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VARIATIONS OF ISOTOPIC COMPOSITION OF CARBON IN THE KARST ENVIRONMENT FROM SOUTHERN POLAND, PRESENT AND PAST

Anna Pazdur[1] • Tomasz Goslar[1] • Mirosława Pawlyta[1] • Helena Hercman[2] • Michał Gradziński[3]

ABSTRACT. We describe a comprehensive study of carbon isotopes in several karst springs and their environs in a contemporary karst environment in the region of the Cracow-Wieluń Upland and Western Tatra Mountains, Southern Poland. We collected samples of water, plants and carbonate deposited on aquatic plants, and obtained ^{13}C values and ^{14}C concentrations. We also investigated a group of the youngest calcium carbonates from caves where deposition is still being observed or ceased no more than a few hundred years ago. The determination of a ^{14}C dilution factor (q) in these carbonates allows us to determine the "true" radiocarbon ages of old speleothems from caves in the area under investigation and enables the use of old speleothems as suitable material for extending the ^{14}C calibration time scale, the "Absolute" age having been determined by U/Th or amino acid racemization (AAR) dating methods. Measurements of δ^{13}C and ^{14}C concentrations were made on dissolved inorganic carbon (DIC) extracted from water samples. Calculated values of q range from 0.55 to 0.68 and δ^{13}C values range from −10‰ to −13‰ versus VPDB with mean values equal to 0.65 and −12‰, respectively. Results indicate that the dissolution process of limestone bedrock is a closed system with the dominating contributor being biogenic carbon dioxide.

Isotopic composition of carbon in contemporary plants collected at the karstic springs at 3 localities is highly diverse, with different species distinctly varying in both q and δ^{13}C values. Extremely light values of ^{13}C (under −40‰), observed in Algae and *Hyloconium splendens*, are correlated with ^{14}C concentrations that are much lower than 100 pMC. Small systematic changes of isotopic composition were found in plants of the same species collected along streams at various distances from the spring. The youngest calcium carbonates from different caves show a relatively high scatter of both δ^{13}C values and ^{14}C concentration. The lower reservoir effect for ^{14}C is observed in samples with higher value of δ^{13}C, indicating equilibrium conditions in the sedimentation of carbonate. Pazdur et al. (1995b) presented ^{14}C dating results and paleoclimatic interpretation of 170 ^{14}C analyses of 89 speleothems from 41 caves obtained through 1994. Investigations continued until early 1997, during which time a speleothem, JWi2, was dated by ^{14}C, U/Th and AAR dating methods, and its stable isotope composition (δ^{13}C and δ^{18}O) analyzed in detail (reported here). Carbon isotope analyses indicate very large differences among results obtained by U/Th, AAR, and ^{14}C dating methods.

INTRODUCTION

It is widely recognized that isotopic studies of carbon and oxygen of freshwater calcite precipitates in the temperate zone have the potential to reconstruct certain parameters of environmental conditions that existed during sedimentation. The isotopic compositions of carbon, oxygen, uranium, and thorium in freshwater carbonates deposited in speleothems (Geyh and Hennig 1986; Geyh and Schleicher 1990; Gascoyne 1992; Harmon et al. 1978; Hennig et al. 1983, Hercman 1991; Pazdur et al. 1995b; Baker et al. 1993; Schwarcz 1986), calcareous tufas (Pazdur et al. 1988; Srdoč et al. 1983; Turi 1986; Usdowski et al. 1979) and lake sediments (Digerfeldt 1988; Goslar et al. 1995; Magny 1992, 1993; Pazdur et al. 1995a) enable reconstruction of the time scale of sedimentary processes and their climatic conditions. Measurement of radiocarbon in carbonates enables us to determine the ^{14}C age of sediments, that is, the time of deposition on the ^{14}C time scale, but with a substantial error that depends on the geochemical cycle of carbon in the investigated area (e.g., "reservoir effect"). The U/Th dating method allows calendar ages to be determined back to about 300 ka but with relatively low precision, particularly for younger sediments. Measured values of the stable isotopes of carbon and oxygen (δ^{13}C and δ^{18}O) in carbonate are indicative of temperature and humidity during the deposition processes.

The isotopic composition of calcareous precipitates under the same thermal conditions is characteristic of the sedimentary environment (caves, springs, lakes), geographical region (altitude, longi-

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[1] Institute of Physics, Silesian Technical University, Krzywoustego 2, PL-44-100 Gliwice, Poland
[2] Polish Academy of Science, Institute of Geological Sciences, Twarda 51/55, PL-00-818 Warszawa, Poland
[3] Jagiellonian University, Institute of Geological Sciences, Oleandry 2a, PL-30-063 Cracow, Poland

tude), type of bedrock in the karst area or carbonate in the soil and source of water infiltrating bedrock (meteoric water, groundwater from different depths), source of CO_2 dissolving the bedrock (atmospheric, biogenic, metamorphic) and type of vegetation covering the study area; incorporation of CO_2 from decomposing plants generally predominates.

Differing conditions during precipitation of freshwater carbonate determine the seasonal changes of carbon isotope composition. These are induced by changes in the isotopic composition of atmospheric CO_2, dissolved inorganic carbon (DIC) in water, and the photosynthetic pathways in plants (Willkom and Erlenkeuser 1973; Horvatinčić et al. 1989; Marcenko et al. 1989; Shore et al. 1995). To try to answer the many questions associated with studies of isotope composition in the environment, the research must continue over several years and isotopic analyses must be performed on all parts of the ecosystem that may be relevant to the geochemical cycle of carbon in the study area.

Simple geochemical models describing the cycle of carbon isotopes in the environment and the isotopic composition of DIC in water (Pearson and Hanshaw 1970; Vogel 1970) predict that the concentration of ^{13}C and ^{14}C isotopes is determined by carbon from different sources and that the ^{14}C concentration at the time of precipitation of carbonates is <100 pMC. This so-called "reservoir effect" is important in the ^{14}C dating of groundwater (Eichinger 1983; Mook 1976, 1980; Mook et al. 1974), speleothems (Geyh and Schleicher 1990; Schwarcz 1986), tufas (Pazdur 1988; Pazdur et al. 1988, Srdoč et al. 1983) and lake sediments (Olsson 1986; Pazdur et al. 1995a). Measurements of carbon isotope composition in different parts of the contemporary environment in the karst area enable one to infer the magnitude of the "reservoir correction" for ^{14}C ages of carbonates from the region of interest. This reservoir correction can then be used to determine the "true conventional radiocarbon age" of a single layer of calcium carbonate in a speleothem. The possibility of U/Th dating the same layer provides the relationship between conventional ^{14}C ages and calendar ages (U/Th method), that is, the possibility of extending the calibration of the ^{14}C time scale to around 50 ka BP (Goslar et al. 1997). A few uncertainties in extending back into the past glacial period are inherent in inferring the ^{14}C age of groundwater, thus of cave carbonates (Pearson 1992).

THE STUDY AREA

The main study area is the Cracow-Wieluń Upland of Southern Poland (Fig. 1; Pazdur et al. 1995b), the largest and best explored karst region in Poland. The Cracow-Wieluń Upland consists of Upper Jurassic limestones and covers about 2900 km^2. Stable isotope data for the bedrock ($\delta^{13}C$ and $\delta^{18}O$, see Table 1) are comparable with results for Jurassic limestones from other regions throughout the world (Keith and Weber 1964; Morse and Mackenzie 1990). Three sites chosen for the study of the contemporary environment were 1) a karst spring and its environs in Będkowska Valley, 2) karst Zygmunt Springs, and 3) several small karst springs and their environs in Zdów. Chochołowska Cave is located in the Western Tatra Mountains; the bedrocks of this karst area consist of Mesozoic limestones and dolomites.

