ACTA CARSOLOGICA	33/2	14	239-248	LJUBLJANA 2004

COBISS: 1.01

COMPARISON OF ^{14}C AND $^{230}Th/^{234}U$ DATING OF SPELEOTHEMS FROM SUBMARINE CAVES IN THE ADRIATIC SEA (CROATIA)

PRIMERJAVA MED METODAMA ^{14}C IN $^{230}Th/^{234}U$ NA PRIMERU DATACIJE SIG IZ PODMORSKIH JAM V JADRANU NA HRVAŠKEM

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Prejeto / received: 8. 9. 2004

Abstract UDC: 551.44(26.03)(497.5)

Maša Surić & Mladen Juračić & Nada Horvatinčić: Comparison of ^{14}C and $^{230}Th/^{234}U$ dating of speleothems from submarine caves in the Adriatic Sea (Croatia)

Among the 16 speleothems that were collected from 7 submarine caves and pits for the purpose of ^{14}C and U-Th dating and reconstructing sea-level changes, two speleothems were dated by both methods. Different environmental conditions during the speleothem deposition and after the submergence resulted with different appropriateness for speleothem dating by these techniques. Well preserved speleothems gave reliable results by both methods, while U-Th method showed disadvantage in the case of carbonates contaminated with detrital material, as well as in the case of carbonate from marine overgrowth that covers the speleothems. However, U-Th method using MC ICPMS technique which requires only 100-300 mg of sample per analysis (instead of ca. 30 g for ^{14}C conventional method), offers better age resolution that is essential for speleothem dating.
Key words: ^{14}C dating, U-Th dating, submerged speleothems, submarine karst, Adriatic Sea, Croatia.

Izvleček UDC: 551.44(26.03)(497.5)

Maša Surić & Mladen Juračić & Nada Horvatinčić: Primerjava med metodama ^{14}C in $^{230}Th/^{234}U$ na primeru datacije sig iz podmorskih jam v Jadranu na Hrvaškem

Z metodama ^{14}C oziroma U-Th smo datirali 16 sig iz sedmih podmorskih jam v Jadranu. Dve sigi smo datirali z obema metodama. Primernost metod za datacijo sig je različna zaradi različnih okoljskih pogojev, ki so vladali med izločanjem sige oziroma po zalitju jame. Obe metodi sta zanesljivi na dobro ohranjenih sigah. U-Th metoda je slabša, ko so karbonati onesnaženi z detritičnim materialom oz. preraščeni s plastjo morskega izvora . Vendar metoda U-Th z uporabo MC ICPMS analize, kjer potrebujemo le 100-300mg vzorca (namesto 30 g pri metodi ^{14}C), omogoča boljšo časovno ločljivost datacij, kar je pri datiranju sig zelo pomembno.
Ključne besede: ^{14}C datacije, U-Th datacije, potopljena siga, podmorski kras, Jadransko morje, Hrvaška.

INTRODUCTION

After the speleothems had been introduced as a relevant source of paleoclimatic proxy records (Hendy & Wilson 1968), they were also recognized as a reliable indicator of paleo sea levels (Spalding & Mathews 1972; Harmon et al. 1978; Gascoyne et al. 1979). Namely, speleothems are typical terrestrial deposits, so their findings below the present sea level indicate former lower sea levels. Dating of the last surface layer of speleothem that is typical subaerial feature, should provide the time when the speleothem was still under the vadose condition i.e. above sea level, whereas the age of the initial part of marine overgrowth that covers the submarine speleothems should indicate the time of establishment of marine conditions.

