

New technologies applied for determination of carbon and oxygen stable isotopes changes

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Abstract

This literature study summarizes information on carbon and oxygen stable isotopes and application of its knowledge for environmental studies. The main focus is development of new methods by using cutting edge technology which will give us a new insight into isotope trends and active system of coral reefs.

Carbon and oxygen stable isotopes

Carbon has two stable isotopes, ^{12}C and ^{13}C with the abundances of 98.93 % and 1.07 %, respectively. It also has a radioactive isotope ^{14}C with relative abundance of 10^{-10} %. ^{14}C is a cosmogenic radioisotope with half-life of 5730 years. Due to the isotopic fractionation in various physical, chemical and biological processes that are occurring in natural geochemical and biological carbon cycle, various carbon-containing compounds have characteristic carbon isotope content (Fig. 1) [1, 2].

Concentration of atmospheric CO_2 , which is the main source of carbon for biosphere, has been changing during glacial and interglacial transitions. During Last Glacial Maximum concentrations of atmospheric CO_2 varied from 180 to 200 and $\delta^{13}\text{C}$ was about -6.7 ‰. During interglacial conditions $^{12}\text{CO}_2$ is removed from the atmosphere by the process of photosynthesis and atmosphere is enriched by $^{13}\text{CO}_2$ [3, 4].

Carbonate minerals are important contributor to dissolved inorganic carbon (DIC) in terrestrial waters together with atmospheric CO_2 and CO_2 in soil. DIC is a common term for various carbon-containing species in water solution (CO_2 dissolved and aqueous, H_2CO_3 , HCO_3^- and CO_3^{2-}). Gaseous carbon dioxide dissolves in water and with this becomes a part of the system in which

carbon species are distributed according to pH of solution. And further, in normal environmental conditions, calcite dissolution occurs in the contact with water.



DIC is present in environmental waters (stream, lakes, and groundwater) at concentrations of up to 10 mmol/L. The $\delta^{13}\text{C}$ of DIC in groundwater can have a wide range of values. Factors that determine carbon concentration in water are, except origin, temperature and pH of the depositional environment. The stable isotopic composition of DIC is a useful tool that can be used in various fields of research. It presents the possibility of studying gas-water and carbonate-water exchange processes, gives the insight into temperature changes, mineral diagenesis, deep water composition, microbial activity and organic matter deposition [5 - 7].

Knowledge and understanding of isotopic fractionations is essential for relating $\delta^{13}\text{C}$ in a proxy indicator of paleoclimate or paleoenvironment to carbon source. Under equilibrium conditions the degree of isotope fractionation depends only on temperature. Knowledge of the magnitude of these isotope fractionations is essential for the interpretation of the isotope variations of C and O in natural calcium carbonate. Gaseous or aqueous CO_2 in equilibrium with dissolved carbonate ions gives raise to the fractionation towards light isotope ratio between different chemical species. Solid carbonate is isotopically heavier than DIC with which it is in chemical equilibrium [5, 8, 9].

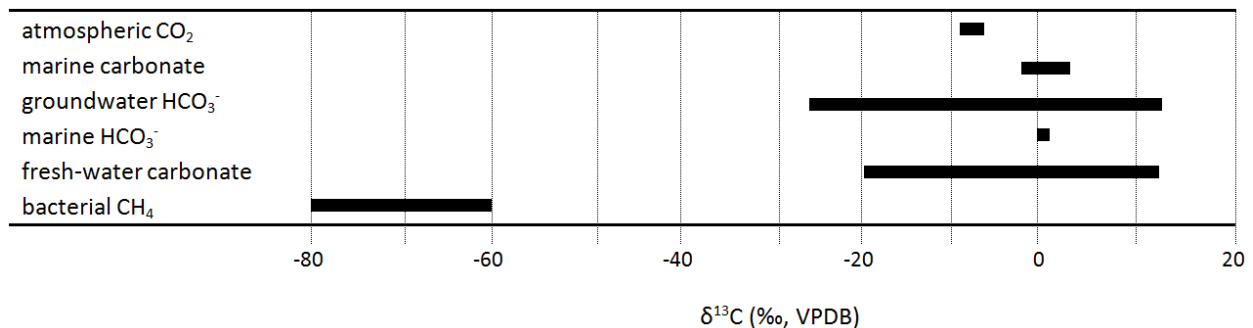


Figure 1. Schematic view of $\delta^{13}\text{C}$ variations in natural compounds.

