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RADIOCARBON DATING OF TRAVERTINES PRECIPITATED FROM FRESHWATER

JOSEP MAS-PLA[1], JOSEP TRILLA and MARIA LLUISA VALLS

Servei de Datació per Triti i Carboni 14, Departament de Geologia, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

ABSTRACT. We have studied the isotopic composition of recently precipitated travertines to determine the initial ^{14}C activity of ancient travertine deposits. We found that the ^{14}C activity of recent travertines of northeastern Spain was a function of the distance from the spring, resulting in variations in the initial ^{14}C activity of the ancient travertine formations. We calculated the ancient travertine radiocarbon ages by using the ratio between the ^{14}C activity of recent travertines and that of present atmospheric CO_2 as the initial ^{14}C activity.

INTRODUCTION

Travertine radiocarbon dating faces the problem of identifying the initial ^{14}C activity of each sample. In the case of travertines precipitated from freshwater, the initial ^{14}C activity is directly related to the chemistry and isotopic composition of the stream waters, which depend on the origin of the water, the equilibrium of the CO_2 - H_2O - $CaCO_3$ system and the isotopic exchange between water and atmosphere. Thus, we can expect changes in the initial ^{14}C activity at any point of the travertine formation.

We have investigated the Llorà travertine formation which developed in spring-fed streams along a hill slope (Ríos & Masachs 1953; Mas *et al.* 1991). Our purpose was to measure the ^{14}C activity of the recently precipitated calcium carbonate along these streams, as well as the chemical and isotopic composition of the stream water, and to estimate the initial ^{14}C activity of the ancient travertines. We investigated the downstream chemical and isotopic variations and used the results to date the oldest layers of the travertine formation.

GEOLOGICAL SETTING

The Llorà travertine formation is located in a small watershed (20 km^2) tributary to the Llémena River in the Sistema Transversal mountain range 15 km NE of Girona (northeast Spain). The watershed is mainly underlain by carbonate sandstones, Rocacorba Formation (Pallí 1972), which are severely faulted in a NW-SE direction (Fig. 1).

The travertines were classified as waterfall tufa (Chafetz & Folk 1984), and they extend along the hill slope in several successive terraces over 0.6 km^2. An erosional discontinuity clearly differentiates an older layer of travertines from a recent one. The origin of both layers can be related to the carbonate-rich spring waters discharging from fractures in the sandstone aquifer. At present, these springs have a perennial flow distributed in several surface streams. Calcium carbonate is actively precipitating in these streams, building travertine structures similar to those observed in the ancient travertines.

THEORETICAL APPROACH

Carbonate precipitation in spring water occurs as it discharges to the surface, where CO_2 partial pressure is lower than in the aquifer. It is governed by the reaction

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[1] Present address: Department of Hydrology and Water Resources, The University of Arizona, Tucson, Arizona 85721 USA