Regarding these facts, submerged speleothems have been studied in order to reconstruct eustatic (global) and relative (local/regional) sea-level changes worldwide (Li et al. 1989; Allesio et al. 1992; Richards et al. 1994; Antonioli et al. 2001; Vrhovec 2001; Bard et al. 2002; Surić 2002; Fornós et

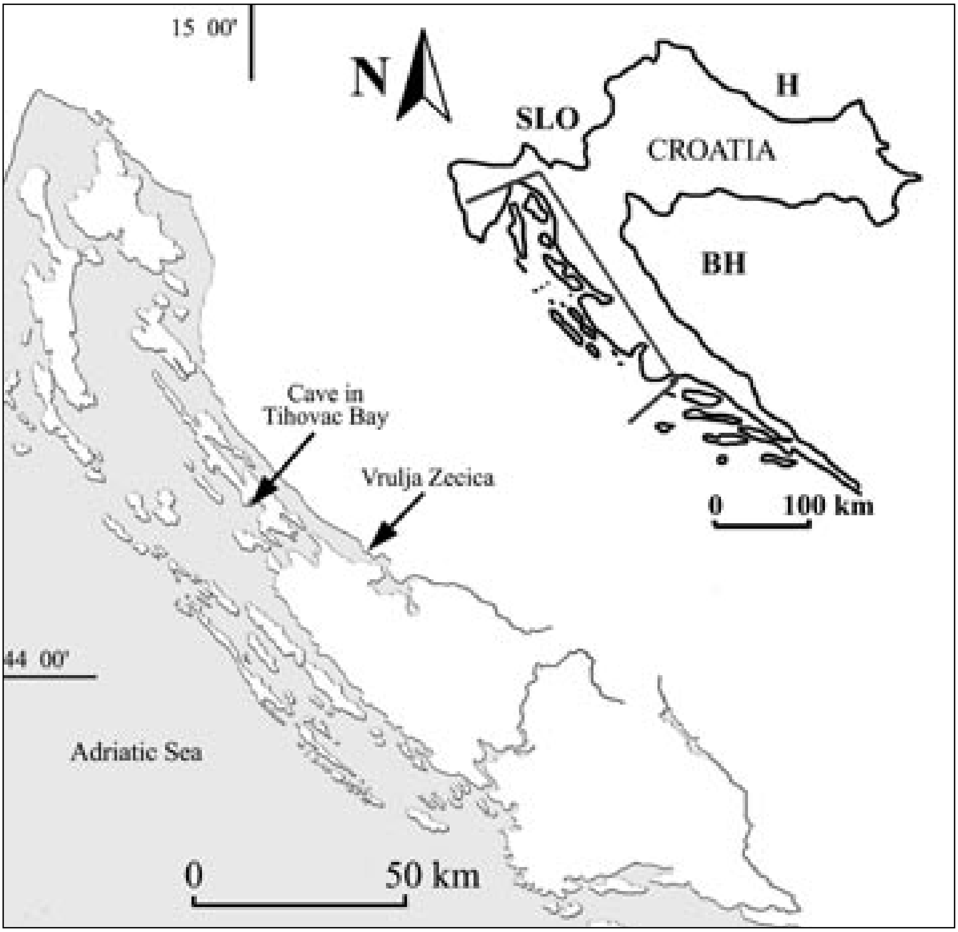

Fig. 1: Study area with sampling sites.

al. 2002). The most frequently used dating methods are ^{14}C and $^{230}Th/^{234}U$. For both methods the good quality of sample is very important, e.g. sample taken from chemically-closed system since the time of deposition, with no sign of any recrystallization, no contamination with detrital material, etc. (Richards & Dorale 2003).

With the intention of reconstructing relative sea-level changes on the Eastern Adriatic coast, 16 samples of speleothems were taken from seven submarine caves (from the depths of 1.5 m to 41.5 m below mean sea level - m.s.l.) located along the mainland and Adriatic islands' coasts. Speleothem samples, as well as marine overgrowth, were dated by conventional ^{14}C method (Surić 2002, Surić et al. 2004, in press).

Here we compare and discuss the results of ^{14}C and U-Th dating of two speleothems from two submerged karst features in the Adriatic Sea: Cave in Tihovac Bay (Pag Island) and submarine spring Vrulja Zečica (Fig. 1).

STUDY AREA – GEOLOGICAL AND ENVIRONMENTAL SETTINGS AND SAMPLING

Both of the studied caves were formed within formerly tectonically disturbed limestones during the periods of lower sea levels, whereas their present positions and hydrological functions were subsequently defined by the last, Late Pleistocene-Holocene transgression (Fig. 2).

