

Is *Cyprideis agrigentina* Decima a good paleosalinometer for the Messinian Salinity Crisis? Morphometrical and geochemical analyses from the Eraclea Minoa section (Sicily)

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a b s t r a c t

The living euryhaline species *Cyprideis torosa* (Jones) undergoes morphometric variations in size, nodding and sieve-pore shape linked to the environmental salinity. In particular it is known that salinity values around 8-9 psu represent the osmoregulation threshold and also the turning point between smaller and greater valve dimensions and prevalingly noded against un-noded valves. The variation of the percentage of round-, elongate- and irregular-shaped sieve-pores on the valves has shown an empiric logarithmic correlation with the water salinity from 0 to 100 psu. Due to this ecologically cued polymorphism, *C. torosa* represents an invaluable paleosalinometer for the Quaternary brackish basins.

In this paper we attempt to verify whether the ecophenotypical behavior of the post-evaporitic Messinian species *Cyprideis agrigentina* Decima was comparable with that of *Cyprideis torosa*. To reach this goal, three morphometric characters have been analyzed: 1) size variability; 2) nodding and ornamentation; and 3) variability of the percentage of the sieve-pore shapes. The paleoenvironmental interpretation was made using synecological and geochemical approaches [stable isotopes, trace elements, Sr-isotopes and natural radioactivity (NRD)]. For this study, the 250 m-thick Messinian Lago-Mare succession of Eraclea Minoa (Agrigento, Sicily) was chosen for the presence of monotypic assemblages made only by *C. agrigentina* for around 70 m of thickness. The results of the morphometric analyses showed that: 1) size variations are not related to the salinity changes recognized both from synecological and geochemical analyses; 2) no noded specimens have been recovered along the Section; 3) the salinities calculated on the basis of the percentage of the sieve-pore shape are not correlated with the salinities inferred from the synecological and geochemical analyses. Thus, in this paper we conclude that *Cyprideis agrigentina* cannot be considered a paleosalinometer for the Messinian Salinity Crisis. There is a correlation of the $\delta^{13}\text{C}$ with the percentages of sieve-pore shapes, linking them to the behavior of the dissolved inorganic carbon (DIC) and to the oxygen availability at the bottom of the basin.

1. Introduction

Since the pioneering studies by Schäfer (1953), Sandberg (1964), Vesper (1975) and Rosenfeld and Vesper (1977), it is known that the living anomalohaline species *Cyprideis torosa* (Jones) undergoes morphometrical variations in size, nodding and sieve-pore shape linked to environmental physical and chemical parameters – especially salinity – showing a clear environmentally cued polymorphism. The species can withstand and thrive in a very wide range of salinity (0.4 to 150 psu according to Neale, 1988 and Griffiths and Holmes, 2000), thus it is commonly regarded as a valuable paleosalinometer

for the Quaternary marginal marine and athalassic brackish deposits (Marco-Barba, 2010; Pint et al., 2012 with references therein). Its slow-Mg calcite shell represents also a source of biogenic carbonate for the geochemical analyses (trace elements, stable isotopes and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios) to infer the chemical composition of past waterbodies, because of its high rate of valve calcification. In many studies, morphometrical variations were coupled with the geochemical approach to make more detailed paleoenvironmental reconstructions of brackish environments (Barbieri et al., 1999; Anadón et al., 2002; Marco-Barba, 2010; Curry et al., 2013; Pint et al., 2013; Rossi et al., 2013). Several studies (Carbonel, 1982; Aladin, 1993; van Harten, 1996, 2000; Keyser and Aladin, 2004; Keyser, 2005; Boomer and Frenzel, 2011; Frenzel et al., 2011, 2012 among others) showed that salinity values around 8-9 psu represent the osmoregulation threshold and also the turning point between smaller and greater valve dimensions

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and prevalingly noded against un-noded valves. Rosenfeld and Vesper (1977) showed an empiric logarithmic correlation between the variation of the percentage of round-, elongate- and irregular-shaped sieve-pores on the valves of *Cyprideis torosa* and the water salinity from 0 to 100 psu. This correlation has been confirmed by subsequent papers (Neale, 1988; Keating et al., 2007; Pint et al., 2012) and Frenzel et al. (2011) elaborated a transfer function based on the percentages of round sieve-pores.

In order to decipher the paleosalinity changes during the end of the Messinian Salinity Crisis (Hsü et al., 1973; CIESM, 2008; Roveri et al., 2014a), Rosenfeld (1977) and Bonaduce and Sgarrella (1999) applied the counting of different sieve-pore shapes to the fossil species *Cyprideis agrigentina* Decima, supposing that also this species could morphologically react as *C. torosa*. In both cases they obtained hyperhaline values for the waters hosting *C. agrigentina* specimens (respectively 35-50 psu and 50-70 psu) considering those values reliable for the evaporative paleoenvironment that yielded the deposition of the gypsum.

