

MINERALOGY AND OXYGEN ISOTOPE PROFILE OF *PELECYORA GIGAS* (VENERIDAE, BIVALVIA) FROM TUSCAN PLIOCENE

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ABSTRACT: a specimen with joined valves of *Pelecycora gigas*, an extinct species, was collected in a sandy layer of Early Pliocene age in the northern part of the Siena Basin (Tuscany, Italy). XRD data demonstrated that the original mineralogical composition of the specimen was aragonitic and it maintained substantially the original structure and composition. Neglecting possible changes in sea salinity during different seasons, we can estimate, using oxygen isotope composition a maximum seasonal temperature differences of ca. 9 °C experienced during the life of the individual. An approximate estimation of past sea water composition allows to calculate an average temperature of 23.0±2.7 °C for the water where the shell lived, whereas calculated temperature extremes are 18.5 °C for the colder season and 27.6 °C for the warmer. These data are in a good agreement with those proposed on the basis of the Pliocene Mediterranean taxa nowadays living along the western African shores.

Keywords: *Pelecycora gigas*, shell mineralogy, isotopic composition, Pliocene temperatures, Tuscany.

1. INTRODUCTION

Many factors may influence the biogeography of shallow marine benthic molluscs such as nutrients, predation, competition, substrate, natural barrier, ocean circulation (Monegatti & Raffi, 2001; Silva et al., 2006). However, it is largely accepted that sea surface temperature (SST) plays the major role in controlling the latitudinal distribution of benthic organisms on the continental slope (Hall, 1964; Petuch, 2004). In this context the critical factor does not lie as much in the temperatures suitable for the survival of specimens but rather the duration of the time interval in which the sea water is at the temperature required for successful reproduction and early growth (Raffi, 1986; Raffi et al., 1985; 1989).

Even though the Pliocene period appears to have been, on average, warmer than present (Jansen et al. 2007), it is characterized by climatic cooling phases recorded in the Northern Hemisphere by paleontological and isotopic data (Stanley, 1986; Stanley & Ruddiman, 1995; Mudelsee and Raymo, 2005; Haug et al., 2005; Lisiecki & Raymo, 2007; Lawrence et al., 2009). The two major cooling events occurred at about 3.1 Ma and 2.7 Ma (the latter just older than the recently revised Plio-Pleistocene boundary, Gibbard et al., 2009) and caused pulses of extinction and local disappearance

among the Mediterranean mollusc fauna (Monegatti & Raffi, 2001; Monegatti et al. 2002; Monegatti & Raffi, 2010). This fact results in a Pliocene decrease of the mollusc diversity because faunal impoverishment is not balanced by recovery phases, probably owing to an upwelling phenomenon along the Northwest African coasts, which appears to have intensified since the Middle Pliocene (Cita & Ryan, 1979; Sarnthein et al., 1992; Monegatti & Raffi, 2001).

During the Early-early Middle Pliocene the Mediterranean Basin was populated by a thermophilic malacofauna thriving in a tropical sea with estimated mean maximum SSTs over 24–25 °C for at least five to six months every year (Monegatti & Raffi, 2001; Silva et al., 2010); the molluscan fauna is categorized as MPMU1 by Raffi & Monegatti (1993) and Monegatti & Raffi (2001). At least as far as molluscan fauna is concerned, this temperature regime remains substantially stable up to about 3.1 Ma, when the first cooling event, even though not so severe as that at 2.7 Ma, has dramatic results for the Early Pliocene thermophilic fauna. The disappearance of *Strombus coronatus* and the drastic decrease of the taxonomic diversity of Conidae and Terebridae are the most relevant events among gastropods whereas bivalves offer a more detailed and quantitative approach thanks to the hundreds of infra- and circalittoral species

taken into account by Monegatti & Raffi (2001). In correspondence to, or just after, the 3.1 Ma event, a percentage of bivalves varying from 15% to 23% (more than 50 and no more than 80 species) disappears from the Mediterranean (Raffi & Monegatti, 1993), owing to both regional disappearances and true extinctions (*sensu* Raffi et al., 1985; 1989). Among 13 and 17 species typical of MPMU 1 are still living along the West African coasts south of latitude 20-22°N (i.e. the tropical Mauritanian-Senegalese province of Hall, 1964) but this stock appears to be negligible in comparison with that of the extinct taxa.

