vienna Pee Dee Belemnite; VSMOW - Vienna Standard Mean Ocean

HISTORY OF THE DEVELOPMENT OF ISOTOPE ANALYZERS

- 1687 - I. Newton published the laws of motion

- 1865 - J. C. Maxwell defined the properties of the electromagnetic field

- 1895 - H. A. Lorentz derived the force acting on an electrically charged particle in a magnetic field (Nobel Prize)

- 1897 - J. J. Thomson demonstrated the existence of a charged particle in the structure of the atom - the electron (Nobel Prize)

- 1899 - W. Wien discovered that a strong electric and magnetic field bends the rays of ionized gas (Nobel Prize)

- 1909 - E. Rutherford confirmed the existence of the proton (Nobel Prize)

- 1913 - F. Soddy, following the suggestion of M. G. Todd, introduced the term "isotope" based on the Greek words "isos" (equal) and "topos" (place) to characterize an element from the same position on the periodic table (with the same chemical properties) but with a different atomic mass (Nobel Prize)

- 1919 - F. W. Aston constructed a device called the mass spectrograph, which allowed for the separation of isotopes of the same element with different atomic masses (Nobel Prize)

- 1932 - J. Chadwick discovered the neutral particle, the neutron (Nobel Prize)

- 1932 - H. C. Urey found that hydrogen has isotopes and discovered deuterium (Nobel Prize). His study of oxygen isotopes in marine sediments contributed to the development of geochemistry

- 1940 - A. Nier, using a mass spectrometer of his own design, successfully separated the isotopes **235U** and **238U** for the American Manhattan Project

- 1947 - L. Jenckel developed the first compact mass spectrometer. He established a subsidiary company called Atlas MAT (Measurement and Analytical Technology) at Atlas-Werke in Bremen, where the first **commercial instruments** of the **IRMS** type were produced from 1953 onwards.
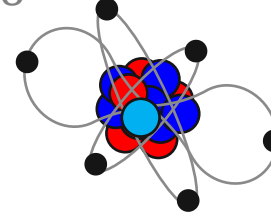
STABLE ISOTOPES

- Isotopes are chemically identical elements with different masses. For mass spectrometry, stable isotopes are suitable, not radioactive ones

- Stable isotopes of **carbon** ^{12}C, ^{13}C (12 = 6p + 6n, 13 = 6p + **7n**)

$$^{12}_{6}C \qquad\qquad ^{13}_{6}C$$
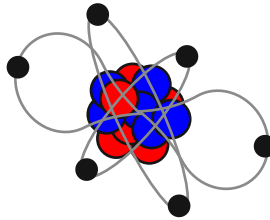
- Natural abundance: 98,9%   1,1%

- Stable isotopes of **oxygen** ^{16}O, ^{18}O (16 = 8p + 8n, 18 = 8p + **10n**)

$^{16}_{8}O$ $^{18}_{8}O$
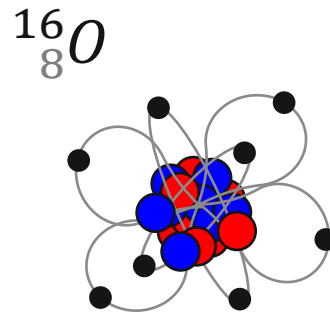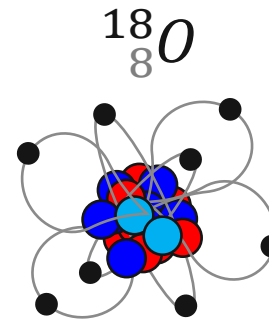
- Natural abundance :   99,8%   0,2%

- Stable isotopes of **hydrogen** ^{1}H, ^{2}H (1 = 1p, 2 = 1p + **1n**)
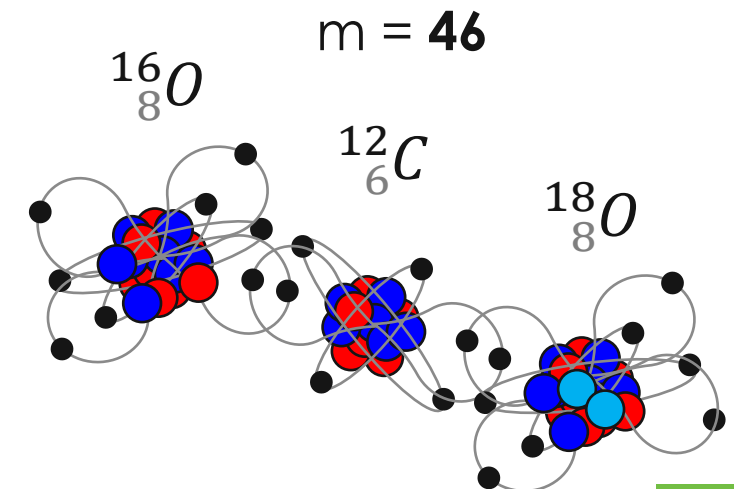
$$\mathbf{^1_1}H \qquad \mathbf{^2_1}H$$
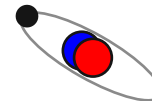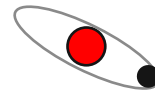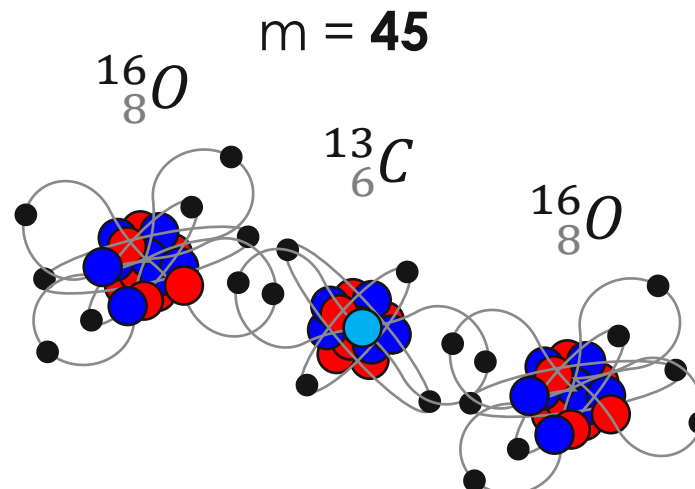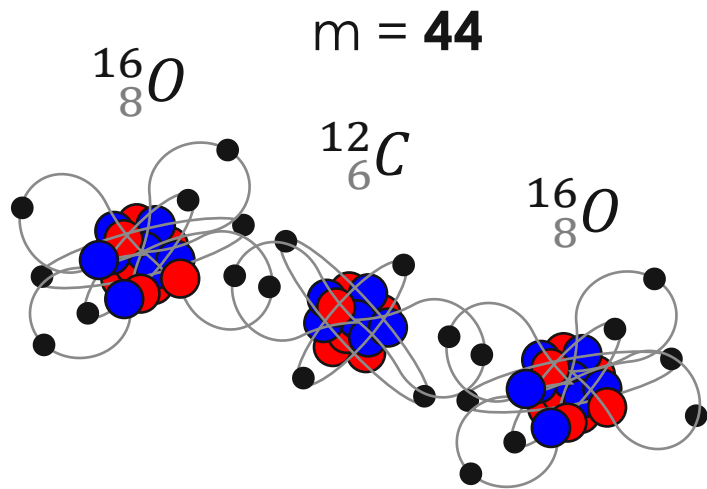