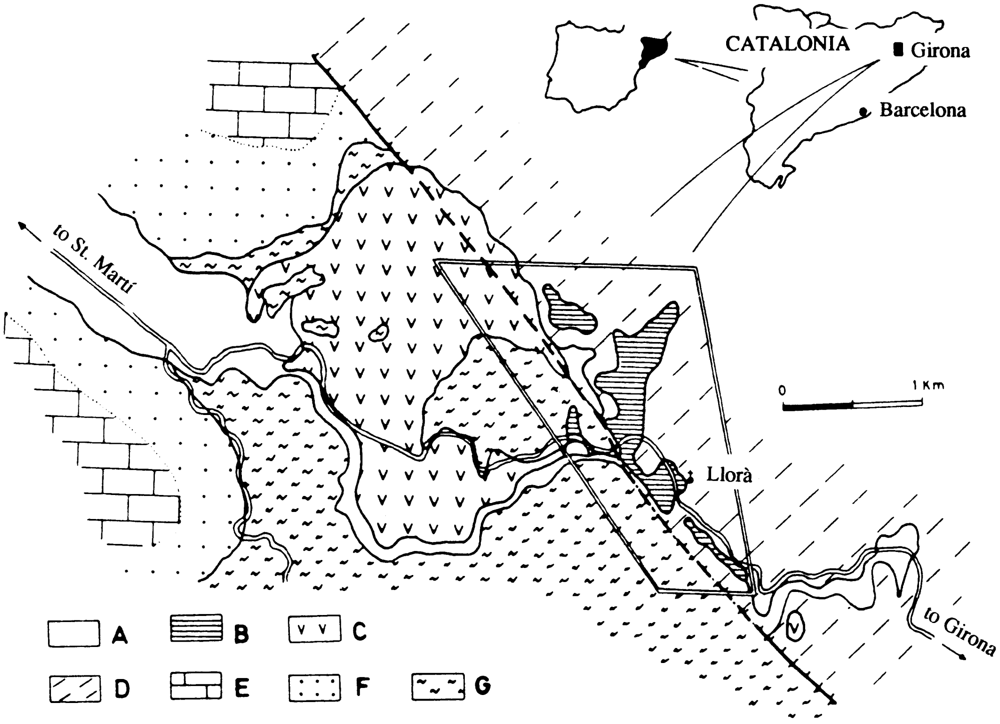

Fig. 1. Geological map of the study zone. A – alluvium; B – travertine; C – volcanic tuff and basalt; D – carbonate sandstone (Rocacorba Formation); E – limestone (Girona Formation); F – siliciclastic sandstones and shales (Pontils Formation); G – schists and slates. (Original by L. Pallí).

$$Ca^{2+} + 2\ HCO_3^- \rightleftharpoons CaCO_3 + H_2O + CO_2\ g\ . \qquad (1)$$

As a result of CO_2 loss, spring water pH and CO_3^{2-} concentration increase, and water tends to reach supersaturation conditions that enable calcite nucleation and precipitation. These processes are controlled by the partial pressure of CO_2, and they will occur until chemical equilibrium is attained between CO_2 partial pressure in water and atmosphere. Runoff dynamic characteristics will also influence the reaction rate (Jacobson & Usdowsky 1975).

Simultaneously, the isotopic composition of water in the aquifer and its variations as it flows as runoff affect the initial ^{14}C activity of precipitated calcium carbonate. ^{14}C content at the spring reflects CO_2 - H_2O - $CaCO_3$ dissolution and exchange dynamics during infiltration and water residence in the aquifer. Under closed-system conditions, the atmospheric ^{14}C activity will decrease due to the dissolution of carbonate rock, presumed to be ^{14}C-free due to radioactive decay (Münnich 1957). Once water flows as surface runoff, the system is definitely open and isotopic exchange between water and atmosphere will determine the ^{14}C activity and ^{13}C content of the dissolved carbon (Wigley 1975) and, consequently, the isotope composition of precipitated carbonate.

In summary, we can expect that the initial ^{14}C activity of recent travertines will be defined by the activity of the dissolved inorganic carbon (DIC) in the aquifer and by the exchange rate of carbon isotopes between DIC and atmospheric CO_2 in streams. The nucleation rate related to the hydrochemical changes downstream from the spring will determine how far from the spring $CaCO_3$ precipitates and, consequently, the extent of the ^{14}C and ^{13}C isotopic exchange.

ANALYTICAL METHODS

We measured temperature and pH in the field. Other analyses were performed in the laboratory less than 8 h after sampling. Alkalinity was measured by titration with 0.02 N H_2SO_4. Ca^{2+} and Mg^{2+} were analyzed by complexometric titration with 0.01 N EDTA. Na^+ and K^+ were measured by atomic absorption spectroscopy. Cl^- was analyzed using the Mohr method and SO_4^{2-} by turbidity. An equilibrium chemistry model, WATEQF (Plummer, Jones & Truesdell 1976), was used to calculate CO_2 partial pressure and the calcite saturation index.

