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U/TH DATING AND GEOCHEMISTRY OF CARBONATE CONCRETIONS ASSOCIATED WITH UPPER PLEISTOCENE FOSSIL SHORELINES OF THE SORRENTO PENINSULA (CONCA DEI MARINI, SOUTHERN ITALY)

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ABSTRACT
U-series dating and geochemical analyses were performed on carbonate concretions in order to put chronological constraints on the associated fossil shorelines. In particular, samples were taken from concretions found at Conca dei Marini Cape where former shorelines ascribed to the Upper Pleistocene are present. From the chronological data the height of sea level during highstands of Late Pleistocene is inferred; moreover, due to the tectonic stability of the area the estimated height could be taken as a close approximation of eustatic sea level position. A +3.5 m a.s.l. sea level highstand which occurred during the end of Oxygen Isotopic Stage (OIS) 5e was recognised by the U/Th age and elevation of the concretion covering a wave-cut platform. Furthermore, new interpretations for more recent sea level highstands were obtained by analyses performed on two calcitic concretions associated with a marine biocalcarenite. They indicate that the sea level at the end of OIS 3 was close to the present day one; such a conclusion disagrees with the generally accepted sea levl position derived from proxy data taken from oceanic cores while it agrees with recent chronological data obtained from marine deposits in the Gulf of Taranto (Southern Italy).

RIASSUNTO
In due siti della Penisola Sorrentina , presso il Capo di Conca dei Marini, sono state rinvenute alcune concrezioni carbonatiche in associazione con depositi e forme marine ascritte in letteratura agli stazionamenti alti del livello marino correlati con lo Stadio 5 della stratigrafia basata sugli isotopi dell'ossigeno. Su queste concrezioni sono state eseguite datazioni U/Th al fine di ottenere ulteriori vincoli cronologici (limiti ante quem *o* post quem*) per la genesi delle linee di riva, ed analisi sedimentologiche e geochimiche indirizzate alla determinazione del loro ambiente diagenetico. Le condizioni di stabilità tettonica tardo quaternaria caratterizzanti l'area in studio hanno consentito, inoltre, di porre in relazione la posizione altimetrica dei depositi e delle forme cronologicamente inquadrati ad altrettante posizioni eustatiche del livello marino durante gli Stadi Isotopici 5 e 3 del Pleistocene superiore. Fra i risultati più interessanti si segnalano quelli ottenuti da una concrezione laminare datata al sottostadio 5d che ricopre una piattaforma di abrasione posta a +3,5 m s.l.m., la cui genesi va così inquadrata nella parte finale del sottostadio 5e, e le datazioni di due concrezioni calcitiche che si intercalano ad una biocalcarenite marina a + 4 m s.l.m. Queste ultime, datate allo Stadio3, suggeriscono una posizione del livello marino per quel periodo prossima al livello marino odierno; tale conclusione da un lato contrasta con quanto sinora proposto in letteratura sulla base di dati indiretti ottenuti da carote oceaniche, d'altra parte è in accordo con recenti dati ottenuti su depositi marini affioranti sulle coste del Golfo di Taranto.*

Key words: emerged shorelines, calcareous concretions, geochemistry, U-series data, Upper Pleistocene, southern Italy.

Parole chiave: linee di riva, concrezioni calcaree, geochimica, datazioni U/Th, Pleistocene superiore, Italia meridionale.

1. INTRODUCTION

The Sorrento promontory is a NE-SW trending *horst* facing Capri island along the coast of the Campania region (Fig.1). Highly resistant rocks – carbonates of Meso-Cenozoic age – displaced by normal faults in structural blocks constitute the promontory. As such, the Peninsula is characterised by a structure-controlled type of coast with high and rectilinear sea cliffs interrupted by angular plan-shaped bays and pocket beaches. Offshore, plunging cliffs alternating with narrow coastal benches are generally present.

