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COMPARISON OF U-SERIES AND RADIOCARBON DATES OF SPELEOTHEMS

Tomasz Goslar[1] • Helena Hercman[2] • Anna Pazdur[1]

ABSTRACT. The paper presents a comparison of U-series and radiocarbon dates of speleothems collected in several caves in central and southern Europe and southeast Africa. Despite a large spread of dates, mainly due to contamination with younger carbon, the group of corresponding ^{14}C and $^{230}Th/U$ ages of speleothem samples seems to be coherent with the previous suggestion of large deviation between the ^{14}C and the absolute time scale between 35 and 45 ka BP. This agrees with the result of frequency analysis of published ^{14}C and $^{230}Th/U$ ages of speleothem.

INTRODUCTION

Calibration of the radiocarbon time scale has been a subject of research for more than 40 years. Recently, the ^{14}C calibration has been extended far beyond the beginning of Holocene, due to the data from corals (Bard et al. 1998), and from annually laminated oceanic and lacustrine sediments (Hughen et al. 1998; Goslar et al. 1995; Kitagawa and van der Plicht 1998). These data indicate deviation between the ^{14}C and the absolute time scale increasing from 1000 to >3000 years between 11 and 24 ka BP.

The ^{14}C calibration is important not only to geochronologists, but it is also related to reconstruction of past geomagnetic fields (e.g. Mazaud et al. 1991; Laj et al. 1996; Bard 1998), solar activity (e.g. Stuiver and Braziunas 1993; Bard 1998), and water circulation in the ocean (e.g. Goslar et al. 1995, 1999; Hughen et al. 1998; Bard 1998). The latter factor appeared best reflected in the Younger Dryas period, and with much lower confidence at the beginning of Bølling interstadial slightly after 15,000 cal BP (Stuiver et al. 1998). For the earlier time, large variations of atmospheric ^{14}C concentration are expected because of the changes of the geomagnetic field (Laj et al. 1996; Tric et al. 1992), connected even with disappearance of deviation between ^{14}C and absolute time scales before 40 ka BP (Mazaud et al. 1991). For the period before 23 ka BP, however, only two ^{14}C dates of corals are available (Bard et al. 1998). They are supplemented by some dates from laminated sediments of Lake Suigetsu, Japan, but the relevant part of the Suigetsu varve chronology is based on only a single core, and therefore, needs to be confirmed (Kitagawa and van der Plicht 1998).

Another material enabling comparison of ^{14}C and calendar time scales is speleothem. Using ^{14}C and $^{230}Th/U$ ages of stalagmite from the Cango Cave in South Africa, Vogel (1983) found large deviations between both time scales in the late Pleistocene, well before the coral dates became available. In recent years, the set of the Cango dates has been enlarged and completed with dates from Lynd's Cave, Tasmania (Vogel and Kronfeld 1997). A similar study was published by Holmgren et al. (1994), who dated stalagmites from the Lobatse II Cave, Botswana. Our goal was to enlarge significantly the set of speleothem dates, by ^{14}C and $^{230}Th/U$ dating of stalagmites from many sites in Europe and Africa.

MATERIAL AND METHODS

In our research, we used speleothem samples collected in several caves (Table 1, Figure 1) in central and southern Europe, and in southeast Africa. For dating, we selected the largest stalagmites accessible. From each specimen, a slice about 1 cm thick was cut out along the stalagmite axis, and for dating we used sections with large and clear carbonate crystals, transparent on the slices. These 0.3–3 cm

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[1] Radiocarbon Laboratory, Institute of Physics, Silesian University of Technology, ul. Krzywoustego 2, 44-100 Gliwice, Poland. Email: goslar@zeus.polsl.gliwice.pl.

[2] Institute of Geological Sciences, Polish Academy of Sciences, ul. Twarda 51/55, 00-818 Warsaw, Poland

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Table 1 ^{14}C and ^{230}Th/U dates for speleothems obtained in the present work. Column 4 gives the ^{14}C age, corrected for the reservoir effect. Columns 6–8 list the activity ratios of the U and Th isotopes, and column 9 the U-series ages adjusted for initial Th.