Pelecypora gigas is a large, thick-shelled bivalve typical of the Early Pliocene tropical environments in the Mediterranean Basin, that became extinct during, or just after, the 3 Ma cooling event. This species has been little studied and research results are restricted to the systematic perspective and are mainly concentrated in the 1960s and 1970s (Tavani & Tongiorgi, 1963; Palla, 1966; Malatesta, 1970, among others).

The aim of the present study is:

- to analyze the shell composition of *Pelecypora gigas* to investigate its original mineralogy;
- to reconstruct the shell growth pattern;
- to measure the oxygen isotope composition of the shell and to interpret these data with regard to climate conditions of the Mediterranean during the Early Pliocene.

Concerning the last point, stable isotope analysis of the Plio-Pleistocene molluscs in Tuscany was pioneered in the late 60s to 70s of the last century and then almost completely forgotten (Longinelli et al., 1961; Vergnaud Grazzini, 1968). To better understand and constrain future climate change in a high CO₂ world, it is essential to study potential CO₂ concentration analogues in Earth's history and the climate at that time. The Pliocene epoch prior to the intensification of Northern Hemisphere glaciation at about 2.75 Ma is a likely candidate for such a high CO₂ analogue (e.g. Bartoli et al., 2011) and this should encourage to a reappraisal of the study of the Pliocene marine successions preserved in Tuscany.

2. GEOLOGICAL AND PALEONTOLOGICAL DATA

The *P. gigas* specimen was gathered from a Pliocene sandy level outcropping near Colle d'Arbia (Monteaperti, Siena) in the northern part of the Siena Basin (Tuscany, Italy). This is part of a broader tectonic depression, NNW-SSE oriented, traditionally interpreted as a half-graben formed in the framework of late Miocene-Quaternary polyphase extensional tectonics of Northern Apennines (Bossio et al., 1993; Carmignani et al., 2001; Brogi, 2011) (Fig. 1).

The Neogene sedimentary infill of the



Fig. 1 - Location map of the fossiliferous outcrop (scale map 1:10.000).

Siena Basin starts with a Miocene (late Messinian) succession overlying the pre-Neogene bedrock composed of several metamorphic and non-metamorphic tectonic units (Brogi, 2011). Miocene sediments are in turn overlain by Pliocene ones with an intervening angular unconformity (Costantini et al., 2009). Pliocene deposits of the northern part of this basin, mainly consisting of sands with gravel and mud intercalations, have been recently mapped as a succession of four depositional sequences (Martini & Aldinucci, 2017; Martini et al., 2011) ranging from early Zanclean to Piacenzian in age.

In particular the sequence S3, the fossil bearing unit, ranges within the late Zanclean-early Piacenzian time span (Martini & Aldinucci, 2017).

From the taphonomic point of view, the fossil speci-



Fig. 2 - *P. gigas* just after the extraction. Note the original horizontal position.

men displays conjoined valves in a nearly horizontal position, which reflects a *post mortem* dislodging due to wave/current sweeping action (Fig. 2)

However, the presence of an articulated individual with nearly complete valves displaying one of these with the ventral margin broken but nearly whole (i.e. each piece of the shell is juxtaposed with the surrounding ones) along with the general good state of shell preservation allow us to infer low energy conditions after the exhumation consistent with minimal *post-mortem* disturbances, very little reworking and negligible transportation. Inconspicuous signs of bioerosion and encrustation suggest a rapid burial, which also promotes the conservation with articulated valves.

P. gigas is a large and thick-shelled venerid reaching the largest dimensions known within this genus, a characteristic which seems typical of species living in tropical environments (Marasti & Raffi, 1980). Regarding the paleoecological evidence, this species has been frequently recognized in inner subtidal sandy bottoms (Bernasconi & Robba, 1993; D'Alessandro et al., 2004; Ferrero et al., 2005), a substrate preference consistent with the grain size (sand 80.07%, silt 17.41%, clay 2.51%) of the siliciclastic sediment of the Colle d'Arbia outcrop. *P. gigas* is considered a suspension-feeder, which lived as a sluggish active shallow-burrower, a life

habit suggested by the shell thickness, shape and size along with the pallial sinus form (Stanley, 1970). However, the relationship between the burrowing depth and the shell/pallial sinus morphology discussed in the pioneering work of Stanley (1970) is not sufficient to be used as a clue to reconstruct the burial depth of extinct species. Taking into account both the horizontal position displayed by the specimen and the average level of sediment reworking in shallow water sandy bottoms (about 15-20 cm), it seems reasonable to consider the above measure as the burrowing depth attained by our individual of *P. gigas*. A closer relationship between burrowing depth and pallial sinus length is suggested by Kondo (1987) on the basis of the ratio of pallial sinus to shell length (Pallial Sinus Index, PSI). This index is very useful in active burrowing, suspension-feeding siphonate bivalves and may be also useful for extinct species. The PSI calculated for our *P. gigas* specimen corresponds to a burrowing depth of 1-2 times the shell length, a result consistent with that previously inferred.