Water samples for tritium analysis were electrolytically enriched. DIC for ^{14}C analysis was precipitated by addition of NaOH and $BaCl_2$ in a 100-liter volume of water (IAEA 1984). The CO_2 obtained by H_3PO_4 dissolution of precipitated $BaCO_3$ and travertine samples was used for benzene synthesis. Tritium and ^{14}C activity were measured by liquid scintillation in a low background counter. Stable isotope ^{13}C and ^{18}O content of carbonate samples was also measured.

RESULTS

Hydrochemistry

Water was sampled monthly (April to October 1989) at 10 points along the Torrent de Can Camps stream (Fig. 2). Points 1 and 3 correspond to springs that presently show a perennial discharge. The Font d'En Dansa spring at Point 1 is the main source of surface runoff in the stream.

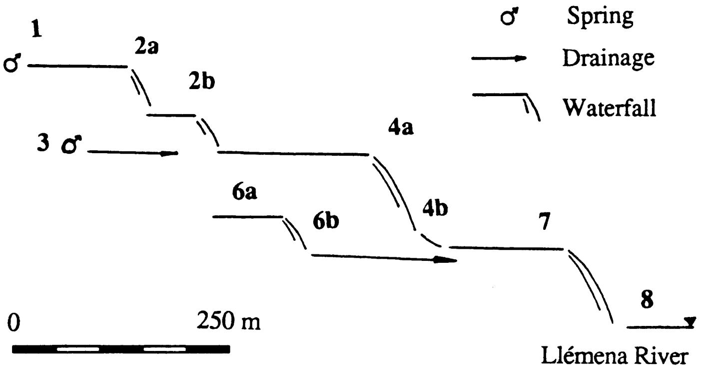

Fig. 2. Profile of the Torrent de Can Camps stream and distribution of the sampling points. Vertical distance between Points 1 and 8 is 160 m (arbitrary vertical scale).

The hydrochemical composition of the Font d'En Dansa spring water (Point 1 in Fig. 2) is characterized by a stable and high concentration of bicarbonate and calcium ions and dissolved CO_2. All other measured ions are present in very low concentrations (Table 1). We estimated CO_2 partial pressure at an average value of $10^{-1.30}$ atm, with a maximum value of $10^{-1.14}$ atm. The calculated saturation index shows that waters are slightly undersaturated with calcite. We conclude that water is in chemical equilibrium in the carbonate sandstone aquifer.

Changes in concentrations of calcium and carbonate species illustrate the chemical evolution of the system (Fig. 3). From Points 1 to 2b (Fig. 2), we observe average losses of $1.94 \cdot 10^{-3}$ M of H_2CO_3 (or CO_2 aq), $0.91 \cdot 10^{-3}$ M of HCO_3^-, and $0.60 \cdot 10^{-3}$ M of Ca^{2+}. In particular, a significant decrease