Cyprideis agrigentina (Fig. 1) is one of the most widespread ostracod that lived in the Paleomediterranean during the latest Messinian Lago-Mare event (5.53-5.33 Ma, CIESM, 2008; 5.55-5.33 Ma, Manzi et al., 2013; Roveri et al., 2014a). It seems to have been the first ostracod that colonized again the sterile bottoms of the Paleomediterranean after the deposition of the Primary Lower Gypsum and the partial desiccation of the basin. It has been recovered both in the Messinian sediments drilled on the Paleomediterranean bottoms and in those cropping out along the peri-Mediterranean chains, from the most western area (Malaga Basin) to the easternmost Adana Basin (Benson, 1978; Bonaduce and Sgarrella, 1999; Iaccarino and Bossio, 1999; Grossi and Gennari, 2008; Guerra-Merchán et al., 2010; Cosentino et al., 2012; Faranda et al., 2013). In their study on the Messinian Lago-Mare paleoenvironments inferred from the ostracod assemblages, Grossi et al. (2008) showed that *C. agrigentina* behaved as a very euryhaline species: it was associated a) with the benthic foraminifer *Ammonia tepida* (“*Cyprideis-Ammonia* assemblage”) in very oligotypic assemblages supposed to be typical of high mesohaline environments; b) with *Loxococoncha muelleri* (Mehés) and *Loxococoncha eichwaldi* Livalent (“*Cyprideis-Loxococoncha* assemblage”) (low mesohaline environment); c) it was also a component, although not dominant, of the “pointed candonids-Leptocytheridae assemblage” and “pointed candonids assemblage”, supposed to be characteristic of oligohaline to low mesohaline environments.

Anyway, despite its apparent capability to withstand different salinities, no noded specimens of *C. agrigentina* have been ever found (Ligios and Gliozzi, 2012) and this could arise some questions about the possible ecophenotypical reaction of *C. agrigentina* to the environment.

In this paper we attempt to verify whether the ecophenotypical behavior of *C. agrigentina* was comparable with that of *C. torosa*. To

reach this goal, adult male and female valves of *C. agrigentina* from the long section of Eraclea Minoa (Agrigento, Sicily) were investigated and three morphometrical characters have been analyzed: 1) size variability; 2) nodding and ornamentation; 3) variability of the percentage of the sieve-pore shapes. The paleoenvironmental framework to which the ecophenotypical characters displayed by *C. agrigentina* will be compared has been built based on synecological analysis (assemblages taxonomic composition and diversity) (Chapter 3) and geochemical approaches [stable isotopes, trace elements, Sr-isotopes and natural radioactivity (NRD)] (Chapter 4).

2. Material and methods

One hundred fifty-two samples have been soaked in a H₂O₂ 5%_{vol} solution for 24 h, sieved with 0.063 and 0.125 mm-mesh sieves and dried in oven at 40 °C. Total manual picking has been carried out on the 0.125 mm dried sieved samples. When possible, up to 300 valves where hand-picked from each sample. Ostracods have been identified and their frequency counted; the obtained values have been normalized to 10 g in order to get comparable figures all along the section to perform a reliable paleoenvironmental interpretation using the synecological approach proposed by Gliozzi and Grossi (2008) and Grossi et al. (2008). Shannon-Wiener index has been calculated on the basis of the normalized matrix.

When possible, supplementary adult specimens of *C. agrigentina* were picked to increase the amount of material on which the morphometrical and geochemical analyses were performed. The morphometrical and geochemical analyses have been carried out on more than 3000 adult valves of *C. agrigentina*, and several thousand juvenile valves were added for Sr-analyses.

2.1. Morphometrical analyses

All juvenile and adult valves of *Cyprideis agrigentina* were observed under the stereo-microscope to investigate the ornamentation and nodding. Over one thousand adult female and male valves of *C. agrigentina* from fifty-three selected samples were measured under the stereo-microscope, using the Leica Application Suite 2.5.0. Mean values were calculated for each sample.

Around 20 adult female and male valves of *Cyprideis agrigentina* from fifty-three samples, chosen on the basis of its high frequency, were observed under the Scanning Electron Microscope (LIME Laboratory, Roma Tre University). Following the methodology proposed by Rosenfeld and Vesper (1977), the rounded, elongated and irregular sieve-pores were counted and each percentage was calculated. To obtain the inferred salinity value, the following transfer function elaborated by Frenzel et al. (2011), based on the percentage of rounded sieve-pores was used:

$$S = e^{-0.06RS + 4.7}$$

where S = salinity (psu) and RS = percentage of rounded sieve-pores.

2.2. Geochemical analyses

2.2.1. Stable isotopes

Carbon and oxygen stable isotope analyses ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) were performed on fifty-three ostracod samples each consisting of eight *Cyprideis agrigentina* clean adult valves. Two splits of each sample (4 valves each) were reacted with anhydrous phosphoric acid at $76 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ in a Finnigan MAT Kiel preparation device directly coupled to the inlet of a Finnigan MAT 251 triple collector isotope ratio mass spectrometer (Stable Isotope Laboratory, University of Michigan, Ann Arbor, MI, USA). The isotopic results of the mean of the two splits are reported in permil (‰) notation relative to the Pee Dee Belemnite (PDB)

