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STABLE ISOTOPE COMPOSITION OF FOSSIL AHERMATYPIC CORAL *CLADOCORA CAESPITOSA* (L.) FROM PLEISTOCENE RAISED MARINE TERRACES OF THE LIVORNO AREA (CENTRAL ITALY)

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ABSTRACT: The Livorno coastal area (coastal Tuscany) preserves evidences of several raised marine terraces. Stratigraphically they have been correlated with MIS 5e, 9c and MIS 11 sea-level high stands. However, no direct dating have been performed so far. Thanks of new findings of fossil specimens of ahermatypic coral of *Cladocora caespitosa* in the terraced units correlated to MIS 5e ("Terrazzo di Livorno") and MIS 11 ("Terrazzo della Fattoria Pianacce") we attempted direct dating using the U/Th technique. Moreover, stable isotopes (oxygen and carbon) were used for attempting environmental reconstruction. Dating support the correlation of the "Terrazzo di Livorno" unit with the MIS 5e but are inconsistent for the older unit indicating diagenetic U-mobilization. Oxygen stable isotopes suggest warmer condition for the MIS 5e and MIS 11 compared to modern conditions, even if the indetermination on the water isotopic composition of past interglacial (i.e. ice volume) hampers our capacity to quantify this values.

Keywords: Raised marine terraces, stable isotopes, *Cladocora caespitosa*, U/Th dating, Livorno.

1. INTRODUCTION

Raised beaches deposits represent an invaluable tools for documenting and reconstructing past relative sea level oscillations (e.g., Bloom et al., 1974; Hearty et al., 2007; Olson and Hearty, 2009; Zanchetta et al., 2012, 2014; Bini et al., 2017, 2018; Boretto et al., 2017), coastal tectonic activity (e.g., Belluomini et al., 2002; Nisi et al., 2003; Ferranti et al., 2006; Pedoja et al., 2011), and climate condition at time of their formation using paleontological and geochemical data (Leone and Rosselli, 1995; Vesica et al., 2000; Aguirre et al., 2002, 2006). The Mediterranean coast preserves important succession of past marine highstands, the most popular of which are the so-called "Tyrrhenian" deposits or terraces (e.g., Hearty et al, 1986; Belluomini et al., 2002; Mauz. 1999; Vesica et al., 2000; Jeoudi et al., 2003), which have been mostly related to the Marine Isotope Stage (MIS) 5e sea level highstand (e.g., Ferranti et al., 2006; Stocchi et al., 2018). Coastal Tuscany (central Italy) does not make exception, and in fact it preserves important succession of Quaternary raised beaches (e.g., Federici and Mazzanti, 1995; Mauz, 1999; Boretto et al., 2017; Sarti et al., 2017). In particular in the Livorno coastal area (Fig. 1) there are several evidences of raised terraces older than MIS 5e (Malatesta, 1942; Barsotti et al., 1974; Boschian et al., 2006; Zanchetta et al., 2006). In this paper, we attempt for the first time to dating these terraces using U/Th method on *Cladocora caespitosa* from raised units correlated from MIS5e to MIS11. We also perform stable isotope (carbon and oxygen) analyses on the same corals, to characterize the marine environment. The isotopic data were compared with samples of modern specimens and samples collected from Lower Pleistocene deposits outcropping in the area. Part of the data were obtained in previous studies conducted in collaboration with F.P. Bonadonna and never published before. In the last years *C. caespitosa* has emerged as a powerful tool to investigate the climatic evolution of the Mediterranean sea from annual-to-sub-annual resolution using growth rate (Peirano et al., 2004), trace elements (Silenzi et al., 2005; Montagna et al., 2007; Royle et al., 2015b) and stable isotopes (Silenzi et al., 2005; Royle et al., 2015a). This calls for a reappraisal of the successions outcropping in the coastal Tuscany also for the concerns related to the present "global warming" and its framing in the natural variability within past interglacial not experiencing human impact.

2. GEOLOGICAL AND GEOMORPHOLOGICAL SETTING

The Livorno area represents a tectonic high, which has shown tendency to a slow uplift during the late Quaternary (Nisi et al., 2003; Zanchetta et al., 2004, 2006), estimated to be ca. 0.1 mm/yr by Nisi et al. (2003). This tectonic regime has produced a succession of raised marine terraces (Fig. 1), the lowest of which is a polycyclic marine terrace knows in literature as "Terrazzo di Livorno" or "Terrazzo II" (Barsotti et al., 1974; Federici and Mazzanti, 1995). At the base of the terrace succession, there is a coastal marine unit for which stratigraphy, paleontological assemblages and regional correlations with successions dated using Optical Stimulate Luminescence (OSL) and aminostratigraphy support a chronological framing within the MIS 5e highstand (Hearty et al., 1986; Mauz, 1999; Nisi et al., 2003; Sarti et al., 2017). Few meters higher than the "Terrazzo di Livorno" there is a poorly expressed morphological unit (the so-called "Terrazzo di Salviano" of Barsotti et al., 1974), whose marine origin is debated (Malatesta, 1942, Barsotti et al., 1974; Boschian et al., 2006). Revision of borehole data and surficial stratigraphy, however, allowed to define the basal part of this morphological unit as still formed by marine coastal deposits (Bossio et al., 2008), representing an older and distinct unit from "Terrazzo II". The age of the deposit of this unit is uncertain, but reasonably related to MIS 9c highstand (Zanchetta et al., 2006). The highest morphological unit is represented by a tilted surface ranging from ca. 120 m to 20 m a.s.l., named "Terrazzo della Fattoria Pianacce" (Barsotti et al., 1974), or "Terrazzo I" (Federici and Mazzanti, 1995). It is discontinuously covered by coastal deposits (i.e. Conglomerati di Villa Umberto I unit, Barsotti et al., 1974), which attest the marine origin of the unit (Boschian et al., 2006). In the northern edge the surface, this terrace is covered by a fluvial to a transitional unit locally named Poggio ai Lecci Formation (Barsotti et al., 1974, Marroni et al., 1990). According to Zanchetta et al. (1998, 2006) the Poggio ai Lecci Formation (specifically the section described by Barsotti et al., 1974) inland is the equivalent of the San Romano Formation outcropping eastward along the Arno Valley. Figure 2 shows the relationships of different stratigraphic and morphostratigraphic units of the Livorno area. The upper part of the San Romano formation contains a thick tephra layers dated using Fission Track (FT) method to 480±50 ka (Bigazzi et al., 1994, 2000; Marcolini et al., 2003), and chemically correlated with the early Plinian activity of Vico volcano and specifically with largest eruptions named Vico α and β (Cioni et al., 1987) and ^{40}Ar/^{39}Ar dated at ca. 420 ka and ca. 403 ka (Barberi et al., 1994), respectively. Recently, tephra with similar composition, equally associated to the early Vico activity, have been found in lake successions of the central Mediterranean area, where act as important tephrostratigrphic markers for the MIS 11 paleoclimatic records (Regattieri et al., 2016; Kousis et al., 2018). Considering the large age uncertainty of FT dating, the ^{40}Ar/^{39}Ar age or that deriving from the climatostratigraphic position of the equivalent distal tephra in Lake Ohrid high resolution record (Kousis et al., 2018) should be assumed as the best age for this layer. This allows correlating this unit with the MIS 11 (Marcolini et al., 2003). For the presence of the mentioned tephra and the correlations proposed, it is reasonable to assume that the "Terrazzo della Fattoria Pianacce" unit was modelled during the MIS 11 highstand (i.e., MIS 11c, Railsback et al., 2015), whose the San Romano Formation is the inland continental equivalent (Fig. 2).

