Comparison of $^{13}C/^{12}C$ Isotope Ratios from the Atmosphere Measured Using Two Different Analytical Techniques

P. Čech,[1] Z. Grolmusová,[1] P. Veis,[1,2] A. Šivo,[3] P. Povinec[3]

[1] Laboratory of Isotope Geology, State Geological Institute of Dionýz Štúr, Mlynská dolina 1, 817 04 Bratislava 11, Slovakia.

[2] Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics Comenius University, Mlynská dolina F2, 842 48 Bratislava, Slovakia.

[3] Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics Comenius University, Mlynská dolina F2, 842 48 Bratislava, Slovakia.

Abstract. In this study we compare two different IRMS approaches of $\delta^{13}C$ measurement in atmospheric CO_2 and investigate the differences in measurement results. Both approaches start with the same nine samples of $BaCO_3$, each prepared from an atmospheric CO_2 sample captured during one month. Then, in the first approach we used Delta V Advantage mass spectrometer with direct on-line preparation of CO_2, while in the second approach we used Finnigan MAT 250 mass spectrometer with off-line prepared CO_2. The two techniques yield very similar $\delta^{13}C$ values with inter-technique differences ranging from 1.11 ‰ (sample BA Feb 2012) to 0.28 ‰ (sample BA Mar 2012).

Introduction

The goal of this study is a comparison of two different analytical techniques used to determine the isotopic composition of carbon (Z = 6) in the atmosphere. Isotopes of carbon can reveal important data that can lead to more detailed knowledge of the sources of CO_2 and geochemical and biological processes that take place on the Earth. Carbon has two stable isotopes: ^{12}C (98.90 %, 12.000000 amu) and ^{13}C (1.1 %, 13.003355 amu), and one cosmogenic radioactive isotope ^{14}C ($14N + p = 14C + n$) that is also produced artificially during atmospheric nuclear bomb tests, as well as in the nuclear industry [*Faure and Mensing*, 2005]. Study of the content of ^{14}C in the atmosphere is important when deciphering the origin, sources and variations of CO_2. It is also important to monitor the ^{14}C atmospheric fluctuations caused by human-induced nuclear reactions. In order to study radioactive ^{14}C it is important to know isotopic composition of carbon that is expressed as $\delta^{13}C$ (standard PDB) where positive numbers mean that carbon contains more ^{13}C, and vice versa.

Analytical methods

Nine samples of CO_2 were extracted from the atmosphere in Bratislava in 2012, each during a period of one month (January–July and October–November). Atmospheric CO_2 was extracted from the atmosphere using absorption on NaOH in a special apparatus:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O\ .$$

After that followed the precipitation of BaCO3 from Na_2CO_3 with the help of ferrous sulphate hydrate and a coagulation agent:

$$Na_2CO_3 + BaCl_2 \rightarrow BaCO_3 + 2NaCl\ .$$

Consequently the precipitated $BaCO_3$ was purified, filtered and dried. These first steps were the same for both analytical methods, but then the first method (Delta method) used direct analytical setup with a Thermo Fisher Scientific Flash HT 2000 peripheral unit connected to Delta V Advantage IRMS spectrometer, while in the second method (MAT method) the $BaCO_3$ was digested in phosphoric acid and the resulting CO_2 was analyzed on dual inlet Finnigan MAT 250 IRMS spectrometer.

Delta V Advantage Flash HT 2000 Setup

Carbon isotopic analyses were performed in the continuous flow mode using Delta V Advantage mass spectrometer [*Thermo Fisher Scientific*, 2012] interfaced with the Flash HT 2000 elemental

analyzer [*Thermo Fisher Scientific*, 2012]. $BaCO_3$ powder samples (ca. 490 μg) were packed into tin capsules that were inserted into the elemental analyzer using a solid auto sampler flushed by helium. Flash HT 2000 allows combined C/N analyses using a combustion quartz reactor filled with chromium oxide, reduced copper and silver cobaltous–cobaltic oxide heated to the temperature of 1020 °C. With the help of oxygen gas pulse and chemical reagents serving as further oxygen donor, the sample was combusted and fully oxidised to CO_2. The post-reactor gas chromatography column heated to the temperature of 50°C provided the CO_2 gas separation. From Flash HT 2000 the sample gas was transferred trough the ConFlo IV unit which carried the sample by continuous flow to the mass spectrometer. The same method was used by *Grolmusová et al.* [2012], when comparing isotopic composition of carbon in cellulose with off-line prepared CO_2 gas prepared by the below mentioned method [*McCrea*, 1950].