- Natural abundance :   99,98%   0,02%

- Particles measurable by mass spectrometry for carbon isotopes are CO_2 molecules. In order to analyze carbon isotopes, a hydrocarbon sample needs to be completely oxidized to CO_2

- The most abundant combinations of stable carbon and oxygen isotopes are:
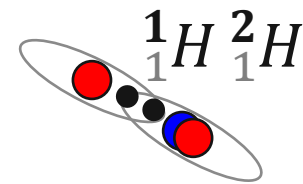
STABLE ISOTOPES

- Particles measurable by mass spectrometry for hydrogen isotopes are H2 molecules. In order to analyze hydrogen isotopes, a hydrocarbon sample needs to be completely pyrolyzed into H_2 (and soot).

- The most abundant combinations of stable hydrogen isotopes are

m =1+1 = **2**

$$^1_1H_2$$

m =1+2 = **3**

$$^1_1H\ ^2_1H$$
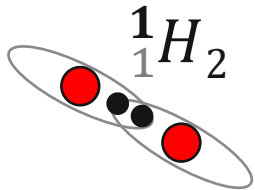
- Magnetic Sector – The essence of a mass spectrometer is as follows: The ion beam of the sample is exposed to the influence of a perpendicularly oriented magnetic force in a vacuum. The magnetic field causes the path of the flying ions to curve. The radius of curvature depends on the strength of the magnetic field **(B)**, the velocity of the ions **(v)**, the charge of the ions **(q)**…
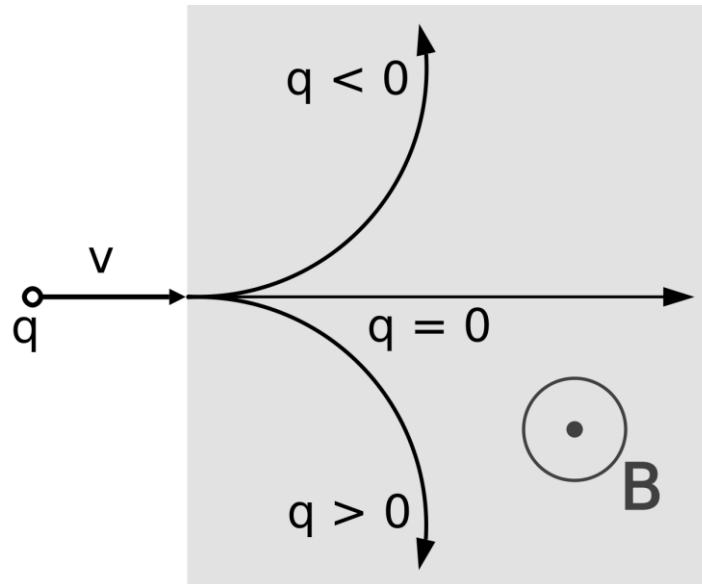
- ... and the magnitude of the bending, r, also depends on the mass of the ions, **m** (at speeds much slower than the speed of light) - greater mass results in a path with a larger radius.

$$m_1 < m_2$$
$$r_1 < r_2$$
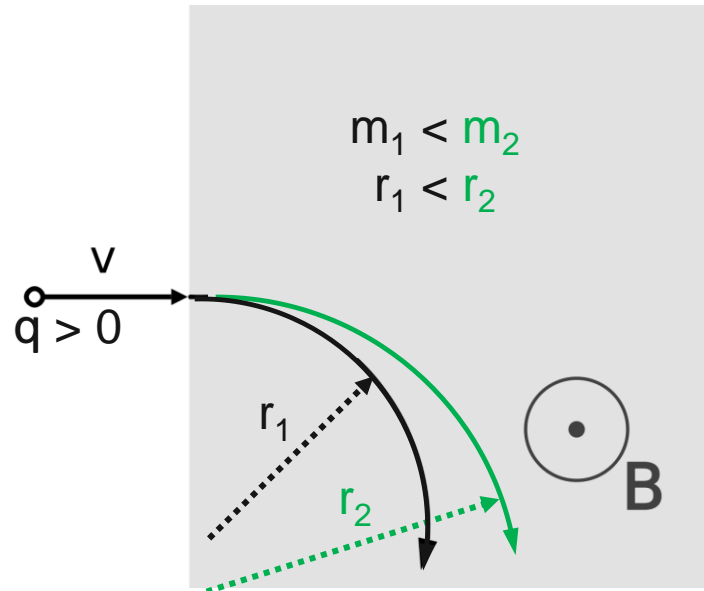
- The relationships for the mentioned mechanical and electrical quantities demonstrate their influence on r and define the fundamental parameter m/z, which allows the mass spectrometer to distinguish individual isotopes

