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DISTRIBUTION OF OXYGEN ISOTOPES IN MOLLUSCAN SHELLS FROM TWO QUATERNARY SHORELINE DEPOSITS (LATIUM, ITALY)

G. Leone(1) - A. Roselli(2)
(1) Dipartimento di Scienze della Terra, Università di Pisa
(2) Museo Provinciale di Storia Naturale, Livorno

ABSTRACT - *Distribution of oxygen isotopes in molluscan shells from two quaternary shorelines deposits (Latium, Italy)* - Il Quaternario, 2, n.1, 1989, p. 41-47 - Thirty-two samples of four species of the molluscan fauna from two Quaternary shoreline deposits of Latium (central Italy) have been analyzed for oxygen and carbon isotopic compositions. The ^{18}O contents of the studied shells cluster separately for the two deposits, thus proving to be a distinctive feature of the studied shorelines. The complex isotopic history of the Mediterranean sea interferes with a simple paleoclimatic interpretation of the obtained results; however the obtained data show that the used type of analyses may be useful in the stratigraphic characterization of fossiliferous deposits. The method can thus be applied to the study of Quaternary Mediterranean shorelines which have markedly been affected by tectonic displacements.

RIASSUNTO - *Distribuzione degli isotopi dell'ossigeno nelle conchiglie dei molluschi di due depositi costieri quaternari (Lazio, Italia)* - Il Quaternario, 2, n.1, 1989, p. 41-47 - Questo lavoro si propone di valutare lo specifico contributo che le misure di composizione isotopica dell'ossigeno nelle faune fossili a molluschi possono apportare allo studio delle linee di costa quaternarie dell'area Mediterranea. In questa prospettiva è stata misurata la composizione isotopica dell'ossigeno e del carbonio di 32 conchiglie fossili appartenenti a quattro specie provenienti da due depositi di fossili di facies costiera situati nel Lazio centrale e settentrionale, rispettivamente a Casale di Statua presso Palidoro e in località Lestra dell'Ospedale presso Tarquinia. Le conchiglie fossili dei due depositi si differenziano nettamente per quanto concerne la composizione isotopica dell'ossigeno $\partial^{18}O$ mentre i valori isotopici del carbonio $\partial^{13}C$ sembrano essere principalmente influenzati da caratteristiche proprie delle singole specie. La complessa evoluzione della composizione isotopica delle acque del Mediterraneo durante il Quaternario ostacola una diretta interpretazione paleoclimatica dei dati ottenuti che però evidenziano l'utilità di questa metodologia come contributo alla distinzione stratigrafica dei vari depositi di fossili. Questo ne suggerisce una più estesa applicazione particolarmente nell'area Mediterranea dove la tettonica ha pesantemente influenzato l'attuale dislocazione delle linee di costa quaternarie.

Key-words: Stable isotopes, shorelines, Latium
Parole chiave: Isotopi stabili, linee di costa, Lazio

1. INTRODUCTION

Paleoclimatic and paleoenvironmental studies based on stable isotopic composition of marine carbonates are common in the literature (e.g. Savin, 1977; Veizer, 1983); in particular, oxygen isotopic ratios $^{18}O/^{16}O$ measured on biogenic calcium carbonates such as foraminifers from deep sea sediments, contributed greatly to a better knowledge of marine climates during Quaternary and it was possible to estabilish an oxygen isotope statigraphy of Plio-Pleistocene with a worldwide applicability (Duplessy, 1981; Odin et al., 1982).

Several factors limit the use of oxygen isotope composition of molluscan shells as a stratigraphic tool. Namely: the discontinous character of the studied deposits; dubious paleoclimatic records partially obscured by events such as the general isotopic fluctuations of marine waters due to icecaps advance or retreat and local variations in evaporation rate and freshwater contribution; differences in the ecological and/or physiological behaviour of single species (Hoefs, 1980 and references therein). Nevertheless, stable isotopic composition of molluscan shells proved their utility to the study of marine Quaternary paleoenvironments mainly if of Holocene age (see Donner and Nord, 1986), and contributed to a better knowledge of the global sea-level changes (Aharon and Chappell, 1986).

