RADIOCARBON DATING OF TRAVERTINE DEPOSITS, ARBUCKLE MOUNTAINS, OKLAHOMA

DUŠAN SRDOČ

Ruđer Bošković Institute, P O Box 1016, 41001 Zagreb, Yugoslavia

HENRY CHAFETZ and NANCY UTECH

Department of Geosciences, University of Houston
Houston, Texas 77004

ABSTRACT. Travertine deposits occur abundantly at past and present sites of waterfalls in the Arbuckle Mountains region of Oklahoma. This area ($1600km^2$) consists of folded and faulted Prepaleozoic and Paleozoic rocks, with abundant outcrops of Paleozoic carbonate rocks. Samples of recently deposited and old travertine from the Turner Falls area were collected during a 1987 field trip and analyzed for ^{13}C, ^{14}C and ^{18}O content. The aquatic chemistry of travertine depositing creeks was investigated systematically and compared with those of similar areas in SE and central Europe.

INTRODUCTION

^{14}C dating of old solidified travertine which forms the Turner Falls dam revealed a pre-Holocene deposit, beyond ^{14}C dating limits. Freshly deposited calcareous mud contains ca 110% modern carbon, part of which is due to bomb-produced ^{14}C. The negative $\delta^{13}C$ values of calcareous deposits of carbonate bedrock prove that part of the carbon in travertine is of biogenic origin, thus making ^{14}C dating feasible. Samples of recent calcareous deposits contains a large proportion of calcite depositing micro-organisms, especially *Oocardium stratum,* indicating biogenically induced precipitation of calcite.

GEOLOGIC SETTING

The travertine deposits comprising this study lie within the Arbuckle Mountains of south-central Oklahoma (Fig 1). The area, ca $1600km^2$, consists of an inlier of folded and faulted Prepaleozoic and Palozoic rocks juxtaposed between the Wichita Mountains to the west and the Ouachita Mountains to the east. Geologically, the Arbuckle Mountains are most widely recognized for substantial outcrops of Paleozoic carbonate rocks exposed as a result of a tumultuous past. Roadcuts along US Interstate 35 between Davis and Ardmore attest to this eventful history as the strata stand in a nearly vertical position.

The 3.5km of Cambrian through Devonian strata comprise the largest exposed area of this sequence in the southern midcontinent region, with sizeable exposures of Prepaleozoic granites, Cambrian rhyolites, and Pennsylvanian conglomerates (Ham, 1973).

The massive accumulation of Paleozoic carbonate rocks, in particular the Ordovician Arbuckle Group, is significant with respect to the travertine deposits. As meteoric water seeps down through crevices into this stratum, the water becomes charged with ions (including Ca^{2+}, Mg^{2+} and HCO_3^-) derived from dissolution of the limestone. This ionically charged water
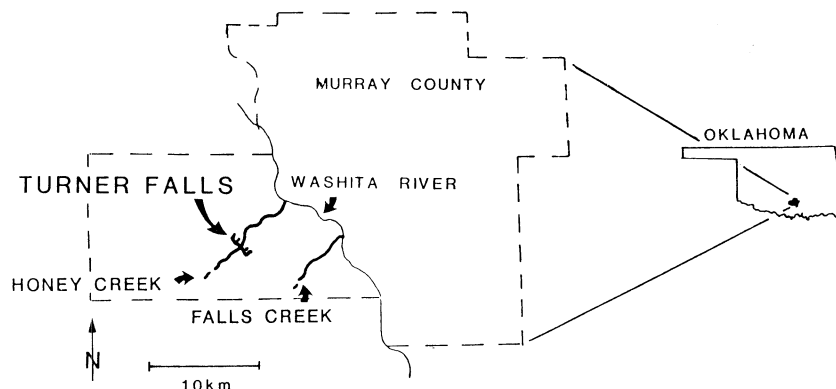
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Fig 1. Location of study site

moves underground along faults and eventually emerges as springs, which feed the streams from which the travertine precipitates.

The travertine deposits of Turner Falls show a very pronounced similarity in morphology with travertine of Czechoslovakia and Yugoslavia. The aquatic chemistry of travertine-depositing streams and the isotopic content of calcareous deposits from the Turner Falls area are compared with those of Plitvice National Park in Yugoslavia and of Český Kras in Chechoslovakia.

CLIMATE

The Arbuckle Mountains are situated near the western edge of the humid, subtropical climatic zone and the eastern edge of the semi-arid climatic zone (Steila, Wilms & Leahy, 1981; Jackson & Hudman, 1982). Annual mean precipitation is 95cm; monthly mean precipitation is highest in April, May and September and lowest in January and February (Robinson & Curtis, 1968).The annual mean temperature is ca 17°C; the daily mean temperature is highest from June through August (ca 27°C) and lowest from December through February (ca 7°C) (Robinson & Curtis, 1868).