MATERIALS AND METHODS

Contemporary Environment

The research included different parts of the local karst ecosystems of the sites of interest. A Pazdur, M F Pazdur and H Hercman collected water samples from karst springs from October 1991 to June 1993 (Table 2). M Gradziński collected samples from Chochołowska Cave. During 1992–1993, recent carbonates deposited on algae, mosses growing in karst springs (Table 3) and some water samples were collected. A Pazdur, M F Pazdur and H Hercman collected plant samples from Octo-

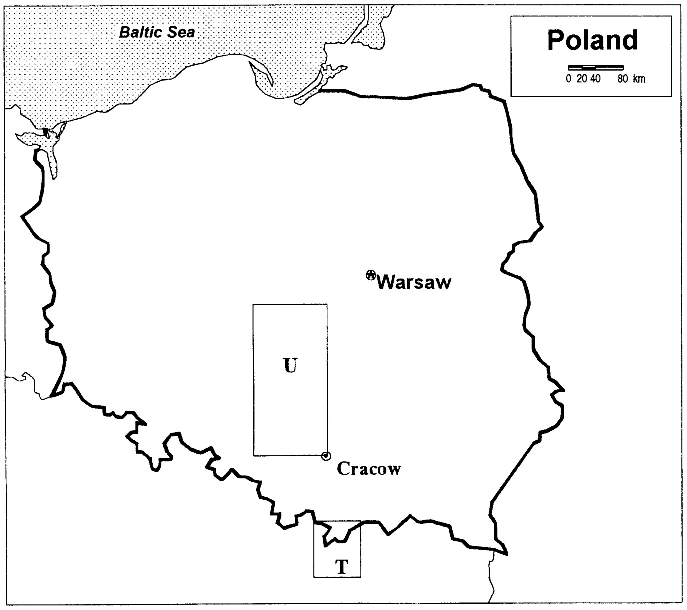


Figure 1 Map of Poland and investigated karst areas. U = Cracow-Wielún Upland, T = Tatra Mountains.

Table 1 $\delta^{13}C$ and $\delta^{18}O$ values in limestones

Sample	$\delta^{13}C$ (‰, VPDB)	$\delta^{18}O$ (‰, VSMOW)	Site
Cracow-Wieluń Upland, Cave			
JM0	+2.53	26.66	Mamutowa
JMd0	+1.16	26.09	Mydlnicka
JD0	+2.95	27.69	Dziewicza
JC0	+2.32	26.40	Ciemna
STG0	+4.24	28.95	Tomaszówki Górne
DB0/2	+3.25	29.22	Będkowska Valley
DB/4	+2.33	34.08	Będkowska Valley
DB0/8	3.33	30.85	Będkowska Valley
JZł0	–0.5	23.40	Złodziejska
"Cracow"	–2.3	26.00	Limestones near Cracow
Western Tatra Mountains, Cave			
JCh0/1	–1.4	23.6	Chochołowska
JCh0/2	–1.0	24.2	Chochołowska
JCh0/3	–4.5	24.0	Chochołowska

ber 1991 to June 1993 (Table 4). J Baryła, botanist at the Jagiellonian University, and T Goslar identified plants.

Most of the plant samples were collected in spring and early summer during the time of intensive growth. One sample series was collected in late autumn (October 1991 and December 1992) from the spring in the Będkowska Valley and along the stream course (Fig. 6). All plants except one moss sample (*Hyloconium splendens* and *Pleurozium schreberi*; Table 4) grew in an aquatic environment in springs with differing rates of water flow, the strongest flow being in the Zygmunt Springs, weaker in

Table 2 Isotopic composition of carbon in DIC of water samples from karst springs under different caves, Chochołowska Cave and atmospheric CO_2 from Dziewicza Cave

Lab nr Gd-	Sample name	Collection date	^{14}C (pMC)	$\delta^{13}C$ (‰, VPDB)	Site
4759	BWW1/91	91.10.01	61.9 ± 0.9	−12.03	Będkowska Valley (main outflow); Caves: Nad Źródłem, Na Tomaszówkach, Łabajowa, Kawiory
4886	BWW1/92	92.09.10	55.7 ± 0.7	−12.94	Będkowska Valley (main outflow); Caves: Nad Źródłem, Na Tomaszówkach, Łabajowa, Kawiory
4921	BWW2/92	92.12.03	58.4 ± 0.8	−11.63	Będkowska Valley (main outflow); Caves: Nad Źródłem, Na Tomaszówkach, Łabajowa, Kawiory
4889	DBW2/92	92.09.10	70.0 ± 1.4	−9.66	Będkowska Valley; Dziewicza Cave
4882	BDzW1/92	92.09.10	70.0 ± 1.2	−11.84	Będkowska Valley Cave; Dziewicza Cave
4836	WWW1/92	92.04.30	63.1 ± 0.8	−11.95	Kluczwody Valley (main outflow); Wierzchowska Cave
4866	WWW2/92	92.06.28	61.5 ± 1.0	−10.11	Kluczwody Valley (main outflow); Wierzchowska Cave
6670	DPnSSW1/92	92.05.27	50.6 ± 0.7	−12.32	Prądnik Valley, outflow below Stokowa Skała; Łykowiec Cave
4880	WSW1/92	92.06.01	67.4 ± 0.8	−13.16	Sąspowska Valley, spring in Sąspów
4847	JCHW1/92	92.04.01	82.2 ± 1.8	−4.90	Chochołowska Cave, outflow inside of cave
9010	ZZWW1/93	93.05.01	66.1 ± 0.8	−12.60	Zygmunt Springs; Wierna Cave
9030	ZDWW1/93	93.06.12	72.8 ± 0.9	−12.00	Springs in Zdów; no clear connection with caves
6577	JD-ATM1/91	91.10.11	112.6 ±1.5	−27.88	Dziewicza Cave; atmospheric CO_2

Table 3 $\delta^{13}C$ and $\delta^{18}O$ in carbonates deposited on aquatic plants growing in different springs

Sample name	$\delta^{13}C$ (‰, VPDB)	$\delta^{18}O$ (‰, VSMOW)	Plant	Site
ZDRW 4/93/C	−0.9	21.9	Alga	Spring in Zdów
ZDRW 7/93/C	−1.0	23.5	Alga	Spring in Zdów
ZRW 1/93A/C	0.0	22.7	Moss	Zygmunt Springs
ZRW 6/93/C	−2.5	23.0	Alga	Zygmunt Springs
ZRW 7/93B/C	−3.0	22.2	Alga	Zygmunt Springs
ZRW 14/93/C	−2.9	21.8	Alga	Zygmunt Springs
DBIM 8/92/C	−3.8	26.1	Moss	Będkowska Valley
DBIM 2/92/C	−0.9	25.7	Moss	Będkowska Valley

the spring in the Będkowska Valley, and very slow flow or almost stagnant water in Zdów. Two characteristic groups of aquatic plants were investigated: submerged and semi-submerged in water.