Cave in Tihovac Bay, formed in Upper Cretaceous limestones, situated ca. 100 m off-shore has no hydrological function and it is entirely within marine environment. Stalactite P-23 was collected from the SE channel, from the depth of 23 m below m.s.l. and it was completely covered with 0.5-1.0 cm thick marine overgrowth (biocenosis of caves and ducts in complete darkness). For ^{14}C measurements, carbonate samples were drilled from overgrowth (layer P), the youngest speleothem layer (A) and from the oldest, central part of the speleothems (B) (Figs. 3a and 3c). U-Th measurements were performed on wafers from marine overgrowth (P1) and from the first two layers beneath the

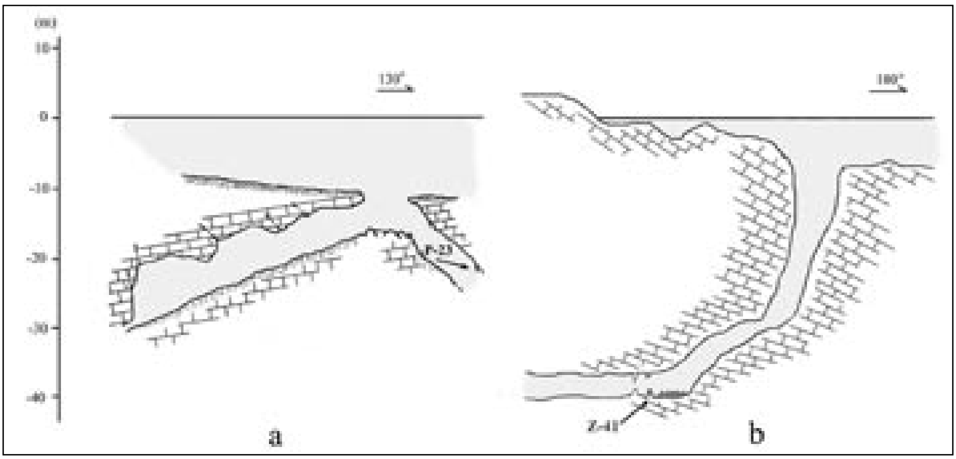

Fig. 2: (a) Cave in Tihovac Bay; (b) submarine spring Vrulja Zečica (after Bakran-Petricioli & Petricioli 1999).

overgrowth (T1 and T2) (Fig. 3b). Both of these samples, T1 and T2, measured by U-Th method overlap with sample A measured by ^{14}C method.

Submarine spring Vrulja Zečica was formed in Tertiary limestones and its outlet is situated 20 m off the coast at the depth of -9 m. Although it is presently periodical freshwater spring, numerous speleothems (stalagmites, stalactites, draperies, etc) at the depth of ca. -40 m are evidence of its former vadose phases. Stalagmite Z-41 was taken from the depth of 41.5 m below m.s.l. Scarce, eroded vermetid tubes on its surface and destroyed side of the stalagmite oriented toward main channel (Fig. 4), suggest very strong periodical freshwater outflow resulting in mechanical erosion. Inner part also shows discontinuities and inhomogeneous clayey layers, probably originating from periodical flooding of the cave during the speleothem growth.

Sample for the ^{14}C measurement (S) was taken after removing 5 mm of speleothem surface, whereas the samples for U-Th dating were drilled from the layers 5 mm (B-40) and 17 mm (B-28) below the stalagmite surface (Fig. 4).