Similarly, the Quaternary fossil shorelines of the Peninsula are represented by scattered and small remnants of marine terraces and by scarce outcrops of coarse-textured beach deposits patched onto the bedrock and usually barren. There are a very few sites where fossiliferous Pleistocene marine deposits are present such as the well known Ieranto and Conca dei Marini bays, where Eutyrrhenian marine deposits were pointed out (Brancaccio *et al.*, 1978).

In this paper we present new chronological data on the Upper Pleistocene fossil shorelines of the Sorrento Peninsula. They have been obtained by U-series data performed on carbonate concretions which we have found closely or directly associated with some sea level stand indicators, both of erosional and depositional origin, in Conca dei Marini area.

2. GEOMORPHOLOGY, STRATIGRAPHY AND SEDIMENTOLOGY

Two Sites of Conca dei Marini promontory (Site I and Site II in fig.1) have been studied in detail in this paper. The Upper Pleistocene shorelines are represented by patches of marine deposits and by bioerosive notches and emerged platforms, located at elevation between +8 and +1.5 m. They were studied in Brancaccio *et al*. (1978), Cinque & Romano (1990), Riccio *et al.* (2001).

In Site I several carbonate concretions associated with a + 8 m high notch have been found (Fig.2). The concretions are finely laminated and fill bowl-like cavities present all along the notch concavity. Microscopically, the concretions consist of alternation of microsparitic laminae. XRD analyses revealed the presence of some aragonite together with calcite. The origin of the cavities and carbonated infilling appears very problematic. Possibly, the cavities originated as *Lithophaga sp*. burrows and were subsequently enlarged by chemical weathering. The former studies carried