Caves

The youngest calcium carbonates (moonmilk, soda straw stalactite, and outer layers of stalagmite) from different caves in the Cracow-Wieluń Upland and Western Tatra Mountains (Table 5) were col-

Table 4 Isotopic composition of carbon (^{14}C and $\delta^{13}C$) in aquatic plants from the Karst area of the Cracow-Wieluń Upland

Collection date	Lab nr. Gd-	Sample	Plant	^{14}C (pMC)	$\delta^{13}C$ (‰, VPDB)
Będkowska Valley					
91.10.18	7131	DBRW1/91	*Campylium elodes*	55.5 ± 0.3	–48.70
91.10.18	6674	DBRW2/91	*Bryophyta*	64.8 ± 0.7	–42.15
92.12.03	6766	DBRW1/92	*Ranunculus scleratus* L.	61.3 ± 0.8	–39.20
92.12.03	6770	DBRW2/92	*Hyloconium splendens* L.	66.8 ± 0.7	–47.14
92.12.03	4945	DBRW3/92	*Mysotis palustris* Nath.	60.0 ± 0.9	[a]
92.12.03	6800	DBRW4/92	*Hyloconium splendens* Helw.	60.5 ± 0.8	[a]
92.12.03	4939	DBRW5/92	*Veronica beccabunga* L.	87.8 ± 0.9	–34.40
92.12.03	6789	DBRW6/92	*Hyloconium splendens* Helw.	69.4 ± 0.8	–43.49
92.12.03	4938	DBRW7/92	Algae	76.7 ± 1.2	–44.30
92.12.03	6794	DBRW8/92T	Graminae	100.2 ± 1.0	–35.55
92.12.03	4942	DBRW8/92M	*Hyloconium splendens* Helw.	57.0 ± 1.0	–47.00
93.05.20	6939	DBRW1/93	*Crateneuron filicinum* Helw.	67.3 ± 0.9	–43.10
93.05.20	9136	DBRW3/93	*Hyloconium splendens* L.	53.9 ± 1.3	–39.20
93.05.20	9119	DBRW6/93	*Ranunculus scleratus* L.	70.8 ± 2.6	–33.70
93.05.20	9137	DBRW7/93	*Ranunculus scleratus* L.	63.6 ± 1.4	–34.40
93.05.20	9140	DBRW9/93	*Hyloconium splendens* L.	63.2 ± 1.6	–39.30
93.05.20	6932	DBRW11/93	*Pleurozium schreberi* (and *Hyloconium splendens*)	118.6 ± 0.6	–26.70
Zygmunt Springs					
93.05.01	9118	ZRW4/93A	*Cardamine amara* L.	116.5 ± 2.5	–29.00
93.05.01	9135	ZRW9/93A	Algae	70.5 ± 1.5	–44.20
93.05.01	9125	ZRW11/93	*Mentha aquatica* L.	118.5 ± 1.8	–39.60
Springs in Zdów					
92.07.12	6682	ZDRW1/92	*Ranunculus scleratus* L.	73.8 ± 0.7	–33.95
92.07.12	6683	ZDRW2/93	*Hyloconium splendens* L.	78.9 ± 1.0	–33.24
93.05.01	9123	ZDRW2/93	*Brachythecium rivulsre* B.S.G.	86.6 ± 2.2	–36.80
93.05.01	9139	ZDRW6/93	*Brachythecium rivulsre* B.S.G.	62.4 ± 1.9	–35.20
93.05.01	9122	ZDRW9/93	*Cratoneuron filicinum* Helw.	72.8 ± 2.3	–33.40
93.05.01	9124	ZDRW11/93A	*Eur. rip.* (Helw.) Richs.[b]	62.6 ± 2.7	–43.80
93.06.12	6909	ZDRW13/93	(?)	93.5 ± 0.9	–25.00
93.06.12	6100	ZDRW14/93	*Mentha longifolia* (L.) Huds.	111.8 ± 1.4	–25.00

[a] Assumed value of $\delta^{13}C = -30.0$‰; [b] *Eurh. Rip.* = *Eurchynhium riparioides* (Helw.) Richs.

lected during cave explorations by M. Gradziński and A. Górny, from the Geological Museum, Academy of Mining and Metallurgy, Cracow.

A stalagmite (JWi2) approximately 30 cm long, found in Wierna Cave, underwent U/Th and AAR dating at the Institute of Geochemistry and Physics of Minerals, Ukrainian Academy of Sciences, Kiev (Pazdur et al. 1995c) and ^{14}C dating at the Gliwice Radiocarbon Laboratory.

METHODS

All samples were analyzed for ^{14}C content, using gas (CO_2) proportional counters at the Gliwice Radiocarbon Laboratory. Plant samples, prior to combustion, were treated with 2% HCl, washed and dried. Calcium carbonate samples were treated with HCl to create CO_2. The pretreatment of water samples was carried out prior to determination of ^{14}C and $\delta^{13}C$ concentration in DIC according to standard IAEA Vienna procedure. The precipitated $BaCO_3$ was reacted with HCl in a sealed reaction vessel connected to a vacuum line and the CO_2 collected.

Table 5. Isotopic composition of carbon (^{14}C and δ^{13}C) in the youngest calcium carbonate from different caves of the Cracow-Wieluń Upland and western Tatra Mountains (Chochołowska Cave)

Lab nr. Gd-	Sediment	Sample[a]	^{14}C (pMC)	δ^{13}C (‰, VPDB)	Cave
5912	Moonmilk (?)	JD2/2	80.5 ± 0.6	−2.48[b]	Dziewicza
7126	Moonmilk	JŁd1	53.1 ± 0.4	−5.12[b]	Ładna
7129	Moonmilk	JŁd2	47.0 ± 0.4	−8.24[b]	Ładna
4850	Soda straw stalactite	JM3	84.0 ± 1.5	−8.00[b]	Mamutowa
7105	Moonmilk	JM4	37.4 ± 0.5	−5.43[b]	Mamutowa
7026	Moonmilk (flowstone)	JSA1/1	47.1 ± 0.5	−6.00[b]	Szeroki Awen
3549	Moonmilk (?)	Schr.Ic37/1	83.6 ± 0.6	−2.67	Schron IIC37
7027	Moonmilk (flowstone)	JSnM1/1	82.6 ± 0.7	−2.15	Schron Nad Młynami
6668	Moonmilk (flowstone)	SWJ1	84.2 ± 1.0	(b)	Schronisko w Wąwozie Jamki
5920	Outer layer of stalagmite	JT1/1	73.5 ± 0.5	−3.67[b]	Towarna
5921	Outer layer of stalagmite	JT1/2	87.9 ± 0.5	(b)	Towarna
5926	Outer layer of stalagmite	JT1/3	88.1 ± 0.5	(b)	Towarna
3562	Moonmilk (flowstone)	JZg1	44.7 ± 0.8	−1.34[b]	Zegar
7154	Moonmilk	JZg2	44.5 ± 0.4	−6.14[b]	Zegar
7128	Moonmilk	JzK1	48.0 ± 0.4	−0.01[b]	z Kominem
7125	Furry moonmilk	JZł1	60.5 ± 0.4	−0.58[b]	Złodziejska
	Furry moonmilk	JZł2	—	−2.3	Złodziejska
4837	Moonmilk (?)	JCh-MW-1/92	54.9 ± 1.0	(b)	Chochołowska
4846	Moonmilk (?)	JCh-MW-2/92	58.7 ± 1.5	−0.7	Chochołowska
Kiev	Felt moonmilk	JCh-MW-1/93/C	78.9 ± 0.9	−0.1	Chochołowska
		JCh-MW-1/93/ORG	—	−30.4	Chochołowska
Kiev	Furry moonmilk (outer part)	JCh-MW-2/93/C	78.3 ± 0.7	0.5	Chochołowska
Kiev		JCh-MW-2/93/ORG	83.2 ± 0.6	−29.4	Chochołowska
Kiev	Furry moonmilk (inner part)	JCh-MW-3/93/C	70.0 ± 0.8	1.7	Chochołowska
Kiev		JCh-MW-3/93/ORG	72.9 ± 0.6	−29.7	Chochołowska

[a] C = carbonate fractions of sample; ORG = organic fractions

[b] = assumed values of δ^{13}C in samples to correct ^{14}C (pMC) values: −2‰ for SWJ1, −3.5‰ for JT1/2 and JT1/3, −1‰ for JChMW2/92.