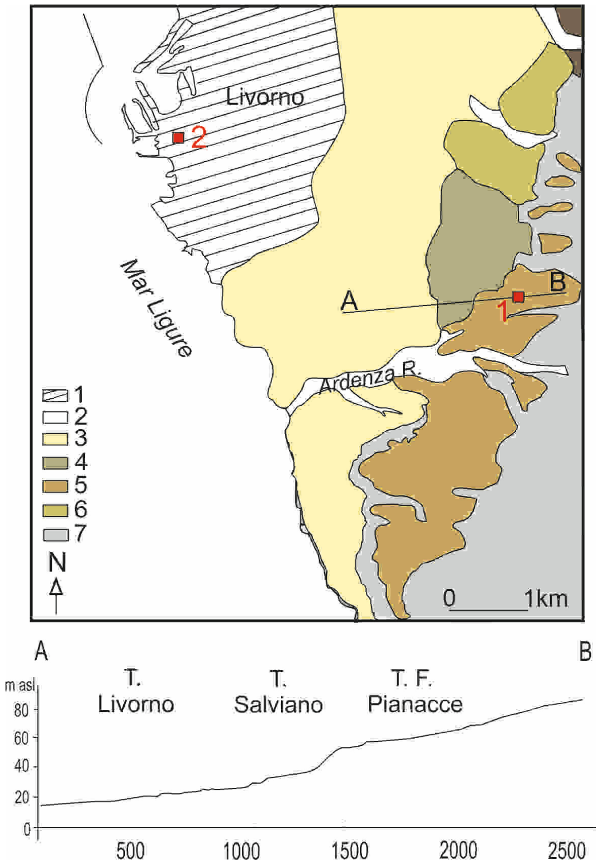

Fig. 1 - Upper panel: Geology of the area (after Barsotti et al., 1974; Lazzarotto et al., 1990; Marroni et al., 1990); 1 Urbanized area; 2) Recent alluvial deposits; 3) Deposits related to "Terrazzo di Livorno"; 4) Deposits related to "Terrazzo di Salviano"; 5) Deposits related to "Terrazzo della Fattoria Pianaccie"; 6) Casa Poggio ai Lecci Formation; 7) Rocky substratum. See also figure 2 for the stratigraphic relations. Lower Panel: topographic profile of the area obtained from DTM LiDAR of the MATTM (Ministero dell'Ambiente per la Tutela del Territorio e del Mare, http://www.pcn.minambiente.it/mattm/procedura-richiesta-dati-lidar-e-interferometrici-ps).

Recently, two new geological sections containing marine fossil remains have been discovered by the collaborators of the Livorno Museum in the "Terrazzo di Livorno" and over the "Terrazzo della Fattoria Pianacce". Detailed stratigraphic and the paleontological description of these two news section will be the focus of a different publication and only the general stratigraphy is reported here. Both sections contained remains of the coral

