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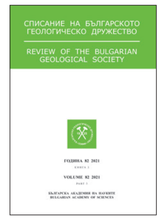

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On the possibility to use $\delta^{13}C$ speleothem records for determination of total freezing of the ground during glaciations

Върху възможността за използване на $\delta^{13}C$ записи в пещерни натеци за определяне на пълно замръзване на почвата по време на заледявания

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Abstract. In a $\delta^{13}C$ speleothem record from Duhlata cave, Sofia region, Bulgaria we found a positive value of $\delta^{13}C$. It is rather unusual and only way to explain it is that all carbon in the speleothem was supplied from the bedrock above the cave during the formation of the corresponding layer in the speleothem. Such situation can happen only during total freezing of the ground above the cave during glaciations. Only in such case both organic and air carbon dioxide cannot reach the cave.

Keywords: caves, paleoclimate, speleothem records.

Introduction

Carbon has two stable isotopes, ^{12}C and ^{13}C, and one radioactive isotope, ^{14}C. The stable carbon isotope ratio, $\delta^{13}C$, is measured against Vienna Pee Dee Belemnite (VPDB). The stable carbon isotopes are fractionated primarily by photosynthesis. The $^{13}C/^{12}C$ ratio is also an indicator of paleoclimate: a change in the ratio in the remains of plants indicates a change in the amount of photosynthetic activity, and thus in how favorable the environment was for the plants (Faure, 1987). During photosynthesis, organisms using the C3 pathway show different enrichments compared to those using the C4 pathway, allowing scientists not only to distinguish organic matter from abiotic carbon, but also what type of photosynthetic pathway the organic matter was using.

C3 plants constitute about 90% of all plants today and include algae and autotrophic bacteria and comprise the majority of cultivated plants, including wheat, rice, and nuts. C4 plants are adapted to hot, dry environments, and include the important human food crops of maize, millet, sorghum, and sugar cane, as well as tropical savannah grasses and sedges. There is a kinetic fractionation associated with carboxylation of ribulose bisphosphate that has been determined by several methods to be –29.4‰ in higher terrestrial plants. Bacterial carboxylation has different reaction mechanisms and a smaller fractionation of about –20‰. Thus for terrestrial plants a fractionation of about –34‰ is expected from the sum of the individual fractionations. The actual observed total fractionation is in the range of –20 to –30‰ (Faure, 1987). The disparity between the observed total fractionation and that expected from the sum of the steps presented something of a conundrum. This solution appears to be a model that assumes the amount of carbon isotope fractionation expressed in the tissues of plants depends on the ratio of the concentration of CO_2 inside plants to that in the external environment: the more photosynthesis depletes the CO_2 in the plant interior, the less the fractionation that occurs.

Some paleoenvironmental information can be obtained only by comparison of different speleothem records in the same sample. For example by comparison of $\delta^{13}C$ and luminescent records can be determined potential temperature dependence of $\delta^{13}C$ variations in a speleothem and the main source of CO_2 in the speleothem.

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Traditional explanation of δ13C variations in a speleothem by variations of the ratio between C3/C4 type plants growing over the cave can not explain observed temperature dependence of δ13C records (Shopov et al., 1994; Shopov, 2006) in some speleothems. The amplitude of the observed δ13C variations is bigger than such, which can be produced by C3/C4 type plants variations. Some variations of δ13C concentration in speleothems are much faster, than the possible variations of the ratio between C3/C4 type plants, which requires major climatic changes and time for forest growth. So it is more likely to be produced by variations of the other major sources of carbon in speleothems, such as the bedrock carbon fraction and soil carbon in many cases (Shopov, 2006).

Experimental techniques

δ13C and δ18O records (Fig. 1A) were measured in McMaster University Stable isotope laboratory on gas mass spectrometer, from CO_2 extracted from the relevant layer in the calcite speleothem along the same traverse in the same sample as the luminescent record.

