# Isotope Composition of Pyrogenic Carbon of Various Origins

D. A. KALASHNIKOVA[1], A. N. MARKELOVA[2], V. N. MELKOV[2] and G. V. SIMONOVA[2,3]

[1]*Tomsk Polytechnic University, Tomsk, Russia*

[2]*Institute of Monitoring of Climatic and Ecological System, Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia*

E-mail: galina_simonova@inbox.ru

[3]*Tomsk State University, Tomsk, Russia*

## Abstract

In the work, the isotopic composition of pyrogenic carbon samples of various origins was studied. The dependence of this composition on the isotopic composition of the source carbon source was determined using isotope ratio a mass spectrometer DELTA V Advantage (Thermo Fisher Scientific/USA−Germany) in the combination with an elemental analyzer Flash-2000. The studies showed that pyrogenic carbon produced after burning kerosene and its derivatives ($\delta^{13}C = -30$ ‰) had the lightest isotope composition. The isotope composition of wood $\delta^{13}C = -27$ ‰, and coal has a heavier isotope composition ($\delta^{13}C = -24$ ‰). The carbon isotope composition of dust particles sampled from the snowpack in different locations in Tomsk showed deviations from the $\delta^{13}C = -28.8$ ‰ to $\delta^{13}C = -21.9$ ‰.

**Key words**: isotope composition of carbon, pyrogenic carbon, soot, black carbon (BC), isotope mass spectrometry, $^{14}C$, snowpack

### INTRODUCTION

Forest fires, auto transport, enterprises of industry and housing and communal services are the sources of emissions into the atmosphere of soot that is the product of incomplete combustion of hydrocarbon fuel and biomass. The main component of soot is pyrogenic or black carbon (BC). According to numerous studies precisely it has a significant impact on population health and climate; therefore, problems of monitoring and control of black carbon in the components in the environment components attract attention of ecologists and climatologists of the entire world [1]. One of these problems is the determination of the sources of BC, typical for this or that territory. We believe that for its solution one can use the connection between the isotopic composition of black carbon (BC) and the substance, the product of which it is.

Carbon is represented by fifteen isotopes. Two of them ($^{12}C$ and $^{13}C$) are stable, the others are radioactive. It is optimal to use stable isotope ratio and the content of BC in compared samples of long-lived radioactive isotope of carbon $^{14}C$ to indicate the origin of BC. The latter is often used to determine the formation time of substances containing carbon. By the activity of $^{14}C$ in BC samples, one can determine, whether it is the combustion product of fossil fuels.

The ratios of stable isotopes of organic substances carbon forming biofuels or objects of nature are different from each other, which can also be used as a label. In practice, there are significant difficulties for using isotope analysis of BC samples collected from atmosphere such as: achieving the required sample masses and separating BC from other pollutants. In this connection, the most convenient object for studies is the snow cover, where deposition and accumulation of BC occur.

In this work, the prospects assessment of applying the isotopic analysis of BC in the snowpack to establish the sources of its origin on the example of Tomsk city was performed.

## MATERIALS AND METHODS

To reveal the origin source of pyrogenic carbon the isotope composition of carbon in wood, peat, coal, kerosene, and then in their combustion products (soot) was originally determined experimentally. The carbon isotope composition of atmospheric suspended matters was determined in the snowpack. The investigation of the snowpack is a convenient and economic method, because snow has a high sorptive capacity. Snow survey was performed in February of 2016. The snow fence was performed in 17 points (Fig. 1). Six points are located outside of Tomsk and they are background once, the rest of them are located in the city, they are situated in areas with different degrees of anthropogenic load.

The snow intake was carried out by the method of the envelope according to the known technique [2]. Snow cores were selected by means of a plastic tube with a diameter of 10 cm and packed in hermetic polyethylene bags. Snow melting was occurred in laboratory setting at room temperature. The average depth of snow cover was 39 cm at the time of sampling. The average snow volume of mixed sample was 3.2 L of water for each sampling point. Melt water was filtered. The mass of dust − atmospheric suspensions deposited on the filter varied from 0.008−0.034 g (for background sites) up to 0.045−3.231 g (in the city).