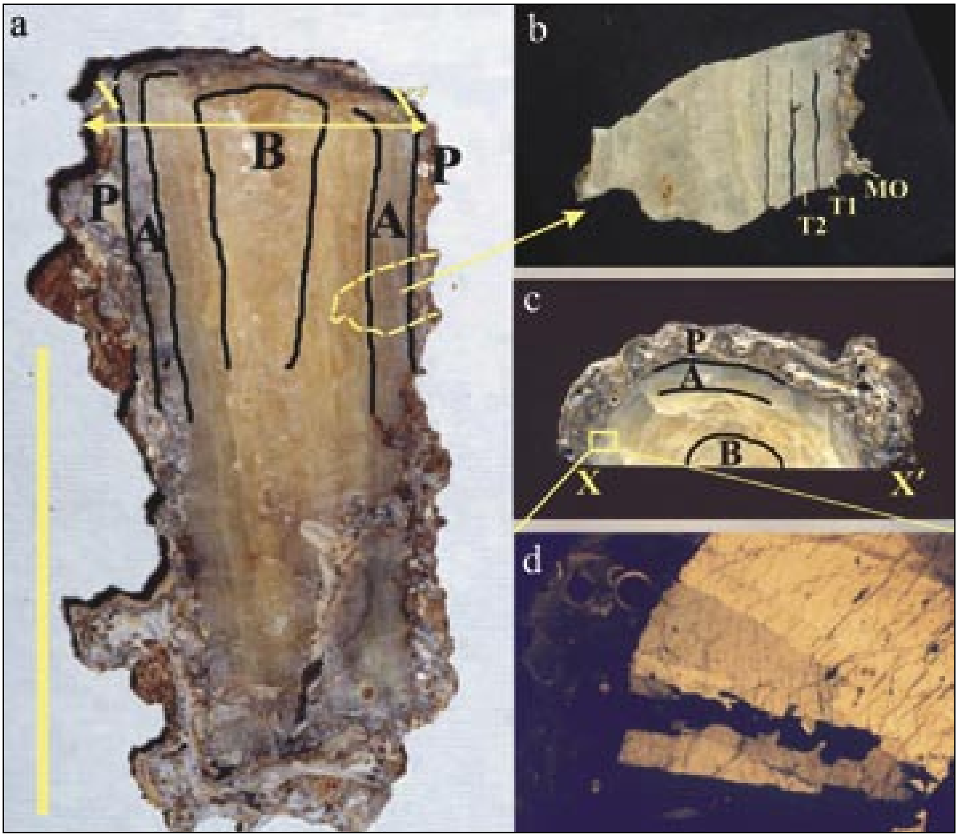

Fig. 3: Stalactite P-23 with marked sampling sites; well preserved upper part and lower part destroyed by boring organisms (scale bar 10 cm): a) longitudinal section; b) slice with wafers from longitudinal section; c) perpendicular section; d) microscopic photo of perpendicular slice. Samples A, B and P were dated by ^{14}C and P1, T1 and T2 by U-Th.

METHODS

Samples were dated at the Ruđer Bošković Institute, Zagreb by conventional ^{14}C method, using gas proportional counter (GPC). For each sample ~30 g of carbonate (speleothem or marine overgrowth) was separated, treated with dilute HCl to obtain CO_2, which was subsequently converted to methane. The conventional ^{14}C ages were corrected for initial ^{14}C activity of 85% and 95% for speleothem and marine overgrowth, respectively. Additional calculation of the starting time of marine overgrowth was made according to mathematical model developed by Allesio et al. (1992) that assumes continuous deposition and simultaneous decay of ^{14}C isotopes within the overgrowth. ^{14}C ages are also expressed in calibrated ^{14}C ages.

Five samples were dated by $^{230}Th/^{234}U$ method using Multi Collector Inductively Coupled Plasma Mass Spectrometry (MC ICPMS) at the Isotope Geochemistry Laboratory and Mass Spectrometry Laboratory, University of Bristol. For each measurement ~300 mg of carbonate was separated, either in the form of powder (from stalagmite Z-41) or in the form of wafer (from stalactite P-23). After the separation of uranium and thorium in ion exchange columns, and plasma ionisation, their amounts were measured by mass spectrometry.

Fig. 4: Longitudinal section of stalagmite Z-41 with marked sampling sites (scale bar 10 cm). Reconstructed part oriented toward recent periodical fresh-water inflow destroyed by mechanical erosion.