Oxygen is the most abundant element on Earth. It has three stable isotopes with the abundances of: ^{16}O : 99.757 %, ^{17}O : 0.038 % and ^{18}O : 0.205 %. Because of the mass difference and the higher abundance the ratio of $^{18}\text{O}/^{16}\text{O}$ is determined as the $\delta^{18}\text{O}$ value and that value is used in environmental research [1, 2]. Measurement results can be expressed in VPDB, VPDB- CO_2 or in VSMOW scale. Conversion equations are given by following equations [7]:

$$\delta^{18}\text{O} (\text{VSMOW}) = 1.03086 \delta^{18}\text{O} (\text{VPDB}) + 30.86 \quad (5)$$

$$\delta^{18}\text{O} (\text{VSMOW}) = 1.04143 \delta^{18}\text{O} (\text{VPDB-}\text{CO}_2) + 41.43 \quad (6)$$

The abundance of oxygen isotopes in global water cycle differs from species to species and also values of $\delta^{18}\text{O}$ show a wide range of variations (Fig. 2). The global water cycle controls much of the oxygen isotope dynamics. It starts with evaporation where major controlling parameters are: isotopic composition of the ocean surface, sea-surface temperature, relative humidity and wind regime. After evaporation, water in the form of vapor is transported until saturation conditions are reached and clouds are formed. With a decrease of temperature rainout occurs and later different pathways lead the water back to the oceans.

Evaporated water is isotopically depleted in comparison with oceanic water and further partial condensation of this vapor associated with cloud formation again leads to isotopically depletion. The reason for that is preferential removal of heavier isotopes by rainout process.

Knowledge and understanding of all these processes is an important key for paleoclimate research and interpretation of paleotemperatures [5, 8, 10].

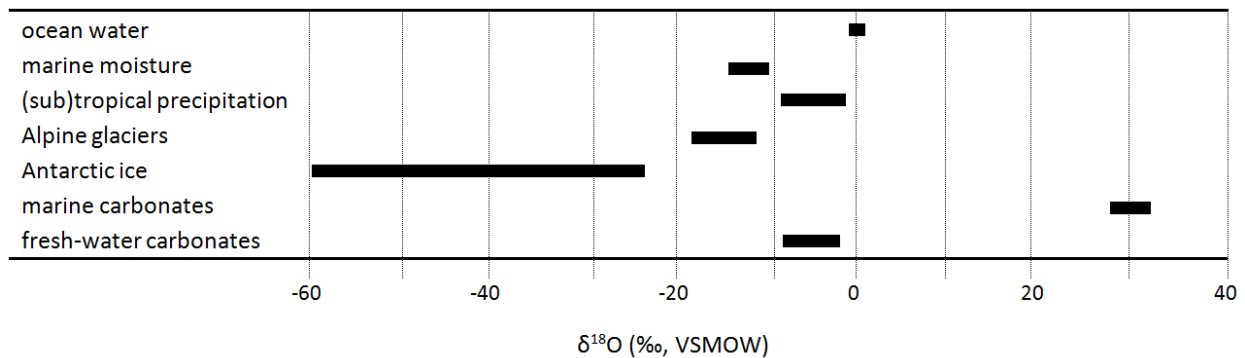


Figure 2. Schematic view of $\delta^{18}\text{O}$ variations in natural compounds.

Instrumentation

The Thermo Scientific Delta Ray with URI Connect is an optical analyzer for continuous measurement of isotope ratio values and concentration of carbon dioxide in ambient air and also, for measurement of discrete samples.

The instrument consists of two main components: The Analyzer and The URI (The Universal Reference Interface); and in addition for measurement of discrete samples CETAC™ ASX-7100 Autosampler.

The Analyzer uses an infrared laser to determine the isotopic composition of a gas. This establishes a new class of isotope analyzers that are portable and need less maintenance than a mass spectrometer.

The Universal Reference Interface is a compact device to deliver sample and reference gas to the optical laser spectrometer. It is composed of two functional units: a reference section and a sample inlet. The URI allows dilution of the supplied gases by mixing various gases with each other to change concentrations of the gas species of interest. The instrument is dedicated to analyze the isotope ratios of $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ from CO_2 in air as well as CO_2 concentration measurements of sample gas.