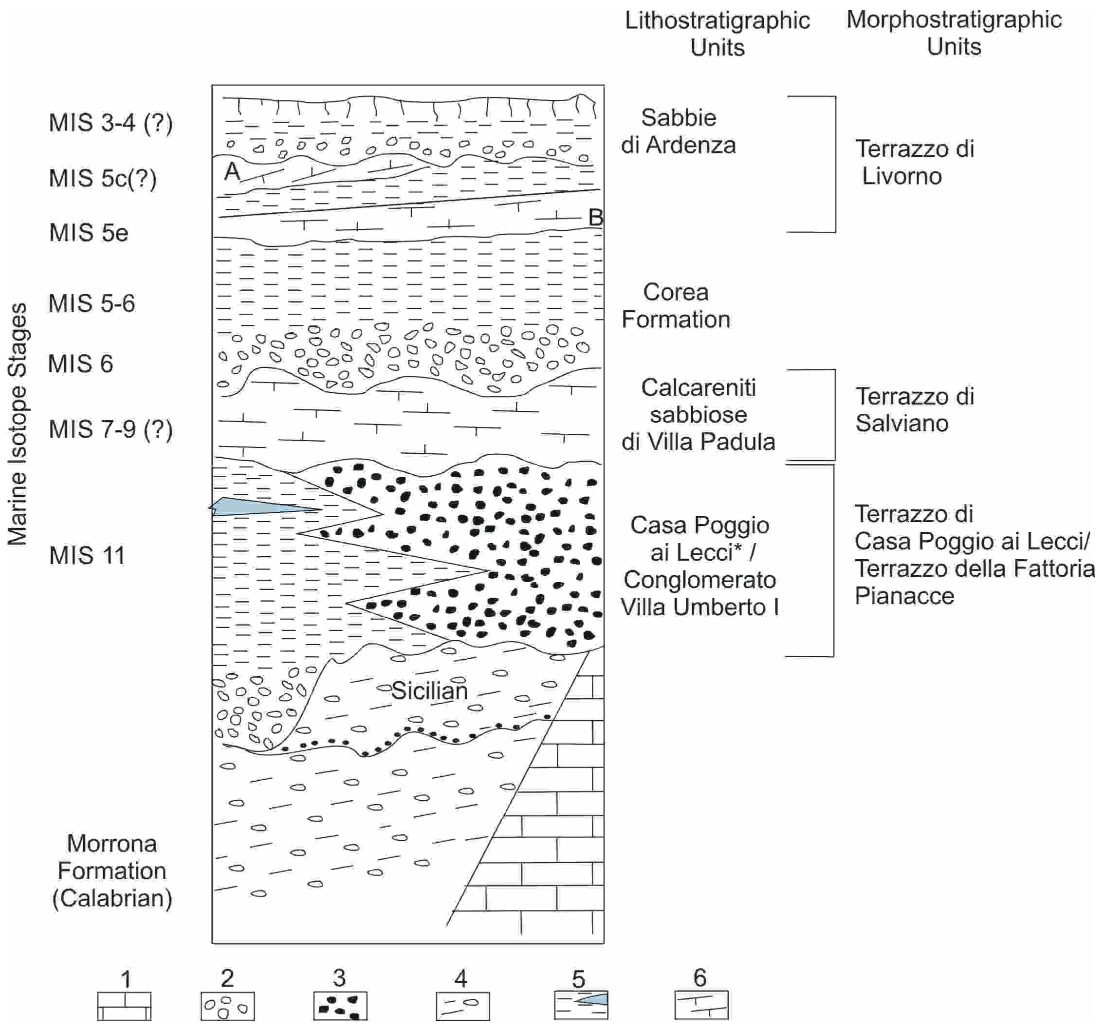

Fig. 2 - Simplified stratigraphic relationship of the Livorno area discussed in the text (modified after Zanchetta et al., 2006). Casa Poggio ai Lecci is considered the equivalent of the San Romano Formation (Zanchetta et al., 1998) containing a tephra which allow a correlation with the MIS11. 1) Rocky substratum; 2) Gravels; 3) Conglomerates; 4) marine sands and gravels; 5) Continental fine grained alluvial deposits; 6) Cemented sands ("Panchina").

Cladocora caespitosa, which gave the opportunity to tempt a direct dating using the U/Th, and to perform a preliminary isotopic study for paleoclimatic purposes.

3. FOSSIL DISTRIBUTION, BIOLOGY AND ECOLOGY OF *CLADOCORA CAESPITOSA*

C. caespitosa is a zooxanthellate and colonial scleractinian species essentially endemic of the Mediterranean Basin (very few records are from adjacent parts of the eastern Atlantic Ocean, i.e. Morocco and Portugal) and it is the sole coral retained as a remnant of the pre-Pliocene Mediterranean reefs (Chefaoui et al., 2017). Large fossil *C. caespitosa* formations have been dated since the Late Pliocene and it seems to be much flourished in warmer climatic phases of the Pliocene and Pleistocene when large bioconstructions have been erected in both the eastern and western Mediterranean Sea (Peirano et al., 2004). The extant distribution of *C. caespitosa* colonies has decreased compared with the fossil one but the causes of this reduction are not fully understood being generically associated with environmentally changes (Kersting and Linares, 2012). Today this species forms still extensive banks mainly near the Tunisian coast, NE Spain, in the Aegean, Ligurian and Adriatic seas (Vertino et al., 2014) but separate colonies in medium or low densities irregularly cover the entire Mediterranean coasts (Chefaoui et al., 2017).

C. caespitosa is a versatile species found in a wide variety of environments, from very shallow waters to no more than 40-50 m in depth because of its photophilous character due to the presence of symbiontic algae. For this reason, it has not been found in dark enclaves but indirect and diffuse light is sufficient to ensure the existence of the zooxanthellae in these conditions (Hoogenboom et al., 2010). This coral may live on hard and soft bottoms both exposed to strong currents and in sheltered places (Bellan-Santini et al., 2002). In terms of sedimentation rate, high values are potentially detrimental for symbiont-bearing corals due to the lowering of photosynthetic production and the obstruction/burial of the polyps (Kruzic and Benkovic, 2008; Lokier et al., 2009; Peirano et al., 2009). However, *C. caespitosa* is tolerant to high input of fines since its polyps are proficient in removing small particles from their oral disk (Peirano et al., 2004; Kruzic and Benkovic, 2008).

The occurrence of *C. caespitosa* in Mediterranean waters with mean winter SST (Sea Surface Temperature) above 12°C suggest that low SST limits its overall distribution. Chefaoui et al. (2017) found that this coral needs higher SST than the mean conditions, both in summer and in winter, to form large buildups: over 20°C in the summer and over 15°C in the winter (see Tab. 2 and Fig. 3 in Chefaoui et al. (2017) for SST mean and range values). These data appear consistent with those of Montagna et al. (2007) who affirm that the growth of this species ceases below 14-16°C. On the other hand the correspondence between the largest *C. caespitosa* bioconstructions and the warmer Plio-Pleistocene phases seems somehow contradictory to the mortality events of this coral in the last decades attributed to prolonged periods of elevated water temperatures (Rodolfo-Metalpa et al., 2000; 2005; Kersting et al., 2013; Kruzic et al., 2016 among others). Different results on *C. caespitosa* thermal tolerance among acquarium and *in situ* experiments suggest that other factor may act together with temperature (Kersting et al., 2013; Chefaoui et al., 2017) but further investigations are clearly required to clarify this point.