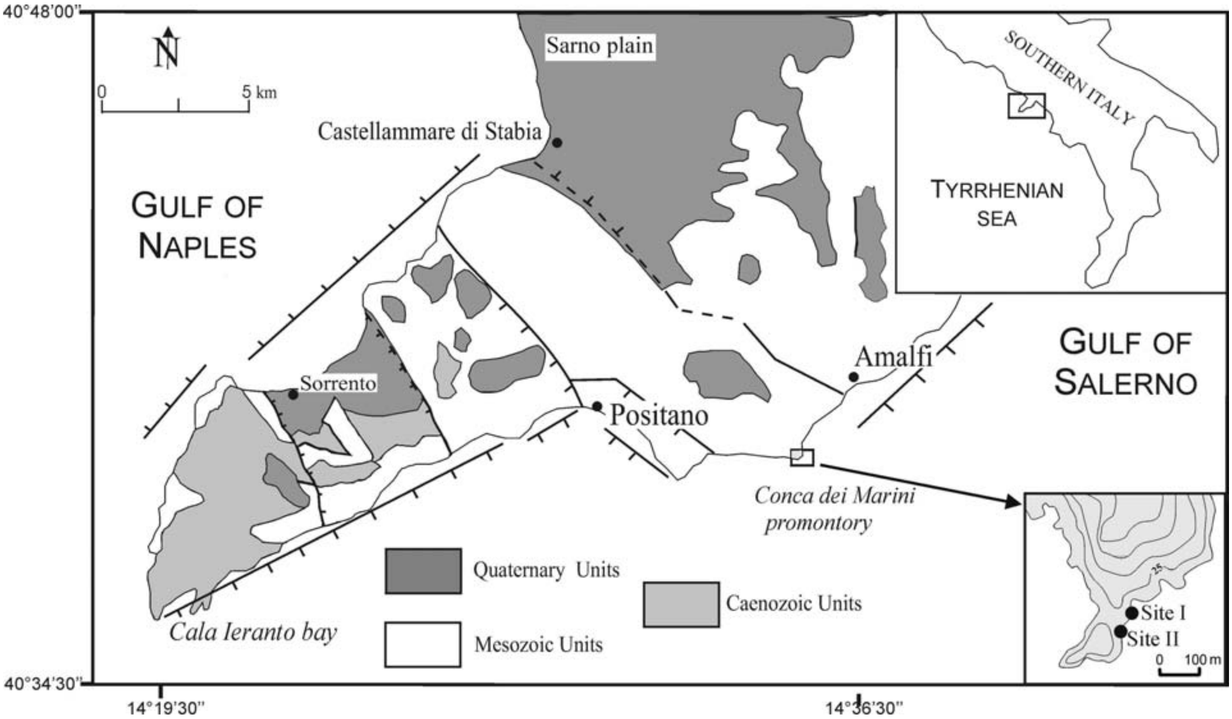

Fig. 1 - Geological scheme of the Sorrento Peninsula with the locations of the Conca dei Marini promontory and of the Site I and Site II bays (after Riccio et al., 2001 modified).

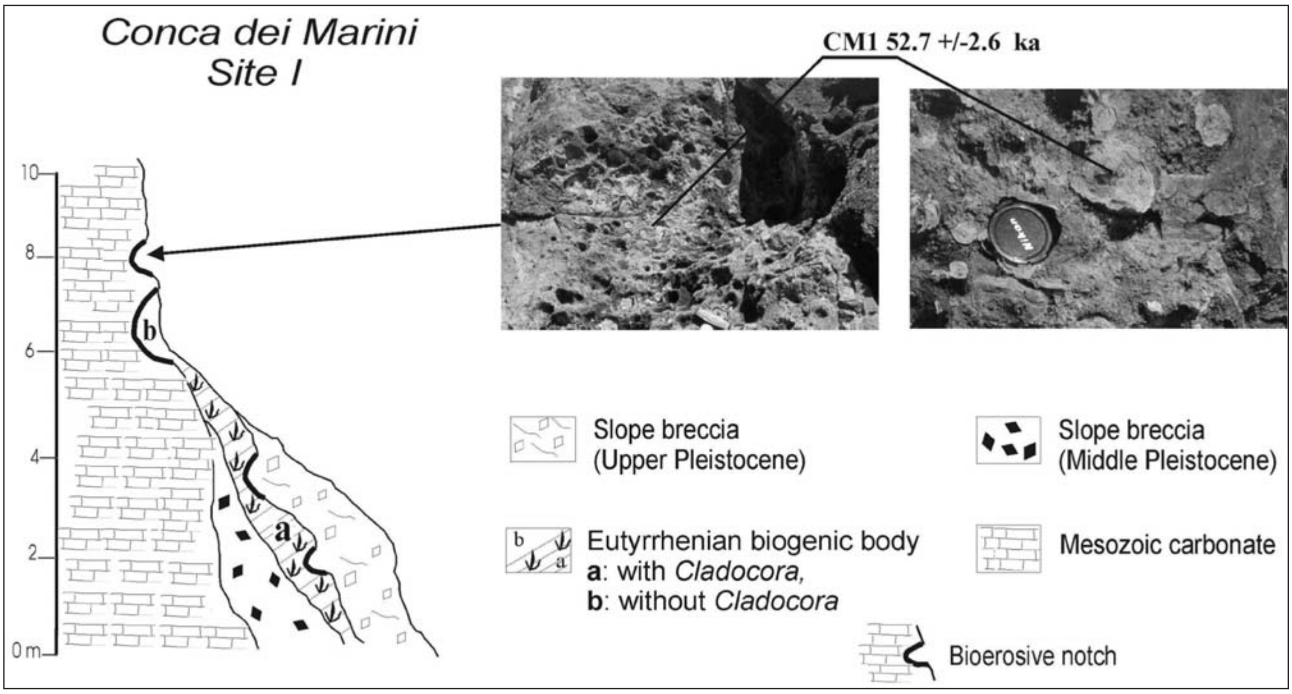

Fig. 2 - Geological section of Site I bay (after Riccio *et al.*, 2001 modified). The photographs show a detailed and a complete view of the concretions present all along the + 8 m high notch.