ISOTOPIC MEASUREMENTS

The number of analyzed samples of travertine from Turner Falls was rather modest, when compared with >500 analyzed samples from Europe. We first analyzed stable isotopes (^{13}C, ^{18}O and ^{14}C) of recent soft calcareous deposits and old solidified travertine to determine the origin and the datability of the travertine. We conducted our work at the Jožef Stefan Institute (Ljubljana) and Ruđer Bošković Institute (Zagreb), respectively.

As opposed to travertines deposited from freshwater around orifices of (often hot) springs, which do not contain measurable concentrations of ^{14}C and have δ^{13}C close to the aquifer matrix value, samples of recent travertine from the Turner Falls area contain a significant concentration of ^{14}C and are depleted in ^{13}C *vs* the PDB standard. Therefore, the Arbuckle Travertine belongs to the same group as in Yugoslavia (Srdoč *et al*, 1987) and Czechoslovakia (Horvatinčić *et al*, 1989). Both ^{13}C and ^{14}C analyses confirmed that part of the carbon in the Turner Falls travertine is of biogenic origin in accor-

dance with the assumed mechanism of dissolution and subsequent precipitation of calcium carbonate (Srdoč *et al*, 1985; Emeis, Richnow & Kempe, 1987).

The $\delta^{18}O$ values from Turner Falls travertine clustered ca $-5.0\pm0.6‰$ *vs* PDB. The difference between the old and the recent travertine $\delta^{18}O$ values was 0.8‰ indicating fairly constant climatic and hydrologic conditions during the calcite precipitation periods. The influence of climate on the chemistry of carbonate groundwater has been studied extensively (Drake & Wigley, 1975; Drake, 1983) as well as the seasonal fluctuations in chemistry of springwater in karst (Srdoč *et al*, 1985) and limestone areas (Shuster & White, 1971). Whereas seasonal fluctuations in chemical and isotopic composition of springwater do not influence the ^{14}C age of large samples of travertine ($\sim$50–100g) needed for conventional ^{14}C dating, long-term changes of climate may introduce an error in ^{14}C age calculation commensurate with the change of ^{14}C activity of groundwater at the time of formation of calcareous deposit. According to $\delta^{18}O$ values, no major changes in isotopic composition of groundwater occurred during the Holocene; thus, we consider ^{14}C dating of travertines from that period quite reliable, as opposed to old, preglacial travertines. In the latter case, several factors, such as unknown groundwater ^{14}C activity, contamination of samples with recent carbonates and low ^{14}C activity of old samples in general, render ^{14}C dating of old travertines unreliable and sometimes even misleading (Horvatinčić *et al*, 1986). In such cases, the $^{230}Th/^{234}U$ dating method may help, providing that adequate samples of clean crystallized calcite embedded in a travertine matrix can be found, and assuming that both travertine and crystallized calcite (eg, in the form of flowstone) were formed within a short period compared to the age of the travertine matrix.

The measured $\delta^{13}C$ values of old and recent travertine ranged between $-7.0‰$ and $-7.8‰$ *vs* PDB standard. The more negative $\delta^{13}C$ values of carbonate bedrock stem from the contribution of biogenically evolved CO_2 from the topsoil, which has $\delta^{13}C$ equal to vegetation ($-24‰$ for C3 plants). The dissolution of mineral carbonates ($\delta^{13}C = 0.0\pm1 \ldots 3‰$ *vs* PDB) by H_2CO_3 derived from decomposed plant detritus in the topsoil ($\delta^{13}C$ $-24‰$ *vs* PDB) results in an intermediate $\delta^{13}C$ value of dissolved inorganic carbon (DIC) in groundwater. Subsequent precipitation of calcite in the form of travertine does not significantly change isotopic content of the precipitate.

The variable content of ^{13}C ($\delta^{13}C = -7.1 \ldots -12.8‰$) and ^{14}C (82 $\ldots$ 113% modern) for travertines shown in Table 1 reflects the extent of the dissolution-exchange process during the seepage of precipitation water, as described by Mook (1976). In principle, the $\delta^{13}C$ values and chemical data listed in Table 1 can be used to calculate the initial activity of deposited travertine (Tamers, 1967; Pearson & Hanshaw, 1970; Mook, 1976; Fontes, 1983). However, the exchange between the dissolved CO_2 in groundwater and the atmospheric CO_2 in the cavernous karstic underground often renders these calculations useless as shown by Krajcar-Bronić *et al* (1986). Thus, we did not attempt to calculate the initial activity of travertines. For a detailed study of physico-chemical and isotopic processes that occur in ground and surface waters, the reader is referred to Wigley, Plummer and Pearson (1987) and Dandurand *et al* (1982).

