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Uranium-series dating of some travertins from the southwestern flank of Mt. Etna

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ABSTRACT. — ^{230}Th and ^{226}Ra methods were used to date some travertins outcropping on the southwestern flank of Mt. Etna, in the area stretching from the towns of Adrano and Biancavilla to the Simeto river. Three date groups were determined: around 20,000 ÷ 24,000 yr, 8,000 ÷ 9,000 yr and 5,000 ÷ 6,000 yr. These ages were correlated with possible volcanic events and related tectonic activity, which may have induced water circulation from which travertin deposited.

Key words: Geochronology, Disequilibria, Travertins, Volcanism, Etna.

RIASSUNTO. — I metodi del ^{230}Th e del ^{226}Ra sono stati impiegati per datare alcuni travertini che affiorano sul versante sudoccidentale dell'Etna, nell'area compresa fra gli abitati di Adrano e Biancavilla, ed il Fiume Simeto. Vengono messi in evidenza tre gruppi di date, attorno ai 20.000 ÷ 24.000 anni, attorno ai 8.000 ÷ 9.000 anni, ed attorno ai 5.000 ÷ 6.000 anni. Queste età vengono messe in relazione ai possibili eventi vulcanici ed al tettonismo ad essi connesso, che possono avere influenzato la circolazione delle acque dalle quali si è depositato il travertino.

Parole chiave: Geocronologia, Disequilibrio, Travertini, Vulcanismo, Etna.

Introduction

Application of the ^{230}Th method to dating of carbonates with high insoluble residue requires corrections for amount of Th (232 and 230) leached by sample dissolution (KU, 1979), (KU and LIANG, 1984 a, 1984 b,), (SCHWARCZ, 1979, 1980), (SCHWARCZ and LATHAM, 1984). On this basis, a chronological study was conducted on some travertins outcropping on the southwestern flank of Mt. Etna. The age of very young material (few thousand yr) was checked by measuring ^{226}Ra activity, whose half-life (1,622 yr) is particularly suitable for ages in this range.

It is reasonable to suppose that travertin deposition was connected with volcanic events allowing upsurge of waters which became enriched with carbonates through interaction with the limestones contained in the «sulphur series». As a result, an attempt was made to correlate ages of the travertins and related volcanic events.

Sampling sites are exhibited in Fig. 1. The travertin area covers a surface of approx. 4 Km^2, extending from the towns of Adrano and Biancavilla to the Simeto river. Here is a detailed list of the samples investigated:

— «Contrada Barcavecchia». A travertin bed, about 6 m-thick, covers an alkali-basalt lava flow, whose morphological discontinuities are sometimes filled with alluvia. The upper