$$\mathbf{F} = \frac{m\mathbf{v}^2}{r}$$

(centrifugal force)

$$\mathbf{F} = q\mathbf{v}\mathbf{B}$$

(Lorentz force)

$$\frac{m\mathbf{v}}{r} = q\mathbf{B}$$

$$E_k = \frac{m\mathbf{v}^2}{2}$$

(kinetic eneregy)

$$E_k = qV$$

(kinetic energy of charged particle)

$$\frac{m\mathbf{v}^2}{2} = qV$$

$$\frac{m}{q} = \frac{r^2\mathbf{B}^2}{2V}$$

$$\frac{m}{q} \times e = \frac{m}{z}$$

MS - MASS SPECTROMETER

- *m/z* represents the ratio of the molar mass to the charge of a particle. This information alone does not describe the chemical nature of the particle. To determine the composition of a sample, additional related data must be known

- A particle with a mass of 50 and a charge of +1 will have the same m/z value as a particle with a mass of 100 and a charge of +2.

$$\frac{m}{z} = \frac{50}{1} = 50 \qquad\qquad \frac{m}{z} = \frac{100}{2} = 50$$

- A **charge of +1** is the most common case of ionization, but it is indeed preferable to know the nature of the sample entering the mass spectrometer in order to gain a better understanding of its composition.

ISOTOPE RATIO

- The initial part of the measurement is based on determining the concentrations of isotopes through molecules that represent them
- The molecules of interest are ionized with a charge of +1, so their m/z values are determined accordingly

for carbon dioxide CO$_2$

$$CO_2^+ \ \frac{m}{z} = 44(^{12}C^{16}O^{16}O)^+, \ \ 45(^{13}C^{16}O^{16}O)^+, \ \ 46(^{12}C^{16}O^{18}O)^+$$

for hydrogen H$_2$

$$H_2^+ \ \frac{m}{z} = 2(\ ^1H\ ^1H)^+, \ \ 3(\ ^1H\ ^2H)^+, \ \ [3(\ ^1H\ ^1H\ ^1H)^+, \ \ 2(\ ^2He\ ^2He)^{++}]$$

- The representation of isotopes in a sample is not practical to express in absolute concentrations. Therefore, the term **"isotope ratio"** is commonly used, comparing the ratio of the **heavier isotope $^H X$** to **the lighter isotope $^L X$** with the **ratio in a defined standard**. It is expressed as **$\delta^H X$**, usually in parts per thousand (‰), as the deviation from the standard is typically small.

$$R_{sample} = \frac{^H X}{^L X}$$

$$\delta^H X = \frac{R_{sample} - R_{standart}}{R_{standart}} \times 1000$$

$$R_{standart} = \frac{^H X_{standart}}{^L X_{standart}}$$

- For carbon measured in the form of ionized molecules CO_2^+ the result is reported as $\boldsymbol{\delta^{13}C}$

- The value $\delta^{13}C$ is calculated as shift with respect to a standart called **VPDB** *Vienna Pee Dee Belemnite ($^{13}C/^{12}C$ = 0,01122)*

$$\delta^{13}C\ [\permil] = \left(\frac{\left(\frac{c[^{13}C]}{c[^{12}C]} \right)_{sample} - \left(\frac{c[^{13}C]}{c[^{12}C]} \right)_{VPDB}}{\left(\frac{c[^{13}C]}{c[^{12}C]} \right)_{VPDB}} \right) \times 1000$$

- For hydrogen measured in the form of ionized molecules H_2^+ the result is reported as **δ^2H**

- The value δ^2H is calculated as a shift with respect to a standard **VSMOW** *Vienna Standard Mean Ocean Water ($^2H/^1H$ = 0,0001557)*

$$\delta^2\text{H} \ [\permil] = \left(\frac{\left(\dfrac{c[^2\text{H}]}{c[^1\text{H}]} \right)_{sample} - \left(\dfrac{c[^2\text{H}]}{c[^1\text{H}]} \right)_{VSMOW}}{\left(\dfrac{c[^2\text{H}]}{c[^1\text{H}]} \right)_{VSMOW}} \right) \times 1000$$