Results of the ^{14}C measurements are presented in the tables and figures as percent of ^{14}C concentration in an undisturbed atmosphere (pMC; Stuiver and Polach 1977). The international ^{14}C dating standard, HOxII, was used as the modern reference material. The δ^{13}C measurements were carried out at the Mass Spectrometry Laboratory in Lublin UMCS University and at the Institute of Geochemistry and Physics of Minerals, Ukrainian Academy of Science, Kiev.

RESULTS AND DISCUSSION

DIC in Water

Table 2 and Figures 2 and 3 show the ^{14}C content and δ^{13}C of DIC in karst spring waters from the Cracow-Wieluń Upland and Chochołowska Cave. The carbon isotope composition of DIC from Będkowska Valley, Zygmunt Springs and springs in Zdów ranges from 55.7 ± 0.7 pMC to 72.8 ± 0.9 pMC for ^{14}C concentration and from −12.94‰ to −9.66‰ for δ^{13}C. The weighted means are 61.8 ± 2.1 pMC and −11.8 ± 1.0‰ (Table 6). These results agree with the model of dissolution of limestone with zero pMC for the ^{14}C concentration and close to zero δ^{13}C from H_2CO_3 derived from microbial degradation of plant detritus in topsoils (A = 110–120 pMC and δ^{13}C = −25‰) and the subsequent

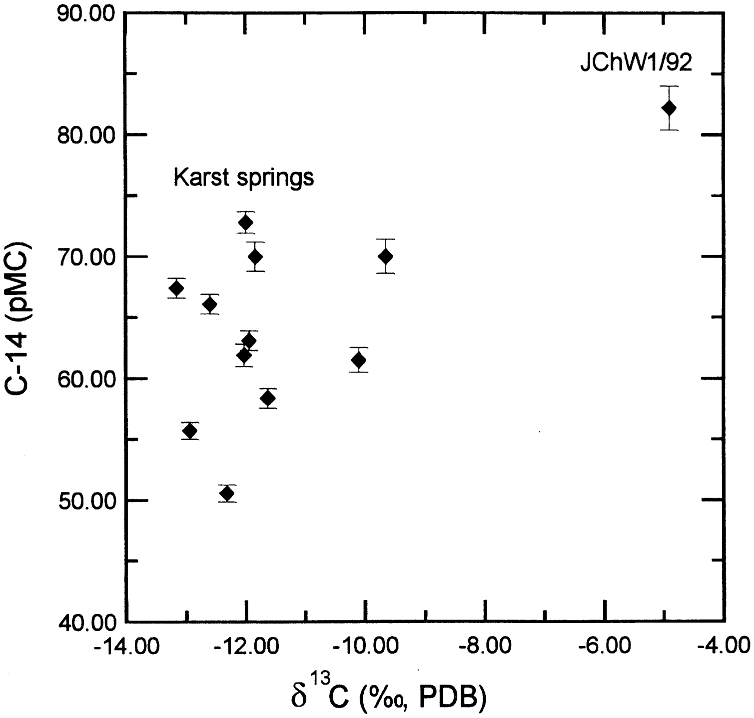


Figure 2 Results of ^{14}C and $\delta^{13}C$ measurements in DIC of waters from different karst springs and from Chochołowska Cave

Table 6 Weighted means of ^{14}C and $\delta^{13}C$ in waters, carbonates and different groups of plants

Sample	$<^{14}C>^a$ (pMC)	Nr of samples	$<\delta^{13}C>$ (‰,VPDB)	No. of samples
Waters	61.8 ± 2.10	11	−11.8 ± 1.0	11
Carbonates on plants	62.6 ± 8.5	3	−2.37 ± 2.2	10
Graminae and others	107.4 ± 4.4	4	−32.3 ± 5.7	4
Other plants	71.2 ± 4.0	7	−34.1 ± 2.5	7
Hyloconium	64.7 ± 1.7	11	−40.5 ± 5.2	11
Algae	74.3 ± 3.0	2	−44.3 ± 0.1	2

[a]< > = weighted means

process of exchange between liquid and gaseous phases (Mook et al. 1974; Mook 1976). Similar results of ^{14}C and $\delta^{13}C$ measurements in DIC in water were obtained by Marcenko et al. (1989) in waters from the karst region in northwest Yugoslavia.

^{14}C and $\delta^{13}C$ values are slightly higher in samples BDzW1/92 taken from stagnant water in Dziewicza Cave and in sample ZdWW1/93 taken from low water flow in Zdów (Table 2). Relatively high values of ^{14}C and $\delta^{13}C$ are observed in DIC from Chochołowska Cave; the water sample was collected as drops falling from the cave ceiling during a 2-week period; exchange of carbon between liquid phase and atmospheric CO_2 cannot be excluded in this sample. There is no significant corre-

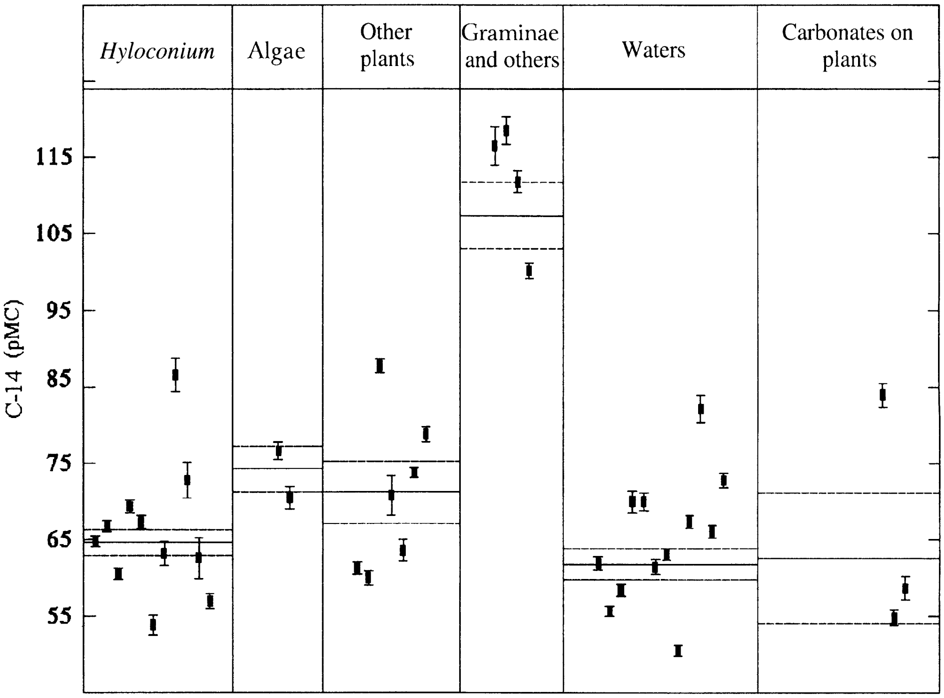


Figure 3 ^{14}C in different groups of aquatic plants. Straight lines indicate weighted means of ^{14}C. Dashed lines indicate ranges of one standard error.

lation between ^{14}C and $\delta^{13}C$ (Fig. 2) in water from Cracow-Wieluń Upland. One sample of atmospheric CO_2 was collected by absorption of CO_2 in a saturated NaOH solution at Dziewicza Cave. A ^{14}C concentration of 112.6 ± 1.5 pMC was measured (Table 2, sample JD-ATM 1/91).