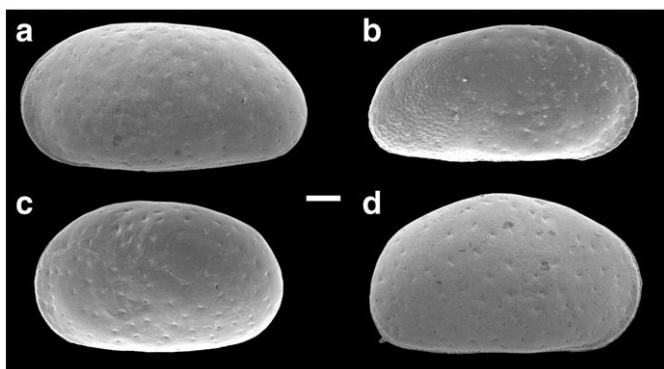


Fig. 1. SEM pictures of *Cyprideis agrigentina* Decima. a. male left valve, sample EM 8-3; b. male right valve, sample EM 7-2; c. female left valve, sample EM 7-2; d. female right valve, sample EM 8-3. White bar corresponds to 0.1 mm.

standard. The measured precision for the analyses was 0.04 for $\delta^{13}\text{C}$ and 0.07 for $\delta^{18}\text{O}$.

2.2.2. Trace elements

Trace and minor element analyses together with Ca on fifty-three ostracod samples, consisting each in 6 to 10 clean adult valves of *Cyprideis agrigentina*, were performed by inductively coupled plasma atomic emission spectrometry (ICP-AES). The ostracod valves were dissolved in 3 ml of ultrapure HNO_3 acid (3%). The solutions were analyzed for Ca (317.9 nm), Mg (285.2 nm), Na (589.5 nm) and Sr (215.2 nm) in the ICP-AES Thermo Jarrell IRIS Advantage Radial device of the Institute of Environmental Assessment and Water Research (IDAEA-CSIC, Barcelona, Spain). The limits of detection were 0.05 ppm for Ca and Mg, 0.01 ppm for Na and 0.005 ppm for Sr. All the analyses were run against multielemental standards prepared from Johnson Matthey™ stock solutions. The obtained results are expressed as metal/calcium ratios of the valves (Me/Ca_v).

2.2.3. Sr isotope analyses

Strontium isotope measurements were obtained from 26 suitable samples of hand-picked valves of *Cyprideis agrigentina*, perfectly preserved. About 10 mg of each sample was subjected to the following procedure: ultrasonic cleaning in double distilled water to remove impurities; gentle crushing and re-washing in double-distilled water; fast dissolution in 4.0 N ultrapure HCl; centrifugation; loading onto standard BIO-RAD AG50-X12 cation exchange resin. The total procedure blank was 0.5 ng. Sr was collected in 2.9 and 6.3 N HCl and evaporated. Isotopic analyses were carried out at IGAG-CNR c/o Department of Earth Sciences, University of Rome – La Sapienza using a FINNIGAN MAT 262RPQ multicollector mass spectrometer with Re double filaments in static mode. The internal precision (within-run precision) of the single analytical value is given as two standard error of the mean. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the samples were normalized to a $^{86}\text{Sr}/^{88}\text{Sr}$ value of 0.1194. The internal precision (within-run' precision) of a single analytical result is reported as 2 standard errors of the mean (2SE) and is obtained as the mean of more than 800-1000 ratios collected in each sample with a stable beam of N 2.0 V. Repeated analyses of NIST-987 during the period of the analyses gave a mean value $^{87}\text{Sr}/^{86}\text{Sr} = 0.710251 \pm 15$ (2σ , $n = 15$).

2.2.4. Natural Radioactivity (NRD)

Natural Radioactivity (NRD) was measured on 27 bulk sediment samples. Uranium, thorium and potassium were determined by high resolution gamma spectrometry using a low background (GEM-EG&G ORTEC) HPGe coaxial detector in a PopTop capsule including detector element, preamplifier and high voltage filter at the Institute of Environmental Geology and Geoengineering (IGAG, CNR, Rome – Italy). The multichannel buffer (16,384 channels, Ethernim-ORTEC 919E), including ADC with extended live time correction, was connected into an Ethernet environment under Windows XP and its control and spectral display was achieved by the use of MAESTRO application software. In particular, ^{232}Th and K were estimated from 583 keV (^{208}Tl) and 1461 keV (^{40}K) peaks, while ^{238}U was estimated by the weighted average of U1 and U2, where U1 is the product of the known $^{238}\text{U}/^{235}\text{U}$ natural activity ratio by the ^{235}U activity (calculated by the 186 keV peak corrected by the ^{226}Ra contribution) and U2 is the ^{238}U activity estimated by the 352 keV peak (^{214}Pb) assuming full equilibrium in the ^{238}U radioactive series. Capo di Bove leucitite (Vologgi et al., 2004) was used as standard, while counting time and amount of each sample were, respectively, 86,400 s and 150 g.

2.3. Statistical analyses

A raw matrix of data was constructed taking into account those samples that provided all the results for the considered types of analyses (9 variables): stratigraphic position, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, Mg/Ca_v , Sr/Ca_v ,

Na/Ca_v , Th/U , assumed salinity after the sieve-pore analysis and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. The statistical software used was STATISTICA 7.0. From the raw matrix, with 9 variables and 20 cases (samples), a correlation matrix was obtained. Moreover from the raw matrix, a set of multivariate analysis techniques, as cluster and principal-component analysis (PCA) was applied. Cluster analysis defines groups of more or less related variables and the corresponding dendrogram (tree clustering) corresponds to the graphic display of the groups. PCA defines eigenvectors showing the position of the variables in the factor plane and revealing the underlying structure of the data set.