- **$\delta^{13}C$** - *Range variations in different types of carbon sources*
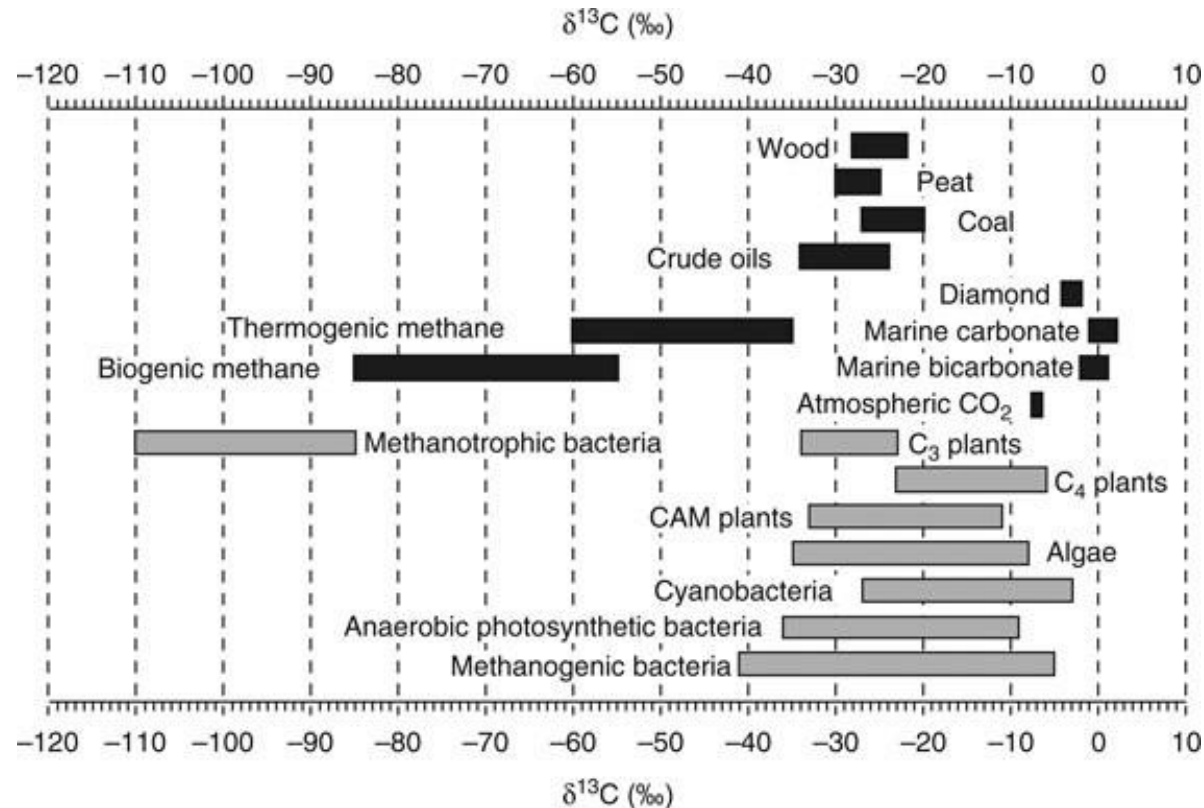
- *δ^2H Range variations in different types of hydrogen sources*