Carbonates on Plants

Some algae and mosses growing in springs were heavily encrusted with calcium carbonate. These carbonate samples were usually too small for ^{14}C measurements; therefore we found only $\delta^{13}C$ and $\delta^{18}O$ values (Table 3; Figs. 3–4). The mean ^{14}C for 3 samples is 62.6 ± 8.5 pMC, which is the same as the mean ^{14}C in DIC of water (61.8 ± 2.1 pMC). The $\delta^{13}C$ values in all samples are relatively lower, compared to values of $\delta^{13}C$ observed in limestones (Table 1), and $\delta^{18}O$ values in these samples are much lower than similar values in bedrock. These results indicate that carbonate samples are indeed calcium encrustations on plants and not the grains of detrital carbonates.

^{14}C and $\delta^{13}C$ in Plants

The results of measurements of ^{14}C concentration and $\delta^{13}C$ values are listed in Table 4 and presented in Figures 3–5. Plants are grouped by species and photosynthetic pathways. In aquatic plants, such as submerged *Hyloconium* and Algae species and the group named "other plants", which contains partly submerged and semi-submerged plants (*Campylium elodes, Crateneuron falicinum, Mysotis palustris, Ranunculus scleratus, Veronica beccabunga,* etc.; Table 4), the concentration of ^{14}C is much lower than 100 pMC. We also found values of $\delta^{13}C$. The mean ^{14}C and $\delta^{13}C$ values are: 64.7 ± 1.7 pMC and –40.5 ± 5.2‰ in *Hyloconium,* 74.3 ± 3.0 pMC and –44.3 ± 0.1‰ in Algae, and 71.2 ± 4.0 pMC and –34.1 ± 2.5‰ in the group "other plants" (Table 6). Similarly, Marcenko et al. (1989)

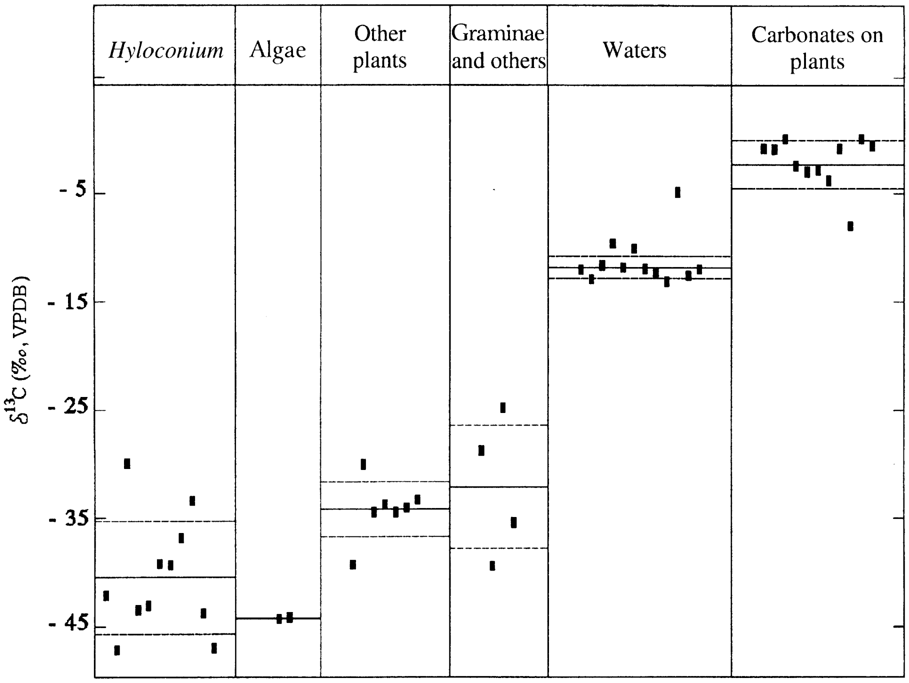


Figure 4 $\delta^{13}C$ values in different groups of aquatic plants. Straight lines indicate weighted means of $\delta^{13}C$. Dashed lines indicate ranges of one standard error.

found low ^{14}C concentrations and $\delta^{13}C$ values were observed for aquatic plants that photosynthesize carbon from freshwater DIC and atmospheric CO_2.

The group "Graminae and others" in Figures 3 and 4 contains plants terrestrial mosses as well as partly and semi-submerged plants (Graminae, *Cardamine amara).* The mean values of ^{14}C concentration and $\delta^{13}C$ for these plants are higher than for the plants from the groups discussed above (107.4 ± 4.4 pMC and −32.3 ± 5.7‰; Table 6). In all groups of plants there is no clear correlation between concentration of ^{14}C and $\delta^{13}C$ value (Fig. 5). Figure 6 shows ^{14}C and $\delta^{13}C$ in different species of plants along the stream course in the Będkowska Valley. ^{14}C pMC and $\delta^{13}C$ values are weakly correlated with distance from point of water discharge.

The Youngest Calcium Carbonate from Caves

Many samples of calcium carbonate in the group of the youngest sediments, taken from different caves, have been identified by M Gradziński as "moonmilk" (Table 5). They were deposited on the walls or found on the floor of caves in the form of flowstones. Moonmilk is white, amorphous crystal, mainly calcite or aragonite. It is suggested that it is of bacterial origin. The crystals usually display needle, branched or helicoidal forms and can be found in 2 shapes, as "furry" and "felt" moonmilk. One sample found was "soda-straw" stalactite, which is a fundamental form of stalactite. It is a single sheath of crystal enclosing a feedwater canal. Growth occurs at the tip, and the c-axis is oriented down the form (Ford and Williams 1994; Ford and Cullingford 1976). Other samples listed in Table 5 are the outermost layers of speleothems. Samples from Chochołowska Cave, where sedimentation is still occurring, were identified as furry moonmilk and felt moonmilk, deposited in the presence of unidentified species of microorganics which grew in the cave (Gradziński et al. 1997). For these sam-