In the URI Connect system, a Variable Volume with a maximum capacity of 100 mL collects the sample gas which comes from the selected Port. The system automatically determines the concentration of the sample in the Variable Volume and adjusts the dilution during measurement. This enables it to perform the isotopic analysis in the Analyzer at an optimal, constant concentration.

Sample introduction into Variable Volume can be done on several ways: 1) Injecting gas samples into Front Port with Sample Processing Method – Inject into Carrier; 2) Measuring Samples from Gas Bags or Flasks with Sample Processing Method – External Container; 3) Measurements from Vials using Sample Processing method: Transfer Sample [11 – 13].

Isotope infrared spectroscopy

The laser light of The Thermo Scientific Delta Ray Spectrometers is generated by a difference frequency generation (DFG) mid-infrared laser that operates at 4.3 μm . In this absorption range lines are about 8000 times stronger than in the near-infrared. This enables a simple direct absorption approach requiring laser path length of 5 m. The absorption lines of

the different carbon dioxide isotopologues are shifted relative to each other which allow calculation of their relative abundance and the stable isotope ratios from spectrum (Fig. 3) [14].

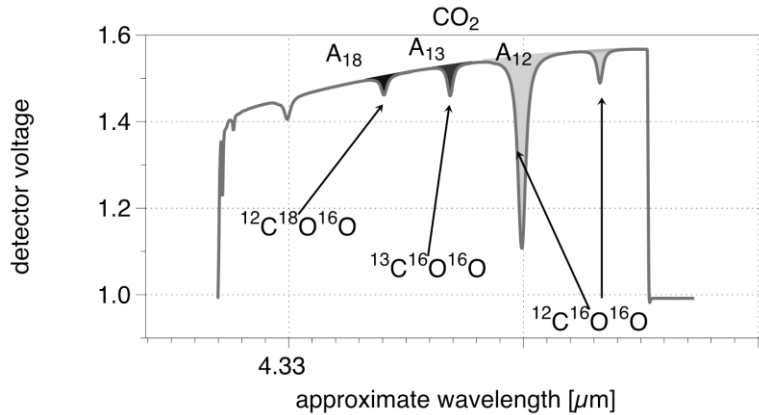


Figure 3. Mid-infrared spectral region at wavelength of 4.3 μm.

Reference materials

Each reference material has to fulfill certain requirements: it has to be homogeneous, easy to handle during preparation of measurement and available in large amount. Due to evaluation process the δ value of the standard must not diverse a lot from the δ values of the samples which are measured [15].

In carbonate materials, as it is calcite, stable carbon and oxygen isotopic composition is useful as environmental tracer to reconstruct paleoclimate and paleo-oceanic circulations. When choosing the reference material for calibration it is important to pay attention on microscale heterogeneities. Some microscale heterogeneities have been observed in the isotopic composition of international reference standards. Ishimura et al. determined grain-scale heterogeneities in the stable carbon and oxygen isotopic composition of the international standard calcite materials (NBS 19, NBS 18, IAEA-CO-1 and IAEA-CO-8) using a continuous-flow isotope ratio mass spectrometry (CF-IRMS). In this study they showed that only standard calcite that has highly homogeneous isotopic composition in grain-scale is NBS 19. NBS 18 is also homogeneous except the presence of the colored grains. IAEA-CO-1 is homogeneous in $\delta^{13}\text{C}$ but it is heterogeneous in $\delta^{18}\text{O}$ so larger quantity (260 μg) of this material should be used for calibration. IAEA-CO-8 shows heterogeneous $\delta^{18}\text{O}$ values and homogeneous $\delta^{13}\text{C}$ but with a disagreement with recommended values [16 – 18].

Carbon and oxygen fluxes in coral reefs

Complex ecosystem of coral reefs is formed through interaction of biological, physical and chemical processes. Coral reefs are important tropical ecosystem characteristic for shallow-water coastal areas. These coastal areas are sites of intense primary production and specific processes which can induce strong variations of dissolved inorganic carbon and associated high air-ocean CO₂ fluxes. Air-ocean CO₂ exchange in coastal areas is a fundamental process in a global carbon cycle [19, 20].

Modern reefs and also fossil reef carbonate structures are indicators of climate changes. Variations in the temperature of the surface tropical ocean and of the global ice volumes leave a quantitative mark on the ¹⁸O/¹⁶O ratios of reef carbonates [21].

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