- Analysis of natural gases - (1) first, the components of natural gas must be separated from each other, (2) quantitatively converted into a suitable form, (3) and sequentially travel with a reference gas towards (4) the MS detector
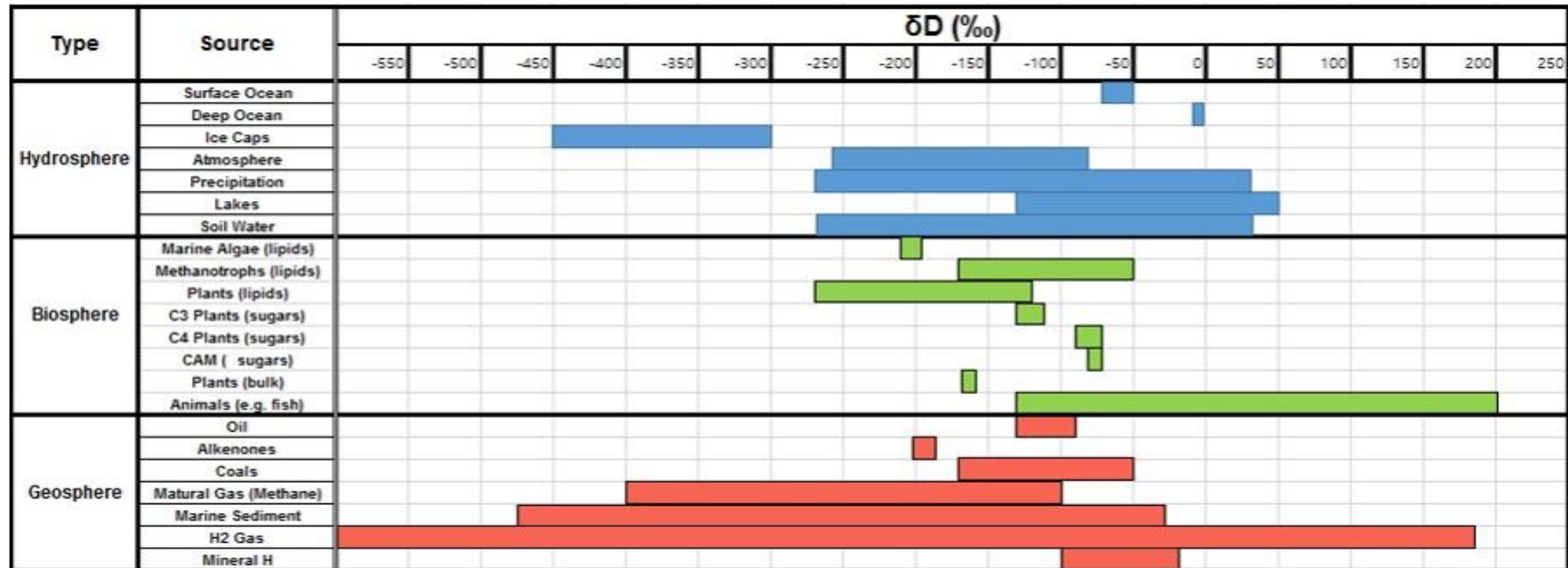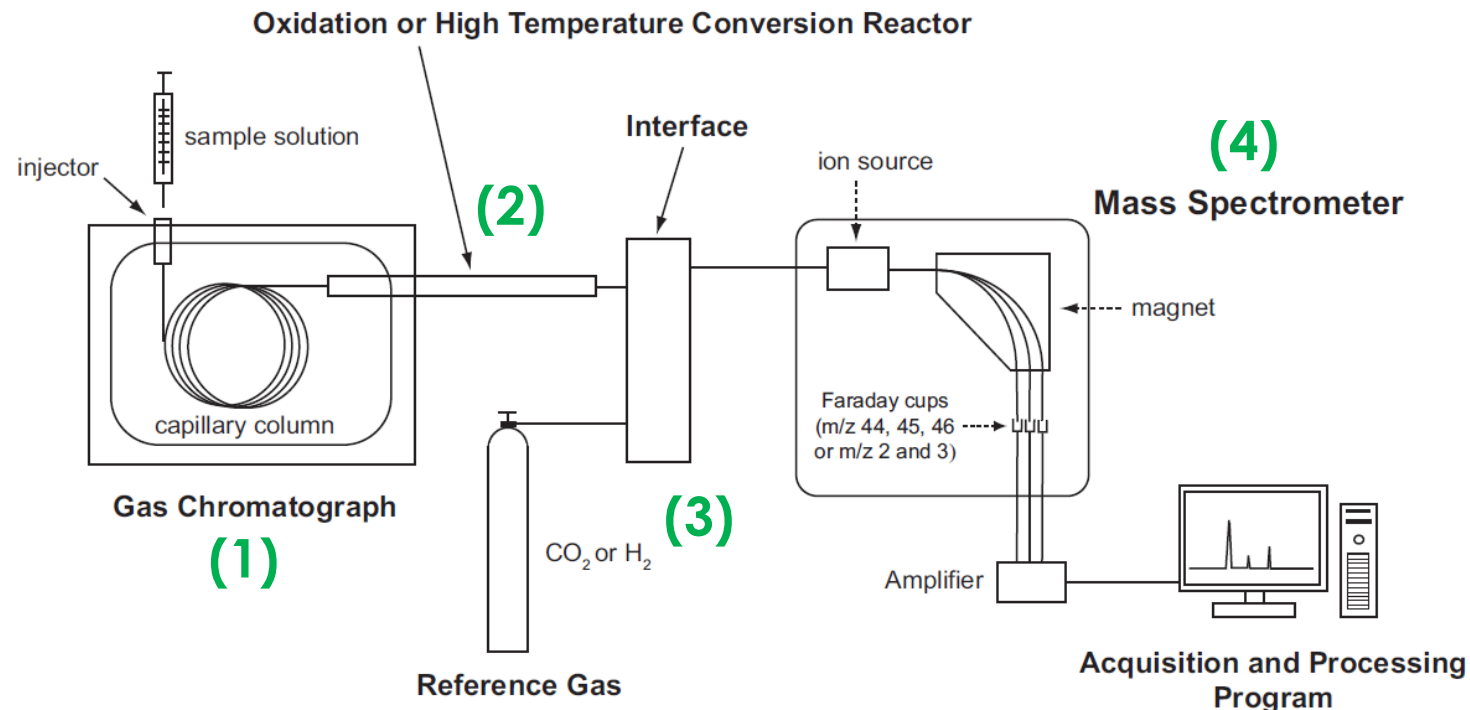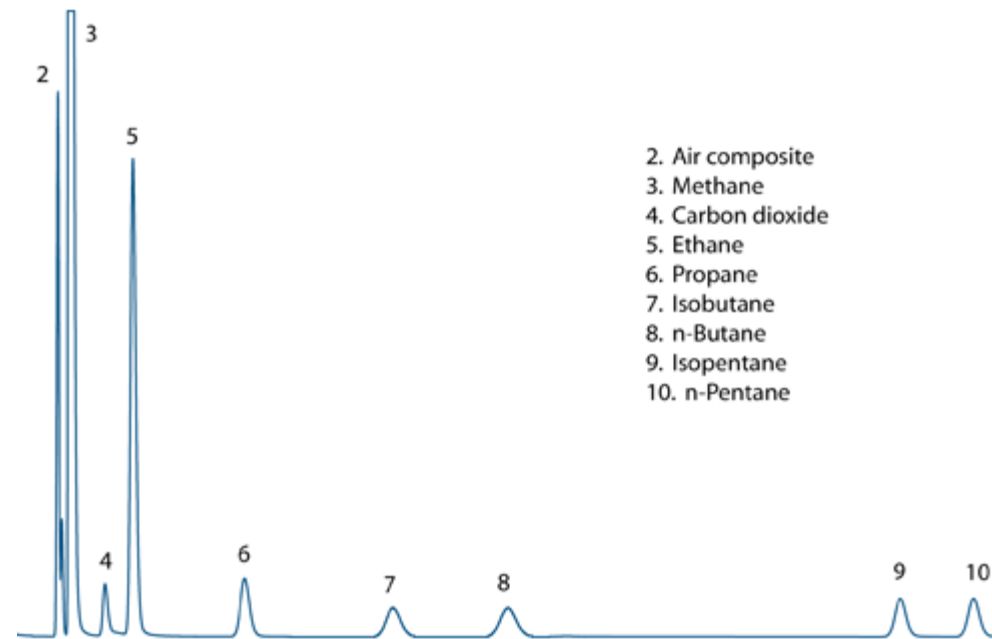
GC-IRMS – ISOTOPE RATIO MASS SPECTROMETER