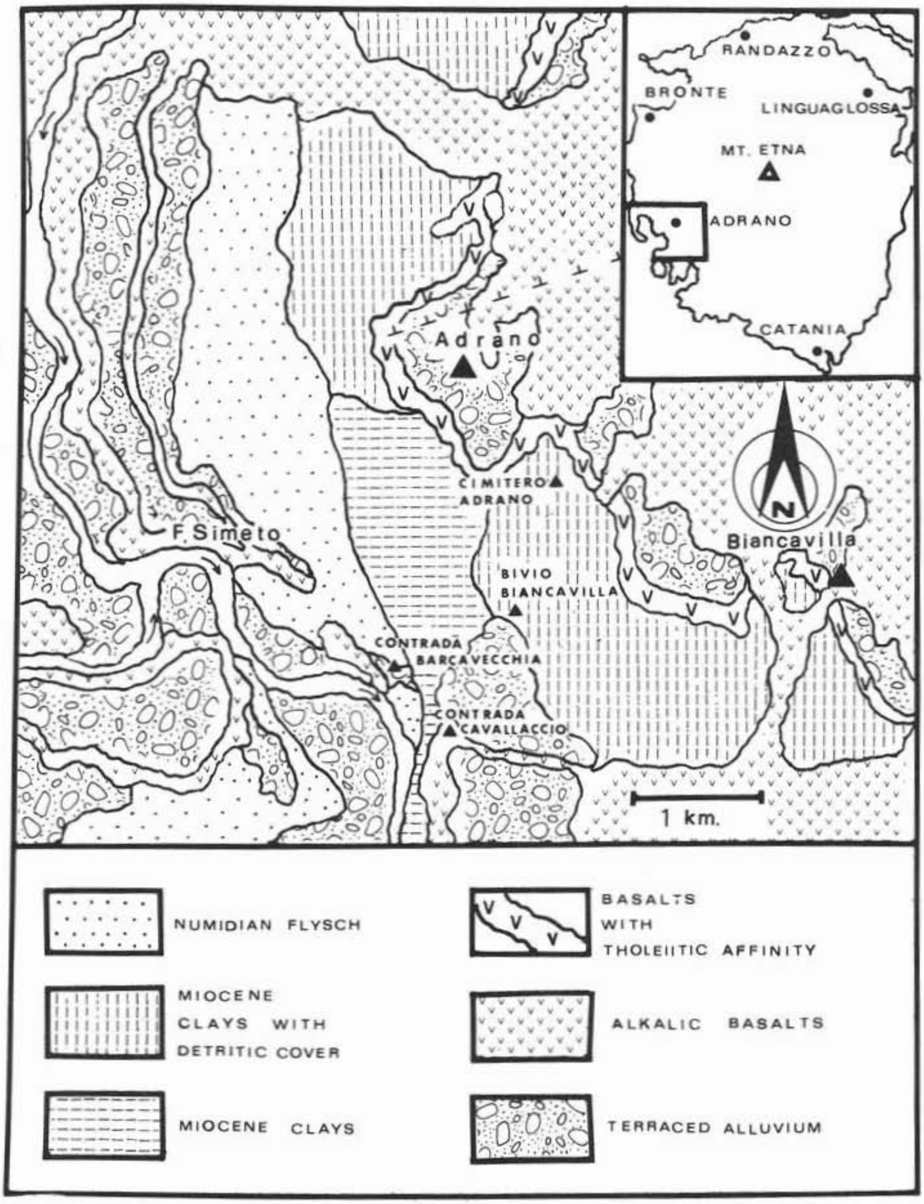

Fig. 1. — Geological sketch of the area and sampling location.

portion of the travertin is interbedded with two levels, approx. 40 cm-thick consisting in fine grain-sized pyroclastics; these levels will be hereafter referred to as «cineritic levels». The two cineritic levels are separated by roughly 40 cm of travertin. The samples collected are as follows (Fig. 2):

CBV 1a, CBV 1b — At the bottom of the bed, just above the underlying alluvia.

CBV 2 — In the upper portion of the bed, just below the lower cineritic level.

CBV 3a, CBV 3b, CBV 3c, CBV 3d — in the lower portion of the travertin layer separating the two cineritic levels. Here, some small gastropods were found: *Lymnea truncatula* (Müller), *Pseudamnicola moussoni* (Calcara) and *Succinea elegans* (Risso), typical of a fresh water environment.

— «Contrada Cavallaccio». A 1 m-thick travertin bed was deposited over an alkali-basalt lava flow. The samples collected are as follows (Fig. 3):