In terms of the bionomic model of Peres & Picard (1964), this venerid is considered an infralittoral species referable to Fine Well Sorted Sand (SFBC) biocenosis (Bernasconi & Robba, 1993; D'Alessandro et al., 2004).

P. gigas ranges from the Early Miocene to the Middle Pliocene. During the Pliocene this venerid is wide-

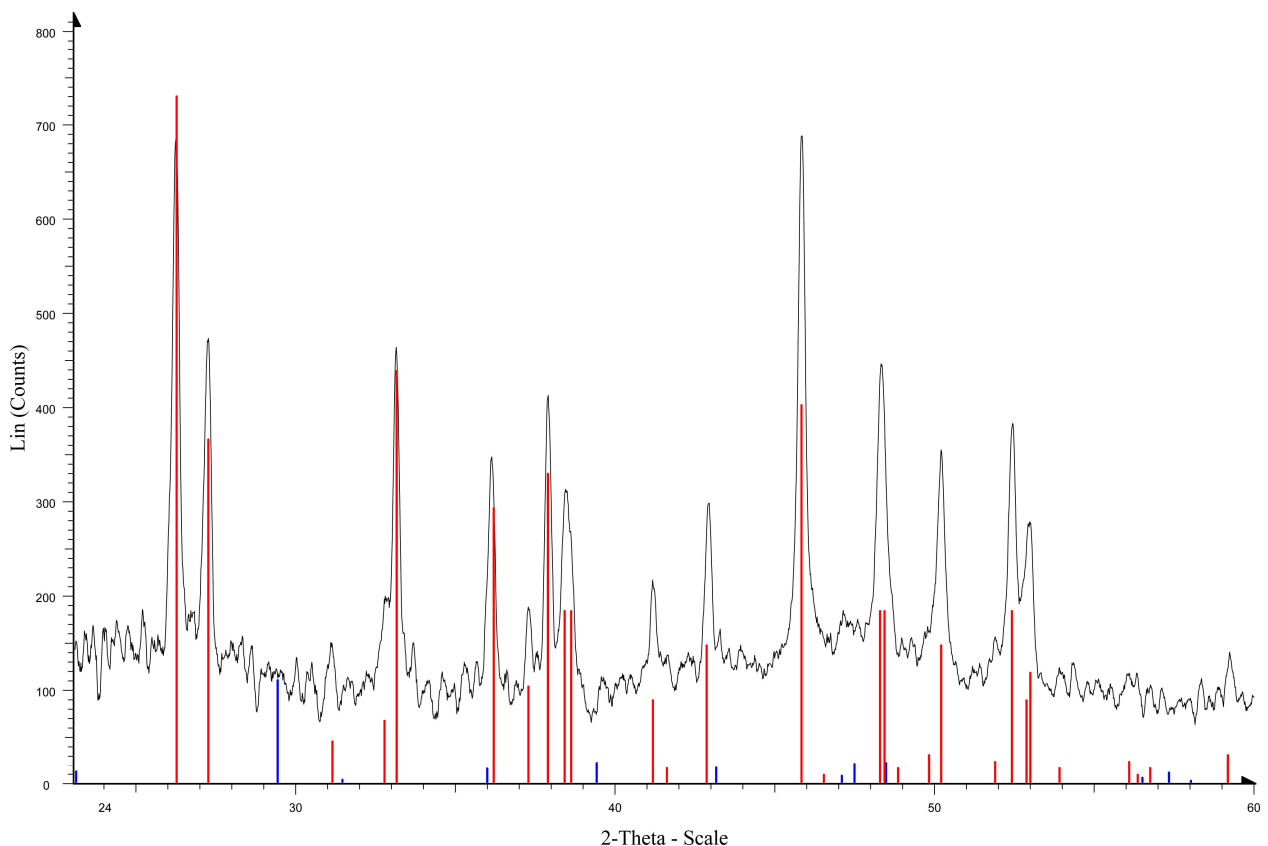


Fig. 3 - Closeup of the X-ray pattern region hosting major diffraction peaks for aragonite and calcite, showing that aragonite is the major phase in the analysed sample.

spread over the whole Mediterranean Basin from the eastern (Turkey) to the western (Andalusia) part (Erunal-Erentoz, 1958; Vera-Pelaez et al., 1995) with a sole Atlantic finding along the Moroccan coast (Lecointre, 1952).