If marine deposits and terraces are considered as paleosea level traces, oxygen isotope data on fossil *Mollusca* can conveniently be used to discriminate between neighbouring shorelines belonging to different paleoclimatic environments. This approach may be very helpful in tectonically active areas where elevations of ancient shorelines and marine terraces are not suggestive of different ages (Bonadonna et al., 1986). Difficulty in discriminating Quaternary raised shorelines is emphasized in the Mediterranean area owing to the tectonic evolution affecting the area during this period, and resulting in various vertical displacements of shorelines of similar age (see Hey, 1978). Further, paleoecological records based on molluscan faunal assemblages from the Mediterranean basin may be misleading because of a high variability of the local climates and of the lithology of the substratum (Butzer, 1983).

Stable isotopes in foraminifera from the Mediterranean sea have widely been investigated (Vergnaud Grazzini, 1985), whereas there are no systematic studies about the oxygen isotopic composition of fossil molluscan shells from Quaternary littoral deposits of the Mediterranean basin after the pioneering work by Emiliani and Mayeda (1964), although many stable isotope analyses of calcium carbonatic shells of living and fossil marine mollusks from this area have been published (e.g., Kaufman and Magaritz,1980; Schifano and Censi, 1983).

The aim of the present work is to check the efficiency of the isotopic method to distinguish among different fossil shoreline deposits belonging to only sligthtly different environments and to make a rough estimate of the isotopic variability within a single deposit.

2. GEOLOGICAL SETTING

The molluscan shells analyzed in this study were collected by Bonadonna (1967a; 1967b) from two fossil assemblages belonging to two Pleistocene deposits of littoral facies located in Northern and Central Latium on the north of Rome (Fig. 1). This area has intensively been investigated as far as the Plio-Pleistocene stratigraphy is concerned (Ambrosetti and Bonadonna, 1967; Bonadonna, 1967a; Bonadonna and Bigazzi, 1970; Ambrosetti et al., 1972; Dai Pra 1978; Conato and Dai Pra, 1980; Conato et al., 1980; Ambrosetti et al., 1981; Bartolini and Bosi, 1983; Radtke, 1983).

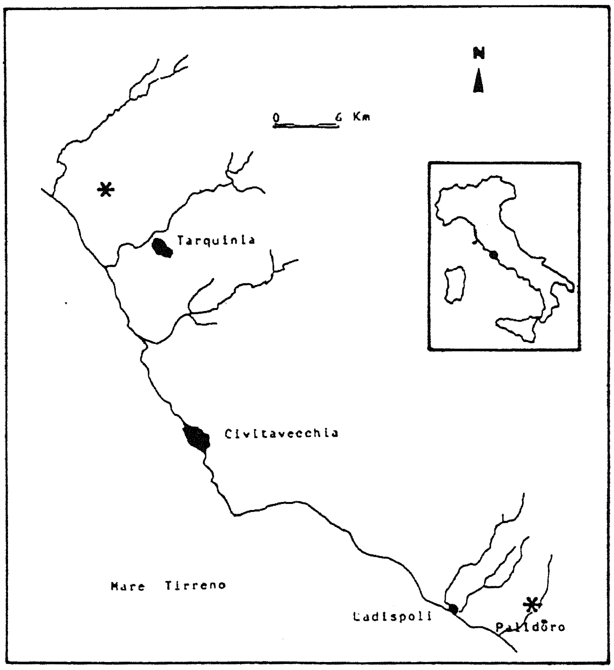

Fig.1 - Map showing locations where shells were collected.
Mappa delle località di raccolta delle conchiglie.

The first considered deposit we have analysed is found at "Casale di Statua", a locality near Palidoro, at an elevation of about 20 m a.s.l. It represents a classic Tyrrhenian ingression shoreline with Senegalese fauna and *Strombus bubonius* (Blanc, 1936; Bonadonna, 1967b). The second outcrop is located at "Lestra dell'Ospedale", near Tarquinia at about 45 m a.s.l. According to Bonadonna (1967a), the deposit is related to a shoreline at 39-48 m a.s.l. of Tarquinian age (Bigazzi et al., 1973). In this very area Dai Pra (1978) recognized a marine terrace between 2-3 and 65 m a.s.l. which was correlated to a single *Strombus bubonius* episode (Eutyrrhenian). On the basis of field observations and amino acid racemization data Bartolini et al. (1984) estimated an approximate age of 200 ka for the Lestra dell'Ospedale fossil samples, which is in agreement with $^{230}Th/^{234}U$ and ESR results by Radtke (1983) suggesting a correlation with the oxygen isotopic stage 7 (Shackleton and Opdyke, 1973). More recently, Hearty et al. (1986) attributed the Lestra dell'Ospedale site to the oxygen isotopic stage 9 in a comprehensive study of the amino acid stratigraphy of the Mediterranean area.

