ISOTOPIC ANALYSES AND ORIGIN OF CO_2 IN SOME MORAVIAN CAVES

IZOTOPSKE ANALIZE IN IZVOR CO_2 V NEKTERIH MORAVSKIH JAMAH

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Jiři Robert Otava: Izotopske analize in izvor CO_2 v nekaterih moravskih jamah

Podani so rezultati preučevanja CO_2 v nekaterih breznih moravskega krasa, kjer so te količine izredno visoke. Izotopske analize so odkrile vsebnost ^{13}C, ki je običajen v kopenski flori. Z globino narašča CO_2, ustrezno pada količina O_2, medtem ko je količina N_2 stalna. Ta pojav je mogoče razložiti z izcedno vodo iz odlagališča odpadkov, ki je nad jamskim sistemom. Biogene reakcije (dezintegracija, razpadanje) sprožajo oksidacijo, za kar se porablja kisik v jami, sproščajo se hlapi, ki se dvigajo (CH_4), CO_2 pa ostaja v spodnjih delih jame.

Ključne besede: speleologija, jamska klima, plini v jamah, izotopske analize, onesnaževanje podzemlja, Češka republika, Moravski kras

Abstract UDC 551.44:551.584(437.1)

Jiři Robert Otava: Isotopic analyses and origin of CO_2 in some Moravian caves

The origin of a sudden contamination by carbon dioxide in several vertical systems of the Moravian Karst was studied. The isotopic analyses of carbon revealed ^{13}C contents common in terrestric flora. Increase of CO_2 content downwards was accompanied by reciprocal O_2 decrease, while the N_2 content remained constant. Such phenomena could be explained by in-washing of liquids from a large dump-hill, over 50m long, 10m wide and several meters high, situated above the system, into the cave. Oxidation caused by biogenic reactions as disintegration and/or mouldering resulted in the consumption of cave oxygen, production of volatiles which escaped upwards (as CH_4), while CO_2 stayed at the lower parts of the cave.

Key words: speleology, cave climate, gas in cave, isotopic analyses, pollution of underground, Czech Republic, Moravian Karst

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INTRODUCTION

Higher carbon dioxide contents in caves are quite well known and a relatively common phenomenon. The most important condition for CO_2 accumulation is a rather static room sealed in lower part e.g. by sump or by clay.

The origin of carbon dioxide could be natural or artifical. Natural carbon dioxide is known for instance from the north Moravian Zbrašov Cave where it is of juvenile origin (see the tab. No. 2). Artifical CO_2 accumulation could be caused by many sorts of human activities e.g. breathing, burning, pollutants, treatment with explosives and so on. Several years ago the speleological public was excited by fatal accident of Pavel Glozar in a cavity opened by the quarry of Mokra Cement Works in the southern part of the Moravian Karst. The abysmal cavity was surveyed too shortly after the explosions and the primary cause of death was the accumulation of higher carbon dioxide content at the bottom of the cavity.

CO_2 contamination has been proved in several vertical cave systems of the Moravian Karst in some cases with quite confused circumstances. That is why we paid attention to the problem.

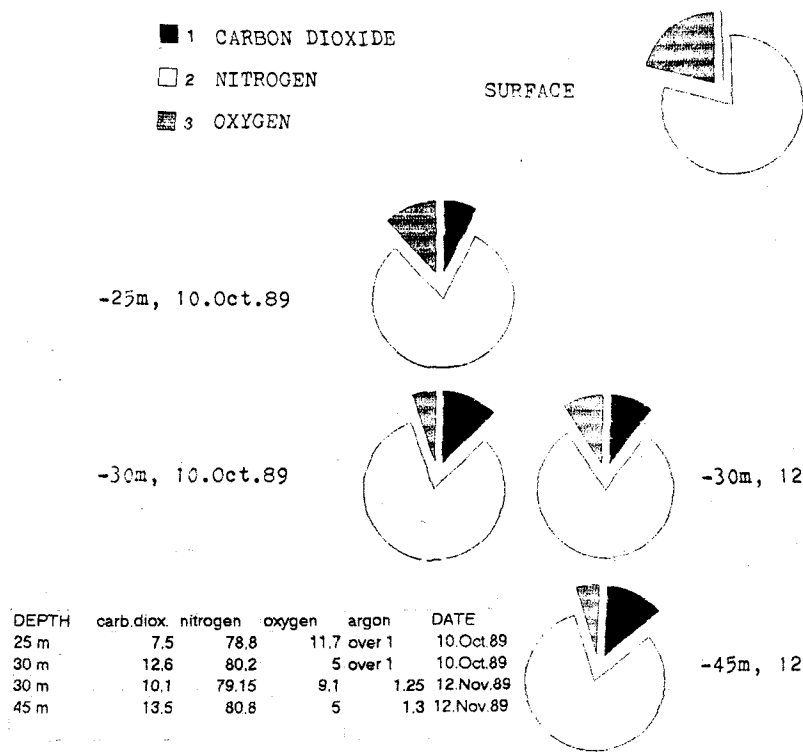
Lažánecký závrt No. 17, Vilémovice-Lažánky Plateau, the Moravian Karst