3. SHELL MINERALOGY

Apart from the presence of trace components, the mineralogical composition of bivalve shells ranges from pure aragonite to pure calcite, the latter being a rather rare case. Usually calcite secreting bivalves are those with an epifaunal life habit whereas those with an infaunal life habit form wholly aragonitic shells. In particular, calcitic continuous layers have been recognized only in some taxa, such as Eupteriomorphs, Hippuritoida (a group of extinct rudists), some mytiloids and chamoids (Carter, 1980; Esteban-Delgado et al., 2008). Within Veneridae, the shell mineralogy is generally uniform being composed of minute aragonite crystals, with some exceptions being representatives of *Saxidomus*, *Protothaca* and *Irus* where small calcitic structures, mainly described as “conellae”, are present in the outer part of the outer shell layer (Carter et al., 1998).

Most of the studies concerning Veneridae shell mineralogy are focussed on the living taxa (Shimamoto, 1986; Glover & Taylor, 2010) and very few data are available on fossil species, such as *P. gigas*. In order to identify the mineral phases in the skeleton of this taxon, an X-ray powder diffraction analysis was carried out. The shell sample was crushed into small pieces and then ground in an agate mortar, with subsequent milling under acetone to produce a fine powder (grain size nearly 5-10 μm) which was loaded into a capillary 0.7 mm in diameter. X-ray diffraction data were obtained using a Bruker D8 Advance diffractometer, equipped with primary Ge (111) monochromator and with a Braun PSD linear detector. The running conditions were: 40 kV, 40 mA, 2θ range 21° to 70° , 2θ step 0.0157° , measurement speed 6 sec/step PSD measurement width 4° . Experimental data were examined through the EVA Bruker software: in Fig. 3 is shown the diffraction pattern after background subtraction, together with the PDF reference patterns for calcite (blue bars, PDF 83-1762) and aragonite (red bars, PDF 41-1475) One can notice that aragonite (red bars) is clearly the major phase, and that the presence of calcite, if any, is very minor.

To precisely evaluate the presence of calcite, the experimental data were elaborated through a Rietveld refinement, performed with the Topas-Academic program (Coelho, 2018) for mineralogical quantitative analysis for mixtures including both crystalline and amorphous phases. In a Rietveld refinement, the difference between the observed and calculated intensities is minimized at every 2θ point of the observed powder diffraction pattern, namely:

$$S = \sum_i w_i [y_i(\text{obs}) - y_i(\text{calc})]^2 \rightarrow \min$$

The weight fractions of the phases in a mixture can be derived from the refined scale factors of each phase

S_p , through the expression:

$$W_p = \frac{S_p \cdot (Z \cdot M \cdot V)_p}{\sum_{i=1}^n S_i \cdot (Z \cdot M \cdot V)_i}$$

where W is the relative weight fraction of phase p in a mixture of n phases, and S , Z , M , and V are, respectively, the Rietveld scale factor, the number of formula units per cell, the mass of the formula unit (in atomic mass units) and the unit cell volume (in \AA^3).

Structural models for the Rietveld refinement were taken from literature (calcite: Effenberger et al., 1981; aragonite: Dal Negro & Ungaretti, 1971), and only aragonite cell parameters were refined.

During the refinement, a parameter taking into account asymmetry, determined from the refinement of SRM 675 NIST standard, was introduced and not refined. Background was modelled with a 12-terms Chebyshev function, and a pseudo-Voigt function was used for peak shape. A common Lorentzian parameter for crystallite size was introduced and refined for aragonite and calcite to model peak width. Final agreement factors for the refinement (Fig. 4) were satisfactory, with the figures $R_{wp}=2.817\%$, $R_p=2.167\%$, $Gof=1.087$.

