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Study of the formation of biogenic speleothems found in submarine caves at the cape of Otranto, Italy, by ^{14}C AMS

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Abstract

Submarine caves at the Cape of Otranto, Italy, contain eccentric stalactites that were recently identified as entirely biogenic. One of these stalactites was sectioned along its longitudinal axis in order to select samples for radiocarbon dating. ^{14}C AMS measurements provided fundamental information for the interpretation of the biogenic process and revealed that the formation of the stalactite continued for approximately 5000 years with a decrease in the longitudinal growth rate over time. Measurements of modern organisms were performed to assess the accuracy of the radiocarbon determinations, calibrated in calendar years by measuring the local marine reservoir age.
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1. Introduction

In the open marine environment, there are many examples of biogenic reef structures formed by organisms which produce carbonate skeletal materials. The two main types of reef structures are coral reefs which are formed from animal carbonates and intertidal algal reefs which are formed from coralline algae. In both cases, the biodiversity of these colonial ecosystems is very high. The final structure of these reef formations is the result of an equilibrium between the biogenic growth process and erosion.

Submarine caves at the Cape of Otranto, southern Italy, contain eccentric stalactites, which hang from the vault and protrude from lateral walls toward the centre of each submerged hall, with a length of 2 m. These structures have only recently been identified as being biogenic formations. At the entrance of the cave they are similar in structure and biodiversity to coralline algal reefs, however toward the inner part of the grottoes they appear to be mostly monospecific and are formed by calcareous tubules of *Polychaeta Serpulidae*.

One of these stalactites was longitudinally sectioned in order to examine its inner texture in detail and select samples for ^{14}C AMS measurements.

In this paper, we present the methodological aspects related to sample selection, processing and the interpretation of the ^{14}C AMS results. A detailed description of the inner texture of the stalactites and the interpretation of the biogenic process will be reported elsewhere.

The methodological aspects related to the ^{14}C dating of the sample are presented primarily with respect to the estimation of the marine reservoir age and the possible presence of ^{14}C-depleted sources in the diet of the organisms under investigation.

2. Sample selection and methods

A stalactite with a length of 37 cm, already detached from an internal wall of the *Lampiùne* submerged cave,

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(lat 40°08′19″ N, Long 18°30′26″ E), was longitudinally sectioned. Four samples of calcareous tubes were selected for AMS analysis along the longitudinal axis of the stalactite at distances of 0, 18.5, 29.0 and 37 cm from the base were isolated from the matrix and sampled by drilling (see Fig. 1). First, the samples were mechanically cleaned in order to remove the outermost layer, which was expected to contain a portion of the matrix. Next, conventional sample processing was performed for carbonates by employing the following procedure [1]:

1. Washing with H_2O in an ultrasonic bath.
2. Drying at 60° for 24 h.
3. Attack with H_2O_2 for 15 min in the ultrasonic bath.
4. Drying at 60° for 24 h.

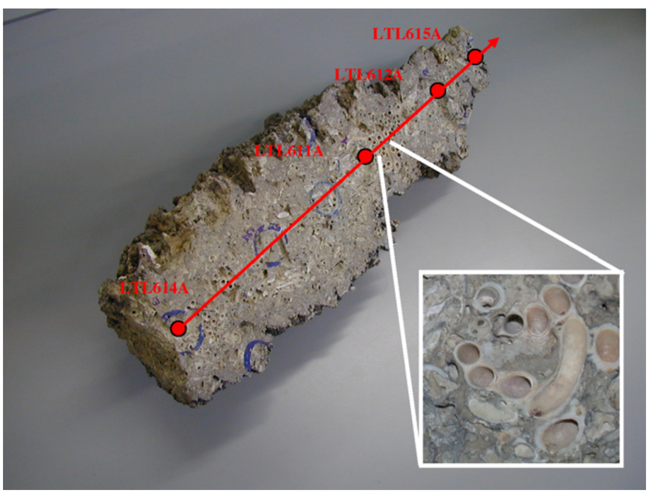

Fig. 1. Sectioned stalactite with four sampling points (red circles). The magnified image shows *Polychaete* tubules which comprise the stalactite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

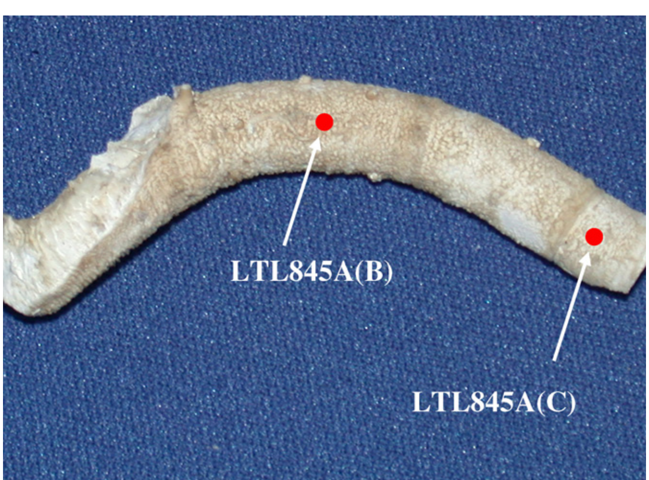

Fig. 2. Modern tubule sampled with the inner living worm. The two sampling points are shown.