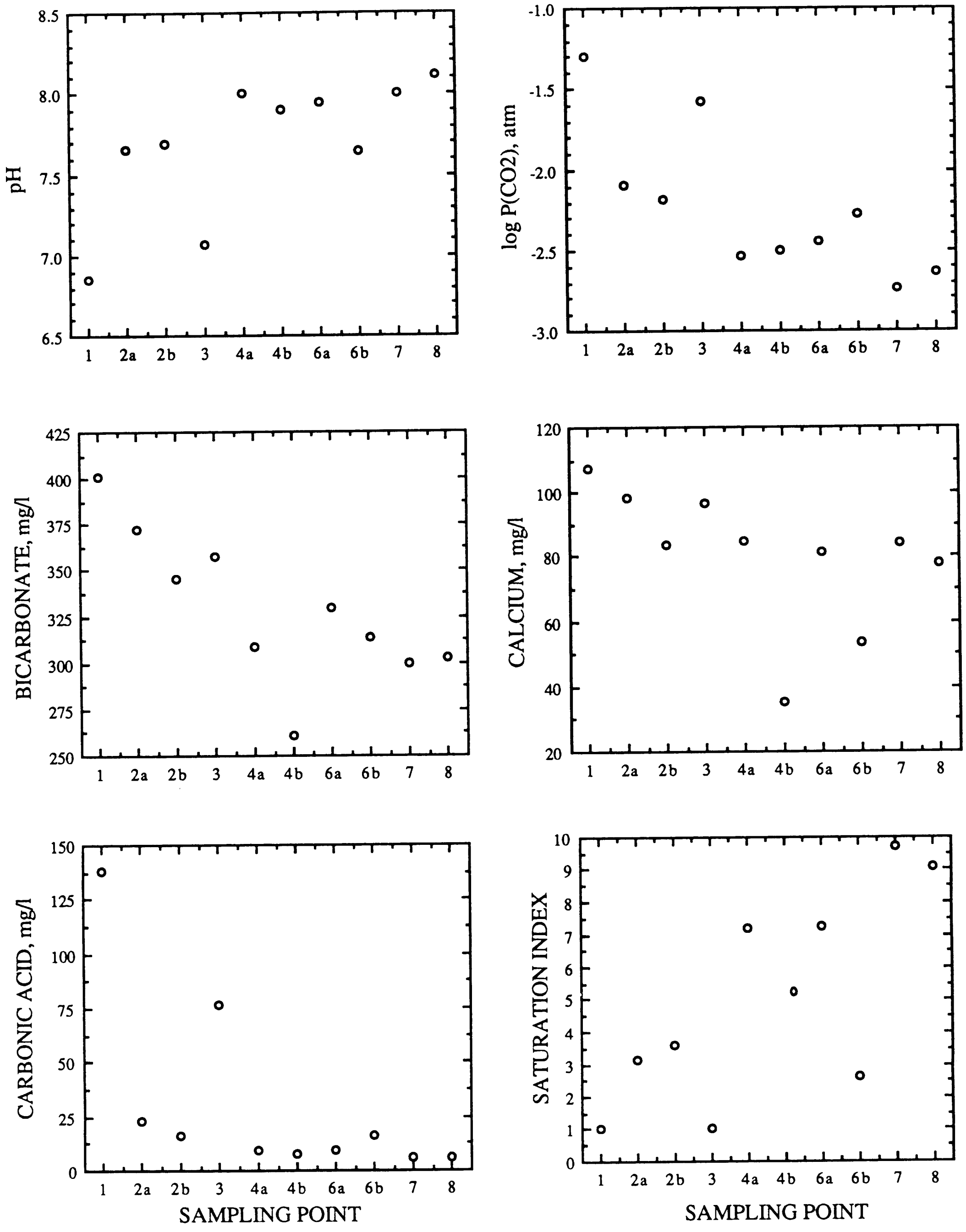

Fig. 3. Variation of the pH, hydrochemical species and saturation index along the Torrent de Can Camps stream. Plotted data are tabulated in Table 1.

TABLE 1. Mean values of chemical composition of water along the Torrent de Can Camps stream*

Point	T (°C)	pH	HCO_3^-	H_2CO_3	Ca^{2+}	Mg^{2+}	K^+	Na^+	SO_4^{2-}	Cl^-	lgP_{CO_2}	SI
1	16.5	6.85	400.8	138.1	107.7	<1.5	<1.0	6.3	30.0	21.6	−1.30	1.01
2a	16.0	7.66	372.7	22.8	98.3	<1.5	<1.0	6.6	30.0	19.5	−2.09	3.17
2b	16.4	7.69	345.1	16.4	83.5	<1.5	<1.0	6.0	27.8	20.6	−2.18	3.62
3	14.3	7.07	357.1	77.0	96.9	<1.5	<1.0	6.6	27.7	18.9	−1.58	1.03
4a	14.7	8.00	309.1	9.1	85.0	<1.5	<1.0	6.5	20.6	19.5	−2.51	7.22
4b	16.5	7.90	261.1	7.8	35.2	<1.5	<1.0	6.5	14.0	17.7	−2.59	4.80
6a	15.9	7.94	329.5	9.1	85.3	<1.5	3.0	9.7	28.3	21.9	−2.44	7.27
6b	17.8	7.65	313.9	16.3	53.5	<1.5	3.0	8.9	35.2	21.7	−2.27	2.64
7	14.3	8.00	299.7	5.8	84.3	<1.5	3.0	5.8	46.8	26.6	−2.74	9.70
8	15.2	8.11	302.7	6.1	78.1	<1.5	2.5	7.9	33.5	24.8	−2.64	9.10