- Thermo Scientific system in laboratory of specialized services division of DPZZP:

(1) Gas chromatograph,
    Trace 1310

(2) Sample conversion,
    GC IsoLink II
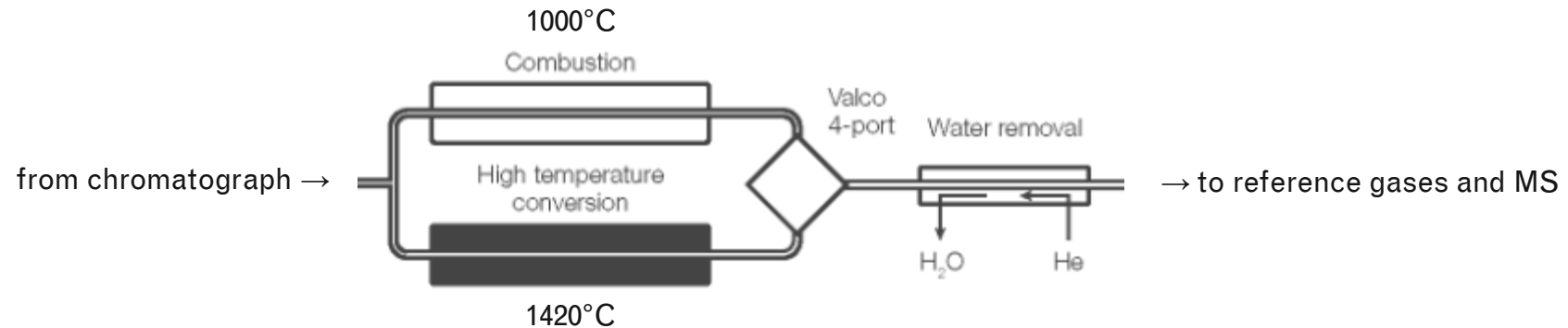
(3) Refference gas mixer, ConFlo
    IV

(4) IRMS,
    Delta V Advantage

(1) Gas chromatograph– GCwhich separates hydrogen, nitrogen, methane, carbon dioxide, ethane, propane, etc.

2. Air composite
3. Methane
4. Carbon dioxide
5. Ethane
6. Propane
7. Isobutane
8. n-Butane
9. Isopentane
10. n-Pentane

(2) Hydrocarbon conversion:

- **combustion oxidation** of CO_2
- **pyrolytic conversion to** H_2 and soot

1000°C
Combustion

Valco
4-port   Water removal

from chromatograph →   High temperature
conversion   → to reference gases and MS

H_2O He

1420°C

▪ Hydrogen and Carbon dioxide from gas are not affected in this process

(3) The current is switched between the reference gases and the sample in the interface for gas dosing, and helium is sometimes used for dilution. The reference gas serves as a control for the MS
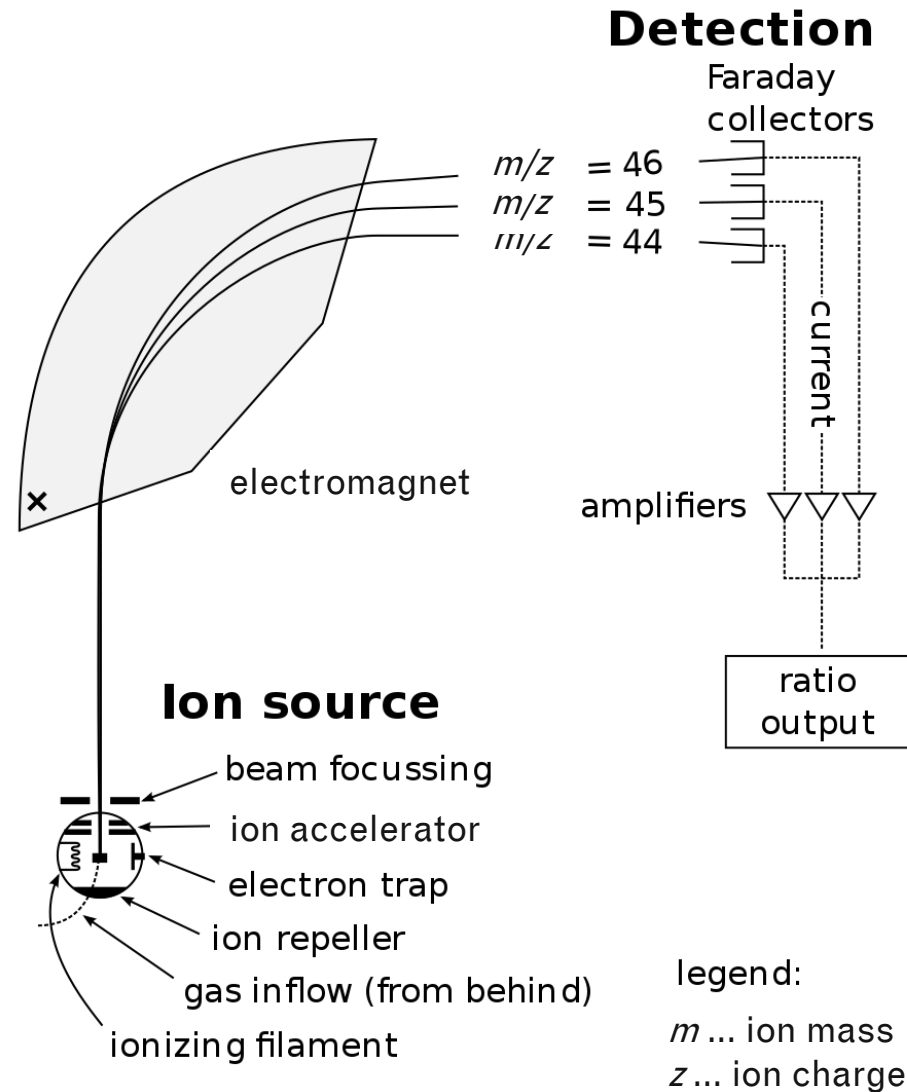
(4) IRMS detector- example for CO_2