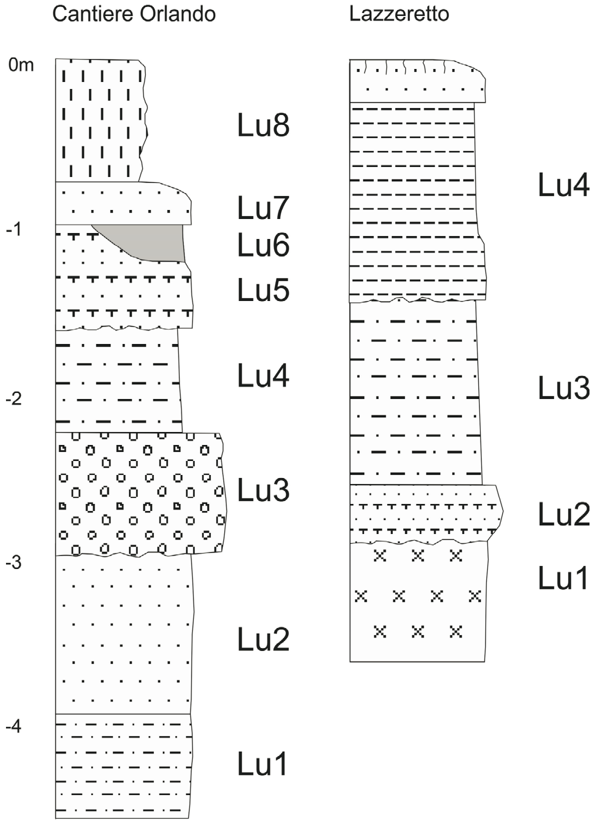

Fig. 3 - Stratigraphy of the a) Cantiere Orlando, b) Lazzaretto sections. See the text for the explanation of lithostratigraphic units (Lu).

4. MATERIAL AND METHODS

4.1. U/Th dating

Three small fragments were extracted from the skeleton of *C. caespitosa* samples from Cantiere Orlando (n=1) and Lazzaretto (n=2) and were analysed for uranium and thorium isotopes at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE, Gif-sur-Yvette, France), following a well-established protocol (Pons-Branchu et al., 2014). Briefly, the samples were mechanically cleaned using a dental drill with diamond-encrusted blades to remove any visible contamination, and finally crushed into a coarse-grained powder with an agate mortar and pestle. An aliquot (~20 mg) of each sample was used for X-ray diffraction analysis (XRD) to identify the bulk mineralogy. The rest (~100-150 mg) was transferred to acid cleaned Teflon beakers, ultrasonicated in MilliQ water, leached with 0.1 N HCl for ~15 s and rinsed twice with MilliQ water to remove any residual contaminants. The cleaned coral carbonate samples were completely dissolved in 3-4 ml dilute (~10%) HCl (optima-grade) and mixed with an internal triple spike with known concentrations of ^{229}Th, ^{233}U and ^{236}U, calibrated against a Harwell Uraninite solution (HU-1) assumed to be at secular equilibrium. The solutions were evaporated to dryness at 70°C and redissolved in 3 N HNO_3. Uranium and thorium were extracted using Eichrom UTEVA ion exchange chromatography and prefilter resins. The isotopes of uranium and thorium were analysed by standard-sample bracketing using a Thermo Scientific^{TM} Neptune^{Plus} MC-ICPMS fitted with an ARIDUS II desolvating system (full details of the analytical method are reported in Pons-Branchu et al. 2014). The ^{230}Th/U ages were calculated from measured atomic ratios through iterative age estimation (Ludwig and Titterington, 1994), using the ^{230}Th, ^{234}U and ^{238}U decay constants of Cheng et al. (2013). Due to the elevated initial δ^{234}U values, the ages were tentatively corrected using the open-system model of Thompson et al. (2003) and the present-day seawater δ^{234}U of 145‰ (Chutcharavan et al., 2018). No correction was applied for the non-radiogenic ^{230}Th fraction. Table 1 shows the results.

4.2. X-ray diffraction analysis

The three samples were crushed into a fine powder with a mortar and pestle and the powder was mounted on a silicon zero background sample holder. The X-ray powder diffraction data were recorded on a Panalytical θ-θ diffractometer at the Department of Geosciences of the University of Padova (Italy). The program High Score Plus was used for phase identification and quantitative analysis by Rietveld refinement (Rietveld, 1967). Refined parameters were scale factors, zero-shift, background, lattice constants, and profile parameters

Sample name	**Cantiere Orlando**	**Lazzaretto_1**	**Lazzaretto_2**
Lab code	LSCE-6002	LSCE-5999	LSCE-6244
^{238}U (µg/g)	2,639 ±0,001	2,603 ±0,003	2,631 ±0,001
^{232}Th (ng/g)	9,25 ±0,003	3,99 ±0,002	1,44 ±0,001
$\delta^{234}U_m$	115,52 ±1,48	120,18 ±1,42	122,3285 ±0,90
(^{230}Th/^{232}Th)	761 ±1,0	1513 ±1,4	4179,111 ±4,3
(^{230}Th/^{238}U)	0,87414 ±0,00119	0,76212 ±0,00069	0,750111 ±0,00077
Age (ka)	159,30 ±1,0	120,64 ±0,5	116,86 ±0,4
$\delta^{234}U_{(initial)}$	181,2 ±2,4	169,0 ±2,0	170,2763 ±1,3
Age (ka)*	143,69 ±1,4	110,99 ±1,0	106,82 ±0,7
Arag (%)	67	98	98
Calc (%)	33	2	2

Tab 1 - Result of the U/Th dating.
$\delta^{234}U_m = \{[(^{234}U/^{238}U)_{sample/}(^{234}U/^{238}U)_{eq}]-1\}$ x 1000, where $(^{234}U/^{238}U)_{sample}$ is the measured atomic ratio and $(^{234}U/^{238}U)_{eq}$ is the atomic ratio at secular equilibrium.
$\delta^{234}U_{(initial)}$ is the initial value and is calculated by the equation: $\delta^{234}U_{(0)} = \delta^{234}U_{meas} \exp^{(\lambda 234\tau)}$, where t is the age in years and λ_{234} is the decay constant for ^{234}U (Cheng et al., 2013).
Dr. W. Thompson kindly provided the Excel spreadsheet to calculate open-system ages.
Arag (%) and Calc (%) are percentage of aragonite and calcite obtained by X-ray diffraction.