In conclusion, shell mineralogical data based on x-ray diffraction suggest that our specimen of *P. gigas* was originally aragonitic and reasonably retained its pristine mineralogy; therefore, it seems very unlikely that diagenesis has reset the shell isotopic composition (Dodd & Stanton, 1976).

4. OXYGEN ISOTOPE COMPOSITION

The external shells were drilled in an ontogenetic sequence, from the umbo towards the ventral margin (e.g. Krantz et al., 1987) using a Dremel microdrill equipped with a 1 mm bit, with average distance between the center of the holes of ca. 1.5 mm. 44 samples were obtained (Fig.5).

Stable isotope analysis on the obtained powder was performed using a Gas Bench II (Thermo Scientific) coupled to a Delta XP IRMS (Finnigan) at the Institute of Geosciences and Earth Resources of the Italian National Research Council (IGG-CNR) in Pisa (Italy). Carbonate samples of ca. 0.15 mg of CaCO_3 were dissolved in H_3PO_4 (105%) for one hour at 70°C . Sample results were corrected using the International Standard NBS-18 and a set of 3 internal standards, previously calibrated using the international standards NBS-18 and NBS-19. Isotopic results are reported using the conventional $\delta^\circ\text{‰}$ notation, with reference to the V-PDB standard; $\delta^{18}\text{O}$ values of water are quoted with the reference to V-SMOW. Analytical uncertainty ($\pm 1\sigma$) for $\delta^{18}\text{O}$ was $\pm 0.20\text{‰}$.

The equilibrium oxygen isotopic composition of marine biogenic carbonates primarily depends on the temperature of carbonate deposition and on the oxygen isotope composition of the surrounding sea-water (Epstein et al., 1953). The latter is globally influenced by continental ice volume and locally by salinity variations (i.e. mixing with freshwater and/or evaporation, e.g.

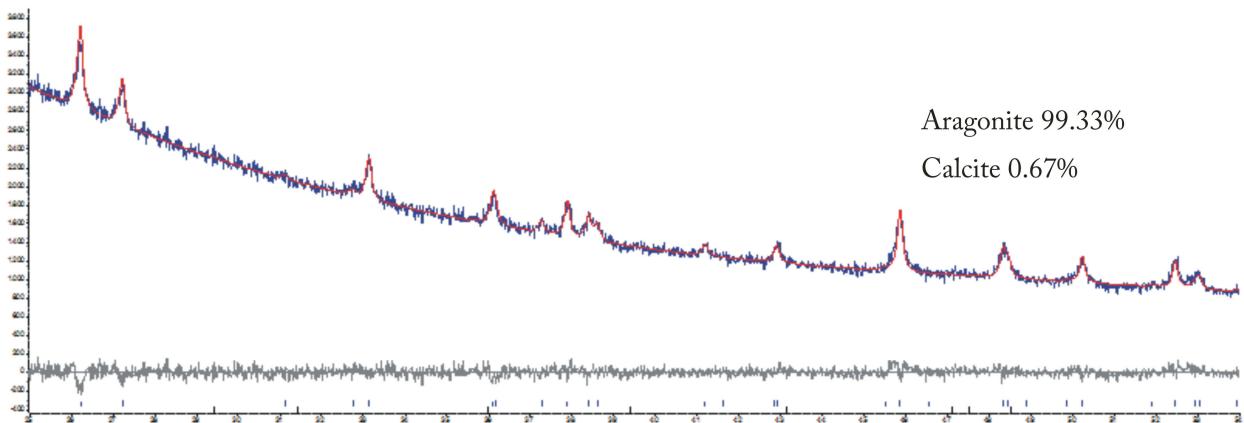


Fig. 4 - Rietveld refinement plot, closeup of the 2θ range 25-50°; dark blue line represents the observed pattern, red line the calculated pattern. Their difference line is represented by the lower trace, with vertical marks showing the calculated positions of Bragg reflections for aragonite and calcite.