Detection

Faraday collectors

m/z = 46
m/z = 45
m/z = 44

electromagnet

current

amplifiers

ratio output

Ion source

beam focussing

ion accelerator

electron trap

ion repeller

gas inflow (from behind)

ionizing filament

legend:

m … ion mass
z … ion charge

- Conditions of the **analytical** process:

  - Ionization, acceleration, and detection of particles occur in a **vacuum**

  - The sample must be in the gas phase, and if it is not, it must be vaporized or converted, preferably into simple gaseous molecules such as H_2, CO_2, N_2, CO

  - Subsequently, the sample is ionized by an electron beam - collisions between electrons and neutral particles result in the formation of positively ionized particles, for example, from CO_2...
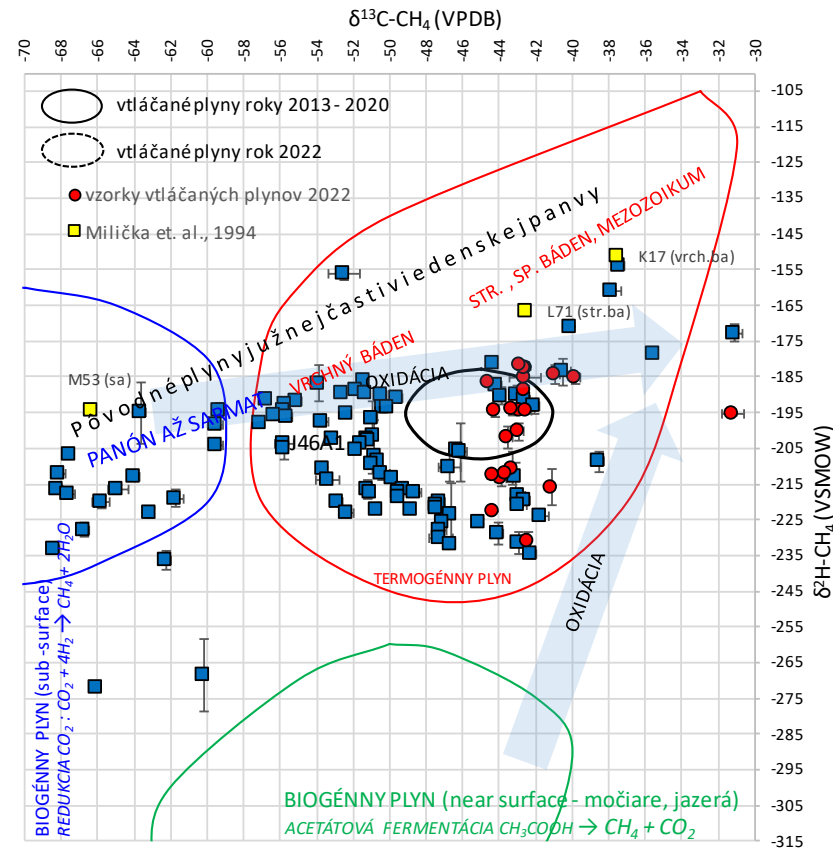
$$CO_2 + e^- \rightarrow \mathbf{CO_2}^{+\bullet} + 2e^-$$
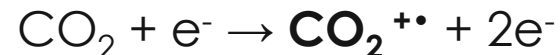
  - Ions acquire a velocity and direction due to a preset electrical voltage and are directed into a magnetic field created by an electromagnet

  - The beam of ionized particles is separated into less curved and more curved streams of particles in the magnetic field, based on the content of heavier and lighter isotopes in the molecule.

  - Detection collectors are set to correspond to specific values of *m/z*

- Necessary **technical** conditions for the functionality of a mass spectrometer:

  - Room with **stabilized** interior temperature of 20-22°C

  - Backup power source with a 400V output and **voltage fluctuation filtration** in the electrical network

  - Pressure connection to **high-purity** technical gases - synthetic air, helium, carbon dioxide, hydrogen, methane, oxygen, nitrogen

  - Certified reference materials - **isotopic calibration gases**

  - Active exhaust for hot exhaust gases

  - Regular checks of **analytical correctness** and instrument reliability

  - Service support and preventive maintenance

- The utilization of **δ¹³C** a **δ²H** z GC-IRMS for determining the origin of gas is based on the processing method developed by Schoell and Coleman, which involves the use of values for methane **δ²H-CH₄** relative to **δ¹³C-CH₄**

Schoell, M., 1980, 1984; Coleman, D. D. et. al., 1993, 1995
VPDB - Vienna Pee Dee Belemnite; **VSMOW** - Vienna Standard Mean Ocean Water