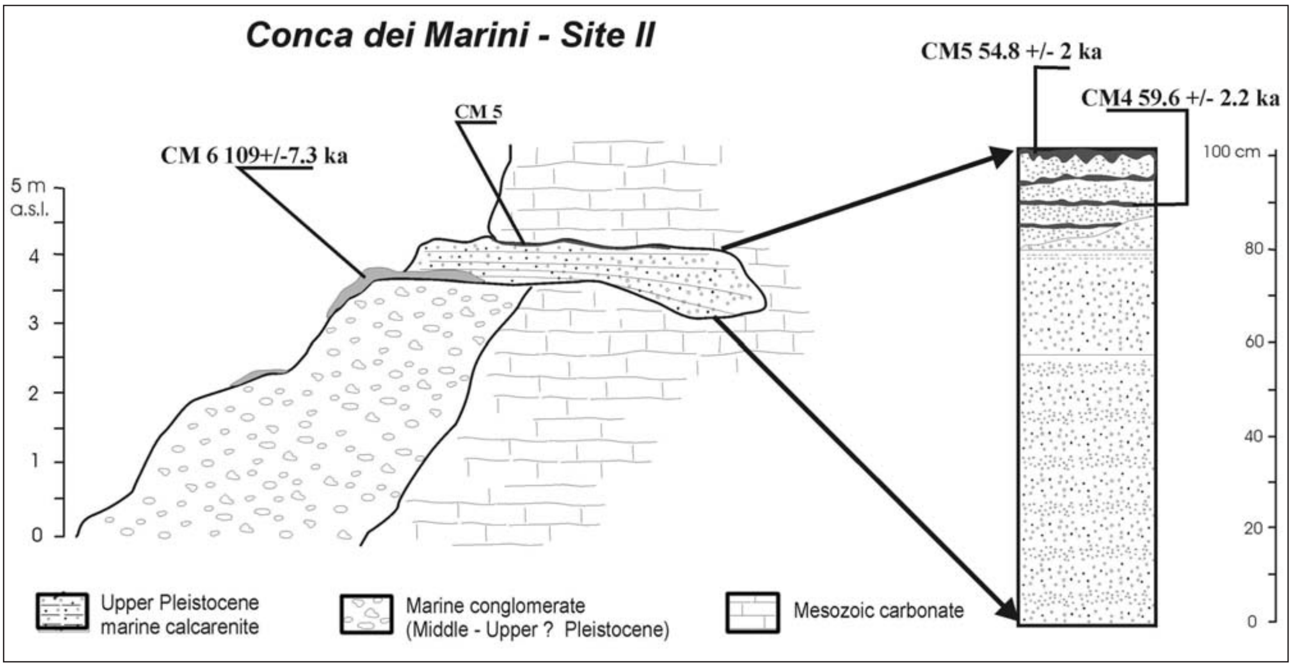

Fig. 3 - Geological section of Site II bay. For details of the concretions see fig. 4.