3. METHODS AND MATERIALS

The factors affecting the stable isotope composition of *Mollusca* have thoroughly been studied. These organisms appear to precipitate their carbonatic shells in isotopic equilibrium with the living environment (Lloyd, 1964; Fritz and Poplawsky, 1974): ^{18}O contents of shell carbonate are a function of the temperature of formation and of the isotopic composition of the mother water, whereas ^{13}C contents are linked mainly to the sources of available dissolved bicarbonate (Mook, 1971).

The assumption that ^{18}O contents of fossil shell carbonate reflect water temperature changes in the studied area and/or worldwide ^{18}O shifts of oceanic waters caused by the ice-effect (Shackleton and Opdyke, 1973) requires that the studied specimens were not affected by local phenomena which can modify their isotopic compositions. Furthermore original isotopic ratios must be unaltered from the time of deposition. In dealing with faunas from shoreline deposits, the ^{18}O content of shells can be influenced mainly by: contamination by ^{18}O depleted fresh-waters, individual response to peculiar environmental conditions and post-depositional isotopic exchange. Mook (1971) proposed a procedure based on the use of the relationship between $\partial\ ^{13}C$ and $\partial\ ^{18}O$ values to detect the extent of fresh-water contamination in not purely marine environments; the physiology of each species or the development of different ecotypes inside the same species (Bianucci and Longinelli, 1982) may require specific ecological niches and/or peculiar life habitats, therefore measurements of more than one species better characterize the studied environment and, finally, following Buchardt (1977), the preservation of original metastable aragonitic composition of shell material strongly supports the lack of post-depositional isotopic exchanges.

TABLE 1 - Isotopic composition of the studied shells in ∂‰vs PDB(*)

Sample	∂ ^{18}O	∂ ^{13}C	∂ ^{18}O	∂ ^{13}C
	Casale di Statua, Palidoro		Lestra dell'Ospedale, Tarquinia	
Mactra (M.) corallina L.				
Sample n° 1	-0.49 ± 0.01	+1.22 ± 0.01	+2.17 ± 0.09	+0.11 ± 0.07
Sample n° 2	-0.12 ± 0.06	+1.29 ± 0.01	+1.96	+1.01
Sample n° 3	+0.11 ± 0.03	+0.51 ± 0.02	+1.81	+0.95
Sample n° 4	-0.08 ± 0.01	+0.64 ± 0.00	+2.08 ± 0.03	+1.01 ± 0.01
Donax (Serrula) trunculus L.				
Sample n° 1	+0.66	+1.08	+1.34 ± 0.03	+1.34 ± 0.04
Sample n° 2	+0.34 ± 0.02	+1.00 ± 0.04	+1.48 ± 0.07	+1.62 ± 0.05
Sample n° 3	-0.24 ± 0.04	+1.10 ± 0.07	+1.93 ± 0.03	+1.77 ± 0.01
Sample n° 4	+0.81 ± 0.06	+0.78 ± 0.06	+2.05 ± 0.01	+1.60 ± 0.05
Chione (Chamelea) gallina L.				
Sample n° 1	-0.36 ± 0.01	-0.59 ± 0.03	+0.97 ± 0.00	+0.58 ± 0.01
Sample n° 2	-0.47 ± 0.04	-0.02 ± 0.02	+1.43 ± 0.06	+0.47 ± 0.04
Sample n° 3	-0.17 ± 0.01	-0.76 ± 0.07	+1.46 ± 0.06	+0.55 ± 0.04
Sample n° 4	-0.36 ± 0.01	+0.10 ± 0.05	+1.05 ± 0.02	+0.38 ± 0.05
Glycymeris cor violacescens LMK.				
Sample n° 1	-0.27	+1.23	+1.97 ± 0.06	+1.40 ± 0.05
Sample n° 2	+0.02	+1.11	+1.45	+1.37
Sample n° 3	+0.22 ± 0.06	+1.12 ± 0.01	+1.60 ± 0.09	+1.34 ± 0.02
Sample n° 4	-0.46 ± 0.03	+1.43 ± 0.08	+1.32 ± 0.07	+1.52 ± 0.03

(*) Analytical precision, when reported, refers to two-fold sample preparation and measurement.