3. The Eraclea Minoa section and its paleoenvironments inferred from ostracod assemblages

The ca. 266 m-thick Messinian Lago-Mare succession of Eraclea Minoa crops out along the south-western coast of Sicily (lat. $37^{\circ}23'30''$ N, long. $13^{\circ}16'50''$ E) along the cliff which borders the village (Fig. 2). The section has been extensively studied since 1971 (Decima and Wezel, 1971) because it is one of the most complete Messinian Lago-Mare section of the Paleomediterranean where several gypsum levels referred to the Upper Gypsum Unit crop out (among the most recent papers: Schreiber, 1997; Caruso and Rouchy, 2006; Van der Laan et al., 2006; Manzi et al., 2009 with references therein), and because it represents the GSSP of the Messinian/Zanclean boundary (Van Couvering et al., 2000 with references therein) (Fig. 3).

The succession is made of a rhythmic alternation of clays and marls interbedded with sandy and fine grained carbonates and seven gypsum bodies made by multiple strata of finely-laminated gypsum and gypsarenites/selenites (Fig. 4). The astrochronological tuning of the Eraclea Minoa section is different according to several authors. As stated by Caruso and Rouchy (2006), six sedimentary cycles covered by the Arenazzolo Fm. up to the Messinian/Zanclean boundary are recognizable, with a possible seventh basal cycle represented by an intensively deformed gypsum deposit located along the fault contact at the base of the succession. Van der Laan et al. (2006) consider the presence of seven cycles and a half, including the Arenazzolo Fm. They are linked to the precessional cyclicity and date the deposition of the Eraclea Minoa succession between 5.508 Ma to 5.332 Ma. Finally, Manzi et al. (2009, 2012) hypothesize the presence of nine to ten sedimentary cycles, including the Arenazzolo Fm., bracketing the depositional age between 5.53 and 5.33 Ma.

Ostracods are discontinuously present at the base of the section, in the marls intercalated between the lowest six gypsum bodies and become abundant in the upper portion, below and above the seventh gypsum level. Assemblages show variable richness from 1 species (monotypic assemblages made only by *Cyprideis agrigentina*) up to 13 species mainly made by the typical Lago-Mare ostracod assemblages of Paratethyan origin.

In the lowest portion from 88 (sample EM 3-3) to 144 m (sample EM 6-7), *Cyprideis agrigentina* is scarce and the assemblages, made by *Loxococoncha muelleri* (Méhés), *Loxococoncha kocki* Méhés, *L. eichwaldi* Livental, *Loxocorniculina djafarovi* (Schneider), *Loxocauda limata* (Schneider), *Camptocypria* sp. 1, *Tyrrhenocythere pontica* (Livental), *Euxinocythere (Maetocythere) praeabaquana* (Livental), *Amnicythere propinqua* (Livental), *A. subcaspia* (Livental), *A. multituberculata* (Livental) and *A. accicularia* Olteanu, are rather diversified. These assemblages can be referred to the “*Cyprideis*-*Loxococonchidae* assemblage” (sensu Grossi et al., 2008), suggesting low mesohaline and shallow waterbodies (supposed salinities b10 psu).

Monotypic assemblages have been recovered in the central portion of the Eraclea Minoa section, from 153 m (sample EM 6'-1) to 227 m (sample EM 7-12) and the collected valves are abundant and well preserved. In this long interval, *C. agrigentina* is the only species present in the samples or is accompanied by the euryhaline benthic foraminifer *Ammonia tepida* (Cushman). Grossi and Gennari (2008) defined the “*Cyprideis*-*Ammonia* assemblage” for some ostracod and forams



Fig. 2. Geographical location of the Eraclea Minoa section.

associations recovered in the Lago-Mare borehole of Montepetra (northern Apennines, Italy) in which, together with *C. agrigentina* and *A. tepida*, also other benthic foraminifers, *Florilus boueanum* (d'Orbigny) and *Elphidium* spp. were seldom present or *A. tepida* was the dominant species of the assemblage. The authors related such "Cyprideis-Ammonia assemblage" to high mesohaline to hyperhaline shallow waterbody. At Eraclea Minoa no other brackish benthic foraminifers have been recovered except *A. tepida*. Moreover, this latter species is not always present and generally is far subordinated to *C. agrigentina*. Thus, the paleoenvironmental interpretation of the interval from 153 to 227 m at Eraclea Minoa could be slightly different. At the moment, we can suppose for this new "Cyprideis assemblage" a relatively high salinity waterbody and/or a dysoxic bottom, based on the capability of the living species *Cyprideis torosa* and *Ammonia* spp. to withstand low oxygen contents (Jahn et al., 1996; Bernhard and Sen Gupta, 2002). Different assemblages, made only by scarce *C. agrigentina* and accompanying *Loxoconcha muelleri* were recovered in the Lago-Mare succession of Colle di Votta (Majella Mt., central Italy) (unpublished data), in oxygen-depleted sediments (Sampalmieri et al., 2010).

In this central portion of the succession there are only five scattered samples in which the dominant *Cyprideis agrigentina* is associated with few other species: with *Loxocornulina djafarovi* (at 182 m, sample EM 6'-29a), pointing to a low mesohaline environment; with *Ilyocypris* sp. (at 198.5 and 201.0 m, respectively samples EM 6"-8 and 6"-11), suggesting two short oligohaline episodes; with *Fabaeformiscandona* sp. (at 213 m, EM 6"-19) pointing to a further oligohaline episode; with *A. accicularia* (at 220.6 m, EM 7-4) indicating a low mesohaline short interval.