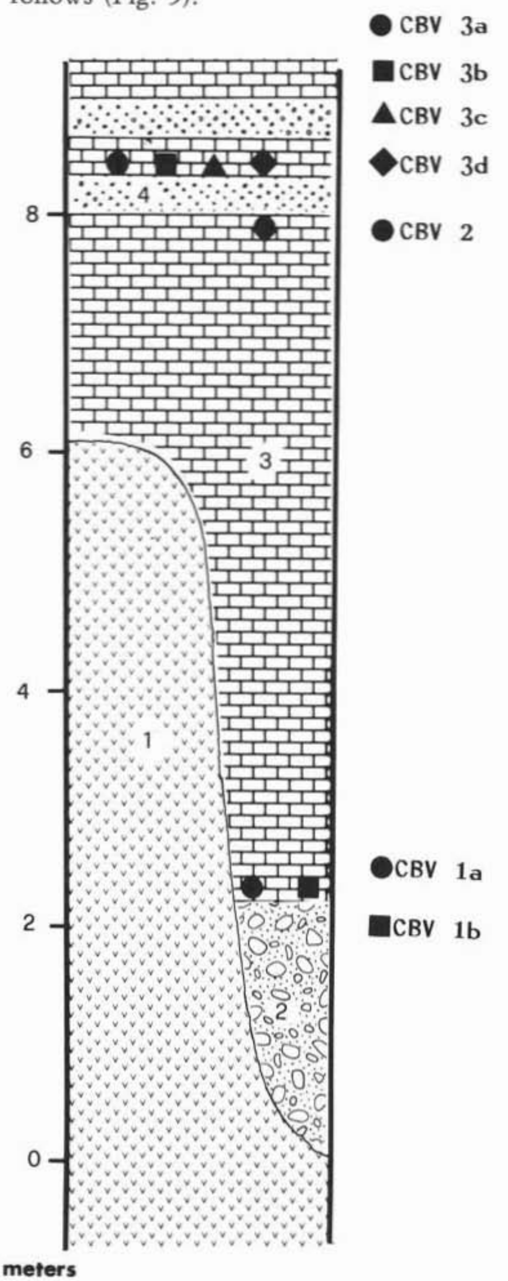

Fig. 2. — Stratigraphic column and sampling location at «Contrada Barcavecchia» (see text). 1: Lava; 2: Alluvia; 3: Travertin; 4: Cineritic levels.

TABLE 1

Uranium and thorium content as measured in the residues from the analysed samples and as calculated in their carbonate fraction

Sample	U_{ppm} (carb.)	% Resid.	U_{ppm} (res.)	Th_{ppm} (res.)	Th/U (res.)
CBV 1a	0.87	21.0	4.63	4.59	0.99
CBV 1b	1.53	22.0	1.18	4.43	3.75
CBV 2	2.84	27.8	1.13	3.23	2.86
CBV 3d	0.38	46.5	1.33	4.21	3.17
CC a	1.59	46.8	2.38	3.93	1.65
CC b	1.16	25.8	1.21	3.64	3.00
AD a	1.41	6.7	0.12	0.32	2.67
AD b	1.34	7.7	0.49	1.91	3.89
BBi	2.38	11.4	1.42	4.34	3.06

— CCa, CCb — In the upper portion of the bed.

— «Cimitero di Adrano». A 2 m-thick travertin bed rests on Miocene clays, just as do some basaltic lavas with tholeiitic affinity, which outcrop further N, a few hundreds of meters away. The travertin is covered with slumping alluvia. The samples collected are as follows (Fig. 4):

— ADa, ADb - In the upper portion of the bed, just below alluvia.

— «Bivio Biancavilla». In this area, the soil consists in alluvia slumping over Miocene clays; numerous lava blocks are encountered (basalt with tholeiitic affinity), which are coated with travertin material; deposition of this material can be observed along the small

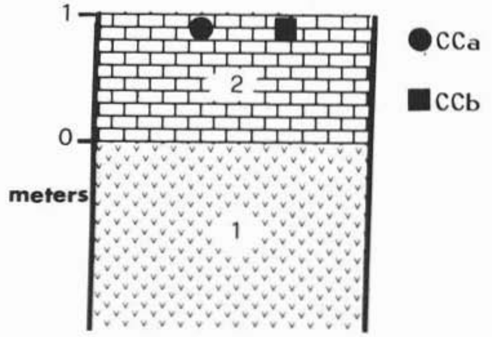

Fig. 3. — Stratigraphic column and sampling location at «Contrada Cavallaccio» (see text). 1: Lava; 2: Travertin.

TABLE 2

Isotopic composition (dpm/g); activity ratios calculated for the carbonate fractions according to KU *and* LIANG *(1984 b) and (*) according to* SCHWARCZ *(1980); ages (years ± 1 σ)*