On this basis thirty-two specimens belonging to four species of *Pelecypoda* (see Table 1) were selected among the forms collected by Bonadonna (1967a; 1967b) in the two considered deposits, each species being represented by four individuals by deposit; the whole valve of large-in-size shells was used for isotopic analyses to minimize seasonal variations. The rigth valve of each shell was carefully cleaned by hand and then by ultrasonic bath. After discarding the umbo the whole valve was crushed and roasted under vacuum at 400 °C for about 40' to decompose organic material and then reacted with 100% H_3PO_4 at 25°C (McCrea, 1950). Mass-spectrometer results are reported using the conventional ∂ ‰ notation relative to the PDB-1 standard (Craig, 1957). The carbonate mineralogy of all the studied samples has been analyzed by X-ray diffraction in order to check for post-depositional alteration which could have affected also the shell isotopic composition. All the analyzed specimens consist of aragonite and no revealable calcitization was detected thus supporting a good preservation of the original isotopic ratios.

4. RESULTS AND DISCUSSION

The isotopic results are reported in Table 1 and plotted in Figs. 2 and 3. Figure 2 shows the relation between ^{18}O and ^{13}C contents of the analyzed 32 shells from the two deposits together with two data from Bonadonna and Fornaca Rinaldi (1974) which refer to the same studied species. The analyzed shells belong to well distinct groups for ∂ ^{18}O whereas the carbon isotopic values do not show this evident partition (Fig. 3). The isotopic variations are comparable in the two areas.

The whole range of ∂ ^{13}C values, from -0.8 to 1.8‰ with 32 values ≥0‰, and the absence of any definite correlation between the oxygen and carbon isotopic abundances inside the same species concur to exclude the presence of fresh-water contamination. On the other hand, ^{13}C contents appear to group according to the species in the same way for the two deposits, particularly in the case of *Chione gallina* which shows the lower ∂ ^{13}C values, the samples from Lestra dell'Ospedale being as a whole slightly enriched in ^{13}C with the exclusion of the species *Mactra corallina* (Fig.3). The carbon isotopes grouping is probably to ascribe to the existence of different but specific microenvironmental conditions in which each species lived (Fritz and Poplawsky, 1974) as well as to vital factors such as the choice of food since the carbon budget of sea cannot be estimated as an infinite reservoir as we do in the case of oxygen.

As it was mentioned previously, the oxygen isotopic data from the two deposits are well distinct: the samples from Casale di Statua have ∂ ^{18}O values of -0.5 to 0.8‰ whereas the ones from Lestra dell'Ospedale show values of 1.0 to 2.2‰, moreover the gap between the two groups increases noticeably if we consider the difference of the isotopic compositions existing between the same species from the two deposits; apart from this feature the distribution of the oxygen isotopic content among the analysed species appear to be quite homogeneous (Fig.3). A beach deposit results from the highly variable actions of waves, currents, tides and