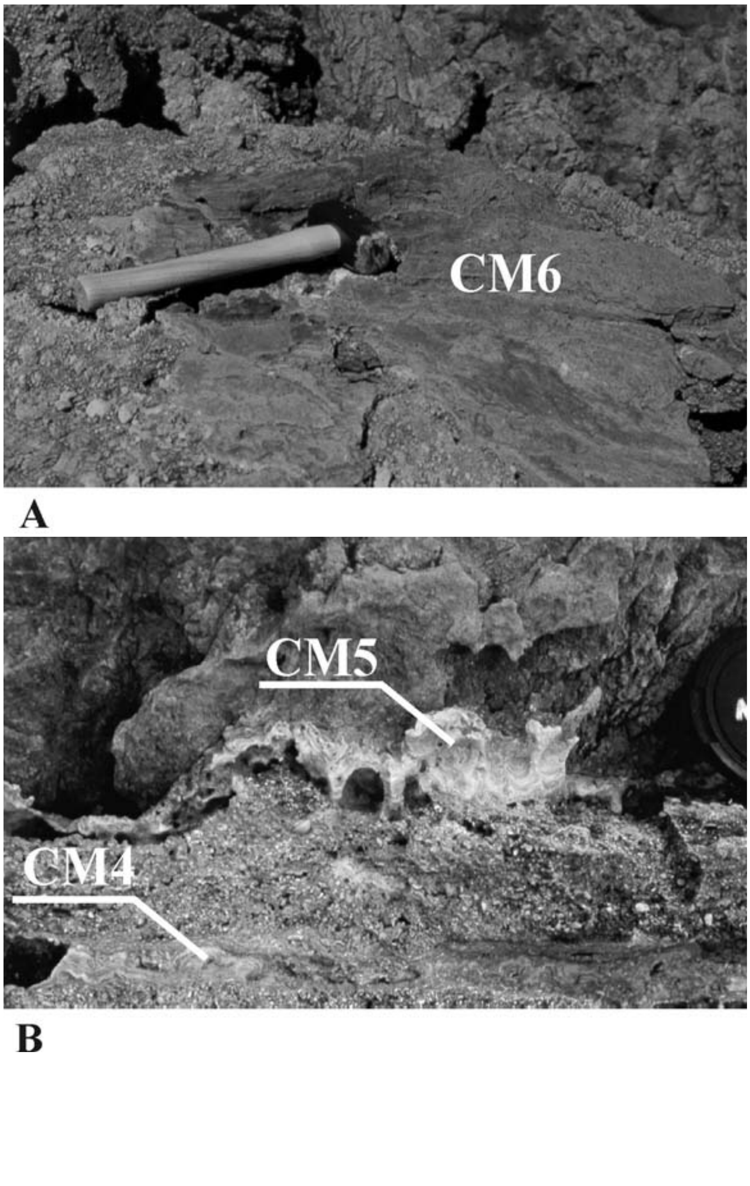

Fig. 4 - Details of the calcareous concretions associated with marine deposits or erosional morphologies at Site II bay. A) the concretion lying onto the +3.5/4 emerged bench, 2/4 cm thick. B) the concretions cementing the upper part of a marine calcarenite, 1/2 cm thick.

out in the area (Brancaccio *et al*., 1978; Riccio *et al*., 2001) indicated an Euthyrrenian age of the + 8 m notch because it is closely associated with a marine deposit with Cladocora coespitosa.

In Site II different generations of calcareous concretions were found closely or directly associated with emerged shorelines (Fig. 3). Some platy, laminated calcitic concretions (Fig.4A) lie onto a +3.5/4 m high wave-cut platform which was tentatively ascribed to a late OI substage 5e sea level stand by Riccio *et al.* (2001).

Other generations of concretions intercalated in the upper part of a marine calcarenite at +4 m a.s.l. (Fig. 3 and Fig. 4B) were observed. The marine deposit covers the +3.5/4 m high emerged platform and there it is only some 60 cm thick; laterally, instead, the deposit thickens to some 100 cm because it fills a sheltered niche whose bottom is 1 m lower than the terrace and is cut directly into the Mesozoic carbonates of the substrate. The deposits are distinctly clinostratified and dip landward with a fan-shaped bedding which progressively compensates the difference in accomodation space between the terrace and the niche. This demonstrates that the protected niche was filled gravitationally by sediments coming from the sea-ward side and washed over the threshold represented by the bench.