RESULTS AND DISCUSSION

Results of ^{14}C and U-Th dating of the submerged stalactite P-23 from the Cave in Tihovac Bay (-23 m) and of stalagmite Z-41 from submarine spring Vrulja Zečica (-41 m) are shown in the Table 1. ^{14}C results are expressed in ^{14}C age corrected for A_0 and in calibrated age as a mean of the calibrated range obtained by OxCal calibration software (Bronk & Ramsey 2003) (with 1 sigma error) for the ^{14}C ages <22000 yr BP, and for ^{14}C ages >22000 yr BP calibrated ages were determined by the proposed extension of the calibration curve (Bard et al. 2004). Results obtained by U-Th dating were corrected for bulk earth value of $(^{230}Th/^{232}Th)_{initial}$ that is 0.8±0.8 (activity ratio) (Wedepohl 1995).

Stalactite P-23

Stalactite P-23 is an example of typical submerged speleothem covered with marine organisms, partially destroyed (Fig. 3a, lower part). However, as indicated in Fig. 3c, upper part of the speleothem was well preserved from boring organisms. $\delta^{13}C$ values measured from the overgrowth (1.8 ‰) and from speleothem samples (-7.5 and -8.5 ‰) showed that there was no contamination of terrestrial carbon with marine one or vice versa (Surić 2002). Microscopic photo of perpendicular slice (Fig 3d) suggests that there was no dissolution on contacts between calcite crystals. It supports the conclusion that there was no dissolution on the surface of the speleothem.

^{14}C age of starting time of P-23 marine overgrowth, calculated by model of Alessio et al (1992) and calibrated (7,920 cal BP), is in good correlation with existing Holocene sea-level curves (Antonioli et al. 2001). Additionally, an attempt was made by U-Th dating of marine overgrowth (sample P1) by U-Th method, despite the likelihood of post-depositional alteration. Uncorrected U-Th age of 52.6 ka was lowered to 28.2 ka by correction for a bulk earth value of $(^{230}Th/^{232}Th)_{initial}$. Anomalously high age could be explained either with uranium loss from the system, or by addition of thorium with $^{230}Th/^{232}Th$ ratio greater then bulk earth. It is interesting that the measured $^{234}U/^{238}U$ activity ratio (1.1511) is close to the modern ocean value of 1.145. It suggests recent U exchange with the ocean reservoir.

As far as the terrestrial part of the stalactite P-23 is concerned, ^{14}C age (30,300 cal BP) is comparable to the U-Th ages of the same part of the speleothem (37 and 33 ka). Obtained U-Th ages are reversed, so apparently, outer part (T1) is older than inner (T2). It indicates that either uranium loss or thorium addition occurred. The latter is more likely because the ^{238}U concentration is actually greater for outer part, and ^{232}Th concentration is also much greater (57 ng g^{-1} compared with 0.84 ng g^{-1} of inner part). Correction for bulk earth value of $(^{230}Th/^{232}Th)_{initial}$ reduces age of T1 from 46.9 ka to 37.3 ka, but it is likely that the true age of cessation prior to submergence is closer to 33 ka (based on T2). Dating of subsequent layer below T2 (not labelled on Fig. 3b) should enable extrapolation and age determination of the outer contaminated layer T1.

Stalagmite Z-41

In case of stalagmite Z-41, results obtained by two methods are in very large discrepancy. ^{14}C age of 11,350 cal BP is expected regarding cessation of stalagmite growth due to Holocene sea-level rise. But, U-Th measurements indicate that this speleothem was contaminated by detrital clays, giving useless results. Namely, sample B-40 has indeterminable age because of too high $^{230}Th/^{238}U$ ratio. That was probably gross error, unless the detrital clay component has a very high initial $^{230}Th/^{232}Th$. However, this is not very likely because the sample B-28 gives a determinable age (although very