Locality (Morphological Unit)	$\delta^{13}C$	$\delta^{18}O$	Estimated age
Living coral	-3.72	-0.57	Modern
Living coral	-3.79	-0.63	Modern
Living coral	-3.90	-0.50	Modern
Mean	***-3.83±0.13***	***-0.57±0.06***	
Leghorn Terrace	-3.93	-1.92	MIS5e
Leghorn Terrace	-3.45	-2.23	MIS5e
Leghorn Terrace	-3.20	-1.91	MIS5e
Mean	***-3.53±0.37***	***-2.02±0.18***	
Fattoria Pianacce Terrace	-2.97	-1.81	MIS11
Fattoria Pianacce Terrace	-2.68	-1.73	MIS11
Fattoria Pianacce	-3.67	-2,39	MIS11
Mean	***-3.11±0.51***	***-1.98±0.36***	

Tab 2 - Stable isotope (oxygen and carbon) data from the Livorno Area.

(Gaussian and Lorentzian coefficients).

4.3. Stable isotopes analyses

Other samples of *C. caespitosa* were soaked in distilled water plus 30% H_2O_2, and cleaned in an ultrasonic bath to remove contaminants. Thereafter, the shells were crushed in agate mortar and homogenized. Stable isotope analyses were performed at the Stable Isotope Laboratory of the Institute of Geosciences and Earth Resources of the Italian National Research Council (IGG-CNR, Pisa, Italy) with a Gas Bench II (Thermo Scientific) coupled to a Delta XP IRMS (Finnigan). About 0.15 mg of carbonate was dissolved in H_3PO_4 (100%), for 1 h at 70°C in a sealed vial flushed with helium. Results were determined relative to the Vienna Pee Dee Belemnite (VPDB) international standard. Sample results were corrected using the international standard NBS-19 and a set of 3 internal standards previously calibrated using the international standards NBS -18 and NBS-19). Analytical uncertainties for replicated analyses of $\delta^{18}O$ and $\delta^{13}C$ were 0.17‰ and 0.15‰, respectively. Table 2 shows the stable isotope results.

5. RESULTS AND DISCUSSION

5.1. New stratigraphic data

A synthetic description of the Cantiere Orlando and Lazzeretto sections (Fig. 3) is reported below.

Cantiere Orlando

In the outcrop is possible to recognize five different lithostratigraphic units (Lu, Fig. 3). From the bottom:

Lu1: massive gray sands to silty sands rich in shallow marine fossils, which can be correlated to Lower Pleistocene (Calabrian) according to the stratigraphic reconstruction from boreholes in the area (Dall'Antonia et al., 2004) and fossil content.

Lu2: well-sorted beige-brown sands, with oxidized layers that contain decarbonated bivalves. The lower boundary is sharp and erosive. The presence of the ostracod *Aurila puncticruciata*, which is restricted to the interval of the late Lower Pleistocene (Ruggieri, 1980), typical of the fauna of local "Sicilian" transgressive deposits (Dall'Antonia et al., 2004), allows to identify a second short sedimentary cycle corresponding to the "Sicilian".

Lu3: fluvial polygenic gravels (mostly carbonates) in sandy matrix (Lu3), upward more clayey. This corresponds to the continental unit of Korea Formation (Zanchetta et al., 2006) of upper Middle Pleistocene.

Lu4: The Lu3 upward passes to Lu4, formed by ochre-orange sandy silts and silty sands, with sand concretions and scarce marine microfauna, indicating nearshore environment.

Lu5: It lies over Lu4 with an erosive surface and consists of a calcarenitic layer rich in marine fossil. In Lu4 remains of *Cladocora caespitosa* are frequent. This unit correspond to "Panchina I" of Federici and Mazzanti (1995).

Lu6: This unit consists of clayey silts green-black in color, and contains abundant wood fragments and peat layers. It is almost barren of fossil remains with few cuticles of oogonium, indicating that it represents a swampy environment.

Lu7: It consists of well-sorted red-brown loose sands of probable aeolian origin representing "Panchina II" of Federici and Mazzanti (1995).

Lu8: It consists of anthropogenic accumulation of briks fragments and reworked material

Lu3 to Lu7 is the typical succession described for the "Terrazzo di Livorno" starting from the lowstand, fluvial deposits of the Korea Formation (MIS 6 to MIS 5/6 transition, Zanchetta et al., 2006) followed by the Lu3-Lu4 representing the typical deposit of the MIS 5e highstand in the area (Boschian et al., 2006).

Lazzeretto section

The section outcrops along a small fluvial incision. Four main lithostratigraphic unit can be distinguished (Fig. 3):

Lu1: Rocky substratum represented by the argillitic Antignano Formation (Marroni et al., 1990).

Lu2: Whitish calcarenites with thin lenses of gravels and marine fossil remains.

Lu3: Bluish sands to silty sands with abundant marine fossil remains with frequent remains of *C. caespitosa*. In the upper part of the visible outcrop Lu3 shows calcarenitic lenses with sparce granules and gravels.

Lu4 Weathered colluvial fine sand to silt deposits.

Lu2 and Lu3 represents the marine sediment of the "Terrazzo della Fattoria Pianacce".

For comparison with fossil samples, a small living colony of *C. caespitosa* was collected near the "Secche della Meloria" shoal, off Livorno coast by a collaborator of the Livorno Museum.

5.2. Chronology

Table 1 shows results of U concentration, activity ratios and $^{230}Th/^{234}U$ ages of the coral fragments analysed in the present study. The three samples have ^{238}U concentration of 2.6 ppm, which is within the reported range of the modern *C. caespitosa* specimens (Montagna et al., 2007). The back-calculated $\delta^{234}U$ values ($\delta^{234}U_{initial}$) range from 169±2‰ for sample "Lazzaretto" to 181.2±2.4‰ for "Cantiere Orlando" one. Those values are significantly above the tolerance intervals recommended for marine samples (e.g. 145±8‰, Chutcharavan et al., 2018), suggesting that the analysed coral samples have behaved as open-systems. We decided to apply the model by Thompson et al. (2003) to correct for open-system behavior, even though we acknowledge that the application of the model to single analyses of corals can be somehow misleading. The corrected ages are of 143.7±1.4 ka for "Cantiere Orlando" sample, and 111±1 ka and 106.8±0.7 ka for "Lazzaretto" sample. The XRD analyses reveal a very high amount of calcite (33%) for the "Cantiere Orlando" sample, which points to a diagenetic alteration of the primary coral aragonite that most likely biased the calculated U/Th age of the sample. However, this age is still in agreement (even if too old) with the unequivocal correlation for these level with the MIS5e (Boschian et al., 2006). Despite the minor degrees of aragonite-calcite