The resulted $\delta^{13}C$ data were processed using Isodat 3.0 software. The stable isotope values were measured relative to international standards and reported using delta notation. Results are expressed in $\delta^{13}C$ parameter defined by the equation:

$$\delta^{13}C = \left(\frac{\left(^{13}C/^{12}C\right)_{sa} - \left(^{13}C/^{12}C\right)_{st}}{\left(^{13}C/^{12}C\right)_{st}} \right) \times 10^3 \text{ ‰} ,$$

where $(^{13}C/^{12}C)_{sa}$ is the ratio of the heavy to the lighter stable carbon isotope in the sample and $(^{13}C/^{12}C)_{st}$ in the standard.

Stable isotope values are expressed in units of permill (‰) and $\delta^{13}C$ is reported relative to the international standard VPDB (Vienna Pee Dee Belemnite) that is a marine carbonate. We used following standards: LSVEC ($\delta^{13}C_{VPDB}$ = –46.6 ‰), IAEA KST ($\delta^{13}C_{VPDB}$ = –5.7 ‰), IAEA C1 ($\delta^{13}C_{VPDB}$ = 2.4 ‰), IA-R022 ($\delta^{13}C_{VPDB}$ = –28.63 ‰) and our laboratory working standard Carrara marble ($\delta^{13}C_{VPDB}$ = 2.4 ‰).

Finnigan MAT 250 Setup

The $BaCO_3$ powder samples were put into a vacuum apparatus and dissolved in phosphoric acid as follows:

$$3BaCO_3 + 2H_3PO_4 \rightarrow Ba_3(PO_4)_2 + 3CO_2 + 3H_2O .$$

Water was removed from the gas mixture by freezing using a dry ice/methanol trap and the resulting CO_2 was extracted into a glass tube using liquid nitrogen bath. The produced CO_2 was then analyzed in the dual inlet Finnigan MAT 250 mass spectrometer. The dual inlet spectrometer is a high accuracy setup with a high static vacuum that enables direct comparative analysis to standardized CO_2 gas (with the known carbon composition) with accuracy of $\delta^{13}C$ measurements under 0.1 ‰. Sample is analyzed in three blocks of ten measurements comparing the measured composition with a known composition of CO_2 standard gas. Measurements are raw measurements without any fractionation correction of the measured data for the mineral content [*Carrothers*, 1988; *Böttcher*; 1996; *Swart,* 1991, *Friedman*, 1977].

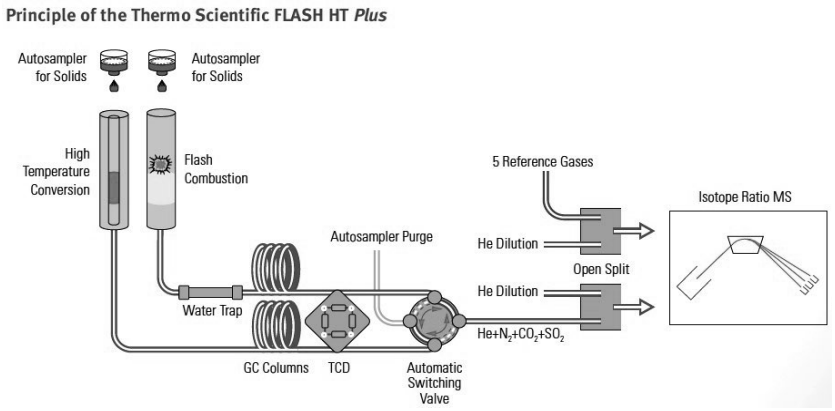

Figure 1. Schematic drawing of the Delta V Advantage Flash HT 2000 Setup [*Thermo Fisher Scientific,* 2012].