Sample	Distance from base (mm)	^{14}C age (BP)	Corrected ^{14}C age (BP)	U (ppm)	$\frac{^{234}U}{^{238}U}$	$\frac{^{230}Th}{^{232}Th}$	$\frac{^{230}Th}{^{234}U}$	^{230}Th/U age (cal BP)	Corrected ^{230}Th/U age (cal BP)
Sudety Mountains (Poland)									
Niedźwiedzia 1A	0–18	10,540 ± 80	8840 ± 1000	0.144 ± 0.004	1.20 ± 0.03	18.5	0.112 ± 0.003	12,810 ± 370	11,830 ± 700
Niedźwiedzia 1B	18–60	10,410 ± 70	8710 ± 1000						
Niedźwiedzia 1C	86–122	9090 ± 80	7390 ± 1000	0.064 ± 0.002	1.53 ± 0.07	6.5	0.103 ± 0.002	11,750 ± 280	9160 ± 1500
Niedźwiedzia 1D	182–217	5380 ± 80	3680 ± 1000	0.060 ± 0.002	1.89 ± 0.09	4.6	0.103 ± 0.002	11,660 ± 240	7970 ± 1500
Niedźwiedzia 5/2		4480 ± 60	2780 ± 1000	0.016 ± 0.002	4.75 ± 0.52	7	0.171 ± 0.035	19,930 ± 4450	16,000 ± 5500
Moravian Karst (Czech Republic)									
Holstynska 2/1				0.34 ± 0.01	1.89 ± 0.03	52	0.130 ± 0.007	15,000 ± 800	
Holstynska 2/2		13,350 ± 170	11,650 ± 1050	0.604 ± 0.010	1.68 ± 0.03	205	0.114 ± 0.005	13,100 ± 600	
Holstynska 2/4		8810 ± 70	7110 ± 1000	0.519 ± 0.01	1.35 ± 0.02	12	0.093 ± 0.006	10,500 ± 700	9230 ± 1100
Kadlec 1		8590 ± 150	6890 ± 1000	0.144 ± 0.008	1.38 ± 0.10	1.6	0.11 ± 0.01	13,400 ± 900	890 ± 5500
Kadlec 2		8140 ± 60	6440 ± 1000	0.115 ± 0.005	1.42 ± 0.07	2	0.171 ± 0.004	20,160 ± 510	5280 ± 5700
Cracow-Wieluń Upland (Poland)									
Dziewicza 1/5		47,800 ± 1500	46,100 ± 1800	0.047 ± 0.003	2.41 ± 0.17	8.8	0.53 ± 0.05	76,100 ± 10,200	66,900 ± 13,400
Bez Nazwy 1/1	30–40	30,400 ± 1900	28,700 ± 2200	0.070 ± 0.003	1.75 ± 0.10	4.8	0.36 ± 0.01	47,040 ± 1420	34,800 ± 1500
Bez Nazwy 1/2	20–30	44,500 ± 2200	42,800 ± 2500	0.054 ± 0.002	2.09 ± 0.11	4.6	0.51 ± 0.01	72,920 ± 2580	55,100 ± 2800
W Tomaszówkach 2		35,200 ± 600	33,500 ± 1200	0.050 ± 0.002	1.99 ± 0.11	3	0.34 ± 0.03	44,130 ± 4270	24,200 ± 6200
Wierna A+B+C	70–180	47,200 + 4300 −2800	45,500 + 4400 −3000						
Wierna B+C	100–180			0.117 ± 0.003	1.09 ± 0.03	84	1.01 ± 0.02	>350,000	
Wierna D+E+F	182–282	>46,000	>44,000						
Wierna D+E	180–250			0.110 ± 0.004	0.976 ± 0.05	29	1.04 ± 0.05	>350,000	
Wierna G	280–300	40,200 + 2600 −2000	38,500 + 2800 −2300						
Wierna H	300–320	>46,300 >46,700	>44,500 >45,000						