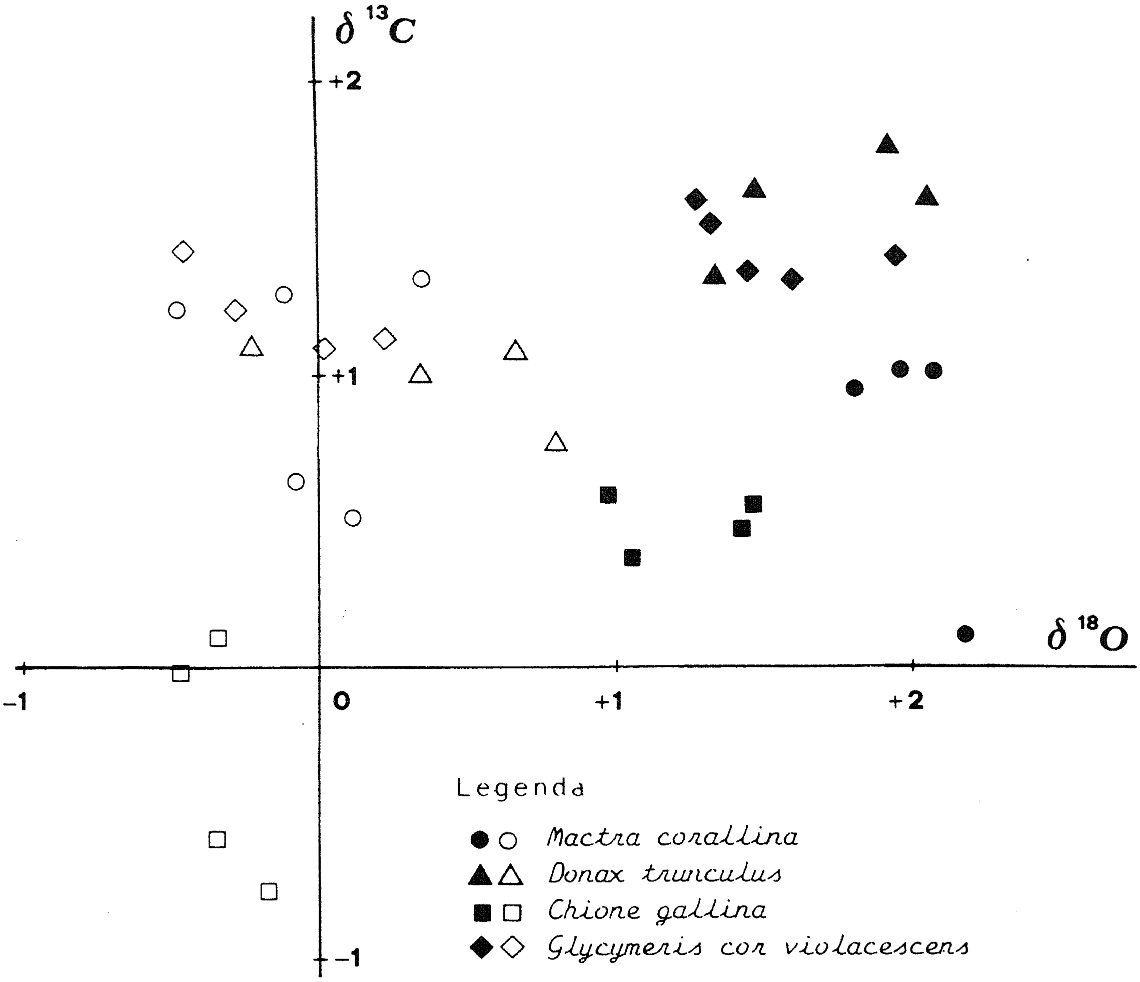

Fig.2 - Plot of $\partial\ ^{18}O$ and $\partial\ ^{13}C$ of shell carbonate from the studied sites. Open symbols: samples from "Casale di Statua"; solid symbols: samples from "Lestra dell'Ospedale".
Diagramma $\partial\ ^{18}O$ - $\partial\ ^{13}C$ del carbonato delle conchiglie studiate. Simboli vuoti: campioni provenienti da "Casale di Statua"; simboli pieni: campioni provenienti da "Lestra dell'Ospedale".

sediments reworking in a high energy environment. Therefore the fossil faunas we found in deposits like the studied ones are death assemblages rather than biocoenoses. Furthermore they cover a time span not negligible even if very short from a Quaternary geology point of view. So, the existence of mixed populations of slightly different ages with faunas from variable habitats can account for the observed scatter of $\partial\ ^{18}O$ values, but the number of studied specimens is not sufficient to speculate about the existence of systematic isotopic differences among the studied species. Probably the knowledge of the isotopic behaviour as deduced from the corresponding living forms could better clarify the causes of the distribution of the isotopic data to find out the species more suitable to develop this technique in a given area. In any case the obtained results show clearly the importance to compare isotopic data that are homogeneous as far as species are concerned.

Vergnaud Grazzini (1985) summarizes the peculiarity of the geochemical behaviour of the Mediterranean with reference to the isotopic composition of carbonate secreting organisms like foraminifera. The resulting picture shows that the oxygen isotopic values of calcium carbonate precipitated in equilibrium with modern surface waters are influenced by the eastward $\partial\ ^{18}O$ enrichment trend which results from the excess of evaporation, compensated by the Atlantic water contribution from Gibraltar. Changes in deep waters circulation patterns between the Eastern and the Western Mediterranean basins followed eustatic fluctuations and modified the distribution of surficial $\partial\,^{18}O$ values. As a consequence it is not possible to read the oxygen isotopic data of Quaternary molluscan marine faunas of the Mediterranean area in terms of thermal gradients and worldwide ice effects only (Magaritz and Kaufmann, 1973). In absence of detailed