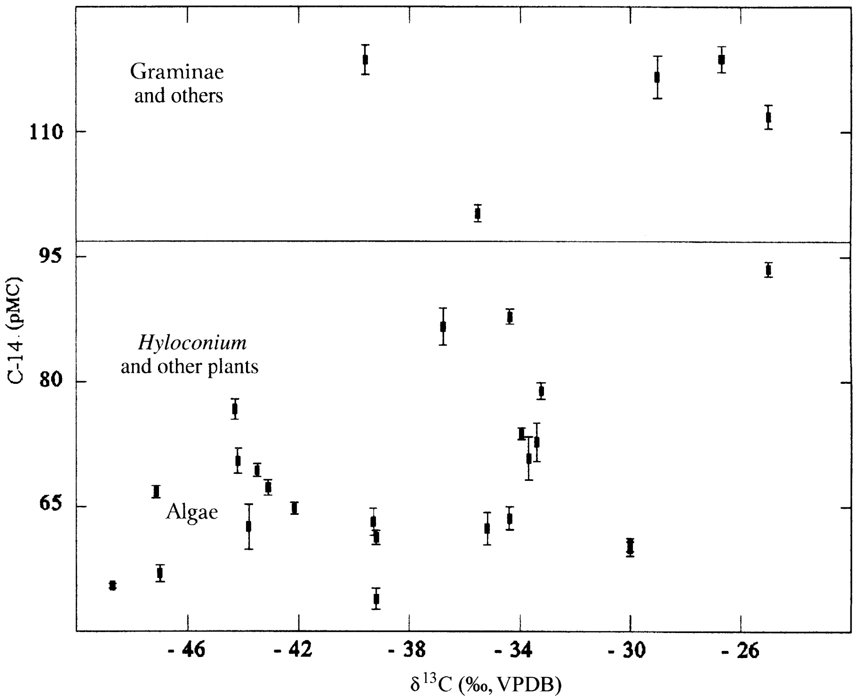


Figure 5 ^{14}C and $\delta^{13}C$ values in different groups of aquatic plants

ples, ^{14}C concentrations and $\delta^{13}C$ values in both carbonate and organic fractions were measured. On the basis of sedimentological observations (soft, porous and white calcium carbonate), other samples belong to the group of youngest sediments.

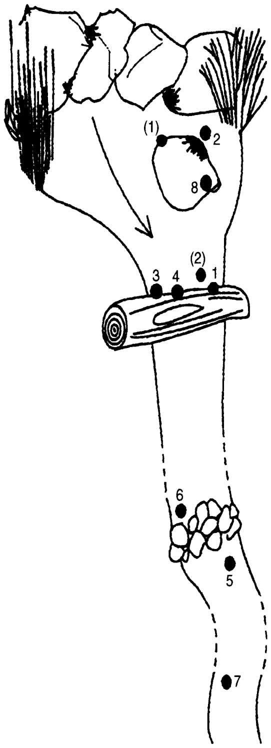
If we assume the model of the sedimentation of calcium carbonate in caves, with carbon sources from limestone and biogenic CO_2, the ^{14}C concentration in contemporary carbonates should be ca. 85 pMC (Geyh and Schleicher 1990; Schwarcz 1986), that is, an apparent age of 1350 yr. Observed values of ^{14}C concentration are much lower than 85 pMC in a group of 10 samples (Table 5), lower than 50% in 6 samples and slightly higher than 50% in 4 samples. Therefore, samples JŁd1, JŁd2, JM4, JSA1/1, JZg1, JZg2, JZK1 and JZł1 are much "older" than other samples from Cracow-Wieluń Upland (Table 5). The conventional ^{14}C age of the "youngest" sample in this group (JZł1) is ca. 4000 BP and the age of the "oldest" sample (JM4) is ca. 7900 BP. The ^{14}C concentration in the second group of samples from Cracow-Wieluń Upland caves ranged from ca. 73 (JT1/1 sample) to ca. 88 pMC (JT1/2 and JT1/3 samples); apparent ages of these samples are 2470 and 1020 BP.

Low ^{14}C concentrations occur in 2 samples from Chochołowska Cave (Table 5): JChMW 1/92 (ca. 55pMC) and JChMW 2/92 (ca. 58.7 pMC), whereas the samples of felt and furry moonmilk from the same cave have much higher ^{14}C concentrations. In both carbonate and organic fractions of furry moonmilk and in carbonate of felt moonmilk, ^{14}C concentration ranges from ca. 70 to ca. 83 pMC. Notable is the correctly higher value of ^{14}C in the outer part, and the lower value in the inner part of the furry moonmilk sample (Table 5).

The $\delta^{13}C$ values are relatively high and scattered, with the lightest being −8.24‰ and the heaviest ca. 0‰. The higher values of $\delta^{13}C$ indicate precipitation of carbonate from DIC in equilibrium with atmospheric CO_2 (Mook 1976). A correlation between ^{14}C concentration and $\delta^{13}C$ values is not

Będkowska Valley

Series: DBRW ()/91 collected in October 1991
DBRW /92 collected in December 1992



Distance	Sample	Plant	^{14}C (pMC)	$\delta^{13}C$ (‰)
ca. 1 m	(1)/91	Moss	55.0 ± 0.3	−48.70
	2/92	Moss	66.8 ± 0.7	−47.14
	8/92	Moss	57.0 ± 1.0	—
	8/92T	Grass	100.2 ± 1.0	−35.55
ca. 6 m	(2)/91	Moss	64.8 ± 0.7	−42.15
	4/92	Moss	60.5 ± 0.8	—
	1/92	*Ranunculus*	61.3 ± 0.8	−39.20
	3/92	*Mysotis*	60.0 ± 0.9	—
ca. 20 m	6/92	Moss	69.4 ± 0.8	−43.49
	5/92	*Veronica*	87.8 ± 0.9	−34.40
ca. 50 m	7/92	Alga	76.7 ± 1.2	−44.30

Figure 6 Changes of ^{14}C and $\delta^{13}C$ values in aquatic plants along the stream course in Będkowska Valley

observed (Fig. 7). It should be noted that "bomb" ^{14}C may affect the calibration of contemporaneously deposited (zero-age) ^{14}C levels. Moonmilk and soda-straw stalactite might contain post-1950 carbon. This could be confirmed by tritium measurements on the water presumed to be currently depositing $CaCO_3$. These investigations have not been made.

The Oldest Speleothems

Detailed studies of isotopic changes recorded in selected speleothems is an effective tool for reconstructing subtle climate changes in the moderate zone (Gascoyne 1992; Harmon et al. 1978). Eighty-9 speleothems from 41 caves in the Cracow-Wieluń Upland were investigated before 1994 and 170 ^{14}C dates obtained (Pazdur et al. 1995b); 45 of these samples yielded infinite dates. One of the speleothems, JWi2, was dated by the U/Th and amino acid racemization (AAR) methods at the Institute of Geochemistry and Physics of Minerals of the Ukrainian Academy of Sciences in Kiev. AAR results were based on experimentally determined relationships between stable and unstable amino acids, Thr/Leu and Thr/Glu (Julg et al. 1987; McCoy 1987). Pazdur et al. (1995b) measured stable isotopes ($\delta^{13}C$ and $\delta^{18}O$) along the growth line and observed a strong correlation between $\delta^{13}C$ and $\delta^{18}O$. Table 7 shows ^{14}C dates on several samples of JWi2 speleothem recently made in the Gliwice Radiocarbon Laboratory.