The sediments, as reported in Riccio *et al*. (2001), consist of a matrix-free coarse calcarenite to calcirudite. The part of deposits closer to the sea is distinctly coarser, with single grains reaching some cm in diameter. Grains are subrounded and show a good sorting within each layer. They consist mainly of bioclasts and lithoclasts of coarse-crystalline dolomites. Only one layer, at 80 cm, consist mostly of more angular and reddened lithoclasts. The bioclasts are represented mainly by fragments of articulate and inarticulate bivalvs, gastropods, bryozoan and echinoderms and of red algae. Frequent are also micritic grains of unknown origin. The deposit is generally highly porous and crumbly because of a very low degree of cementation. In fact, in the thin section, only an irregular, discontinuous rim of limpid, equant calcite cement is present showing frequently meniscus textures. Only a few layers in the upper part of the deposits are heavily cemented by several laminated carbonate concretions.

The concretions are represented by several mm thick laminated layers consisting exclusively of precipitated carbonate which interrupt the sedimentary layering (Fig 4B and 5). However, there are also calcarenite layers made harder by the presence of the same carbonate precipitate covering the sigle grains. The geometric relations between cement and sediment layers demonstrate that most of the cementation took place during deposition. Moreover, it is clear from field relations that for the latest concrections, downward, stalactitic growth on cavity floor was contemporaneous with upward growth on the sediment surface, probably as a flowstone. The microstructures are characterised by alternating laminae of spar and microspar often showing the presence of fibrous structures due to the crystallographic continuity of single crystals of each superposed lamina. This especially occurs when the laminae are not planar but form domes and arches. In the case of upward growth on the sediment surface these structures are comparable to those of stromatolites according to the definition of De Micco & Hardie (1994). Otherwise, they

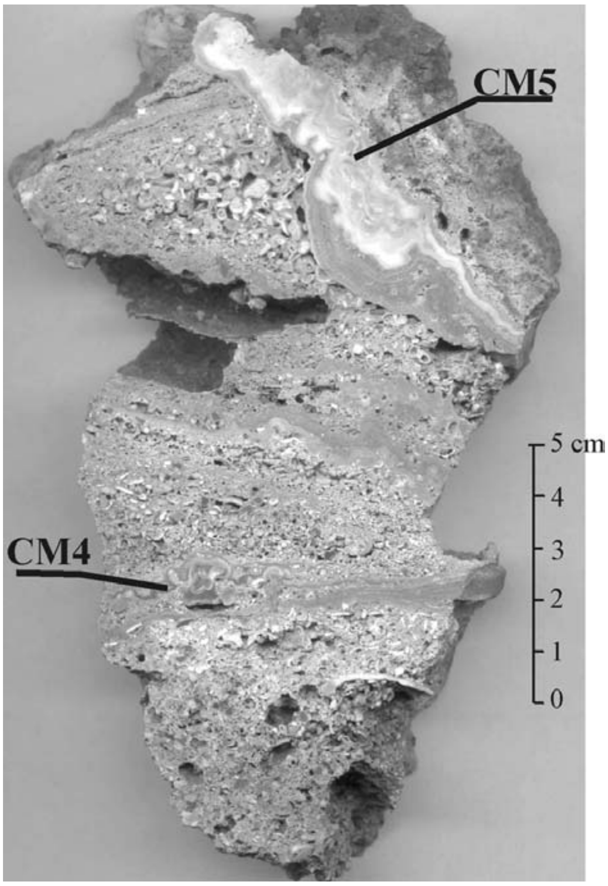

Fig 5 - Details of the stalactitic (CM4) and the stalagmitic (CM5) portions of the concrections cementing the marine calcarenite at Site II.

are typical of coconut calcite in stalactitic growth. These concrections are morphologically comparable to many spleothems but also to some carbonates formed in special conditions in supersaturated marine waters, as suggested by Riccio *et al*. (2001).

3. GEOCHEMISTRY

The several carbonate concrections at Conca dei Marini are the only available material to constrain cronologically the associated sediments and erosional features. To this aim, several samples have been collected from:

- the concrections cementing the upper part of the biocalcarenite at Site II, both in the stalactitic (samples CM5) and stalagmitic (sample CM4) portions;
- the problematic circular concrections partly covering the +8 m notch at Site I (sample CM1);
- the concrection covering the coastal bench at 3.5-4 m at Site II (samples CM6);

From the collected material, four samples have been analysed by U-series disequilibria, nine for O and C stable isotopes. The list of samples and results are shown in Tables 1 and 2.