Finally, in the uppermost part of the section [from 228 m (sample EM 7-13) to 265.5 m (sample EM 8-20)], *Cyprideis agrigentina* is again accompanied by the Paratethyan assemblage in which Loxoconchidae are slightly less abundant and two more leptocytherid species are included, even if with scarce frequency: *Amnicythere litica* (Livental) and *Amnicythere costata* (Olteanu). On the whole, this topmost interval seems again to be referable to the "Cyprideis-Loxoconchidae assemblage" (Grossi et al., 2008), pointing to shallow waterbodies with supposed salinities b 10 psu. Within this uppermost interval, it is possible to identify three horizons [from 228 m (sample EM 7-13) to 232 m



Fig. 3. Panoramic view of the Eraclea Minoa section. In evidence the gypsum levels of the Upper Gypsum Unit from gypsum body 3 to gypsum body 6 (marked by numbers) and the Messinian/Zanclean boundary.

(sample EM 7-19), at 234 m (sample EM 7-21) and from 235 m (sample EM 7-25) to 238 m (sample EM 7-28)] in which *C. agrigentina* shares its dominance only with two candonids species, *Fabaeformiscandona* sp. and *Cypria* sp., testifying an oligohaline and shallow environment, and two short levels [at 252.8 m (sample EM 8-3) and 257.8 m (sample EM 8-7)] in which *C. agrigentina* is again the only ostracod species of the assemblage.

4. Geochemical analyses and inferred paleoenvironmental features

4.1. Stable

isotopes

Cyprideis agrigentina calcite valves display a wide range of stable isotopic values. $\delta^{13}\text{C}$ ranges from -6.40 to 1.91‰ ; $\delta^{18}\text{O}$ ranges from -4.08 to 7.95‰ (Table 1; Figs. 5, 6). The $\delta^{13}\text{C}$ values of the ostracod valves show a slight increase from 153 to 189 m (interval A) to 198–225 m (interval B). Significant, rapid variations are shown around 198–204 m and in the upper portion of the section around 253–260 m (interval E).

The $\delta^{18}\text{O}$ values of the ostracod valves show a slight increase from 153 to 189 m (interval A), a rapid variation around 198–204 m (lower interval B), and decrease from 204 to 225 m (upper interval B). In the upper portion of the section, from 257.8 to 258.5 m (interval E), a significant decrease in $\delta^{18}\text{O}$ values, from 8‰ to -1.4‰ is observed.

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values from 153 to 189 m (interval A) display small fluctuations, suggesting minor variations in the paleohydrological conditions. On the contrary, the valves from 198 to 204 m (interval B) and 253 to 260 m (interval E) display significant oscillations, both in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, suggesting instabilities in the paleohydrological conditions related to these intervals. In both cases the larger instabilities (major $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ oscillations) may be linked to significant detrital and freshwater inputs as reflected by the coarse-grained detrital beds at 199 m and 256–264.5 m.

The distribution in a X-Y plot (Fig. 6) shows that the isotopic values from 153 to 216 m (interval A and lower B) display a negative covariant trend with a significant correlation ($R = -0.894$). This is mainly due to the negative correlation of the interval 198–216 m (lower B, $R = -0.903$) and the almost invariant values in the interval 153–189 m (interval A).

4.2. Trace elements

For *Cyprideis agrigentina* calcite valves, the Mg, Sr and Na content expressed as Mg/Ca_v , Sr/Ca_v and Na/Ca_v molar ratios are listed in Table 1 and represented in Fig. 5. The Mg/Ca_v values range from 0.0052 to 0.0158, the Sr/Ca_v range from 0.0022 to 0.0054 and the Na/Ca_v from 0.0032 to 0.0046.

The Mg/Ca_v values show a significant drop from 189 to 198.2 m (intervals A and B boundary) towards the upper portion of the succession, with a rapid variation around 153–156 m (lower interval A). An overall increase trend in Mg/Ca_v is recorded in the interval 198.2–225 m (interval B) and a significant increase is observed also in the upper part of the section (interval E). This is parallelized with a similar increase in the $\delta^{13}\text{C}$ values.

The Na/Ca_v values show a slight decrease from 153–189 m (interval A) to 198–216 m (interval B), with a rapid variation around 198.2–201 m. A significant decrease of Na/Ca_v is observed in the upper portion of the section (interval B). This is parallelized with the decrease in Sr/Ca and $\delta^{18}\text{O}$ values.