Sample	^{234}U	^{238}U	^{230}Th	^{232}Th	$^{230}Th/^{234}U$	$^{234}U/^{238}U$	Age
CBV 1a Leached	1.266 ±0.016	1.263 ±0.016	0.318 ±0.005	0.197 ±0.004	0.198 ±0.032	0.974 ±0.098	24,000 ±4,000
CBV 1a Residue	3.540 ±0.078	3.431 ±0.075	1.094 ±0.061	1.092 ±0.061			
CBV 1b Leached	1.502 ±0.048	1.422 ±0.045	0.444 ±0.016	0.289 ±0.013	0.167 ±0.024	1.133 ±0.077	19,800 ±3,200
CBV 1b Residue	0.813 ±0.024	0.875 ±0.026	0.863 ±0.025	1.054 ±0.028			
CBV 2 Leached	2.333 ±0.032	2.286 ±0.031	0.273 ±0.011	0.170 ±0.008	0.056 ±0.005	1.030 ±0.077	6,300 ±1,300
CBV 2 Residue	0.766 ±0.034	0.839 ±0.037	0.754 ±0.052	0.769 ±0.052			
CBV 3a W.R.	0.798 ±0.013	0.784 ±0.012	0.473 ±0.015	0.567 ±0.016			
CBV 3b W.R.	0.979 ±0.014	1.016 ±0.015	0.631 ±0.018	0.745 ±0.020	(*) 0.048 ±0.052	(*) 1.020 ±0.212	5,300 ±5,300
CBV 3c W.R.	0.907 ±0.011	0.904 ±0.011	0.555 ±0.017	0.674 ±0.018			
CBV 3d W.R.	0.978 ±0.028	0.982 ±0.028	0.823 ±0.025	1.003 ±0.031	0.051 ±0.026	1.096 ±0.106	5,700 ±3,000
CBV 3d Leached	0.450 ±0.007	0.441 ±0.007	0.150 ±0.005	0.165 ±0.006			

stream flowing along the road. The following sample was collected here:

— BBi — This represents an approx. 1 cm-thick travertin incrustation covering the volcanic alluvia.

Methods

Elementary and isotopic composition of uranium and thorium was determined via α-spectrometry with a method now commonly in use (GASCOYNE et al. 1978). Ages were computed by accounting for the ^{230}Th from the non-carbonate fraction, based on the methods suggested by KU and LIANG (1984 b) and SCHWARCZ (1980).

^{226}Ra activity was also determined via α-spectrometry, after separating the isotopic complex of radium according to the KOIDE and BRULAND method (1975). The ^{224}Ra contained in the material was used as internal spike.

Experimental results and discussion

Analytical results on uranium and thorium content of the material investigated are displayed in Table 1; those on isotopic composition of these elements, as well as on sample ages are shown in Table 2; those relevant to radium measurements are exhibited in Table 3.

Uranium in carbonates

The first column of Table 1 shows uranium concentrations calculated in the travertin car-

(Table 2 continued)

Sample	^{234}U	^{238}U	^{230}Th	^{232}Th	$^{230}Th/^{234}U$	$^{234}U/^{238}U$	Age
CC a Leached	1.754 ±0.019	1.685 ±0.019	0.384 ±0.010	0.271 ±0.009	0.082 ±0.017	1.057 ±0.074	9,300 ±2,000
CC a Residue	1.768 ±0.023	1.759 ±0.023	0.891 ±0.028	0.936 ±0.030			
CC b Leached	1.161 ±0.018	1.151 ±0.018	0.379 ±0.015	0.280 ±0.012	0.073 ±0.024	1.008 ±0.080	8,200 ±2,800
CC b Residue	0.906 ±0.026	0.896 ±0.026	0.982 ±0.028	0.867 ±0.025			
AD a Leached	1.117 ±0.009	1.073 ±0.009	0.115 ±0.003	0.025 ±0.001	0.073 ±0.006	1.043 ±0.060	8,200 ± 700
AD a Residue	0.073 ±0.005	0.092 ±0.008	0.114 ±0.005	0.077 ±0.005			
AD b Leached	1.082 ±0.017	1.006 ±0.016	0.101 ±0.003	0.017 ±0.001	0.074 ±0.008	1.086 ±0.090	8,400 ± 900
AD b Residue	0.367 ±0.017	0.366 ±0.017	0.635 ±0.020	0.456 ±0.018			
BBi Leached	1.868 ±0.041	1.812 ±0.040	0.146 ±0.005	0.051 ±0.003	0.036 ±0.007	1.025 ±0.061	4,000 ± 700
BBi Residue	1.104 ±0.028	1.048 ±0.027	1.664 ±0.070	1.035 ±0.055			

bonate fraction. These concentrations appear to be quite homogeneous, except for samples CBV 3d and perhaps CBV 1a, which are significantly poorer in this element. This non-homogeneity can be ascribed to: 1) different amount of uranium in the waters, which may in turn depend on lithotypes with which they interacted and on residence time; 2) possible presence of a uranium-rich soluble phase (organic matter ?). However, as shown in Table 2, the initial $^{234}U/^{238}U$ activity ratio remains more or less constant in all the materials.