Shackleton, 1987). With only the $\delta^{18}\text{O}$ of carbonate, neither the $\delta^{18}\text{O}$ of water nor paleotemperature can be reliably determined without independent quantification of one or the other. Although complex in detail, oxygen isotope composition of samples collected along the shell growth have been demonstrated to be related to changes of seasonal conditions like in change in temperature and salinity (e.g. Schöne et al., 2007; Leng et al., 1998; Collareta et al., 2018). Therefore, analysing isotopic composition along the shell growth, it is possible to calculate the seasonal changes in temperature, reasonably assuming constant isotopic composition of sea water during the year. Moreover, for most bivalves, precipitation close to equilibrium can be assumed (Wefer & Berger, 1991) even in absence of calibration of a single species. There is discussion concerning the best equation for calculating paleotemperature (Patterson et al., 1993; Kim & O'Neil, 1997; White et al., 1999; Zanchetta et al., 2005) and the ideal would be to have specific equation for each species. However, different calibrations usually differ only slightly in the term of rate of change in $d\alpha/dt$, where α is the fractionation factor between water and calcite and t is the temperature (White et al., 1999) but can differ for the absolute value of temperature determined.

For the reconstruction of the paleotemperatures (SST °C) from shell oxygen isotopes we used the equation for aragonite given by Grossman & Ku (1986), with a correction for the conversion of V-SMOW to V-PDB (Dettman et al., 1999).

$$\text{SST}(\text{°C}) = 20.60 - 4.34[\delta^{18}\text{O}_{\text{shell-V-PDB}} - (\delta^{18}\text{O}_{\text{water-V-SMOW}} - 0.27)] \quad (1)$$

This implies that for a constant isotopic composition of seawater the $\Delta\delta^{18}\text{O}/\Delta T \sim 0.23\text{‰}/\text{°C}$.

The average $\delta^{18}\text{O}$ values measure along the profile is $0.06 \pm 0.61 \text{‰}$ the maximum values and the minimum

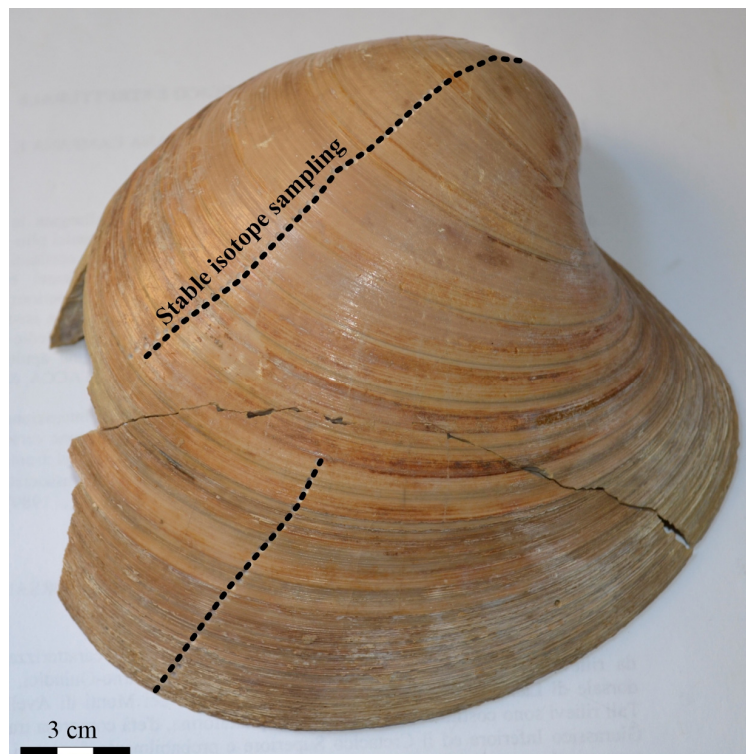


Fig. 5 - The specimen of *P.gigas* showing the stable isotope sub-sampling tracks.

are 1.12‰ and -0.99‰ respectively. This implies a maximum difference in temperature during the life of the mollusc of ca. 9.2°C . At least three clear seasonal oscillations are visible (Fig. 6) in the $\delta^{18}\text{O}$ profile. At the edge of shells the ontogenetic reduction of shells growth (e.g. Aguirre et al., 1998) complicate the identification of seasonal cycles at the resolution adopted. However, it seems reasonable to assume that the specimen represents more than 2 yr of $\delta^{18}\text{O}$ record.

To calculate past "absolute temperature" is difficult because of the absence of accurate evaluation of past

sea water isotopic composition. Current $\delta^{18}\text{O}$ values of western Mediterranean can range from ca. +1.3 to +1.4‰ (Pierre, 1999). Mediterranean is today considered a concentration basin due to the deficit in the hydrological budget and this has been probably true already during the Pliocene (Bianchi et al., 2012). This implies that local isotopic composition is higher than the ocean average owing to evaporation. In addition, it must be considered that Pliocene sea level was higher than today associated to lower isotopic composition of seawater for a lower mass of continental ice. Multiple lines of evidence suggest that the sea level during the middle Pliocene was >20 m above present sea level and a value of +25 m is often adopted in numerical climate model simulations (Dwyer and Chandler, 2009; Miller et al., 2012; Rohling et al., 2014 and reference therein).