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Sample	Distance from base (mm)	^{14}C age (BP)	Corrected ^{14}C age (BP)	U (ppm)	$\frac{^{234}U}{^{238}U}$	$\frac{^{230}Th}{^{232}Th}$	$\frac{^{230}Th}{^{234}U}$	^{230}Th/U age (cal BP)	Corrected ^{230}Th/U age (cal BP)
Wierna H+M	300–410			0.118 ± 0.004	1.06 ± 0.05	62	1.04 ± 0.03	>350,000	
Wierna L+M	350–420	>46,900	>45,000						
Wierna N+O+P	420–540	42,400 + 3100 −2300	40,700 + 3300 −2500						
Wierna P	530–540	34,100 + 2500 −1800	32,500 + 2700 −2100						
Wierna O+P	460–540			0.126 ± 0.004	1.12 ± 0.04	34	0.975 ± 0.029	310,000 + 36,000 −29,000	
Tatra Mountains (Poland)									
Czarna 8/1		5140 ± 60	3440 ± 1000						
Czarna 8/2		1750 ± 80	50 ± 1000	0.131 ± 0.005	2.57 ± 0.10	2.8	0.075 ± 0.001	8370 ± 140	4050 ± 1600
Low Tatra Mountains (Slovakia)									
Lodowa 2/4		6160 ± 60	4460 ± 1000	0.490 ± 0.011	2.90 ± 0.05	>1000	0.042 ± 0.003	4700 ± 300	
Slobody 7/1	1–11			2.74 ± 0.04	1.47 ± 0.02	382	0.091 ± 0.004	10,300 ± 450	
Slobody 7A	31–50	11,400 ± 180	9700 ± 1050	3.14 ± 0.07	1.45 ± 0.03	67	0.088 ± 0.003	10,000 ± 370	
Slobody 7B	105–120	7650 ± 140	5950 ± 1000	3.78 ± 0.07	1.46 ± 0.02	261	0.052 ± 0.001	5740 ± 160	
Slobody 7/2	170–180			4.30 ± 0.07	1.32 ± 0.01	155	0.031 ± 0.002	3400 ± 190	
Slobody 7/3	184–197			4.27 ± 0.07	1.33 ± 0.02	>1000	0.029 ± 0.002	3200 ± 170	
Slobody 7C	205–217	5280 ± 130	3580 ± 1000	3.95 ± 0.07	1.47 ± 0.02	23	0.028 ± 0.0005	3050 ± 50	
Slobody 7D	282–290	3830 ± 110	2130 ± 1000	3.69 ± 0.05	1.38 ± 0.01	28	0.013 ± 0.0002	1420 ± 30	
Slobody 7/4	295–303			5.62 ± 0.11	1.15 ± 0.02	>1000	0.008 ± 0.001	820 ± 90	
Pieniny (Poland)									
Pieniny 1/1	1–10	5050 ± 60	3350 ± 1000	0.184 ± 0.006	1.66 ± 0.06	7.7	0.124 ± 0.002	14,230 ± 290	11,600 ± 1200
Pieniny 1/2	18–29	4700 ± 60	3000 ± 1000	0.193 ± 0.005	1.72 ± 0.04	3.8	0.040 ± 0.001	4490 ± 70	2730 ± 650
Pieniny 1a/1		4750 ± 60	3050 ± 1000	0.188 ± 0.005	1.63 ± 0.04	2.8	0.036 ± 0.001	3980 ± 80	1880 ± 780
Pieniny 1a/2		4170 ± 60	2470 ± 1000	0.217 ± 0.006	1.71 ± 0.05	2.7	0.033 ± 0.001	3640 ± 70	1620 ± 740
Pieniny 2.1/1	1–6	4250 ± 80	2550 ± 1000	0.152 ± 0.005	1.71 ± 0.06	3.2	0.095 ± 0.002	10,720 ± 200	5720 ± 1910