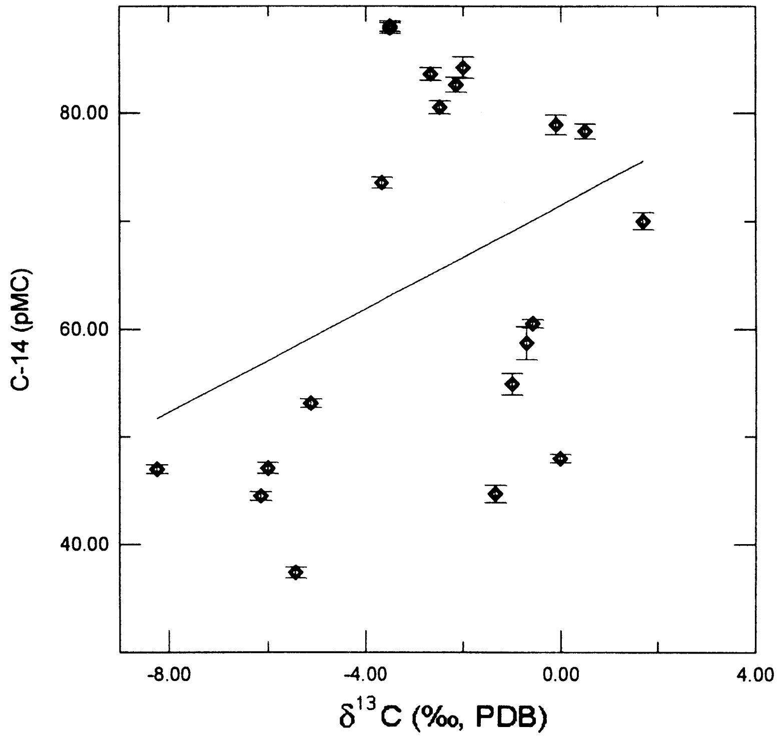


Figure 7 ^{14}C and δ^{13}C values in the youngest calcium carbonate (moonmilks, soda straw stalactite, outer layers of speleothems) from different caves. Straight line is linear approximation of results by the least squares method.

Table 7 ^{14}C dating results for speleothem JWi2

Lab no. Gd-	Distance (cm)	Age (ka BP)	δ^{13}C (‰, VPDB)
6736	0.5 ± 0.5	25.7 ± 0.2	−9.29
7871	8.2 ± 4.8	47.2 +4.3 / −2.8	−8.50
7873		>45.9	−9.30
10558	16.0 ± 3.0	>46.7	−8.50
10573	20.5 ± 1.0	40.2 +2.6 / −2.0	−7.80
7874	25.5 ± 3.4	>46.9	−9.06
7870	32.5 ± 3.5	41.2 +3.1 / −2.3	−9.10
10560(?)	36.5 ± 0.5	34.1 +2.3 / −1.9	−9.80
6735	37.0 ± 0.2	23.7 ± 0.2	−10.15

The cone-shaped stalagmite JWi2, 35 cm high, was examined and sedimentological analysis revealed it to be composed of 3 parts. The lower part contains many detrital components (i.e., quartz grains, Fe and Al oxides and hydroxides, and small bones), indicating that the crystallization of this part of the stalagmite occurred in wet conditions. The central part consists of a number of large calcite crystals with some brown laminae resulting from clastic or organic impurities. Competitive growth of crystals is visible and inclusions are abundant, characteristics that indicate the stalagmite grew in favorable conditions. Its upper part contains smaller and irregularly shaped calcite crystals with numerous brown laminae, indicating that the upper part of the stalagmite grew in unstable conditions.

The first ^{14}C measurements of speleothem JWi2 were to determine the time of its initiation and the end of calcium carbonate sedimentation (Pazdur et al. 1995b). The ^{14}C age (25,730 ± 200 BP) obtained from the bottom of the speleothem (the beginning of the sedimentation) was much younger than the U/Th and AAR ages (Table 8). The ^{14}C date on the outer layer at the top of the speleothem (23,700 ± 200 BP) is much older, by about 4 ka, than U/Th and AAR ages. Dates on several layers between the bottom and top of speleothem JWi2 indicated much older ^{14}C ages, both in comparison to the earlier ^{14}C dates and the U/Th and AAR dates. The first ^{14}C dates received from the top and bottom of the speleothem are probably too young because of contamination of speleothem outer layers by younger carbon (Srdoč et al. 1986); they are excluded from discussion and presentation in Figure 8.

Table 8 Results of U/Th and AAR dating and calculated ^{14}C ages of speleothem JWi2

Distance (cm)	Method	AAR or U/Th (ka)	^{14}C age (ka BP)
0.5 ± 0.5	U/Th	28.4 ± 1.1	49.5 ± 4.1
0.5 ± 0.5	U/Th	29.0 ± 1.0	49.5 ± 4.1
0.5 ± 0.5	AAR	33.7 ± 2.2	49.5 ± 4.1
2.0 ± 0.5	AAR	31.0 ± 1.8	49.0 ± 4.1
3.4 ± 0.4	U/Th	27.0 ± 1.1	48.5 ± 4.2
11.5 ± 1.5	U/Th	25.6 ± 1.0	45.5 ± 4.5
20.3 ± 1.7	AAR	28.6 ± 1.0	42.2 ± 5.2
21.3 ± 0.7	AAR	28.6 ± 1.0	41.9 ± 5.3
21.3 ± 0.7	AAR	25.5 ± 0.8	41.9 ± 5.3
20.9 ± 0.4	U/Th	22.9 ± 0.9	42.0 ± 5.2
23.7 ± 0.3	U/Th	24.2 ± 1.0	41.0 ± 5.5
25.6 ± 0.7	U/Th	24.2 ± 1.0	40.3 ± 5.7
25.6 ± 0.7	AAR	23.0 ± 0.8	40.3 ± 5.7
35.7 ± 0.5	U/Th	20.2 ± 0.8	36.6 ± 6.9
36.0 ± 0.5	AAR	18.0 ± 0.7	36.4 ± 6.9
36.0 ± 0.5	U/Th	18.9 ± 0.8	36.4 ± 6.9
36.0 ± 0.5	U/Th	19.5 ± 0.8	36.4 ± 6.9
36.5 ± 0.5	U/Th	19.5 ± 0.8	23.7 ± 0.5

Dating results are presented in Figure 8. It is worth noting that the least-squares lines fitted to ^{14}C data and AAR results, as a function of the sample distance from the bottom of speleothem, are parallel (see line equations in Fig. 8). On the basis of the linear relation between measured ^{14}C conventional ages (excluding the first 2 values) and distance, the ^{14}C conventional ages were calculated for all layers dated by AAR and U/Th methods. These results are shown in Table 8 and Figure 9.

If we assume that AAR ages obtained from the organic fractions of the samples are "true, calendar ages" of dated layers, the reservoir effect can be estimated as apparent age (T_{app}) of calcium carbonate sample dated by ^{14}C (Pazdur 1988). Apparent ages of dated samples as differences between conventional ^{14}C ages and AAR ages are 15.9 ka at the bottom (x=0) and 16.3 ka at the top (x=35 cm) of the speleothem. The dilution factors (q) calculated on the basis of relation

$$T_{app} = -8033 \ln q \tag{1}$$

are q = 0.14 at the bottom and q = 0.13 at the top, in other words the same along the whole growth line. Similarly, T_{app} and q values estimated on the basis of comparing ^{14}C conventional ages and U/Th ages