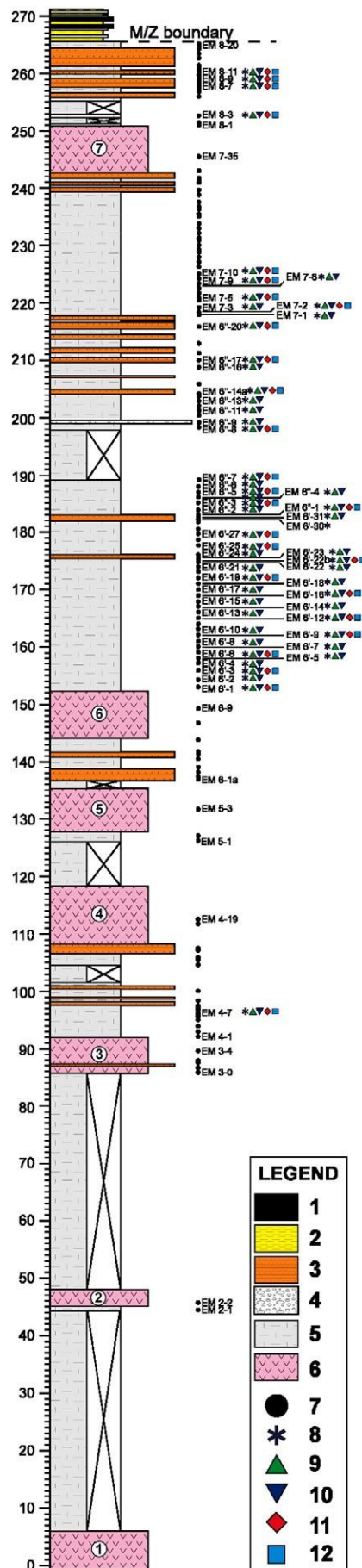


Fig. 4. Simplified stratigraphic log of the Eraclea Minoa section (modified from Manzi et al., 2009). Legend: 1. sapropels; 2. clays; 3. sandstones/sandy levels; 4. microconglomerate levels; 5. marls; 6. gypsum bodies (Upper Gypsum Unit); 7. samples for paleontological analyses; 8. samples for morphometrical analyses (ornamentation, dimensions and percentage of sieve-pore shapes) on *C. agrigentina* valves; 9. samples for stable isotopes analyses on *C. agrigentina* valves; 10. samples for trace elements analyses on *C. agrigentina* valves; 11. samples for Sr-isotopes analyses on *C. agrigentina* valves; 12. samples for NRD analyses on marls.

Table 1
Stratigraphic position and lithology of the samples, and geochemical analytical results from *C. agrigentina* valves: stable isotope data ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$; PDB notation), Mg/Ca, Sr/Ca, and Na/Ca, in molar ratios, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