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Sample	Distance from base (mm)	^{14}C age (BP)	Corrected ^{14}C age (BP)	U (ppm)	$\frac{^{234}U}{^{238}U}$	$\frac{^{230}Th}{^{232}Th}$	$\frac{^{230}Th}{^{234}U}$	^{230}Th/U age (cal BP)	Corrected ^{230}Th/U age (cal BP)
Pieniny 2.1/2	6–13	4440 ± 80	2740 ± 1000						
Pieniny 2.1/3	13–20	4120 ± 60	2420 ± 1000	0.147 ± 0.005	1.84 ± 0.07	3.2	0.061 ± 0.002	6870 ± 180	3660 ± 1270
Slovak Karst (Slovakia)									
Krasnohorska 1A		35,500 ± 1700	33,800 ± 2000	0.035 ± 0.002	2.17 ± 0.16	5.9	0.44 ± 0.01	58,880 ± 1900	47,200 ± 6200
Krasnohorska KZSA		36,600 ± 5000	34,900 ± 5100	0.185 ± 0.011	3.80 ± 0.25	22	0.42 ± 0.03	52,000 ± 4500	
Ruse region (Bulgaria)									
Bulgaria OCz 1		37,000 ± 1400	35,300 ± 1700	0.092 ± 0.004	1.46 ± 0.07	>1000	0.33 ± 0.02	42,700 ± 3600	
Bulgaria OCz 2		12,900 ± 150	11,200 ± 1000	0.167 ± 0.005	1.67 ± 0.06	>1000	0.19 ± 0.02	22,400 ± 2600	
Bulgaria Bulg 1		38,300 ± 700	36,600 ± 1250	0.096 ± 0.007	1.08 ± 0.11	31	0.38 ± 0.03	52,000 ± 5000	
Bulgaria Bulg 2		21,650 ± 280	19,950 ± 1100						
Bulgaria Bulg 3		15,650 ± 100	13,950 ± 1000	0.132 ± 0.005	1.14 ± 0.06	10	0.18 ± 0.05	21,450 ± 7000	18,500 ± 8000
Bulgaria Bulg 4		11,250 ± 140	9550 ± 1000	0.105 ± 0.003	1.17 ± 0.04	22	0.019 ± 0.06	2000 ± 7000	
Tanzania									
Tanzania MAF1A	0–26	33,700 ± 1100	32,000 ± 1500	0.509 ± 0.013	1.10 ± 0.03	24	0.31 ± 0.01	40,190 ± 850	
Tanzania MAF1B	90–104	36,700 +3700 −2600	35,000 ± 3800	0.231 ± 0.005	1.12 ± 0.03	18	0.31 ± 0.01	39,600 ± 720	37,000 ± 1000
Tanzania MAF1C	151–165	32,000 ± 1600	30,300 ± 1900	0.226 ± 0.008	1.31 ± 0.05	33	0.34 ± 0.01	44,400 ± 2000	
Tanzania MAF1D	244–258	33,800 ± 1700	32,100 ± 2000	0.26 ± 0.01	1.02 ± 0.05	28	0.288 ± 0.007	37,000 ± 1000	
Tanzania MAF1E	282–296	31,600 ± 1600	29,900 ± 1900						
Tanzania MAF1F	334–346	29,800 ± 1300	28,100 ± 1700	0.183 ± 0.006	1.17 ± 0.05	8.8	0.36 ± 0.01	47,160 ± 1130	40,000 ± 2000

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(most frequently 0.5–1.5 cm) wide sections were cut out along growth layers, and divided in two portions. The edges of some stalagmites had fine-grained structure, and these sections were avoided. Also, we did not use sections containing depositional discontinuities.

One portion was dated by the ^{14}C method in the Gliwice Radiocarbon Laboratory, using the CO_2-filled proportional counters. Prior to separation of CO_2 for dating the outer part of the sample (about 20% of sample mass) was leached out with 4% HCl. Table 1 lists the ^{14}C dating results.

The twin sample was dated by the ^{230}Th/U method at the Institute of Geological Sciences, Polish Academy of Sciences, Warsaw. Standard radiometric dating procedure of the ^{230}Th/^{234}U method was used (Ivanovich and Harmon 1992). Samples of 10–40 g were dissolved in about 6 mol nitric acid. Uranium and thorium fractions were separated by chromatography. ^{234}U, ^{238}U, ^{230}Th, and ^{232}Th activities were measured by using isotope dilution with a ^{228}Th/^{232}U spike. All measurements were done with alpha spectrometry using OCTET PC (EG&G ORTEC). The ages were calculated by standard algorithm (Ivanovich and Harmon 1992). Reported errors are 1 sigma. For the samples with ^{230}Th/^{232}Th <20, correction for detrital thorium was performed using an assumed initial ^{230}Th/^{232}Th of 1.5 ± 0.5. Results of the measurements are listed in Table 1.

Figure 1 Map showing regions in Europe, where the samples listed in Table 1 have been collected. 1. Sudety Mountains (Poland), 2. Moravian Karst (Czech Republic), 3. Cracow-Wieluń Upland (Poland), 4. Tatra Mountains (Poland), 5. Low Tatra Mountains (Slovakia), 6. Pieniny (Poland), 7. Slovak Karst (Slovakia), 8. Ruse region (Bulgaria), 9. One speleothem comes from Tanzania, Africa (collected by K Holmgren).

DISCUSSION

^{14}C dates of speleothem samples are obviously affected by the "reservoir effect" because the ^{14}C in precipitating speleothem is diluted with the ^{14}C-free carbon from leached carbonate rocks. Therefore, the ^{14}C age of speleothem is greater than that of organisms deriving carbon from the atmosphere. So-called "apparent ages" are obtained. In the range of the ^{14}C calibration curve, the dilution

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factor can be assessed when the absolute age of the speleothem is known. Recent compilation of bibliographic data (Genty and Massault 1997) suggests that the dilution factors usually range between 0.7 and 0.9 (corresponding to apparent ages between 2750 and 750 yr), with the mean value of about 0.8 (apparent age of 1700 yr). In our studies the reservoir corrections of the speleothem samples from the Slobody Cave (Figure 2) are fairly constant over the whole Holocene and range from 2300 to 2700 yr. However, for most of our samples the reservoir correction is not exactly known, and (cf. Table 1) we used a value of 1700 ± 1000 yr.