Luminescent record (Fig. 1B) was obtained by microphotometry of a photometric quality photographic image of phosphorescence of a double side polished crossection of the sample along its growth axis, which was scanned on a high resolution scanning microdensitometer Joyce Loebl with 10 mμ step and 20 x 200 mμ window, allowing optical smoothing of the scan. Phosphorescence of the speleothem calcite was excited by impulse Xe-lamp. Such excitation produces luminescence of fulvic and humic acids incorporated in the relevant layers of calcite speleothems during their growth (Shopov et al., 1994, Shopov, 2006). Their concentration in each layer is proxy of the soil temperature during its formation, which is determined by solar insolation of the surface in the case of grass cover over the cave like the one over Duhlata cave.

Results and discussion

The aim of this work is to study the possibility to use δ13C speleothem records for determination of total freezing of the ground during glaciations. We studied the region near Bosnek on the south slope of Vitosha Mt., Bulgaria. Careful study of this speleothem shows that it grew continuously during the last 250 000 years (Stoykova et al., 2003). This is rather unusual for speleothems, because during full glaciations there is no water supply for speleothem growth. This suggests that Bosnek region was never completely glaciated during the last 250 000 years, thus allowing continuous water supply through the limestone bedrock over the cave.

We studied a calcite flowstone growing over the floor of Urinarnika hall of Duhlata cave. The sample is located approximately 50 m below the surface and 500 m far from the cave entrance. We measured a paleoluminescence record from this speleothem, with time step of 251 to 445 years (Fig. 1A) as established by Stoykova et al. (2003), who determined precisely the variations of the growth rate of this speleothem. This record has constant linear step of 0.0208 mm/px, but variable growth rate measured in mm/yr, which produce variable time step of the record. We measured also δ13C and δ18O records allong the same path in the same sample (Fig. 1A). δ18O record correlates with the paleoluminescence record suggesting positive correlation with the paleotemperature. It has deep minima during the studied glaciation producing positive value of δ13C (Fig. 1A). This sample was dated with 7 TIMS U/Th dates in 2 independent labs (Table 1) and one 14C date.

Studied speleothem exhibits negative correlation between δ13C (Fig. 1A) and paleotemperature as presented by the paleoliuminescence record from the same sample (Fig. 1B). It can be explained by following way. The main part of CO_2 in karst waters came from soils. There are two sources of CO_2 in the soils (Faure, 1987):

(1) respiratory CO_2, which is enriched by δ13C, and

(2) CO_2 formed by soil decomposition (which is depleted to δ13C).