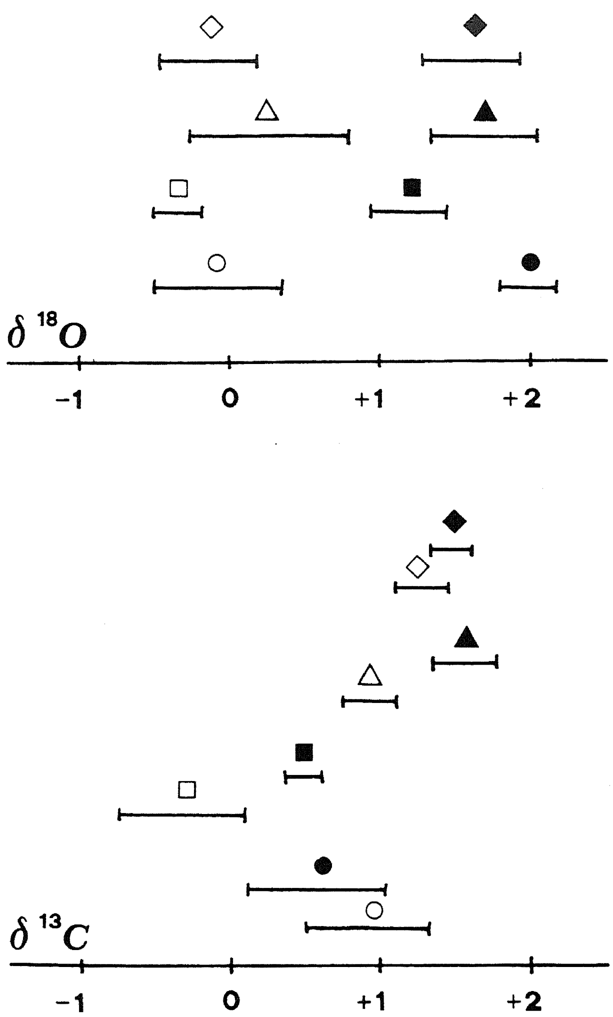

Fig.3 - ^{18}O and ^{13}C distribution of the studied shells, symbols are the same as in Fig. 2.
Distribuzione dei contenuti in ^{18}O e ^{13}C delle conchiglie studiate, simboli come in Fig. 2.

studies that let us to compare the isotopic data from different species we can only notice that the $\partial\,^{18}O$ results reported by Cortecci and Longinelli (1971) for living specimes of *Mactra corallina*, 0.20‰, and *Donax trunculus*, 0.50‰, collected at Tirrenia, about 200 km to the north of the studied sites, agree with the present $\partial\,^{18}O$ found in the samples from Casale di Statua and that the average $\partial\,^{18}O$ of 0.46‰ found by Vergnaud Grazzini (1986) for the modern planktonic foraminifera *Globigerinoides ruber* in the West Mediterranean, taking into account the oxygen isotope fractionation between aragonite and calcite (Veizer, 1983), correspond to the lower values measured for the samples from Lestra dell'Ospedale. Clearly these comparisons, based on very scanty data, can suggest only that the present $\partial\,^{18}O$ values of calcareous secreting organism living in shallow marine waters of the considered area fall in the range which includes the results obtained in the fossils from the deposit of Casale di Statua and the lower values from Lestra dell'Ospedale. On the basis of the similarity of the faunas collected in the two deposits, the ^{18}O average enrichment of about 1.7‰ measured in the samples from Lestra dell'Ospedale with respect to the ones from Casale di Statua deposit seems to be related mainly to a worldwide positive ^{18}O shift of sea waters caused by the ice effect and/or to variations in the isotopic balance of the Mediterranean rather than to a thermal shift towards a lower temperature in the studied area.

As above mentioned, different stratigraphical attributions have been proposed by several authors for the Lestra dell'Ospedale site. The average oxygen isotopic difference observed between the two deposits is comparable with the ones measured for the peaks of minimal $\partial\,^{18}O$ values in the isotopic curve from Mediterranean foraminifera (Cita et al., 1977; Vergnaud Grazzini, 1985). Clearly to develop on these basis a correlation with the events recorderd by the foraminiferal isotopic stratigraphy it is necessary to analyse shells from the fossil deposits of the numerous shorelines both in the considered area and in the whole Mediterranean.

5. CONCLUSIONS

Fossil shells from the two studied sites have well distinct oxygen isotopic composition, therefore the considered deposits are distinguishable by means of their $\partial\,^{18}O$ values. The distribution of carbon isotopes appears to depend partly on the considered species showing similar variations in the two groups.

The chief aim of this work was to evaluate the actual suitability of the isotopic method to help to mark some Quaternary shoreline deposits on the basis of the oxygen isotopic values of their molluscan fauna: the consistence of the obtained results suggests that this methodology, if widely applied, can further contribute to Mediterranean Quaternary stratigraphy.

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