The precision of the ^{230}Th/U ages strongly depends on the concentrations of uranium and detrital thorium. In our collection, the lowest U concentration (usually <0.1 ppm) was revealed by the samples from the Cracow-Wieluń Upland. Activity of detrital ^{230}Th, which is not produced from the decay of ^{234}U in the speleothem, is routinely subtracted from the measured total ^{230}Th activity (if ^{230}Th/^{232}Th activity ratio is less than 20). It is determined through the measurement of ^{232}Th activity, and an assumed initial activity ratio of ^{232}Th and ^{230}Th in the detrital minerals. This ratio is, however, usually not exactly known, but ranges between 1 and 2 according to bibliographic data.

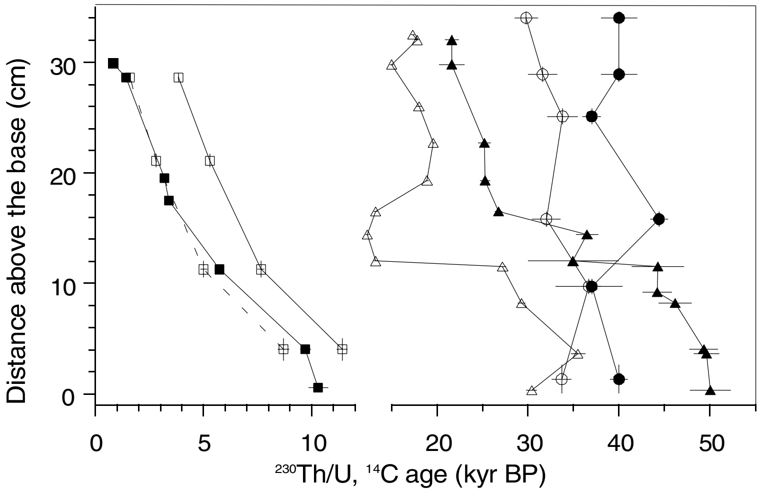

Figure 2 Profiles of ^{230}Th/U (solid symbols) and ^{14}C (open symbols) age of selected stalagmites. Squares = Slobody Cave; circles = MAF, Tanzania (this work); triangles = Lobatse II, Botswana (Holmgren et al. 1994). Open squares connected with dashed line represent ^{14}C ages of samples in equilibrium with atmospheric carbon, obtained from ^{230}Th/U ages using the ^{14}C calibration curve.

The uncertainty of the ^{230}Th/^{232}Th activity ratio affects the accuracy of the ^{230}Th/U age, especially when the activity of ^{232}Th is high. For a few samples, the error in ^{230}Th/U age reached as much as several thousand years (Table 1).

In Figure 3 we compare the ^{14}C and ^{230}Th/U ages of our samples, together with the earlier published datings of speleothem and lignite (Goede and Vogel 1991; Holmgren et al. 1994; Vogel and Kronfeld 1997; Geyh and Schlüchter 1998), and with the coral ^{14}C calibration data (Bard et al. 1998). The spread of our data points (Figure 3) is large. Comparison with the calibration dates suggests that many ^{14}C ages are too low, or ^{230}Th/U ages too high. The former case appears more probable, as young (or modern) carbonate might be deposited in the original structure of porous speleothem or in fractures. Such contamination distinctly affects ^{14}C ages of old samples, while its influence on the