The samples were then converted into CO_2 by acidification with H_3PO_4 and finally into graphite by using H_2 as a reducing agent and Fe powder as a catalyst [2]. The AMS radiocarbon measurements were performed at CEDAD, the AMS radiocarbon dating and ion beam analysis facility of the University of Lecce, Italy [3].

Modern tubes, that still contained living worms of the same species found in the stalactite were sampled in order to asses the accuracy of the ^{14}C measurements (Fig. 2). However, the main aim was to estimate the time required for the formation of the tubule and to exclude the presence of sources of ^{14}C-depleted food in the diet of the organism.

3. Results and discussions

Table 1 summarizes the AMS ^{14}C results obtained for both the modern and stalactite tubule samples .

For the modern tubule, we measured radiocarbon concentrations of 106.73 ± 0.46 and 106.16 ± 0.41 pMC from the middle and upper parts, respectively. There was no significant difference between the values measured for the two parts of the same organism (0.57 ± 0.62 pMC) therefore our results are compatible with a time range of the tubule formation of 3 y or less. The comparison of these data with the global marine curve did not indicate any obvious radiocarbon depletion, thereby allowing the exclusion of the presence of the "aging" effect due to the ingestion of ^{14}C-depleted food [4].

For the stalactite samples, calibration of the ^{14}C data in calendar years was obtaining by estimating the marine reservoir age by selecting paired marine gastropod and terrestrial charcoal samples taken from a well defined layer of a geological sequence of a dune ridge found in a nearby area. The results of the ^{14}C measurements of the samples are listed in Table 1. Based on geomorphological considerations, the samples were expected to be contemporary and the age difference between the marine and terrestrial

Table 1
Results of the ^{14}C AMS dating results of samples along the stalactite axis, modern tubule and samples used for the determining the marine reservoir age

Sample	Position	^{14}C age ($\pm 1\sigma$)	Calibrated age ($\pm 1\sigma$)
Stalactite samples			
LTL614A	0 cm	6056 ± 55 BP	6530 ± 90 cal BP
LTL611A	18.5 cm	4926 ± 45 BP	5345 ± 85 cal BP
LTL612A	29.0 cm	3661 ± 65 BP	3620 ± 110 cal BP
LTL615A	37.0 cm	1928 ± 30 BP	1530 ± 80 cal BP
Living sample			
LTL845A(C)	Middle part	106.73 ± 0.46 pMC	–
LTL845A(B)	Upper part	106.16 ± 0.41 pMC	–
Reservoir age samples			
LTL175A (Cuttlefish)	–	340 ± 25 BP	–
LTL184A (Charcoal)	–	20 ± 30 BP	–

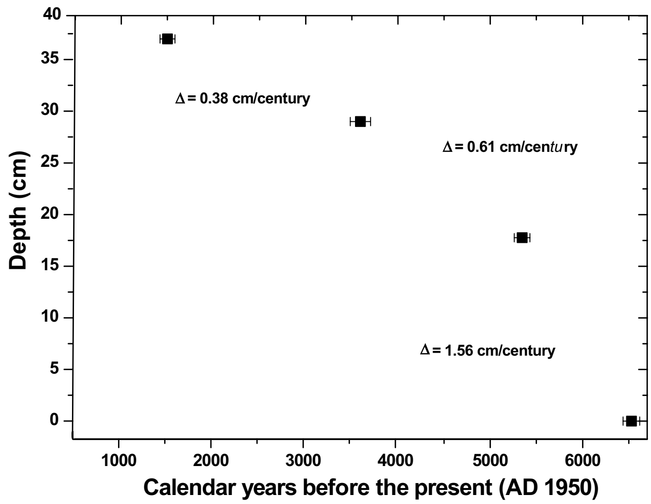

Fig. 3. Age of the samples taken along the longitudinal axis of the stalactite (in calendar years BP) plotted against the distance from the base.

samples was used to estimate the pre-bomb reservoir age of 320 ± 40 y [5]. Based on a comparison with MARINE04 data, this value corresponded to a ΔR value of −45 ± 40 y, which was used for the calibration with OxCal [6].

Fig. 3 shows the calibrated ^{14}C ages (expressed in calendar years BP) of the samples as a function of the distance along the stalactite axis (0 corresponds to the base). The ^{14}C age measurements indicate that stalactite formation proceeded quite regularly and continued for 5000 ± 120 y from 6530 ± 90 cal BP to 1530 ± 80 cal BP; our estimated growth rates appear to decrease progressively from an initial value of 1.56 cm/100 y to a final value of 0.38 cm/100 y. This progressive decrease of the growth rate of the stalactite can be interpreted as the result of a change in the environment which resulted in unfavourable conditions for *Polychaete* growth by approximately 1530 y ago. Possible environmental conditions influencing the growth rate could be caused by changes in the marine circulation and restriction of food supply (suspended particles) for the living worms as the result of sea-level rise [7].

4. Conclusions

^{14}C AMS measurements of modern and fossil *Polychaete* worm tubules provides the first estimation of growth rates of biogenic stalactites found in submarine caves at the Cape of Otranto, southern Italy. Measurements of modern tubules produced by living organisms show that worms may occupy the tubules for less than 3 y. ^{14}C ages for the fossil tubules were calibrated to calendar years by estimating the pre-bomb reservoir age by measuring paired marine and terrestrial materials.

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