Height (m)	Sample	Lithology	Stable Isotopes (n. of valves)	$\delta^{13}\text{C}$ (VPDB)	$\delta^{18}\text{O}$ (VPDB)	Trace elements (n. of valves)	Me/Ca molar			$^{87}\text{Sr}/^{86}\text{Sr} \pm \text{se}^*$	
							Mg/Ca	Sr/Ca	Na/Ca		
259.1	EM 8-11	Sandstone	8	-2.68	-1.37	10	0.0082	0.0025	0.0032	0.708640	± 6
258.5	EM 8-9	Marl	8	-2.29	-1.02	10	0.0092	0.0025	0.0035	0.708630	± 8
257.8	EM 8-7	Sandstone	8	-4.70	7.83	10	0.0060	0.0051	0.0041	0.708647	± 10
252.8	EM 8-3	Marl	8	-5.24	7.95	10	0.0058	0.0051	0.0046	0.708704	± 7
225.0	EM 7-10	Marl	8	-2.67	-1.44	10	0.0115	0.0034	0.0039	0.708637	± 11
224.3	EM 7-9	Marl	8	-2.47	-1.52	10	0.0098	0.0035	0.0039	0.708602	± 2
223.5	EM 7-8	Marl	8	-2.87	-0.37	8	0.0086	0.0040	0.0039		
220.9	EM 7-5	Marl	8	-3.01	-1.27	9	0.0085	0.0039	0.0038	0.708629	± 7
219.1	EM 7-3	Marl	8	-2.63	-0.98	9	0.0083	0.0040	0.0041		
218.5	EM 7-2	Marl	8	-2.46	-3.20	10	0.0102	0.0042	0.0035	0.708552	± 9
218.0	EM 7-1	Marl	8	-2.76	-2.40	9	0.0078	0.0042	0.0040		
216.0	EM 6"-20	Sandstone	8	-2.92	-1.01	8	0.0094	0.0048	0.0035	0.708666	± 10
210.0	EM 6"-17	Sandstone	8	-2.88	-1.79	7	0.0066	0.0050	0.0034	0.708510	± 7
208.9	EM 6'-16	Marl	8	-2.00	-2.81	8	0.0070	0.0045	0.0036		
204.2	EM 6"-14a	Marl	8	-3.27	-1.26	8	0.0100	0.0031	0.0040	0.708511	± 6
203.0	EM 6'-13	Marl	8	-2.46	-0.69	8	0.0085	0.0029	0.0040		
201.1	EM 6"-11	Marl	8	-2.48	-0.43	8	0.0081	0.0038	0.0038		
199.2	EM 6"-9	Gravel	8	-6.14	2.72	10	0.0095	0.0030	0.0048		
198.2	EM 6"-8	Marl	8	1.91	-4.08	10	0.0055	0.0054	0.0034	0.708685	± 11
189.0	EM 6"-7	Marl	8	-5.53	1.99	8	0.0131	0.0029	0.0046	0.708609	± 7
188.0	EM 6"-6	Marl	8	-5.08	1.93	8	0.0132	0.0030	0.0046		
187.0	EM 6"-5	Marl	8	-5.20	1.46	8	0.0137	0.0029	0.0046	0.708654	± 9
186.0	EM 6"-4	Marl	8	-4.56	1.69	9	0.0124	0.0030	0.0043		
185.0	EM 6"-3	Marl	8	-5.88	1.65	8	0.0115	0.0029	0.0043	0.708608	± 9
183.9	EM 6"-2	Marl	8	-4.57	1.90	8	0.0128	0.0027	0.0041		
183.1	EM 6"-1	Marl	8	-4.35	1.52	6	0.0152	0.0028	0.0041		
182.8	EM 6'-31	Sandstone	8	-4.74	1.63	8	0.0122	0.0028	0.0038		
180.0	EM 6'-27	Marl	8	-4.93	1.55	9	0.0149	0.0028	0.0040	0.708663	± 7
177.8	EM 6'-25	Marl	8	-5.44	1.33	10	0.0139	0.0029	0.0042	0.708729	± 10
176.0	EM 6'-24	Marl	8	-4.89	1.55	8	0.0144	0.0028	0.0043		
175.5	EM 6'-23	Sandstone	8	-4.82	1.58	7	0.0137	0.0028	0.0046		
175.1	EM 6'-22b	Sandstone	8	-4.83	1.49	8	0.0130	0.0028	0.0039	0.708619	± 6
174.6	EM 6'-22	Marl	8	-5.08	1.38	8	0.0127	0.0028	0.0039		
173.9	EM 6'-21	Marl	8	-5.25	1.46	7	0.0131	0.0028	0.0046		
172.0	EM 6'-19	Marl	8	-5.35	1.50	7	0.0125	0.0029	0.0045	0.708671	± 6
171.0	EM 6'-18	Marl	8	-5.27	1.39	7	0.0122	0.0029	0.0042		
169.9	EM 6'-17	Marl	8	-5.15	1.29	9	0.0126	0.0029	0.0044		
169.0	EM 6'-16	Marl	8	-5.87	1.21	8	0.0132	0.0027	0.0044	0.708602	± 7
168.0	EM 6'-15	Marl	8	-6.05	1.05	8	0.0134	0.0029	0.0046		
167.0	EM 6'-14	Marl	8	-5.02	1.28	8	0.0125	0.0027	0.0043		
166.0	EM 6'-13	Marl	8	-5.13	0.94	8	0.0129	0.0028	0.0044		
165.0	EM 6'-12	Marl	8	-5.17	1.57	8	0.0136	0.0026	0.0041	0.708658	± 9
163.0	EM 6'-10	Marl	8	-5.60	1.76	8	0.0120	0.0026	0.0043		
162.0	EM 6'-9	Marl	8	-5.74	1.56	8	0.0122	0.0027	0.0044	0.708614	± 6
161.0	EM 6'-8	Marl	8	-5.52	1.28	9	0.0132	0.0028	0.0043		
160.0	EM 6'-7	Marl	8	-5.48	1.17	7	0.0128	0.0027	0.0043		
159.1	EM 6'-6	Marl	8	-5.55	1.12	8	0.0131	0.0027	0.0045	0.708685	± 5
158.0	EM 6'-5	Marl	8	-4.80	1.02	8	0.0135	0.0027	0.0042		
157.1	EM 6'-4	Marl	8	-5.35	1.07	9	0.0123	0.0028	0.0041		
156.0	EM 6'-3	Marl	8	-6.40	1.12	8	0.0133	0.0028	0.0046	0.708675	± 10
154.3	EM 6'-2	Marl	8	-5.00	1.30	7	0.0158	0.0025	0.0044		
153.0	EM 6'-1	Marl	8	-5.34	1.14	6	0.0111	0.0028	0.0044	0.708612	± 11
96.2	EM 4-7	Marl	8	-1.81	-3.00	7	0.0052	0.0022	0.0032	0.708729	± 10

4.3. Sr isotopes

Different from the ratios of cation concentrations and oxygen isotopes, no Sr isotope fractionation occurs during chemical and biological processes within the marginal basin (Faure and Powell, 1972). Considering that Ostracoda are good monitors of the composition of the aquatic environment (De Deckker et al., 1988), the Sr isotopic composition of ostracod shells allows us to evaluate the connectivity of the basin with the open ocean and the paleoclimatic conditions and hydrography.

The Eraclea Minoa section shows that the $^{87}\text{Sr}/^{86}\text{Sr}$ values from the *Cyprideis agrigentina* valves are comprised between 0.708510 and 0.708729 (Table 1). The range of values is high in the lower analyzed interval (153-189 m – interval A) and decreases in the portion comprised between 198 and 225 m (interval B), reaching the minimum values

(0.708510 and 0.708511) in the interval 204.2-210 m (low interval B), in correspondence of low $\delta^{18}\text{O}$, Sr/Ca and Na/Ca values. In the upper portion of the section (253-260 m – interval E) the $^{87}\text{Sr}/^{86}\text{Sr}$ values rise again, with a maximum (0.708704) at 253 m (Fig. 5). Sr isotopic data of *C. agrigentina* are markedly different with respect to coeval global ocean values (Henderson et al., 1994; McArthur et al., 2001) being significantly lower than the marine waters at that time, but this is a common feature for latest Miocene-earliest Pliocene strontium values of the Paleomediteranean Basin carbonates.