*Concentrations are expressed in mg liter^{-1} and log P_{CO_2} in atm. SI, calcite saturation index. The mean values are calculated over the sampling period and their standard deviations are mostly <10%. (See Figure 2 for sampling point locations).

of the CO_2 aq occurs between Points 1 and 2a (Fig. 2), whereas HCO_3^- and Ca^{2+} show an approximately constant loss rate (Fig. 3). Relevant increases in pH and saturation index also occur downstream from the spring.

Field observations show that efficient calcium carbonate precipitation starts downstream from Point 2a (Fig. 2), with maximum development near Points 4a and 4b where pH and saturation index show high values. According to Dandurand *et al.* (1982), supersaturation is not sufficient for precipitation, and a nucleation threshold (represented by a small increase of pH) has to be reached before calcite precipitates.

In agreement with the hydrochemical data, travertine precipitation is controlled by the rate of concentration change in stream waters. Travertinization occurs along the stream segment where dissolved carbon species reach the equilibrium referred to in Equation (1). This process may explain the local distribution of travertine deposits in the Llorà site and must be considered when evaluating ^{14}C ages.

Stable Isotope Content

$\delta^{13}C$ and $\delta^{18}O$ in Water (Table 2). DIC in spring water (Point 1) has an average $\delta^{13}C$ of −14.4‰ (Fig. 4). However, it is a more positive value compared to Deines, Langmuir and Harmon (1974) data for a carbonate system with a CO_2 partial pressure of $10^{-1.30}$ atm. The differences between Deines' values and our data is 4‰ for an open system and 2‰ for a closed system. These differences may be mainly attributed to the difference between the end-point $\delta^{13}C$ values for CO_2 and calcite used by these authors and the ones in the Llorà area. Isotopic exchange with the atmosphere is clearly reflected by the variation of $\delta^{13}C$ in the DIC along the stream. In particular, an increase of +3.75‰ is recorded between Points 1 and 4b (Fig. 4). ^{18}O content of the $BaCO_3$ precipitated from water samples is consistent with the results reported by Sanz, Bach and Trilla (1982) for an aquifer located near our study area.

$\delta^{13}C$ and $\delta^{18}O$ in Travertines (Table 2). Recently precipitated calcium carbonate has a higher $\delta^{13}C$ content than DIC, mainly because of the fractionation process during calcite precipitation. Considering an enrichment factor between bicarbonate, as the dominant carbon species, and calcite of 1.00185 ± 0.00023 at 20°C (Emrich, Ehhalt & Vogel 1970), the estimated values of $\delta^{13}C_{CaCO_3}$ are −11.07‰ at Point 2a and −8.67‰ at Point 4b.

TABLE 2. Stable isotope content in water and travertine

	Water				Travertine			
	July		October		Recent		Ancient	
Point	$\delta^{13}C$*	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
1	−14.53	−9.60	−14.25	−7.31	--	--	--	--
2a	−12.94	−8.28	−12.92	−7.16	−11.05	−6.21	−11.18	−6.16
2b	−12.13	−9.44	−12.74	−8.77	--	--	--	--
4a	--	--	−10.50	−7.40	−9.97	−5.98	−9.80	−5.93

*$\delta^{13}C$ and $\delta^{18}O$ are expressed in parts per mil (‰) with respect to standard PDB. The error is ± 0.05‰. (See Figure 2 for sampling point locations.)