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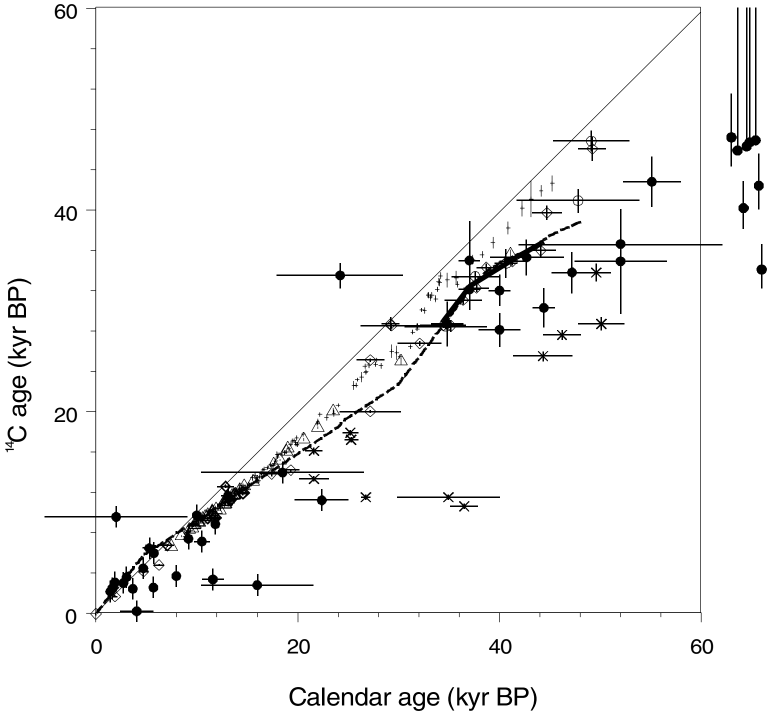

Figure 3 Comparison of ^{14}C and $^{230}Th/U$ ages of speleothem samples used in this work (●) with other relevant dates. The circles beyond the right edge of the plot represent samples from the Wierna stalagmite, dated with $^{230}Th/U$ to >300 ka BP. Δ = corals from Barbados, Tahiti and Mururoa Atoll (Bard et al. 1998); ◊ = stalagmites from Cango Cave, South Africa and Lynd's Cave, Tasmania (Vogel and Kronfeld 1998); × = stalagmite from Lobatse II Cave (Holmgren et al. 1994); ○ = lignite from Kärnten and Gossau, Switzerland (Geyh and Schlüchter 1998); † = annually laminated sediments of Lake Suigetsu, Japan (Kitagawa and van der Plicht 1998). ^{14}C ages of our samples have been corrected for the apparent age 1700 ± 1000 yr. Dashed line shows relationship between ^{14}C and absolute time scales, obtained by analysis of frequency distributions of not-paired ^{14}C and $^{230}Th/U$ ages of speleothem samples (discussed in the text).

$^{230}Th/U$ ages is much smaller. For example, 5% contamination of 40 ka old speleothem would change the $^{230}Th/U$ age by less than 2000, and the ^{14}C age by almost 15,000 years. Such an effect was observed for the stalagmite from the Lobatse II Cave (Holmgren et al. 1994) through the non-monotonous profile of ^{14}C age between 10 and 20 cm (Figure 2). Contamination with younger carbon is also evident in the speleothem from the Wierna Cave. This speleothem, dated with a $^{230}Th/U$ age to >300 ka BP, gave four finite ^{14}C ages, one of them even less than 40,000 BP (Figure 3). With this explanation in mind, one could expect the "true" relationship between ^{14}C and calendar time scales represented by the upper edge of the range covered by our dates. Such an edge can be traced between 35 and 45 ka BP, and indeed, it well agrees with the other dates.

On the other hand, profiles of ^{14}C and $^{230}Th/U$ ages in the stalagmite from Tanzania (MAF, Figure 2) suggest some problems with the $^{230}Th/U$ dates rather than ^{14}C dates. This could be due to open-system conditions, which affected $^{234}U/^{238}U$ as well as $^{230}Th/^{234}U$ activity ratios (cf. Figure 4). It is worth noting, that the two MAF dates, outlying from the monotonous $^{230}Th/U$ profile (Figure 2), are just those producing the large spread of dates between 35 and 50 ka BP (Figure 3).

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The large spread of our dates precludes detailed conclusions concerning ^{14}C calibration. Nevertheless, a lack of dates with ^{14}C ages older than the ^{230}Th/U one between 35 and 45 ka BP is coherent with the suggestion from earlier ^{230}Th/U and ^{14}C dates (Vogel and Kronfeld 1997; Geyh and Schlüchter 1998; Bard et al. 1998) that the deviation between both time scales was large in that period. The cluster of ^{230}Th/U-^{14}C dates (Figure 3) clearly disagrees with the comparison of ^{14}C and varve ages from Lake Suigetsu (Kitagawa and van der Plicht 1998), perhaps an effect of non-continuous varve chronology in the oldest part of the Suigetsu sediments.