For U-series disequilibria measurements, samples were crushed into several-millimetre-diameter pieces with a stainless-steel chisel. These fragments were examined under a binocular microscope and any piece that

Table 1 - U-series data, mineralogy and inferred isotope stage of samples from Conca dei Marini (Italy). Quoted ratios are activity ratios and errors are expressed as 1 sigma. ($^{234}U/^{238}U$)init. represents the initial uranium ratio.

Sample	Mineralogy	U ppm	($^{230}Th/^{232}Th$)	($^{234}U/^{238}U$)	($^{230}Th/^{234}U$)	($^{234}U/^{238}U$)init.	Age (ka)	Stage
CM1	aragonite+ Mg calcite	3.439 ± 0.098	25 ± 1	1.126 ± 0.014	0.387 ± 0,015	1.146 ± 0.016	52.7 ± 2.6	3
CM4	calcite	1.878 ± 0.035	75 ± 10	1.059 ± 0.017	0.424 ± 0.012	1.07 ± 0.02	59.6 ± 2.2	3 -- 4
CM5	calcite	1.211 ± 0.022	34 ± 3	1.043 ± 0.017	0.397 ± 0.011	1.050 ± 0.020	54.8 ± 2	3
CM6	calcite	0.514 ± 0.016	856 ± 792	1.057 ± 0.034	0.638 ± 0.025	1.078 ± 0.046	109.1 ± 7.3	5d

Table 2 - C and O isotope ratios measured on Conca dei Marini concretions.

Sample	$\delta^{13}c$	std.dev.	$\delta^{18}O$	std.dev
CM1	-0.8	0.02	-0.2	0.02
CM 4a	-7.2	0.03	-3.0	0.03
CM 4b	-8.1	0.02	-3.5	0.02
CM 4c	-5.5	0.02	-3.2	0.04
CM 4d	-5.5	0.03	-3.3	0.06
CM 5a	-5.7	0.02	-2.5	0.03
CM 5b	-6.1	0.02	-2.4	0.05
CM 5c	-3.7	0.02	-2.2	0.06
CM 5d	-5.5	0.01	-2.6	0.02
CM 6	-6.5	0.04	-4.1	0.04

showed signs of secondary alteration was discarded. The remaining portion was ultrasonically cleaned in distilled water twice. The analytical procedure used for U and Th separation was that reported by Bischoff *et al.* (1988). Three to six gram samples were spiked with a ^{228}Th + ^{232}U tracer (in secular equilibrium) and activity ratios were counted in an EG&G ORTEC 920-8 alpha spectrometer system. The ages and the initial $^{234}U/^{238}U$ activity ratios were calculated by means of ISOPLOT, a plotting and regression program designed by Ludwig (1994) for radiogenic-isotope data. The uranium contents, the activity ratios and the calculated ^{230}Th ages are listed in Table 1; all errors are reported as 1 sigma.

For O and C isotope ratios measurements, a few mg of powder have been obtained with a dental drill from areas which are exclusively formed of precipitated carbonates. Carbonate powders were reacted with 100% phosphoric acid at 75 °C and analysed in a carbonate preparation line connected to a Finnigan Mat 252 mass spectrometer. The analyses have been carried out at the Stable Isotope Laboratory of Erlangen University (Germany). Results are shown in Table 2.

All the subsamples extracted from CM4 and CM5 samples have $\delta^{13}C$ and $\delta^{18}O$ isotope values ranging from -3,7 to -8,1 and from -2,2 to -3,5 (PDB) respectively. These values, especially the C-isotope ratios, indicate precipitation from meteoric waters. The relatively marked variation within the sample set cannot be explained precisely and has to be attributed to temperature and compositional variation in the parent fluid, both possibly linked to seasonal or climatic factors. The initial $^{234}U/^{238}U$ activity ratios calculated from two samples of the same concretions are 1.05 and 1.07, both not consistent with the average uranium composition of the oceans (about 1.15).