TABLE 1

The comparison of isotopic and chemical composition of DIC in several calcite-depositing streams of North America and Europe

	Isotopic analyses				Chemical analyses						
Sampling location	^{14}C activity (% modern) water	recent tufa	$\delta^{13}C$ (‰ vs PDB)	^{3}H (Bq/l)	t (°C)	pH	CO_2 $\log P_{CO_2}$ (atm)	HCO_3^- (mmole/l)	Ca (mmole/l)	Mg (mmole/l)	I_{sat} (IAP/K_{CaCO_3})
North America											
United States											
Honey Creek											
- 1. headwater	109.0±1.5		-7.1±0.4		17.30	7.23	-1.70	5.65	2.10	0.16	1.46
- 2. Turner Falls, 4 km downstream from headwater					19.20	8.30	-2.83	4.88	1.35	0.27	9.79
Falls Creek											
- 1. (see map)	113.0±1.5		-7.74±0.4		18.10	7.96	-2.93	5.40	1.35	0.49	4.76
- 2. (see map)					21.10	8.25	-2.74	5.14	1.32	0.51	9.56
Europe											
Czechoslovakia											
Cisarska rokle	78.7±1.2			4.7±0.2							
- spring		81.8±1.2	-9.27±0.4		9.7	7.35	-1.86	5.78	3.3	0.7	2.30
- 150 m downstream		89.2±1.2	-7.12±0.4		9.2	8.02					
- 300 m downstream											
Koda near Srbsko	87.1±1.1			5.7±0.2							
- spring		91.9±1.3	-9.03±0.4		10.8	7.4	-1.92	5.67	3.92	0.5	3.12
- 300 m downstream					10.3	8.13	-2.78	4.28	3.06	0.38	9.72
Yugoslavia											
Plitvica	82.5±0.9		-12.8±0.8	3.1±0.2							
- spring		86.8±0.7			7.3	7.60	-2.22	4.56	1.53	0.9	1.35
- 3 km downstream		91.2±0.7			7.3	8.20	-2.87	4.56	1.43	0.93	5.89
- 5 km downstream					8.7	8.34	-2.98	4.34	1.44	0.89	6.83
Bijela rijeka	82.7±2.4		-12.8±0.4	4.1±0.2							
- Spring		85.3±0.8			7.5	7.46	-2.05	4.87	1.46	1.17	0.99
- 2 km downsream					7.9	7.80	-2.37	4.65	1.38	1.11	2.10

The ^{14}C activity of recently deposited calcite from Honey Creek substantiated the conclusion about the biogenic origin of travertine. The ^{14}C activity ranged from 109–113 pMC, part of which should be attributed to bomb-produced ^{14}C in the atmosphere. ^{14}C was incorporated in travertine in much the same way as ^{13}C. ^{14}C dating of travertine is made possible by its radioactive decay within the time scale of the method (Srdoč *et al*, 1980).

The initial ^{14}C activity of recently deposited calcite is distorted by bomb-produced ^{14}C and cannot be used for age correction of older travertine. This correction – usually of the order of one up to several thousand years – becomes less significant for very old samples. It turned out that the age of solid travertine from the Turner Falls barrier exceeds the lower limit of the ^{14}C dating method where any age correction is irrelevant. The true age of the formation of the Turner Falls travertine barrier cannot be determined by ^{14}C dating. By analogy with similar travertine deposits in Europe (Srdoč *et al*, 1985) this pre-Holocene barrier was most likely built during the last interglacial.

PHYSICO-CHEMICAL CONDITIONS FOR CALCITE PRECIPITATION

The concurrent studies of travertine (or tufa) formation in Yugoslavia (Srdoč *et al*, 1985) and Czechoslovakia (Horvatinčić *et al*, 1989) resulted in relatively well-defined physico-chemical conditions for calcite precipitation in freshwater. Basically, the following conditions were satisfied at all sites in karst areas of both countries where calcite was copiously precipitated in the form of tufa or lake sediment:

1) The water must be supersaturated with calcium carbonate; the saturation index (I_{sat} = IAP/K) must exceed 3. Most streams and lakes where intensive precipitation of calcite occurs have saturation indexes of 5–7.

2) The pH value must be over 8.0; mostly, the pH is between 8.2–8.4 at locations of intensive calcite precipitation.

3) The concentration of dissolved carbon (DOC), consisting in non-polluted waters mostly of humic and fulvic acids, must not exceed several mg/L of carbon.