Comparing the theoretical and experimental values (Table 2), we observe that the isotopic composition between both phases is in equilibrium at Point 2b. In contrast, a difference of 1.30‰ appears between the theoretical and experimental values of $\delta^{13}C_{CaCO_3}$ at Point 4b. Calcite precipitation in supersaturated solutions can be faster than the isotopic equilibrium process (Usdowsky, Hoefs & Menschel 1979), and may cause some differences in the stable isotope compositions of the solid calcium carbonate.

Thus, data indicate that non-equilibrium conditions exist during calcite precipitation, as evident from ^{13}C data, and suggest that the same effect must also be expected for the ^{14}C activity. If we assume that ^{14}C will have an enrichment factor twice that of ^{13}C (Craig 1953), the calculated difference will correspond to an increment of the ^{14}C activity <0.3 pMC, which is far smaller than the one standard deviation error (1 σ) of the measured ^{14}C activity.

Isotopic fractionation is also responsible for the differences existing between $\delta^{18}O$ in DIC and the precipitated calcium carbonate.

The similarity in $\delta^{13}C$ and $\delta^{18}O$ data between ancient and recent travertines supports the idea that both travertines formed under similar hydrological conditions. The similarity is significant to show that ancient and recent travertine ^{14}C data can be compared with an acceptable level of confidence.

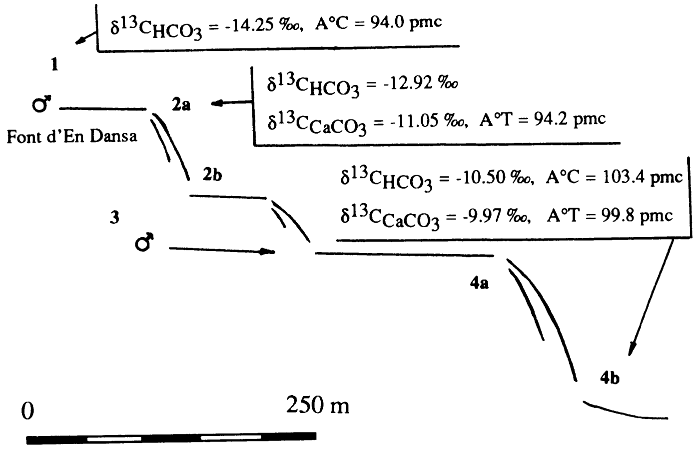

Fig. 4. Changes in the isotopical composition of water ($\delta^{13}C_{HCO_3}$ and A°C) and travertine ($\delta^{13}C_{CaCO_3}$ and A°T) along the monitored segment of the Torrent de Can Camps stream

Radiocarbon Activity in Water and Recent Travertines

We analyzed twice the ^{14}C activity of the DIC in the Font d'En Dansa spring, Point 1, in July and October 1989, and once at Point 4b, in October 1989. We also sampled recent travertines in Points 2a and 4b (Fig. 4).

^{14}C Activity of the DIC. Prior to the ^{14}C analysis, tritium content was measured in the spring samples. The average content was 21.6 ± 3 TU, which is close to the recent rainwater tritium content and indicates that groundwater has a short residence time in the aquifer. Thus, changes in the dissolved carbon ^{14}C activity cannot be justified by isotopic decay, and must be explained by geochemical processes.

Two measurements of the DIC ^{14}C activity at the Font d'En Dansa spring gave values of 96.6 ± 0.7 and 94.0 ± 0.8 pMC in July and October 1989, respectively. These activities are lower than 116 pMC, the atmospheric ^{14}C activity measured in areas of Barcelona and Alt Camp, Tarragona (J. S. Mestres and G. Rauret, personal communication 1990), indicating that calcite dissolution inside the aquifer did not occur under complete open-system conditions.