An abysmal cave system about 90m deep was discovered under the sinkhole at the Vilémovice-Lažánky Plateau of the Moravian Karst in 1988. No carbon dioxide content was observed during the discovering and surveying activities in 1988 and earlier. A group of cavers noticed higher carbon dioxide content at a depth of 25-30m in August 1989. The visitors quickly escaped upwards to the surface because of breath troubles and flame extinguishing. During cave-rescue team training actions (even with oxygen apparatus) several samples of the cave athmosphere were taken from depths of -25, -30 and -45m. The quantitative analyses revealed several interesting facts:

1/ Increase of carbon dioxide content in the deeper parts was always accompanied be reciprocal decresase of the oxygen content, while the content of nitrogen remained constant.

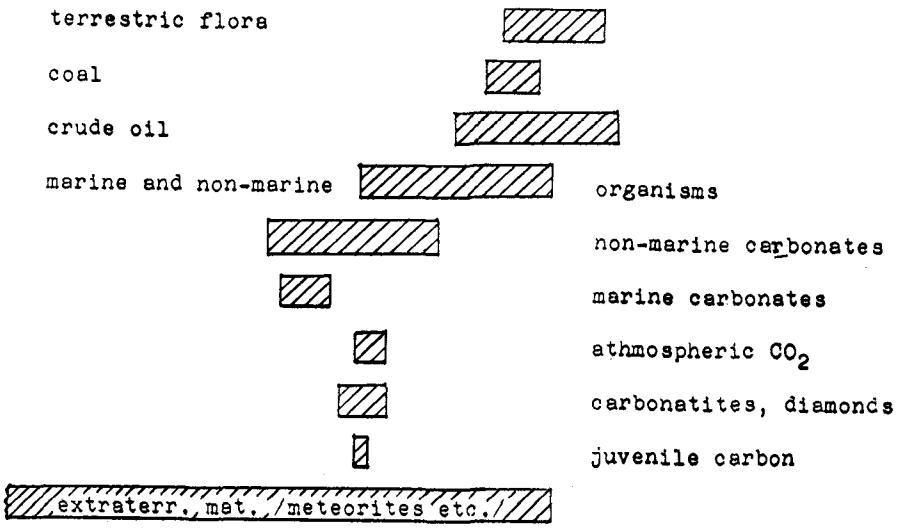
2/ Gradual decrease of carbon dioxide content and lowering of the CO_2 lake surface accompanied the decrease of ou ter temperatures.

However the origin of the gas remained unclear. It is known from the literature (e.g. Castany, 1963) that humic acids and other organic acids could



DEPTH	carb.diox.	nitrogen	oxygen	argon	DATE
25 m	7.5	78.8	11.7	over 1	10.Oct.89
30 m	12.6	80.2	5	over 1	10.Oct.89
30 m	10.1	79.15	9.1	1.25	12.Nov.89
45 m	13.5	80.8	5	1.3	12.Nov.89

Fig. 1 Ležánecký závrt N° 17 Cave. Comparison of the CO_2 content /1/, N_2 /2/ and O_2 /3/ contents at various depths and times. Anal. Z. Boháček, Czech geological survey, Brno.



N°	SITE	material	$\delta^{13}C$ value
1	Moravian Karst	devonian carbonates	0-5,5‰
2	Zbrašov Cave, c.Moravia	juvenile CO_2	-5‰
3	Sedma Cave M. Karst	CO_2	-21,0‰
4	Ležánecký z.17 Cave, MK	CO_2	-30,1‰

Anal. F. Buzek, Czech geological Survey, Prague.

Fig. 2 Variations of $\delta^{13}C$ values in various geological materials. After Hledíková, 1988, erranged.

Comparison with several values measured in the karst terrains of Moravia.

react with carbonates and release carbon dioxide. Other ways of CO_2 production are connected with breathing of plants and other biogenic and biochemical processes as mouldering, disintegration and fermentation. Rather of theoretical value were the chances of juvenile origin of the carbon dioxide, due to distinct N-S dislocation which strongly predisposed the cave system.

The variation of content of the ^{13}C stable isotope in various materials and environments inspired us to apply the isotopic analyse of the carbon stable isotops in solving the problem. The result confirmed the biogenic origin of CO_2 present in the cave (note Tab. No. 2).