The increase of I_{sat} accompanied by the rise of pH is a consequence of CO_2 outgassing (Herman, 1987). According to our observations, the actual precipitation of calcium carbonate does not occur spontaneously. Recent research (Chafetz & Folk, 1984; Srdoč *et al*, 1985; Emeis, Richnow & Kempe, 1987) showed that *biota* play a decisive role in travertine buildup, as well as in nucleation of calcite crystals which form lake sediments. Travertine from Plitvice National Park, Yugoslavia, contains numerous species of diatoms, whereas a sample of recently deposited mud from Honey Creek is composed of calcareous remains of *Oocardium stratum*.

The reasons calcite precipitation stopped despite persistent supersaturation along the water course in the lowland areas remain obscure. We found that all streams in which calcite does not precipitate despite high I_{sat}, share a common feature: their DOC level is several times higher (up to 10) than the DOC in carbonate-precipitating waters. This was demonstrated by DOC measurements along the Korana River in Yugoslavia (Srdoč *et al*, 1985), where abundant calcite precipitation ceased near the point where DOC con-

centration reached 10mg/L, the other parameters (I_{sat}, pH) remaining essentially constant. Due to the short course of travertine-depositing creeks, this phenomenon was not confirmed in Turner Falls. It is assumed that a high level of DOC inhibits the precipitation of calcite in a way similar to that observed in a marine environment (Chave & Suess, 1970).

Chemical analyses of stream water of calcite-precipitating creeks in the Arbuckle Mountains (Honey Creek, Falls Creek) showed a remarkable similarity, as far as conditions for calcite precipitation are concerned, with calcite-precipitating streams of SE and central Europe. A comparison is given in Table 1, showing results of isotopic analyses, *in situ* measurements of temperature and pH, concentrations of major ionic species and the calculated

TABLE 2

The comparison of predicted and observed calcite precipitation from streamwaters at several sites in North America and Europe

Sampling location	pH	I_{sat}	DOC* (mg/L)	Calcite precipitation** (in form of tufa or travertine)	
				Predicted	Observed
North America					
United States					
Honey Creek					
– 1. Headwater	7.23	1.46	5.2†	No	No precipitation
– 2. Turner Falls, 4 km downstream from headwater	8.30†	9.79†	5.2†	Yes	Very intensive precipitation
Falls Creek					
– 1. (see map)	7.96	4.76†	22.9	No	Weak precipitation
– 2. (see map)	8.25†	9.56†	2.67†	Yes	Intensive precipitation
Europe					
Czechoslovakia					
Koda near Srbsko					
– spring	7.4	3.12	10†	No	No precipitation
– 300 m downstream	8.13†	9.72†	10†	Yes	Precipitation
Yugoslavia					
Plitvica					
– spring	7.60	1.35	2.0†	No	No precipitation
– 3 km downstream	8.20†	5.89†	2.5†	Yes	Weak precipitation
– 5 km downstream from the spring	8.34†	6.83†	3.5†	Yes	Intensive precipitation
Bijela rijeka					
– spring	7.46	0.99	2.0†	No	No precipitation
– 2 km downstream	7.80	2.10	2.5†	No	No precipitation
– 6 km downstream from the spring	8.2†	5.1†	2.5†	Yes	Intensive precipitation

* DOC = dissolved organic carbon in water
** Calcite will start to precipitate when pH and I_{sat} exceed a certain level (8.2 and 3, respectively, in temperate zones), and the concentration of DOC is <10mg/L
† Denotes conditions favoring calcite precipitation

index of saturation. The conditions for calcite precipitation may vary slightly from site to site. Table 2 shows a comparison of physico-chemical conditions for calcite precipitation for areas in the US, Czechoslovakia and Yugoslavia.

The differences in pH and I_{sat} values for various sites (Table 2) can be explained by the variability of geomorphologic and especially climatic characteristics of each site, eg, the mean annual temperature is 17°C in the Arbuckle Mountains *vs* 8° at Plitvice National Park.

CONCLUSIONS

Although the actual mechanism of calcite deposition (pure chemical or biogenically induced) does not influence the ^{14}C dating of travertine, it is interesting to note that *biota* played a dominant role in Arbuckle Mountains travertine formation. Algological analysis (Marčenko, pers commun, 1987) revealed that the largest fraction of calcareous deposit consists of calcite encrustion of *Oocardium stratum,* an alga known for its ability to form a calcite sheath around soft tissue.

Isotopic composition of carbon from travertine confirms biogenic origin of calcite (which makes up 97% of dry material) and enables ^{14}C dating of travertine within the range of the method. Physico-chemical conditions for calcite precipitation from freshwaters seems to be very stringent, notably the calcite supersaturation and pH.

The role of biota and DOC was prominent. Whereas micro-organisms (mostly algae and cyanobacteriae) serve as nucleation centers, promoting calcite precipitation, a high DOC concentration, >10mg/L, inhibits calcite precipitation and subsequent formation of travertine.

ACKNOWLEDGMENTS

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