^{230}Th chronology

Fig. 2 shows the stratigraphic column of the travertins collected from «Contrada Barcavecchia». The significant error in age computation of samples CBV 1a and CBV 1b (collected from the bottom of the travertin formation) is definitely due to their high isoluble residue (21 ÷ 22%); within this error, ages are consistent.

Indirect dating of the lower one of the two cineritic levels in the upper part of the travertin bed is of particular interest.

TABLE 3

Excess $^{226}Ra^*$ (dpm/g) as measured in the leached and residual fractions and as calculated for the carbonate fractions. Activity ratio for the two carbonates, and age difference (yeras ± 1 σ)

Sample	$^{226}Ra^*$ Leach.	$^{226}Ra^*$ Resid.	$^{226}Ra^*$ Carb.	$^{226}Ra^*(BBi)/^{226}Ra^*(CBV)$	ΔT
CBV 3d	0.466 ±0.045	1.374 ±0.083	0.320 ±0.045	1.916 ±0.320	1,500 ± 250
BBi	0.625 ±0.050	0.860 ±0.052	0.613 ±0.055		

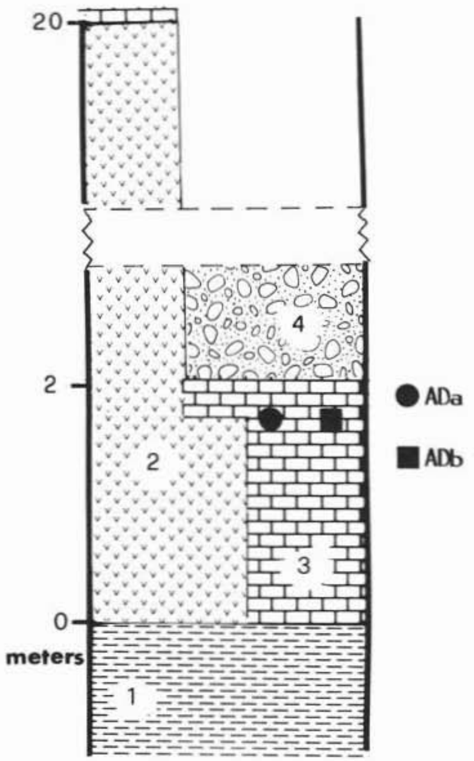

Fig. 4. — Stratigraphic column and sampling location at «Cimitero di Adrano» (see text). 1: Miocene clays; 2: Lava; 3: Travertin; 4: Alluvia.

Sample CBV 2 (collected just below this level) is approx. 6,000 yr old: immediately overlying samples (CBV 3a, CBV 3b, CBV 3c and CBV 3d) yield a 5,300 yr date, corrected with the method proposed by SCHWARCZ and a 5,700 yr date, corrected with the KU and LIANG one. Both dates have a considerable error, owing to the large amount of cineritic material in the travertin. Furthermore, as regard the date corrected according to SCHWARCZ, the error depends also on the fact that as high as three out of four samples have very similar amounts of residue (33 ÷ 37%). It is thus reasonable to assume a ^{230}Th age of between 5,000 and 6,000 yr for deposition of the lower cineritic level. As will be pointed out later, this date is better estimated via the ^{226}Ra method.

At the «Contrada Barcavecchia» site, travertin deposition rate was also measured (approx. 0,4 mm/yr). However, if a comparison were made with the deposition rate of other travertins, account should be taken of the high amount of detrital material enclosed in the carbonate.

At «Contrada Cavallaccio» (Fig. 3), the top of the travertin bed revealed a date of 8,000 ÷ 9,000 yr. Here too, error is large, owing to the amount of the non-carbonate residue, ranging from 26 to 47%, but dates are consistent.