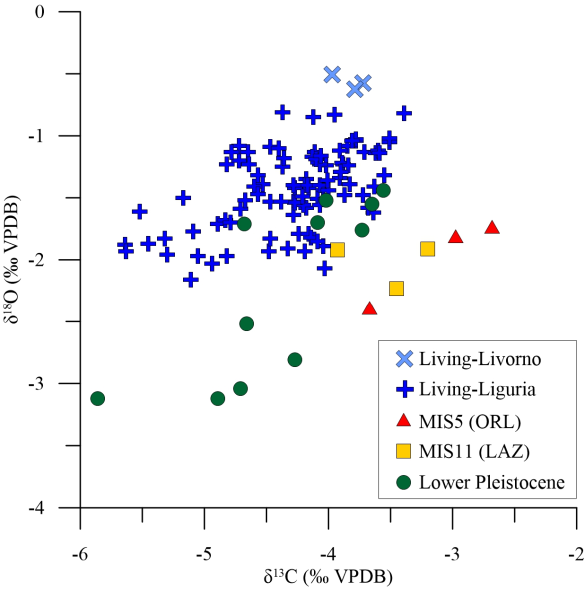

Fig. 4 - Diagram $\delta^{13}C$ and $\delta^{18}O$ of samples discussed in the text.

transformation for the Lazzaretto (2%) sample the age completely disagrees with the morphological and stratigraphic position of "Terrazzo della Fattoria Pianacce", confirming a diagenetic alteration for the U/Th system, possibly related to a recent uptake of U. The different sediment (relatively coarse, well-sorted and cemented sand for "Panchina I" of Cantiere Orlando section, more fine grained and uncemented for Lazzeretto section) can justify the different degree of aragonite-calcite transformation in these two sites, being higher in Cantiere Orlando section, where diagenesis appear more evident for the cementation of the sand deposits.

5.3. Stable isotopes

Table 2 shows the isotopic data. Fig. 3 shows the biplot diagram of $\delta^{13}C$ vs $\delta^{18}O$ isotopic values, whereas Fig. 4 shows the data against presumed ages. For comparison, we have inserted the unpublished data of *C. caespitosa* collected in different outcrops of Lower Pleistocene age in the "Colline Pisane" hills (Table 3), just north-east of Livorno, analysed in the past by students of Prof. Bonadonna during master thesis (Tani, 1996; Gazzerro, 1996). There is a quite detailed information on the stratigraphic position of these samples, even if the original samples are lost and most of the outcrops quoted in the text are not visible anymore. The stratigraphic data permit to confirm that all the samples have been collected in the "Morrona Formation" (Marroni et al., 1990; Boschian et al., 2006) or stratigraphically lateral equivalents (Zanchetta, 1995; Zanchetta and Mazza, 1996; Sarti et al., 2008). The age of the formation is not well-constrained. However, paleomagnetic and paleontological evidences indicate a "Calabrian" (Lower Pleistocene) and possibly late Gelasian (Upper Pliocene) age, indicating a chronological range from ca. 2 to 1.4 Ma (Ambrosetti et al., 1975; Bedini et al., 1981; Zanchetta and Mazza, 1996; Boschian et al., 2006 and references therein).

Figure 3 also shows the isotopic data from a sample of living colony in the continental shelf of the Ligurian Sea collected by Silenzi et al. (2005). According to Silenzi et al. (2005), isotope data of this sample are considered to cover a period of 96 yrs (1906-2000 AD), with annual resolution (assessed through band-counting). On the other hand, our fossil and living bulk samples represent an unknown period of growth, probably lasting several years (samples crushed for stable isotopes were several mm-long), therefore representing the average isotope composition of different years.

Aragonite forms skeleton of living samples of *C. caespitosa* (e.g. Silenzi et al., 2005). Samples from the "Cantiere Orlando" section show a partial recrystallization from aragonite to calcite, with the analyzed sample for XRD showing up to ca. 33% of calcite. Samples from "Lazzaretto" section show almost completely preserved (2% calcite) aragonite compositions. For the Pleistocene samples, the data reported in Tani (1996) show that samples analyzed for XRD showed an almost pure (calcite below the detection limits, which would have

Locality	***$\delta^{13}C$***	***$\delta^{18}O$***	***Estimated Ages***
Soiana	-5.86	-3.12	Lower Pleistocene
Soiana	-4.89	-3.12	Lower Pleistocene
Soianella	-4.27	-2.81	Lower Pleistocene
Casa Vecchia	-3.73	-1.76	Lower Pleistocene
Usigliano	-3.56	-1.44	Lower Pleistocene
Lari	-4.68	-1.71	Lower Pleistocene
Lari	-4.09	-1.70	Lower Pleistocene
Lari	-3.65	-1.55	Lower Pleistocene
Podere Conchiglia	-4.02	-1.52	Lower Pleistocene
Peccioli	-4.66	-2.52	Lower Pleistocene
Scolmatore	-4.71	-3.04	Lower Pleistocene
Clad B	-6.32	-3.34	Pliocene (?)

Tab. 3 - Stable isotope data on Lower Pleistocene from Colline Pisane.