The isolation of BC from the filtered atmospheric suspensions was carried out by the technique described in [3]. There are three types of carbon: inorganic carbon (*e. g.*, carbonates), organic carbon (*e. g.*, humic substances and plant material) and pyrogenic (black) carbon.

The removal of carbonates concluded in the treatment of samples by a solution of 3 M HCl. After this, the treatment with a mixture of HF (10 M)/HCl (1 M) was conducted to remove silicon compounds. Then, for the removal of organic substances and kerogen the samples were treated by an oxidative solution containing a solution of 0.1 M $K_2Cr_2O_7$ in 2 M $H_2SO_4$ at 55 °C during 60 h. Thereafter, the samples were washed with deionised water, centrifugated and dried. The resulting samples of BC of the mass of 500 μg were placed into tin capsules and burned in an oxidation-reduction reactor of an element analyzer.

The measurement of the isotope composition of atmospheric suspensions, as well as wood, peat, coal, kerosene and products of their combustion (soot) was conducted jointly with the determination of the percent content of carbon. The analysis was conducted on the equipment, consisting of a DELTA V Advantage isotope ratio mass spectrometer and Flash EA 2000 elemental analyzer (TomTsKP, SB RAS, Russia) at the Institute of Monitoring of Climatic and Ecological Systems, SB RAS (Tomsk, Russia). The isotopic composition $\delta^{13}C$ was expressed in per mille (thousandths of the deviation of the standard) according to the equation

$$\delta^{13}C\ (‰) = 1000[(R_{sam} - R_{st})/R_{st}]$$

where $R_{sam}$ is $^{13}C/^{12}C$ ratio in sample; $R_{st}$ is $^{13}C/^{12}C$ ratio in the standard, which is carbon of fossilized mollusc *Belemnitella americana* (PDB [4]).

The error of the analysis results of the isotopic composition of carbon did not exceed ±0.15 ‰. The radiocarbon analysis of coal, peat and wood was conducted by liquid scintillation method [5] using a Quantulus radiometer-spectrometer (TomTsPK, SB RAS).



Fig. 1. Places of sampling.

## RESULTS AND DISCUSSION

### Isotopic analysis

For the urban environment, the sources of BC are auto transport, industrial enterprises and houses with stove heating. Auto transport and enterprises are the sources of emissions of fossil fuel combustion products. It is known that its carbon isotope composition ($\delta^{13}C = -50... -20$ ‰) is significantly depleted in heavy isotopes compared with the composition of modern vegetation ($\delta^{13}C = -30...-10$ ‰) and $CO_2$ atmosphere ($\delta^{13}C = -8$ ‰). Mainly wood and less coal are used for furnace heating of houses. There are whole areas of such houses in Tomsk.

The isotopic composition of biofuels and modern biomass varies within wide limits and depends on the locus of the plants and their type. The isotopic composition of plants is lighter than the isotopic composition of atmospheric $CO_2$ consumed by them due to fractionation during photosynthesis.

Higher plants have three different mechanisms of photosynthesis (C3, C4, and CAM) and three types of plants, accordingly. Fixation of carbon for C3 plants occurs in the Calvin cycle. Such plants usually grow in areas of temperate climate. Their value of $\delta^{13}C$ varies from $-30$ to $-20$ ‰. Fixation of carbon for C4 plants occurs in the Hatch−Slack cycle. Plants belonging to this type of photosynthesis are common in tropical and subtropical areas. Their value of $\delta^{13}C$ varies from $-15$ to $-10$ ‰. CAM plants are often found in arid desert areas. Isotope compositions of C3 and C4 plants differ from each other significantly, therefore, it is possible to determine the type of plant and as a consequence the geographical position of the ignition source using the isotopic composition of the pyrogenic carbon, formed during plants combustion. For example, the main source of fires in tropical savannah is grasses biomass related to C4 plants [8]. In this case, the isotopic composition of BC $\delta^{13}C$ is about $-15$ ‰, while $\delta^{13}C$ is about $-27$ ‰ at burning wood of trees.