In many estimate for the Quaternary Period, the relation of ca. 0.009 ‰/m of eustatic sea level variation has been found (Rohling et al., 2014). Assuming an eustatic component of +25 m, the isotopic water should be on average ca. -0.25 ‰ lower than today. More recently, estimates of isotopic composition of global ocean for the eustatic component suggest an average value ca. -0.5‰ less than today for the Pliocene at around ca. 3 Ma (Rohling et al., 2014). These differences in estimate may insert some uncertainty in the final temperature estimate of ca. 1°C or more, if the sea level was higher than assumed. The subdued variance of oxygen isotopic time series on benthic foraminifera during the interval of 3-5 Ma (Lisiecki & Raymo, 2005, 2007) suggest a very minor "ice volume effect" (Shackleton, 1987); nevertheless this can introduce additional uncertainty to our estimation.

Assuming a similar relation between salinity and oxygen isotope composition of sea water in western Mediterranean, a reasonable estimate using the discussed figures would be ca. +0.9‰ for the oxygen isotopic composition of western Mediterranean sea water. This does not account for local changes in salinity and in the following calculation, we neglect seasonal change in salinity. This can introduce further error in the proposed calculation. Therefore, the average temperature obtaining from these figures is $23.0 \pm 2.7^\circ\text{C}$, whereas extremes calculated temperature are 18.5°C and 27.6°C respectively. The average maximum temperature obtained for each cycle is $26.6 \pm 0.7^\circ\text{C}$, whereas the minimum is $19.3 \pm 0.7^\circ\text{C}$.

P. gigas belongs to the MPMU1 mollusc group including a stock of thermophilic taxa that no longer exist in the Mediterranean waters. About fifteen species of this stock (named "Mediterranean Pliocene Tropical Survivors", MPTSs) are living along the coast of West Tropical Africa south of latitude N 21° (Cape Blanc) (Monegatti & Raffi, 2001), the northern limit of the Northern Alternance Region of Le Loeuff & Von Cosel (1998). Taking into account that the areas currently populated by these taxa are characterized by SSTs over 24°C for at least five to six months per year and never cooler than 19°C (data from NOAA-CIRES Climate Diagnostic center) and that the MPTS and the most common tropical extinct species were living everywhere in the Mediterranean Basin before 3.1 MA, an analogous SST pattern has been suggested for MPMU1 time interval

(Monegatti & Raffi, 2001, 2007; Silva et al., 2006, 2010).

Our temperature estimations based on *P. gigas* isotope composition are in very good agreement with the aforementioned data and strongly support typical tropical conditions in the Mediterranean during the Zanclean-early Piacenzian. This fact confirms the thermophilic character of *P. gigas* and that its extinction was caused by the first Pliocene climatic cooling at around 3.1 MA.

5. CONCLUSION

In this paper we describe the mineralogy and the oxygen isotope composition of a fossil shell of *Pelecypora gigas* found in a Pliocene sandy layer in central Tuscany (central Italy). *P. gigas* is an extinct thermophilic species of the Lower Pliocene of the Mediterranean Basin, disappearing during the first cooling step at ca. 3 Ma (Monegatti & Raffi, 2001). New data on mineralogy indicate that the shell was aragonitic as are most bivalves. Petrography and XRD indicate that the selected specimen was perfectly preserved and suitable for stable isotope analyses. Neglecting possible changes in sea salinity during different seasons, $\delta^{18}\text{O}$ values allow calculating a maximum seasonal temperature differences during the life of the shell of ca. 9°C . A crude estimation of past sea water composition allows to calculate an average temperature of $23.0 \pm 2.7^\circ\text{C}$, whereas extremes of calculated temperature are 18.5°C for the colder season and 27.6°C for the warmer. These preliminary data indicate that *P. gigas* would represent an interesting archive to reconstruct seasonal climatic variation during the warmer part of the Pliocene, a period which, to some extent, represents a potential analogue for future projection owing to increasing of atmospheric CO_2 concentration toward values typical of the Pliocene (Bartoli et al., 2011).

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