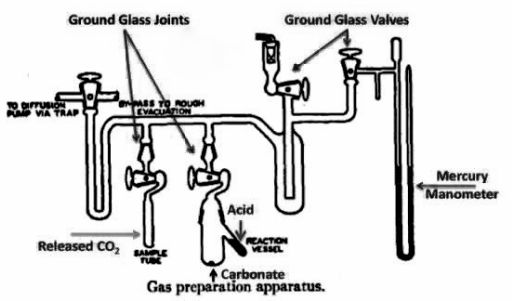

Figure 2. Principle of the vacuum apparatus for preparation of CO_2 from carbonates [*McCrea*, 1950].

Results

Delta measurements were calibrated against certified standards in the $\delta^{13}C$ value range from –46.6 ‰ to 2.4 ‰. Certified $\delta^{13}C$ values of standards correlated very well with measured values, with the regression coefficient of 0.99993 (Figure 3). The analytical error of this measurement was 0.5 ‰. On the contrary MAT measurements are of high precision with error up to 0.1 ‰ because during the dual inlet measurements the analyzed sample is immediately compared with the standard (the Carrara marble).

Nine samples of the atmospheric CO_2 were taken in Bratislava in 2012 and were analyzed. All of them were air samples processed in the first step to obtain carbon in the $BaCO_3$ powder form suitable for both analytical techniques. Subsequently, we analyzed all of them using two different analytical procedures described above. The $\delta^{13}C$ values both of Delta and MAT measurements generally show a similar trend. Delta measurements have bigger scatter due to bigger error (up to 2 ‰) of the measured ratios. 66 % of samples showed higher error than the analytical error of the method (0.5 ‰). We assume that the cause of the bigger scatter of individual measurements by Delta spectrometer are inhomogeneities of $BaCO_3$ powder subsampled for small-size samples (490 micrograms) for in-line combustion (Flash HT 2000).

Measurements of the two techniques yielded $\delta^{13}C$ values with differences ranging from 1.11 ‰ (BA Feb 2012) to 0.28 ‰ (BA Mar 2012). As the CO_2 gas for the MAT 250 preparation method comes from large amount (grams) of $BaCO_3$, the problem of homogeneity is not relevant for this method.