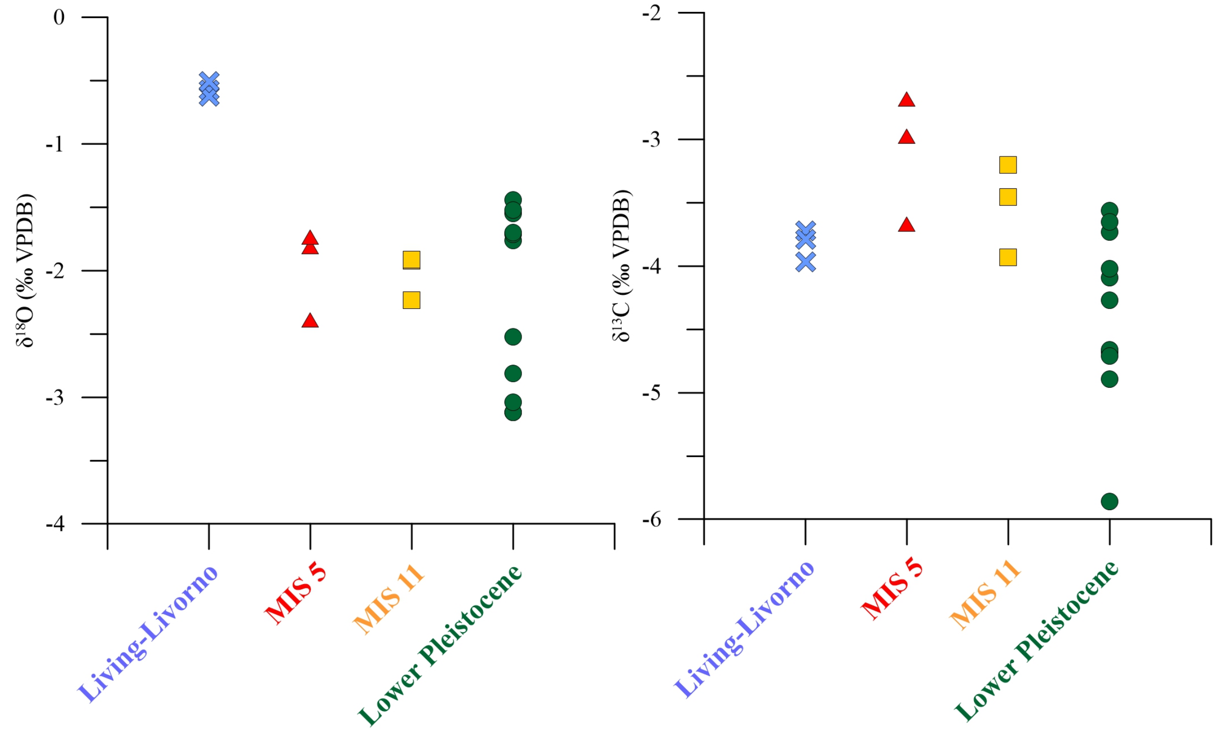

Fig. 5 - Diagrams showing $\delta^{18}O$ vs time and $\delta^{13}C$ vs time.

been ca. 1-2%, for what it is possible to understand for the method used) aragonitic composition. For most of the samples, we can assume a substantial preservation of the pristine isotope signal, even if some samples can have had experienced a partial reset as effect of recrystallization, as evident in the sample from "Terrazzo di Livorno" unit.

We note that $\delta^{18}O$ values of living specimen from Livorno are clearly more ^{18}O-enriched compared to older samples. Instead, there is substantial overlaps between MIS 5e and MIS 11 oxygen values (Fig. 4, 5). Lower Pleistocene samples (Table 3, Fig. 4, 5)) show the largest range of $\delta^{18}O$ values, overlapping those of the MIS5e and MIS11, but not the modern (Fig. 4, 5). The data from Silenzi et al. (2005) show a $\delta^{18}O$ range of values, which overlap with most the MIS 5e and MIS 11 values and partially with those of the Lower Pleistocene, but not those of living *C. caespitosa* collected from Livorno area (Fig. 4).

$\delta^{13}C$ values show almost overlapping values from Modern to MIS 11. The Lower Pleistocene samples show a very large range of values and, on average, appear ^{13}C-depleted compared to living, MIS5e and MIS11 samples.

Oxygen isotope composition of marine carbonates depends on temperature of precipitation and isotopic composition of seawater (Epstein et al., 1953), plus different kinetic and biological effects related to physiology of different species (e.g. Wefer and Berger, 1991) and the eventual presence of symbiotic photosynthetic organisms. Corals are known to show various deviation from isotopic equilibrium condition (both for oxygen and for carbon) owing to different processes (e.g. McConnaughey, 1989a, 2003; Adkins et al., 2003). Despite this complexity, $\delta^{18}O$ is one of the most used proxy for reconstruction of past changes in SST and salinity (e.g. Tudhope et al., 1995; Felis et al., 2000; Rimbu et al., 2003). Data collected from living species in the Ligurian sea by Silenzi et al. (2005) clearly show that at higher temperature the carbonate is ^{18}O-depleted and at lower temperature the carbonate is ^{18}O-enriched, as predicted by the empirical and experimental determination of the dependence of oxygen isotope fractionation factors in relation to the temperature changes (e.g. Grossman and Ku, 1986; Patterson et al., 1993; Kim and O'Neil, 1997). However, Silenzi et al. (2005) noted that a statistically significant correlation could not be found between available sea surface temperature (SST) and $\delta^{18}O$, suggesting that, apart from temperature, a change in salinity (i.e. $\delta^{18}O$ of seawater) may have occurred during years. So this prevent to have a robust equation to calculate, at least, SST relative variability, even if a values of -0.17‰/°C was found, very close to what usually expected for biogenic carbonates and inorganic precipitates, showing a value close to ca. -0.2‰/°C (e.g. Dettman et al., 1999) for the range of ambient temperatures.

$\delta^{18}O$ average value from Silenzi et al. (2005) is -1.44±0.31‰, which is lower than average values of bulk samples from the coral colony in the Meloria shoal (-0.57±0.06‰). This may suggest for them lower temperature of growth and/or higher local salinity. The *C.*