Tamers (1975) defined a correction factor for the initial ^{14}C activity of groundwater using the carbonate species concentration and assuming that dissolution occurred under closed-system conditions. Using the corresponding data for [HCO_3^-] and [CO_2 aq], the calculated correction factors are 0.60 in July and 0.58 in October. Accordingly, the ^{14}C activity of groundwater would be 69.6 and 67.3 pMC, respectively. These results are significantly lower than the measured activities. Thus, an entirely closed system during calcite dissolution cannot be assumed. Nevertheless, additional dissolution of CO_2 during seepage could explain higher ^{14}C activity of DIC.

We observed open-system conditions downstream from Point 1. As shown in Figure 4, an increase of the ^{14}C activity from 94.0 pMC at point 1 to 103.4 pMC at Point 4b was recorded in October 1989. Similar to the changes in $\delta^{13}C$ content, the increase of ^{14}C activity in surface water is attributed to the isotopic exchange between DIC and atmospheric CO_2. Because the turbulence and agitation of the runoff strongly influences the rate of exchange, the measured variations of the ^{14}C activity cannot be directly extrapolated to other streams where travertine formations occur.

^{14}C Activity in Recent Travertines. The ^{14}C activity in recent travertines precipitated at Points 2a and 4b are 94.2 ± 0.8 and 99.8 ± 0.8 pMC, respectively (Fig. 4). This represents an increment of 4.6 pMC between the two sampling points, in accordance with the postulated increase of the DIC activity along the water course.

Because of fractionation, we expect that the ^{14}C activity of the travertine is higher than the activity of the DIC. At Point 4b, where the two activities were measured, the activity of DIC was slightly higher than that of the travertine, contrary to what was expected. We think that this disagreement can be explained by the fact that DIC activity represents a single data point, whereas travertine activity is an average of several years. An extensive record of data would probably offer more accurate results.

Measured ^{14}C activities in the recent travertines at Points 2a and 4b were normalized to the standard activity of 100 pMC, yielding 81.2 and 86.0 pMC, respectively.

Radiocarbon Dating of the Ancient Travertines

^{14}C activity of the ancient travertines sampled in the uppermost layer of the so-called "old deposit" are 49.8 ± 0.5 pMC at Point 2a and 51.3 ± 0.5 pMC at Point 4b. The ^{14}C age of old travertine has been calculated using the initial ^{14}C activity 81.2 pMC for Point 2a and 86.0 pMC for Point 4b. The corresponding ages are 3930 ± 80 BP for Point 2b and 4150 ± 80 BP for Point 4b. Thus, the uppermost layers of the Llorà travertine formation date to approximately 4 ka BP. We conclude that this formation developed during the Holocene.

As the calculated initial ^{14}C activity is only an estimate, the magnitude of its error term can be evaluated. For example, assuming an error of ± 5 pMC for the initial ^{14}C activity at Point 2a (81.2 pMC), the positive error (+5 pMC) will give an age difference of −480 yr, and for the negative value (−5 pMC) the difference is 510 yr. It is worth noting that these errors are independent of the age of the sample.

CONCLUSIONS

We have investigated the ^{14}C activity of a recent travertine formation by studying the hydrochemical processes that change both isotopic and chemical compositions of the carbonate precipitating springwater. Chemical data show that calcium carbonate precipitation occurs once supersaturation has been reached as a result of the re-equilibration of the dissolved carbon species exposed to atmospheric conditions. Simultaneously, isotopic exchange between DIC and atmospheric CO_2 takes place as water flows from the spring, thus modifying groundwater isotopic composition to approach that of the atmosphere. As a result, the ^{14}C activity of the precipitated calcium carbonate becomes a function of the rate of both reactions or, simply, the distance from the spring.

We have recorded a ^{14}C activity difference of 4.8 pMC in recently precipitated travertines between two points 400 m apart in the same stream. We used different initial ^{14}C activities (81.2 and 86 pMC) to obtain the corrected ^{14}C age of the two samples of ancient travertines. Similarity of the two results indicates travertine formation around 4 ka BP.