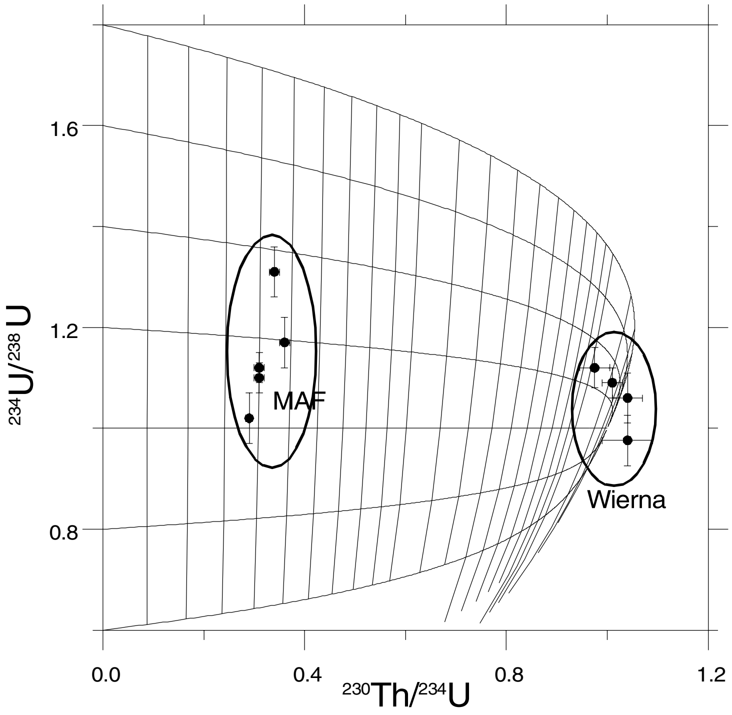

Figure 4 Plot of ^{234}U/^{238}U vs. ^{230}Th/^{234}U activity ratios for the samples from Wierna Cave and MAF, Tanzania

Comparison of Frequency Distribution of ^{14}C and ^{230}Th/U Ages of Speleothems

Though few speleothem samples have been dated by both the ^{14}C and ^{230}Th/U methods, there are many speleothem samples dated by only one of these methods. Looking through our bibliography, we found 133 "single" ^{14}C dates and 252 ^{230}Th/U dates of speleothem samples (younger than 60 ka) from Europe (Table 2). These dates are not uniformly distributed in time, reflecting some periods more favoring speleothem growth than the other ones.

The maxima of distributions of ^{14}C and ^{230}Th/U ages (Figure 5a) are not synchronous, most distinctly for period before 30 ka BP, an effect presumably reflecting deviation between both time scales. We tried thus to find such dependence between ^{14}C and calendar time scales (the so-called "transfer function", Figure 5b) which explains most of the time lags between both distributions. This function transfers the horizontal scale of distribution of ^{14}C dates (Figure 5c). The clue is to find such a function, which gives a minimum sum of squares of differences between the ^{230}Th/U and transferred ^{14}C distribution curves.

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Table 2 Sources of dates used in comparison of frequency distribution of ^{14}C and ^{230}Th/U ages of speleothem

Location	Nr of dates	References
Radiocarbon method		
Croatia, Slovenia, Bosnia	73	Srdoč et al. (1973, 1975, 1977, 1979, 1981, 1982, 1984, 1989, 1992)
Germany	10	Geyh and Hennig (1986)
Tatra Mountains, Poland	13	Duliński M. (1988); Hercman (1991)
Slovakia	5	Hercman et al. (1994)
Cracow-Wieluń Upland, Poland	32	Pazdur et al. (1994)
Total	133	
Uranium-Thorium method		
Crakow-Wieluń Upland, Poland	10	Głazek (1986); H Hercman, unpublished
Tatra Mountains, Poland;	31	Duliński M. (1988); Hercman et al. (1998); H Hercman, unpublished
Sudety Mountains, Holy Cross Mountains, Poland	18	Hercman et al. (1995); H Hercman, unpublished
Great Britain	116	Hennig et al. (1983); Atkinson et al. (1986); Rowe et al. (1989); Gascoyne et al. (1983); Ford et al. (1983); Sutcliffe et al. (1985)
Moravian Karst, Czech Republic	11	Hercman et al. (1997); H Hercman, unpublished
France	18	Bakalowicz et al. (1984); Maire and Quinif (1987)
Germany	33	Hennig et al. (1983
Low Tatra Mountains, Slovakia	15	Duliński M. (1988); Hercman et al. (1997); H Hercman, unpublished
Total	252	

The optimal transfer function has been found with the computer algorithm VARFIT (Goslar 1993). This algorithm searches the optimum in the large class of allowed transfer functions, using the dynamic programming method (Bellman and Dreyfus 1962). In our case, the class of allowed transfer functions was limited by two conditions. First, we allowed that for any age the ^{14}C time scale could be stretched or stressed by no more than 50%. This limitation obviously reflects the fact that the concentration of ^{14}C in the atmosphere never changed too abruptly. Second, we fixed the age of 34,000 BP transferred at 38 ka BP, to synchronize distinct maximum in both distributions. Without such a fixation, the VARFIT synchronized 34,000 BP with another maximum of the ^{230}Th/U distribution, at 44 ka BP, the result being completely unlikely, in view of other calibration data.