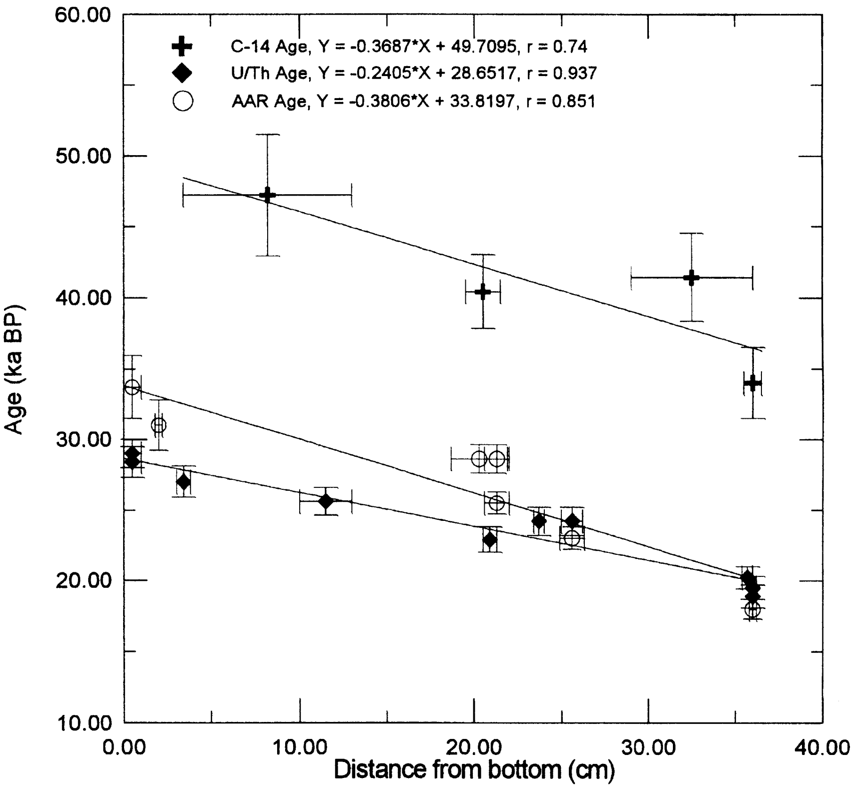


Figure 8 Results of ^{14}C, U/Th, and AAR dating of speleothem JWi2. Samples were taken from different distances from the bottom. Straight lines are linear approximations of results by the least squares method (note the equation lines).

are: 21.1 ka and 0.07 for x = 0 and 16.5 ka and 0.13 for x = 35 cm. The estimated values of apparent ages are extremely high and dilution factors extremely low. In the above estimations, changes of ^{14}C concentration in the past are neglected.

The relation between ^{14}C and U/Th ages (Fig. 9) is the reverse of that reported by Goslar et al. (forthcoming) for the long series of ^{14}C and U/Th dates in the interval 20–60 ka, obtained for speleothems from other caves in Europe. In relation to U/Th ages, the ^{14}C dates are younger by ca. 5 ka for 20 ka U/Th age and ca. 15 ka for 60 ka U/Th age with a plateau in the range 30–50 ka of U/Th ages.

In the light of these observations, comparison of the results of ^{14}C and U/Th and AAR dating for speleothem JWi2 requires additional explanation. The observed low value of the dilution factor indicates a significant contribution of old ^{14}C-free carbon in the calcium carbonate of the speleothem. The source of old carbon may have been old bedrocks if the speleothem was subject to diagenesis or redeposition, or both processes. Another possible cause for the incorporation of old carbon is the presence of ^{14}C-free metamorphic CO_2 during dissolution of limestone. This process should be excluded as the only cause of the sedimentation of calcium carbonate of speleothem JWi2, with low values of $\delta^{13}C$, which change from ca. –7 to ca. –11‰ in different layers.

Measurements of carbon isotope composition in the youngest (contemporary) calcium carbonate from caves, in DIC of water, and in aquatic plants are background for measurements of radiocarbon

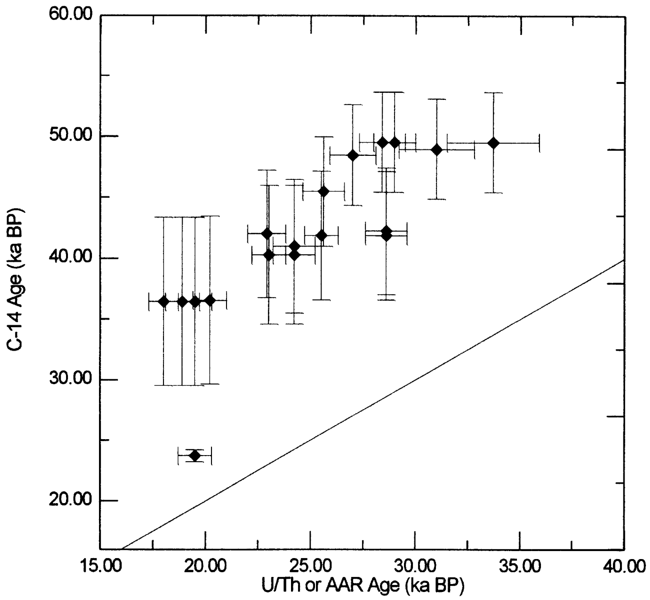


Figure 9 Comparison of calculated ^{14}C and U/Th and AAR ages. The conventional ^{14}C ages were calculated using the relation between measured ^{14}C ages and distance of the dated samples from the bottom of the speleothem. Straight line is described by equation Y=X.

content in the speleothem from the Wierna cave (stalagmite JWi2). The highest observed value of apparent age of the contemporary calcium carbonate is 7.89 ka (Table 5) from moonmilk sample JM4 with 37.4 pMC of ^{14}C content. The results of ^{14}C and $\delta^{13}C$ in DIC of water (Table 2) indicate a closed system of the carbon cycle in the study area.

We assume that, in the karst area, processes of the bedrock dissolution and precipitation of $CaCO_3$ occurred in the presence of the biogenic CO_2 and strong kinetic isotope effect. Suppose that, as a result, $CaCO_3$ with ca. 37 pMC of ^{14}C and $\delta^{13}C$ of ca. –9.5‰ (i.e., 37% of –25‰ in biogenic CO_2) was formed. The second step of the geochemical process was dissolution of deposited calcium carbonate in the presence of old metamorphic CO_2 with $\delta^{13}C$ ca. –8‰ and the same dissolution factor for ^{14}C isotope, q ca. 0.37. Successive precipitation of $CaCO_3$ from that solution would result in calcium carbonate with a dissolution factor ca. 0.14 and almost the same value of $\delta^{13}C$.

The above simple considerations give a ^{14}C isotope content consistent with the estimated value of the dilution factor for speleothem JWi2, obtained on the basis of the comparison of ^{14}C and AAR ages. The estimated $\delta^{13}C$ value is consistent with measured values of different layers (Pazdur et al. 1995b).

CONCLUSION

Measurements of carbon isotope values in the contemporary karst environment of Southern Poland proved that the karst area of Cracow-Wieluń Upland establishes a closed geochemical system for carbon. The $\delta^{13}C$ values in most species of aquatic plants reflect C_3 photosynthetic carbon pathways. The reservoir effect determined for recent calcium carbonate from caves may help in estimating the apparent ages of speleothems dated by the ^{14}C method.

The determination of a ^{14}C dilution factor in carbonaceous deposits is necessary to study speleothems as a suitable material for extending the ^{14}C calibration time scale. The possible use of old speleothems requires both the absolute age and the "true" ^{14}C age of the sample. But, in turn, the "true" ^{14}C age of the speleothems is possible only if the dilution factor is known and must be determined independently, in this case by using the measurements of contemporary carbonates.

Observed results of ^{14}C, AAR and U/Th datings for speleothem JWi2 indicate the possibility of errors in the application of dates from speleothems in order to calibrate the ^{14}C time scale and the need to select speleothems to solve the problem. If our considerations are correct, we may assume that on the Cracow-Wieluń Upland, in the period of 20–30 ka BP (AAR or U/Th time scale), geophysical processes resulted in the evolution of metamorphic CO_2.

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