Speleothem	Sea depth (m)	Lab. no.	Sample	Description	Mass (g)	^{14}C age			U-Th age					
						A_0 corr. (yr BP)	Calc. overgr. starting time (yr BP)	Calibrated age (cal BP)	^{238}U (ng g^{-1})	^{232}Th (ng g^{-1})	$^{234}U/^{238}U$ activity	$^{230}Th/^{238}U$ activity	Uncorr. age (ka)	Corr. age (ka)
P-23	23.0	Z-3053	P	marine overgrowth	41.0	3,381 ± 118	7,090 ± 270	7,920						
		Z-3054	A	youngest part of stalactite	35.0	25,480 ± 1,230		30,300						
		Z-3055	B	oldest part of stalactite	32.0	29,730 ± 2,110		34,800						
		MS 09	P1	marine overgrowth	0.192				1247	1196	1.1511	0.4447	52.6	28.2
		MS 10	T1	youngest part of stalactite	0.225				148	57	1.0987	0.3867	46.9	37.3
		MS 11	T2	layer below T1	0.233				104	0.84	1.0833	0.2884	33.6	33.4
Z-41	41.5	Z-2857	S	youngest part of stalagmite	30.0	9,840 ± 165		11,350						
		MS 12	B-40	5 mm from stalagmite surface	0.304				75	261	1.1156	1.6565	nd#	nd#
		MS 13	B-28	17 mm from stalagmite surface	0.310				49	122	1.1778	1.1764	350.6	287.0

indeterminable age

Table 1. Results of ^{14}C (Z-#) and U-Th dating (MS-#) of the submerged stalactite P-23 from Cave in Tihovac Bay (-23 m) and of stalagmite Z-41 from submarine spring Vrulja Zečica (-41 m). ^{14}C results are expressed in ^{14}C age corrected for A_0 and in calibrated ages using OxCal calibration software (Bronk Ramsey, 2003) (with 1 sigma error) for the ^{14}C ages <22000 yr BP and for ^{14}C ages >22000 yr BP by the proposed extension of the calibration curve (Bard et al., 2004). For detailed description of samples see Figs. 3 and 4.

old, >280 ka) with similar detrital component ($^{230}Th/^{232}Th$ concentration ratio of B-40 and B-28 are 7.89×10^{-6} and 7.82×10^{-6}, respectively). In order to improve obtained results, beside the correction for bulk earth value of $(^{230}Th/^{232}Th)_{initial}$, isochron method should be employed.

Apart from the dating limitations, sampling of speleothems from submarine caves along the Eastern Adriatic coast also has some limiting factors comparing with sampling of speleothem from terrestrial caves: (i) stalactites are more frequent since the stalagmites are usually buried by fine grained clastic sediment deposited within marine environment, or by the material from collapsed roofs; (ii) marine overgrowth, where abundant, conceals the real shape of speleothem that is crucial for choosing the samples; (iii) the speleothems could partially be destroyed by boring organisms and/or in the case of submerged springs, by mechanical erosion and corrosion (Juračić et al. 2002)

CONCLUSIONS

Our study showed that both dating methods, conventional ^{14}C and U-Th MC-ICPMS, give reliable results for well preserved submarine speleothem (terrestrial carbonate). ^{14}C age of marine overgrowth, and then model calculation, give reliable result of overgrowth starting time, while U-Th result is not acceptable.

However, due to a small amount of carbonate samples for U-Th MC-ICPMS method (100-300 mg per analysis) dating by this method provided much better age resolution of single speleothem layer than conventional ^{14}C method (requiring ca. 30 g per analysis). In the same time, U-Th MC-ICPMS method is much more sensitive to the contamination by detrital material, whereas ^{14}C dating method has a problem of determination of the initial ^{14}C activity of carbonates. Combination of both methods and, if possible, using ^{14}C AMS method could give most reliable results.

ACKNOWLEDGMENT

We thank speleodivers Tonći Rađa, Petronije Tasić, Branko Jalžić, Anđelko Novosel and Mladen Kuhta for providing us samples from submarine caves. We also thank David Richards and Dirk Hoffmann (School of Geographical Sciences, University of Bristol) for U-Th analyses and helpful suggestions.

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