The most probable way how to explain the contamination of the cave follows both from the isotope study and from the ratios of nitrogen, oxygen and carbon dioxide in various depths. We think, that the carbon dioxide did not replace the original cave-air, because the normal athmospheric ratio of O_2 : N_2 = approx. 1:4 changed to the ratio of 1:7at the depth of -25m and to the ratio of 1:16 at -30m (October 10th). Next month (November 12th) the O_2 : N_2 ratio was 1:9 in -30m and 1:16 in -45m. We have to suppose that the biogenic reactions consuming oxygen and producing carbon dioxide took part inside the cave. Disintegration seems to be the most relevant process in our case. It is defined as a stage in decomposition of vegetable and animal substances which takes place in the presence of oxygen and moisture. It may be regarded as a slow combustion of organic substance leaving no solid carbon compounds and producing only volatile substances, namely carbon dioxide and water. Mouldering is less suitable as it is characterized with inadequate air available for complete disintegration which, because it is incomplete, leaves small quantities of substances rich in carbon as residual. Fermentation needs only a small amount of oxygen and sometimes produces acids besides carbon dioxide.

The above described case is interesting not only from the scientific point of view, but for ecological purposes and for the safety of the cave visitors too. The deposition of dump-hills on the carbonate surface is dangerous not only for the ground water pollution, but also in special cases for CO_2 contamination of caves. It is further serious argument in favour of excluding dump-hills from the karst terrains or at least for arranging a waterproof deposition sealed e.g. by clay. The outwashing of liquids has to be blocked.

It is probably worthwhile to mention briefly the destiny of carbon dioxide contamination of the cave since the autumn 1989 sampling. During the check-descent at January 13th 1990 no carbon dioxide was noticed at the depth of -45m. In summer 1993 high concentrations of the gas were observed again at the depth of -25m.

The Sedma Cave and the Ve Ćlopech Cave, Babice Plateau, the Moravian Karst

The history of the abysmal Ve Ćlopech Cave includes repeated contami-

nation by up to 8,5% of carbon dioxide. The details are described by Havel (1991) and the origin of the gas is again ascribed to the biochemic reactions and suitable morphology of the cave.

The other cave at the Babice plateau, the abysmal system of Sedma was discovered in 1991 and it contained since the beginning about 3% of carbon dioxide (Šeda, 1992). One sample of the cave air from the depth of about 40m was analysed both for carbon dioxide content and for the stable isotops of carbon composition:

The CO_2 content was 2,05%, N_2=78,1 and O_2=17,73%. It is clear, again that a part of the cave oxygen was converted to carbon dioxide by biogenic reactions inside the cave. The content of $\delta^{13}C$ = -21‰ is somewhat different from the value measured carbon dioxide of the former site. The final conclusion on the difference between the two samples could not be done from the two analyses, nevertheless there are at least two ways how to explain it. The first one considers the fact that the differences in isotopic composition of carbon in plant tissues are influenced by different mechanisms of photosynthesis. The other explanation could follow from mixing of carbon dioxide of different origin (athmosphere, soil, organic remnants, see tab.) which is favoured by relatively low concentration of the gas.

The recent investigations of the regional contamination of the ground water under the Babice plateau proved that it is connected not only with dump-hills but even more probably with industrial waste including oil derivates etc. The carbon dioxide contents in the local cave systems could be probably influenced by such a source too.

CONCLUSIONS AND ACKNOWLEDGEMENTS

Analyses of carbon dioxide, nitrogen and oxygen volume contents (partial pressures) and analyses of the isotopic composition of carbon enabled us to decipher the origin of carbon dioxide in several caves. Nevertheless the complicated history of the reappearing and disappearing of the contamination remains confused and surely needs much more regular observation, sampling and analysing.

Finally it is a pleasure for me to thank my colleagues, cavers from Suchý žleb and Babice Clubs and from the Cave Rescue Group, for help with the taking of samples. I am obliged to my geochemist colleagues for much valuable advice and analysis.

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IZOTOPSKE ANALIZE IN IZVOR CO_2 V NEKATERIH MORAVSKIH JAMAH

Povzetek

Prispevek podaja rezultate preučevanja CO_2 v treh breznih moravskega krasa, kjer so te količine izredno visoke. Izotopske analize so odkrile vsebnost ^{13}C, ki je običajen v kopenski flori, kar tudi potrjuje biogeni nastanek CO_2. Z globino narašča CO_2, ustrezno pada količina O_2, medtem ko je količina N_2 stalna. Ob padanju zunanje temperature se tudi količine CO_2 zmanjšujejo. V drugem primeru je ta pojav mogoče razložiti z izcedno vodo iz odlagališča odpadkov, ki je nad jamskim sistemom. Biogene reakcije (dezintegracija, razpadanje) sprožajo oksidacijo, za kar se porablja kisik v jami, sproščajo hlapljevine, ki se dvigajo navzgor (CH_4), CO_2 pa ostaja v spodnjih delih jame.