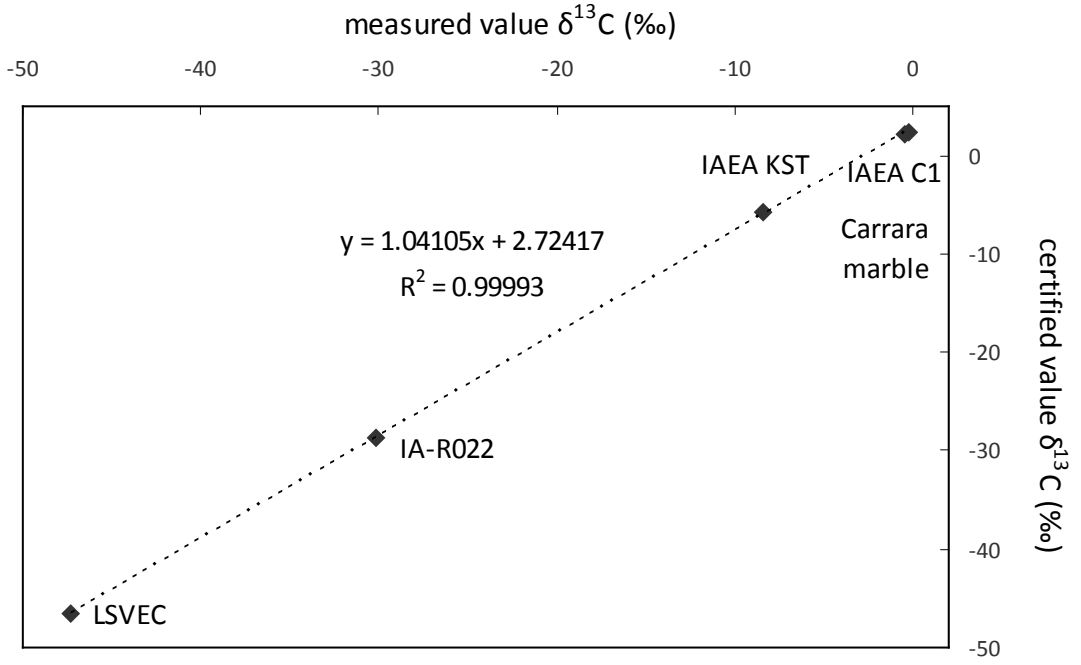

Figure 3. Calibration curve of measured standards using Delta method with the regression coefficient.

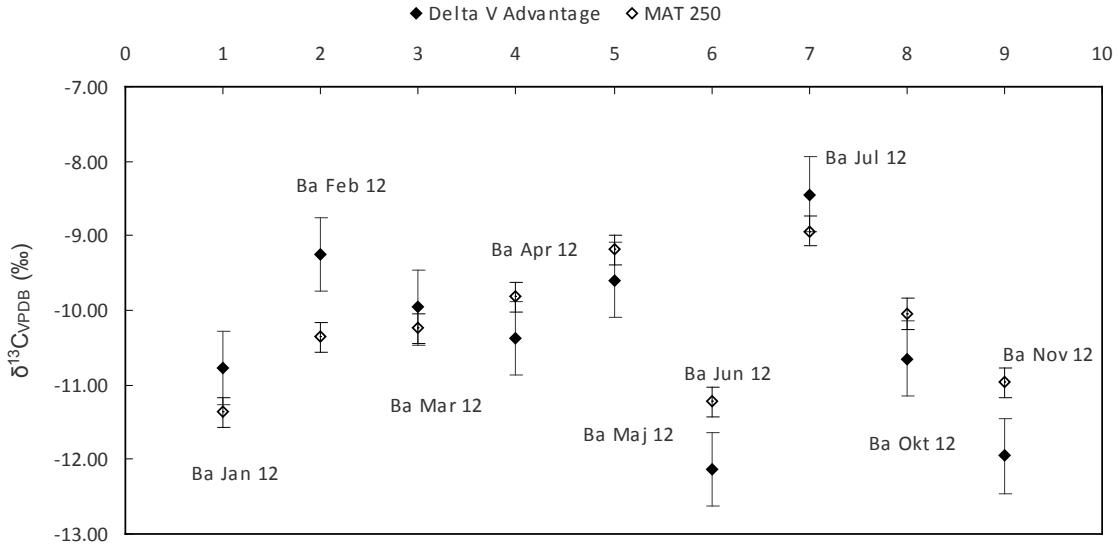

Figure 4. Comparison of the results from nine samples for both Delta and MAT 250 Setups with analytical errors.

Conclusion

^{14}C can give us crucial information on the origin and behavior of CO_2 in the nature. In order to study ^{14}C in the atmosphere it is very important to know the isotopic composition of carbon in the atmosphere, and in the samples for the calculation of usual corrections. The authors investigated and compared two analytical procedures that can be used to determine the isotopic composition of carbon. The two investigated analytical techniques yielded very similar $\delta^{13}C$ values with inter-technique differences ranging from 1.11 ‰ (BA Feb 2012) to 0.28 ‰ (BA Mar 2012). Considering the errors of the preparation techniques and IRMS measurements the Delta method showed more data scatter coming from analysis using the Flash HT 2000 combustion method and from possible inhomogeneities in 490 μg $BaCO_3$ powder samples (up to 0.5 ‰), while in the MAT method with a high accuracy dual inlet measurements, the error comes mainly from complicated chemical and vacuum preparation techniques preceding the IRMS analysis. The Delta method is more suitable for making of large number of isotope analyses due to its simplicity and low demands on the laboratory personnel and the analytical time.

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