The obtained transfer function agrees well (Figure 3) with the coral data in the period 0–20 ka BP, and between 35 and 45 ka BP it fits very well with the line traced by the pairs of ^{14}C and ^{230}Th/U ages of speleothems. Some offset between 20 and 35 ka BP is insignificant as only few ^{14}C and ^{230}Th/U-dated speleothem samples from this period are available. This result seems to confirm that large deviation between ^{14}C and calendar time scales did not disappear before 35,000 BP. However, as the uncertainty of the transfer function is not known, the transfer function approach yields only tentative conclusions.

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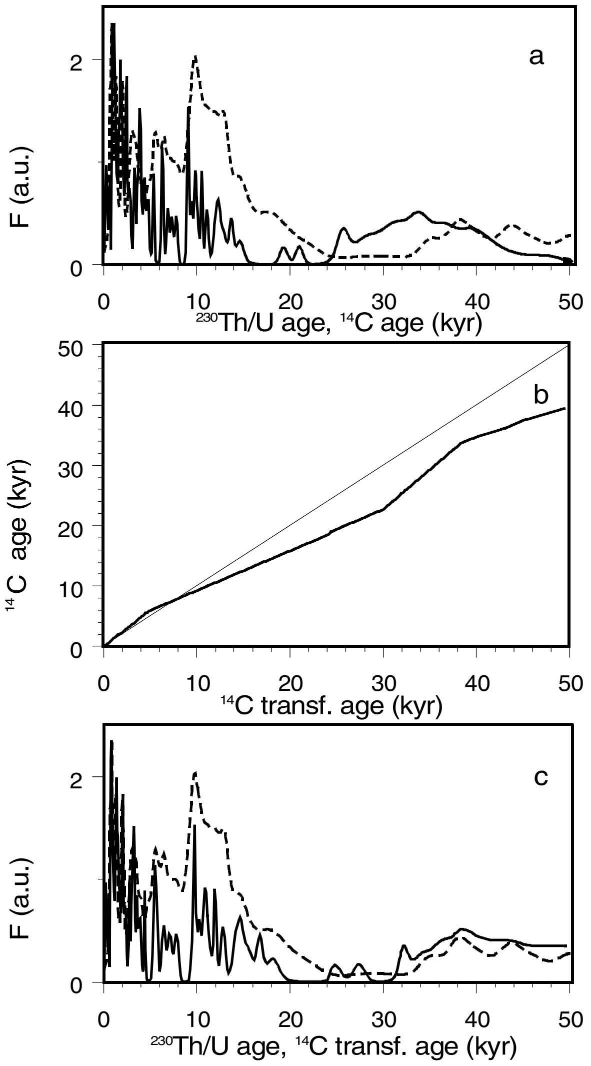

Figure 5 **a**: Comparison of frequency distributions of ^{14}C (solid line) and ^{230}Th/U (dashed line) ages of speleothem, selected from literature. **b**: relationship between ^{14}C and ^{230}Th/U time scales (transfer function) which best explains the time lags between distributions from section **a**. **c**: as in section **a**, with the time scale of ^{14}C distribution modified according to the transfer function shown in section **b**.

CONCLUSION

^{14}C dates of speleothem are commonly treated with caution because of the reservoir effect, producing an apparent age that is usually not accurately known. However, in light of our data and some previous research (Holmgren et al. 1994), the reservoir effect may be of minor importance when compared to contamination with younger carbon. The latter effect can alter ^{14}C ages of old (>30 ka) samples by several thousand years. Despite the large spread, our pairs of ^{14}C and ^{230}Th/U ages of speleothem samples seem coherent with the previously published data on corals, speleothem and lignite, which suggested a large deviation between ^{14}C and absolute time scales between 35 and 45 ka BP. The around 4000-year deviation seems also supported through the analysis of frequency distributions of ^{14}C and ^{230}Th/U ages of speleothem. In this analysis, a much larger set of ages, obtained with one of these methods only, was used.

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