At the «Cimitero di Adrano» site (Fig. 4), the dates obtained, which always refer to the top portion of the travertin formation, are very similar to the previous ones, but the error is more limited thanks to a non-carbonate residue of only 7%. In this area, travertin is overlain by slumping alluvia. As a result, the slumping movement must have started after 8,000 ÷ 9,000 yr. The same slumping material can be sighted on an extensive area stretching from «Cimitero di Adrano» down to «Bivio Biancavilla». This detrital cover, slumping over Miocene clays, contains numerous travertin-coated lava blocks.

Sample BBi, collected from the alluvial cover, yelded a ^{230}Th age of approx. 4,000 yr (Table 3); error is quite limited (for so young ages): ± 700 yr.

^{226}*Ra chronology*

The age of sample BBi was compared with that of the travertin collected above the lower cineritic level, in the upper part of the bed outcropping at «Contrada Barcavecchia» (CBV 3d), whose ^{230}Th age (corrected according to KU and LIANG) had been estimated at 5,700 yr; this age, however, had a large error: ± 3,000 yr. The comparison was conducted by determining ^{226}Ra activity in the two materials (corrected for radium contained in the insoluble residue).

Since the travertin-depositing water at the «Bivio Biancavilla» site is the same as the one giving rise to the «Contrada Barcavecchia» deposits, it is justified to suppose that the amount of radium co-precipitated in the carbonates is identical in the two sites.

Now, Table 3 shows that both samples have excess ^{226}Ra and that the activity of this isotope is higher in travertin BBi than in CBV

3d. The activity ratio reflects an age difference of 1,500 ± 250 yr. The computation neglected radiogenic ^{226}Ra, whose amount is undoubtedly minimum, given the young age and poor uranium content of the materials.

Consequently, it can be inferred that the most reliable age for sample CBV 3d is 5,500 ± 750 yr.

Isotope ratios in the residues

Looking at the isotopic composition of U and Th in the insoluble residues of the travertins investigated, the following points can be made:

— The $^{238}U/^{232}Th$ activity ratio falls within the 0,80 ÷ 1,16 range in almost all residues, except for those from sample CBV 1a, with a much higher value (3,06), and for sample CCa, whose value is 1,83. Since in levels CBV 1 and CC samples were collected a few cm apart each other, the non-carbonate fraction of these travertins is highly inhomogeneous.

— The residues of travertins collected from the «Cimitero di Adrano» and «Bivio Biancavilla» sites (deposited by waters which had been drained over Miocene clays) have a $^{238}U/^{232}Th$ activity ratio which is very similar to the remaining ones (except, as pointed out, for travertin residues CBV 1b and CCb). Neverthless, they have a patent disequilibrium, which is shown by the presence of excess ^{230}Th. This fact can be regarded as the result of the predominantly clayey composition of the residue: in effect, as is known (MEGUMI, 1979), clay mineral may become enriched with this isotope by adsorption.

Conclusions

The 20,000 ÷ 24,000 date group marks the start of travertin deposition at the «Contrada Barcavecchia» site. Previous Authors determined that the start of the ancient Mongibello is definitely younger than 50,000 yr, but older than 18,000 yr (TANGUY et al., 1985), (KIEFFER, 1979) (ROMANO, 1982). The tectonic events connected with the start of the ancient Mongibello activity can thus ben thought to have triggered the travertin-depositing water circulation in the predominantly ENE-WSW-trending fault system which is present in the area under review (LO GIUDICE et al., 1982).

The 8,000 ÷ 9,000 yr date group marks the end of travertin deposition at the «Cimitero di Adrano» and «Contrada Cavallaccio» sites. At that age, an event must have occurred which interrupted water circulation in these sites alone (while, at the «Contrada Barcavilla» site, travertin continued to be deposited). On the other hand, as is known, a series of ^{14}C dates estimated on materials occurring in the volcanics connected with the early stages ot the «Valle del Leone» caldera collapse are also concentrated around 8,000 ÷ 9,000 yr (ALESSIO et al., 1986); their correlation is evident.

The age of the lower cineritic level located in the upper part of the travertin bed at the «Contrada Barcavecchia» site ranges from 5,500 to 6,000 yr. Another group of ^{14}C dates, measured on materials occurring in the volcanics related to the terminal stages of the «Valle del Leone» caldera collapse, is centered around the same age (ALESSIO et al., 1986).

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