- ...and according to Bernard, where the dryness coefficient is used **mol% C$_1$/ mol% (C$_2$ + C$_3$)** in reference to **δ^{13}C-CH$_4$**
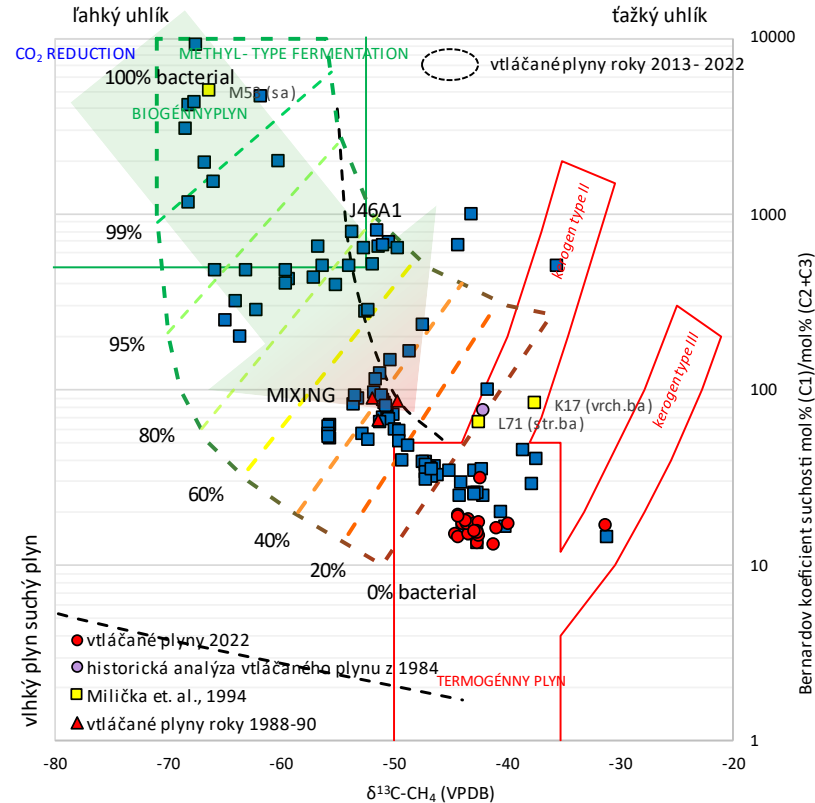
Bernard, B., et. al., 1978; Faber, E. and Stahl, W., 1984; Whiticar, M.J., 1999; Golding, S. D., et al., 2013

- Thermo Fisher Scientific: „Detecting ^{13}Clues, tracking ^{18}Origin, unravelling ^{2}History with isotope **fingerprints**".

ENVIRONMENTAL CASES FOR IRMS

- Analysts can track the origin, authenticity, and identity using isotopic **fingerprints** that remain in gases, liquids, fibers, or stones since their formation. IRMS can help reveal these **"isotopic signatures"** and provide information about the geographic source, natural processes, soil characteristics, cultivation practices, as well as environmental pollution.

- https://www.thermofisher.com/sk/en/home/industrial/mass-spectrometry/isotope-ratio-mass-spectrometry-irms/isotope-fingerprinting.html

    - Environmental analysis

ENVIRONMENTAL CASES FOR IRMS

- Obstacle in interpretation - isotopic **fractionation**...
- ... refers to processes that lead to **partial** changes in isotopic ratios:
  - transitions between gaseous, liquid, and solid **states**
  - **chemical interactions** of the analyzed substance with the surroundings
  - If these processes are well-known, the results are interpreted with consideration for possible fractionation
  - The migration of methane from a "reservoir" gas in one horizon to another can influence the results through diffusive fractionation. If bacterial oxidation occurs during migration, the δ13C and δ2H values of the remaining methane will shift closer to zero - indicating a higher abundance of heavier isotopes

- ... In the case of δ13C from CO2, the reactivity of carbon dioxide and changes in the environment where it is found need to be taken into account....
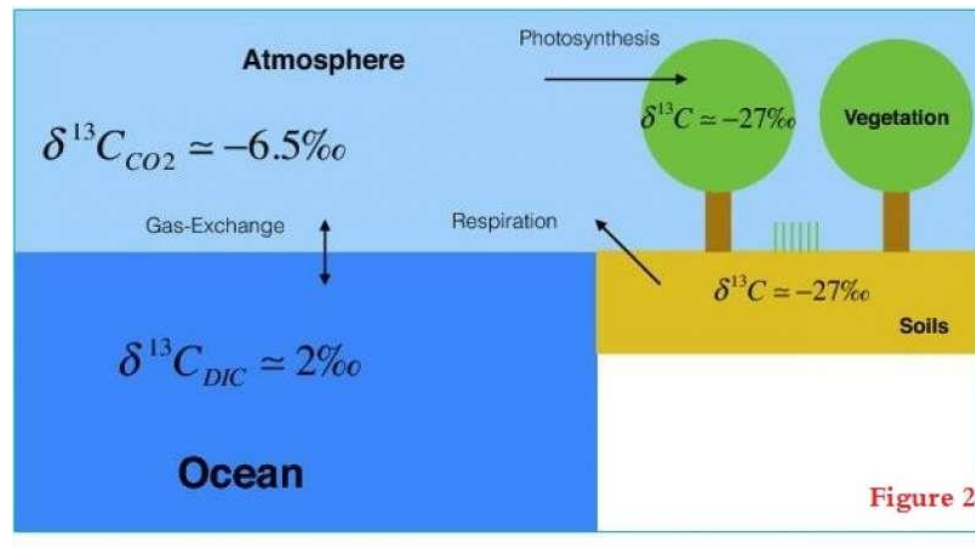

Figure 2: *The ^{13}C isotope fractionation in the Carbon Cycle (Schmittner, 2017)*

CONTACTS

- For analyses using GC-IRMS in the configuration of carbon and hydrogen isotopes in gases, it is necessary to contact the laboratory of the Special Services Department (OSaV, DPZZP) at Plavecký Štvrtok. You can reach them at laboratorium@nafta.sk

- The GC-IRMS instrument is operated by laboratory technician Jakub Zajac jakub.zajac@nafta.sk

- The data manager is geochemist Radoslav Vaverčák radoslav.vavercak@nafta.sk

THANK YOU FOR YOUR ATTENTION