The only isotopically different carbonate is represented by the cavity-filling concretions found at +8 m at Site I (CM1). In fact, a single measurement performed on this material gave $\delta^{18}O$ and $\delta^{13}C$ values of -0.1 and -0.8 (PDB) respectively, distinctly heavier than the other samples. Part of this difference can be attributed to the presence of aragonite in these concretions, which has a slightly higher fractionation factor with respect to calcite, both for carbon (1.8 per mil) and oxygen (0.6 per mil). However, the measured value implies at least a partial contribution of marine waters during precipitation. A simple evaporation effect on meteoric waters can be excluded because this would have raised the measured O-isotopes ratios but not the C-isotopes ones. This interpretation is further strengthened by U-geochemistry. In fact, both U-content and $^{234}U/^{238}U$ activity ratios are higher than in the CM 4 and 5 samples, this again suggesting a marine contribution in the precipitation of these concrections.

For CM6, sample U-data suggest a meteoric origin and a single $\delta^{18}O$ and $\delta^{13}C$ measurement seems to confirm this.

4. DISCUSSION

The chronological data obtained at Conca dei Marini (Table 1) permit to infer the height of sea-level during high-stands of the Late Pleistocene. The estimated height can be taken as a close approximation of eustatic sea level positions. In fact, as pointed out in Brancaccio *et al.* (1978) and Riccio *et al.* (2001), the Conca dei Marini sites have suffered a maximum uplift of 1.5 m since the Eutyrrhenian, corresponding to a mean rate of 10^{-2} mm/a.

The calculated age for the concrection covering the +3.5 m bench (CM6) is 109.1 ka (Table 1), which falls within OI substage 5d (Martinson *et al.* 1987). This only represents an upper limit for the age of the bench. The lower one is the Eutyrrhenian because the bench can be correlated to a +3.5 notch cutting the *Cladocora* deposit (see Fig. 2), as discussed in Riccio *et al.* (2001). Thus, the geochronological data confirm the hypothesis that this highstand occurred during late substage 5e.

However, the ages of the other concrections provide new interpretations for more recent sea level highstands. In fact, U-series data indicate an age of approximately 54-59 ka for the CM 5 and CM 4 concrections respectively (table 1), which can be considered as an estimate of the age of the bioclastic deposits. These ages correspond to the beginning of OIS 3. The sedimentological evidence indicates clearly that the deposits formed as a backshore deposit washed over the bench into a sheltered niche on the rocky coast during storms. Considering the height of the marine calcarenite, this would indicate that the contemporaneous sea level was not so far from the present day one. Such a conclusion disagrees with the largely accepted assumption that the sea level during the whole OIS 3 was some tens of meter below the present one. This conclusion is generally derived from proxy data, specifically by assuming a more or less direct relationship between O-isotope values in oceanic foraminifers and ice-volume (Chappel & Shakcleton, 1986). However, recent research in the Mediterranean area has found a little sedimentological evidence, supported by geochronological data, of a highstand above the present sea level during OIS 3 (Belluomini *et al.*, 2002). Our data provide further support to these findings.

The U- and O-C isotope geochemistry of the problematic concrections of + 7/8 m at Site 1 represents a further possible evidence that sea level was close to the present one during OIS 3. In fact, the calculated age is 52 ka and U content and O and C isotope ratios indicate a precipitation by a fluid with a partial marine contribution. A possible explanation is that sea water came from marine spray over the rocky cliffs.

We think that the data of Conca dei Marini and those reported by Belluomini *et al* (2002) impose further research in other areas, coupled with a critical review of published data concerned with recent sea level highstands, in order to definitively verify the validity of the generally accepted Late Pleistocene sea level curves.

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