The measurements results of carbon isotopic composition for four types of wood, peat, coal, kerosene and their combustion products are given in Table 1.

The isotope composition of wood of various species of wood varies from $-27$ to $-24$ ‰ (see Table 1). For all samples of charcoal obtained from wood of these species, the isotope composition of carbon is eased. This can be explained by the kinetic effect [6].

At chemical reactions, molecules with light isotopes, as a rule, react with high rates than molecules with heavy isotopes during chemical reactions [7]. The average value of isotope composition of soot carbon is $\delta^{13}C = -26.87$ ‰ for four types of wood. The isotope analysis showed that carbon had the heaviest isotopic composition and kerosene − lightest. Soot samples corresponding to these substances showed the same picture.

Isotope analysis has shown that kerosene has the lightest isotope composition ($\delta^{13}C = -31.74$ ‰), and coal has the heaviest one ($\delta^{13}C= -24.05$ ‰). Soot samples corresponding to these substances have similar isotope compositions. It will be easy to identify the sources of pyrogenic carbon by its isotopic composition by comparing isotopic compositions of soot and raw materials if the pyrogenic carbon releases during combustion in the initial state without additional pollutants and retains its original form through the time.

Actually, pyrogenic carbon is ejected together with organic carbon (OC) and other suspended particles and gases, inorganic materials (met-

TABLE 1

Isotope composition $\delta^{13}C$ of wood, coal, peat, kerosene and their soot obtained after burning, ‰

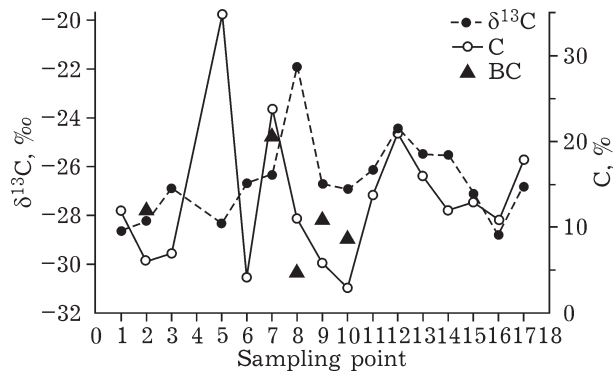| Samples | $\delta^{13}C$ isotope composition | | | | | | |
|---|---|---|---|---|---|---|---|
| | Pinus Sylvestris | Larix | Abies | Betula | Peat | Coal | Kerosene |
| Initial | −27.33±0.1 | −25.69±0.1 | −24.05±0.15 | −26.62±0.05 | −26.75±0.12 | −24.05±0.08 | −31.74±0.07 |
| Charcoal | −28.65±0.09 | −27.13±0.08 | −27.17±0.1 | −28.72±0.12 | − | − | − |
| Soot | −29.27±0.06 | −27.47±0.09 | −25.63±0.08 | −25.12±0.1 | −25.12±0.1 | −24.20±0.05 | −30.02±0.06 |

Fig. 2. $\delta^{13}$C isotope composition of atmospheric dust and soot deposited on the snowpack.

als and sulphates). Volatile organic compounds can condense on BC. The ratios of OC to BC can vary in a soot mixture. For example, the average OC/BC ratio among global sources of diesel exhaust is approximately 1 : 1. For biofuel burning, the ratio is approximately 4 : 1 and for biomass burning it is approximately 9 : 1 [9]. By the colour of soot, one can determine which fraction of carbon dominates. In our experiment, soot obtained when burning peat, had a yellow-brown colour. This evidences the predominance of organic carbon. Darker soot was obtained when burning kerosene.