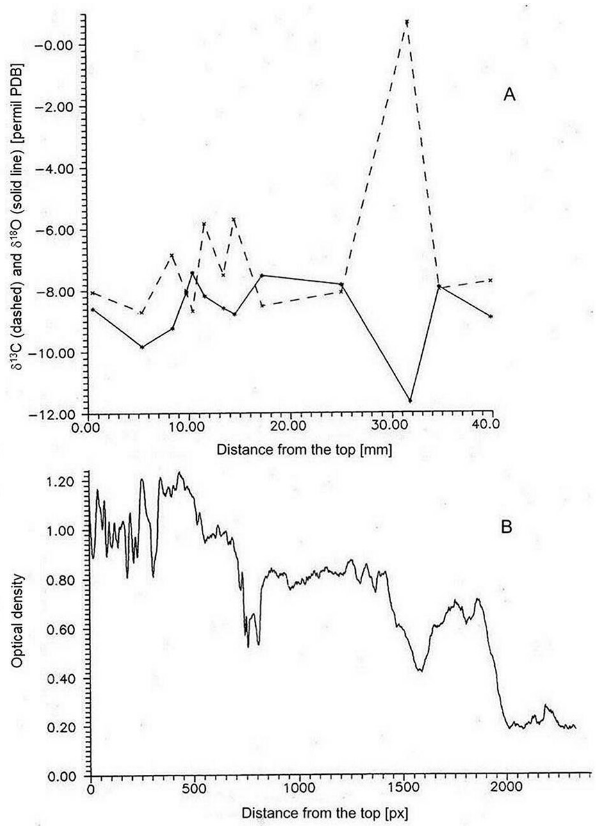

Fig. 1. Speleothem paleoclimatic records from Duhlata cave near Bosnek, Bulgaria**:** *A* (up), δ13C (dashed) and δ18O (solid line) records (in permil PDB) from a flowstone; *B* (down), paleoluminescence proxy record, with time step from 251 to 445 years/px (in dependance on the growth rate of the speleothem) along the same path in the same sample as the record on Fig. 1*A*. Linear step of this record is 48 px/mm (0.0208 mm/px).

Table 1. TIMS U/Th dates of the studied speleothem

Sample	Distance from the top [mm]	$^{230}Th/^{234}U$ [10^3 years]	2σ error [10^3 years]
I 9	12–13	89	+/– 4
Bu1	13–15	93	+/– 1
N I4	19–20.5	243	+24 –19
Bu2	18.5–22	258	+44 –30
O15	20.5–22.5	314	+32 –25
Bu3	25–28	323	+60 –39
S19	25.5–26.5	382	+58 –36
U21	27–28.5	infinite	N/A
Bu4	31–36	infinite	N/A

Note: dates Bu1–Bu4 are made by Derek Ford in McMaster University, while this in italic – by Joyce Lundberg, Carleton University, Canada

The rate of soil decomposition (producing CO_2 of type (2)) is exponentially dependent on temperature thus producing anticorrelation between $\delta^{13}C$ and paleotemperature. In average there is equal amount of CO_2 of types (1) and (2) in soils (Faure, 1987). But in some places type (2) can dominate if the region is covered only by grass and is heated directly by solar irradiation. Indeed the studied Bosnek region (hosting Duhlata cave, Bulgaria) exhibiting such negative correlation is covered by grass and soil temperature reaches 55 °C during summer times. Observed anticorrelation (Fig. 1) results from decomposition of the soil.

In the case of positive correlation (which is more usual) the main source of CO_2 during the formation of the speleothems is plants respiration above the cave.

In this $\delta^{13}C$ record in calcite cave flowstone from the Duhlata cave, Sofia region, we found a positive value of $\delta^{13}C$. This is a very unusual value of $\delta^{13}C$ in cave calcite. In fact, there is no other such case known in the specialized literature. The only way to explain this is that all the carbon in the runoff comes from the limestone bedrock above the cave during the formation of the corresponding layer in the calcite flowstone, because only the carbonate rocks have a positive values of $\delta^{13}C$ (Faure, 1987). Such situation can occur only during the complete freezing of the ground above the cave during a glaciation. In this case, the organogenic and airborne carbon dioxide cannot reach the cave and do not participate in the deposition of calcite in the cave deposits and all CO_2 in the speleothems came from the bedrock (which have positive $\delta^{13}C$ values, like the one observed in the studied speleothem – Fig. 1A).

To specify the age of this event, absolute dating of the studied sample is required. First Timothy Jull tried to date several calcite layers in this speleothem with AMS ^{14}C dating in the University of Arizona. Only one of the samples at 10 mm from the top of speleothem was within the datable range of the method. It produced age of 35 +/– 0.6 kyrs Cal BP.

We tried to date the corresponding calcite layer with the generally accepted method for absolute dating of such samples: U/Th dating (Table 1), but it turned out that the age of the layer in the sample, which was deposited during total freezing of the ground during glaciation is greater than the maximum dating limit with this method (400 000 years). This way so far it is impossible to determine the precise age of this most interesting event with the existing dating methods applicable for dating of cave calcite speleothems.

Conclusions

We demonstrated the possibility to use $\delta^{13}C$ speleothem records for determination of total freezing of the ground during glaciations. This way we found a glaciation in Sofia region, Bulgaria which produced total freezing of the ground in the region.

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