caespitosa precipitates two bands per year, a high-density band forming during periods of lower temperature and lower light intensity, and a low-density band corresponding to high temperature and high light intensity (Peirano et al., 1999). For obtaining data close to average SST, considering water stratification, Silenzi et al. (2005) selected only high-density bands, and this may have produced a further bias between the data collected in the Northern Ligurian Sea and Meloria shoal bulk data (in particular high-density bands may have formed during phases of lower salinity and then lower δ^{18}O of seawater). However, data from Northern Ligurian Sea are of particular relevance because they give a range of values associated with a range of SST of ca. 4°C (estimated using Sr/Ca calibrated against measured temperature from 1982-2000). Even if salinity variability is unknown, MIS5e (average δ^{18}O: -1.93±0,38‰) and MIS11 (average δ^{18}O: -2.02 0,18‰) appear to compare with the lower range of δ^{18}O values of Northern Ligurian Sea and are more ^{18}O-depleted than the average values of coral from Livorno. This suggests that past interglacials have an average temperature some degrees higher than present day. This seems to fit well with general evidences of higher temperature during the last interglacial (e.g. Clark and Huybers, 2009). However, ice volume during the MIS5e and MIS11 interglacials would not be identical to present interglacial conditions. Indeed, higher eustatic sea level during the last interglacial is well known globally (Dutton and Lambeck 2012; Bini et al., 2018), and it is supposed for MIS 11, even if the eustatic component of this period is still debated (e.g. Olson and Hearty, 2009; Bowen, 2010). Recent estimations using SST record to calculate past δ^{18}O of sea water (i.e. the most direct proxy of ice volume) from planktonic δ^{18}O record (Shakun et al., 2015), show that the MIS5e has lower δ^{18}O of sea water (ca. -0.45‰), whereas MIS 11 has higher values (ca. -0.30‰). In the same reconstruction, average global SST seems to be higher for MIS 5e (ca. 1°C) than for MIS 11. Higher temperature and lower ice volume (i.e., lower δ^{18}O value of seawater), explain well the apparent similarity of these two interglacials, in the benthic isotopic stack of Lisieki and Raymo (2005) compared to Holocene. This also would explain the evident similar values found in MIS5e and MIS11 samples of *C. caespitosa* from raised marine terraces of Livorno, and the difference with the living specimens. Considering the global lower δ^{18}O value of seawater during MIS 5e and MIS 11 reported by Shakun et al. (2015), there is still ca. 1‰ of residua in the δ^{18}O values from Livorno, which should be accounted for higher temperature and eventual lower salinity of local seawater. This is in agreement with the results form speleothem from Apuan Alps (Drysdale et al., 2005; Regattieri et al., 2014;, Tzedakis et al., 2019) showing increased rainfall during MIS5e over central Italy, but in particular with lower salinity of the Ligurian sea reconstructed by Toucanne et al. (2015), during MIS5e and MIS11c, in response to the intensification of Mediterranean storm track along the northern Mediterranean borderlands in autumn/winter in correspondence of deposition of sapropels in the eastern Mediterranean. Then, living specimens from Livorno suggest then cooler seawater, higher ice volume and higher salinity conditions compared to MIS5e and MIS11, in a combination, however, difficult to be disentangled from our data.

Lower Pleistocene samples show a large δ^{18}O range partially overlapping MI5e, MIS11 and the lower values (i.e. presumably the warmer counterpart) of living samples from Northern Ligurian Sea. This suggests that samples from different localities all included in the Lower Pleistocene captured different glacial/interglacial cycles characterized by different temperature and ice volume. The presence of two clusters of δ^{18}O values for samples originated by different localities (Fig. 4) may suggest the presence of two specific intervals containing *C. caespitosa*, an eventuality that future stratigraphic research in the area should confirm, but suggested by Tani (1999). Possibly, the lowest values may represent a particularly prominent interglacial and according to Lisieki and Raymo (2005) stacked isotopic records we speculate that this would be MIS 42. The thickness of the Morrona formation (more than 100 m), indicate a clear deposition within a subsiding basin (Boschian et al., 2006), which indicates that this succession has recorded several glacial to interglacial cycles, which potentially can be disentangled and used as important archives for reconstruction of past coastal condition. However, the apparently low δ^{18}O values of some samples accompanied by lower δ^{13}C values may also suggest that, despite the relatively well-preserved aspect, the isotopic composition may have been partially resetted by diagenetic meteoric fluids. Meteoric waters often originate percolating waters, which have lower δ^{18}O and δ^{13}C, compared to marine waters, so the final isotopic composition of altered carbonate would be the results of different effects, including water/rock ratio, temperature and isotopic composition of diagenetic fluids (Lohmann, 1988). We have to note that for samples having preserved mostly the aragonite composition this effect would be minor because during diagenesis aragonite is highly prone to dissolution, followed by precipitation of more stable low-Mg calcite (e.g. Brand, 1989). However, this cannot verified anymore for all samples from Lower Pleistocene, even if the samples analysed by XRD reported in Tani (1999) suggest aragonite preservation. The range of δ^{13}C values of living specimen from Northern Ligurian Sea (from ca. -3.4 to -5.6‰) covers almost all the values of fossil samples (from -2.7 to -5.9‰), suggesting that these values are usual and no necessarily suspect of alteration (as indicated by most XRD). Therefore, we believe that most of the data represent genuine pristine isotope composition of aragonitic coral, with some doubt for more altered samples from Panchina I, which shows significant amount of calcite from XRD. However, these samples are not located at the lower end of the range of isotope values and possibly still retain most of the original stable isotope signal. The large spread of δ^{13}C values from lower Pleistocene corals (covering most of the interval of annual data from Ligurian sea) is then more related to changes in isotopic composition of the dissolved inorganic carbon (DIC) of local water and to effects linked to metabolic and kinetic processes (i.e. the so-called vital effect, e.g. McConnaughey, 1989ab), which is particularly pronounced in corals (Wefer and Berger, 1991). Assuming that metabolic and kinetic effects have a substantial similar influence on $\delta^{13}C$ values between present and past condition, it seems that the carbon isotope composition of the DIC should have remained over a range of values substantially compatible to present day conditions. Even if the Lower Pleistocene may indicate a tendency to have average values ^{13}C-depleted compared to younger samples (Fig. 4).

6. CONCLUDING REMARKS

Despite, our attempt to use *C.* caespitosa to date directly (and for the first time) some terraced units of the Livorno area failed, due to diagenetic alteration of the analysed specimens, the data presented in this work seems to suggest that *C. caespitosa* would have retained unaltered the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios and thus can be useful for the reconstruction of past coastal water condition during different interglacial cycles. Compared to present condition, MIS5e and MIS11c seems to have been characterized by higher temperature accompanied by lower salinity, in agreement with regional paleoclimatic data. This preliminary attempt also shows the potential to expand this investigation to the Lower Pleistocene. Future researches should also be implemented by trace element analyses, and by stable isotope analyses performed at annual to sub-annual resolution.

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