The next step of our research was the determination of the isotope composition of air pollutants and soot particles deposited on the snow cover. The isotope composition of dust (Fig. 2) in different sampling points is distinct by 7 ‰. The percentage content of carbon ranges from 3 to 24 %. It means that the soot has many impurities.

Only five of seventeen samples have BC in an amount sufficient for detection. These samples were obtained at sites within the city, exposed to the maximum pollution. The BC isotope composition in samples Nos. 8 and 10 is $\delta^{13}$C = −30 ‰. These samples were selected near major highways with heavy traffic.

Soot samples from the car park, where drivers leave their cars working a long while winter to warm car engine, have $\delta^{13}$C = −29 ‰. The $\delta^{13}$C value of −24.7 ‰ was obtained for sample No. 7. It was selected in area with the stove heating houses. The BC isotope composition of the sample No. 7 corresponds to the isotope composition of coal.

The predominance of wood soot has been fixed in samples Nos. 2 and 9. The BC isotope composition $\delta^{13}$C of these samples has a value of −28 ‰.

*Radiocarbon test*

According to studies (see Table 1), the isotope compositions of Abies wood and coal are the same and their value is −24.05 ‰. However, the radiocarbon ages of these samples are different. The radiocarbon analysis of soot samples allows uniquely identifying the source of pyrogenic carbon. The content of $^{14}$C in coal soot sample is equal to zero, and the activity of the soot formed during the combustion of modern wood corresponds to the activity of modern $^{14}$C in $CO_2$ atmosphere. If the $^{14}$C activity is below current one, then the ignition source is peat.

**CONCLUSION**

The analysis of the isotopic composition of fossil fuel carbon, several types of wood, peat and their combustion products was carried out. It was found that the isotopic composition of soot and BC was somewhat lightweight, in comparison with the original material, which is due to the kinetic effect.

Joint measurements of $^{14}$C and $\delta^{13}$C allow identifying the origin of pyrogenic carbon. The measurement of the radiocarbon ($^{14}$C) content in soot is an important tool to assess the contribution of fossil pyrogenic carbon into the environment contamination.

The isotopic composition of BC contained in the snow cover allows detecting the sources of its origin. The snowpack reflects the contours of the aerogenic pollution by BC and allows judging about the dynamics of occurring emissions in the winter time. The isotopic analysis opens up new possibilities for monitoring and controlling the content of BC in the environment components, what is shown on the example of the snowpack.

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# Изотопный состав пирогенного углерода различного генеза

Д. А. КАЛАШНИКОВА[1], А. Н. МАРКЕЛОВА[2], В. Н. МЕЛКОВ[2], Г. В. СИМОНОВА[2,3]

[1]*Национальный исследовательский Томский политехнический университет, Томск, Россия*

[2]*Институт мониторинга климатических и экологических систем Сибирского отделения РАН, Томск, Россия*

[3]*Национальный исследовательский Томский государственный университет, Томск, Россия*

**Аннотация**

В работе исследован изотопный состав пирогенного углерода образцов различного генеза. Зависимость этого состава от изотопного состава исходного источника углерода определяли с помощью изотопного масс-спектрометра DELTA V Advantage (Thermo Fisher Scientific/США−Германия) в конфигурации с элементным анализатором Flash-2000. Исследования показали, что пирогенный углерод, образующийся после сжигания керосина и его производных ($\delta^{13}C = -30$ ‰), имеет самый легкий изотопный состав. Изотопный состав древесины $\delta^{13}C = -27$ ‰, а уголь имеет более тяжелый изотопный состав ($\delta^{13}C = -24$ ‰). Изотопный состав частиц пыли, отобранных из снежного покрова в различных местах Томске, характеризуется отклонениями от $\delta^{13}C = -28.8$ ‰ до $\delta^{13}C = -21.9$ ‰.

**Ключевые слова:** изотопный состав углерода, пирогенный углерод, сажа, черный углерод, изотопная масс-спектрометрия, $^{14}C$