A locality where recent and ancient travertines coexist is necessary for the application of the described method. Further, the initial ^{14}C activity is site-specific and cannot be applied to different travertine formations because of differences in hydrology. Consequently, the use of an estimated average value seems to be unavoidable. From our study, an initial ^{14}C activity of 85 pMC appears to be an adequate approximation, and it agrees with the findings of Srdoč *et al.* (1986). Nevertheless, the interpretation of the absolute ages must consider ^{14}C activity variations with distance in larger travertine deposits. It is worth noting that the older the sample, the less significant is the error.

We finally conclude that ^{14}C dating of travertines precipitated from freshwater must be considered approximate, useful in determining geochronological ages, but unsuitable for obtaining chronological sequences or precise correlations.

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REFERENCES

Chafetz, H. S. and Folk P. L. 1984 Travertines: Depositional morphology and the bacterially constructed constituents. *Journal of Sedimentary Petrology* 54 (1): 289–316.

Craig, H. 1953 Carbon 13 in plants and the relationship between carbon 13 and carbon 14 in nature. *Journal of Geology* 62: 115–149.

Dandurand, J. L., Gout, R., Hoefs, J., Menschell, G., Schott, J. and Usdowsky, E. 1982 Kinetically controlled variations of major components and carbon and oxygen isotopes in a calcite-precipitating spring. *Chemical Geology* 36: 299–315.

Deines, P., Langmuir, D. and Harmon R. S. 1974 Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate ground waters. *Geochimica and Cosmochimica Acta* 38: 1147–1164.

Emrich, K., Ehhalt, D. H. and Vogel, J. C. 1970 Carbon isotope fractionation during the precipitation of calcium carbonate. *Earth and Planetary Science Letters* 8: 363–371.

IAEA 1984 Muestreo de aguas para análisis de carbono 14. Isotope Hydrology Section, International Atomic Energy Agency. Laboratory report.

Jacobson, R. L. and Usdowsky, E. 1975 Geochemical controls on a calcite precipitating spring. *Contributions to Mineralogy and Petrology* 51: 65–74.

Mas, J., Trilla, J., Valls, M. L. and Pallí, L. 1991 Cronologia de les formacions travertíniques de Llorà (Girona). *Scientia Gerundensis* 17: 91–104.

Münnich, K. O. 1957 Messung des ^{14}C-Gehaltes von hartem Groundwasser. *Naturwissenshaften* 44: 32–38.

Pallí, L. 1972 *Estratigrafía del Paleogeno del Empordà y Zonas Limítrofes.* Publication of the Universitat Autónoma de Barcelona 1: 388 pp.

Plummer, L. N., Jones, B. F. and Truesdell, A. H. 1976 WATEQF – A FORTRAN IV version of WATEQ. *U.S. Geological Survey Water Resources Investigation* 76–13: 61 p.

Ríos, M. and Masachs, V. 1953 Mapa geológico "Banyoles" 295. Madrid, IGME.

Sanz, M., Bach, J. and Trilla, J. 1982 Aplicación del oxígeno 18 al sistema cárstico de Banyoles-La Garrotxa. *Reunión Monográfica Sobre el Karst.* Larra.

Srdoč, D., Krajcar-Bronić, I., Horvatinčić, N., and Obelić, B. 1986 Increase of ^{14}C activity of dissolved inorganic carbon along a river course. *In* Stuiver, M. and Kra, R. S., eds., Proceedings of the 12th International ^{14}C Conference. *Radiocarbon* 28(2A): 515–521.

Tamers, M. A. 1975 Validity of radiocarbon dates on groundwater. *Geophysical Survey* 2: 217–239.

Usdowsky, E., Hoefs, J. and Menschel, G. 1979 Relationship between C-13 and O-18 fractionation and changes in major element composition in a recent calcite-depositing spring. *Earth and Planetary Science Letters* 42: 267–276.

Wigley, T. M. L. 1975 Carbon 14 dating of groundwater from closed and open systems. *Water Resources Research* II(2): 324–328.