4.4. Natural radioactivity

^{232}Th and K measured in bulk sediment samples are highly correlated ($R = 0.94$) suggesting that ^{232}Th is mainly contained in the detrital

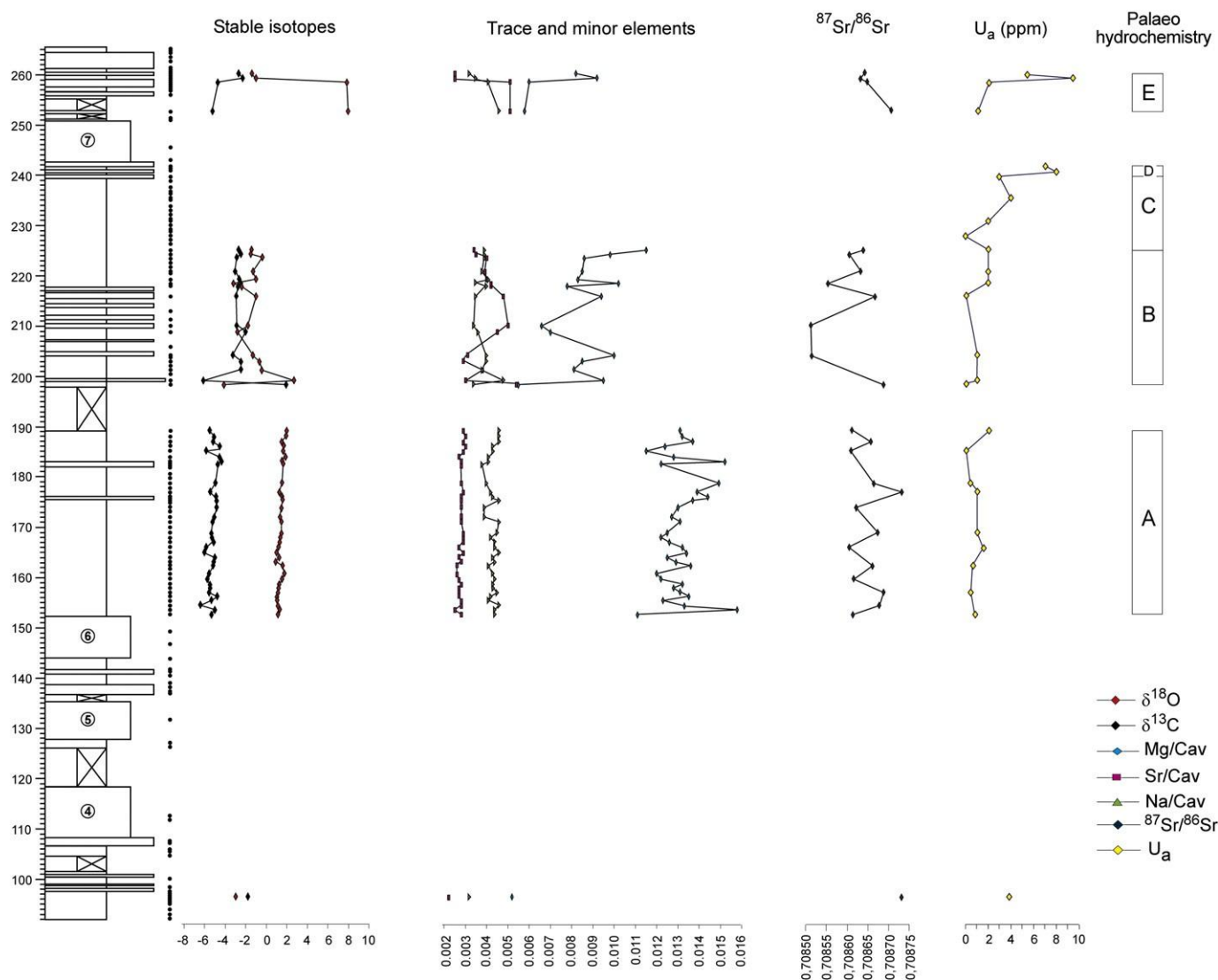


Fig. 5. Stable isotopes, trace and minor elements, $^{87}\text{Sr}/^{86}\text{Sr}$, and authigenic uranium curves plotted against the stratigraphic log of the Eraclea Minoa section. For the descriptions of the intervals, see the text.

fraction. Detrital uranium, in turns, was calculated by the product of measured ^{232}Th and the average $^{238}\text{U}/^{232}\text{Th}$ weight ratio of pelagic sediments, considered close to 0.25 (Mangini et al., 2001). Finally, authigenic uranium, $^{238}\text{U}_a$, was estimated by subtracting the detrital ^{238}U from measured ^{238}U (Table 2). Authigenic uranium as well as the Th/U ratio was proposed by Wignall and Myers (1988) as an index of bottom-water oxygenation; the U_a values tend to increase in a reducing environment, where uranium is immobile as tetravalent ion. According to Wignall (1994) U_a values comprised between 2 and 10 are indicative of dysoxic environments; similarly for Th/U values, Th/U b b 1 indicate anoxic conditions, Th/UNN 1 indicate oxic conditions, while values in the range 1 b Th/U N 1 point to dysoxic conditions. Even if the use of authigenic uranium as proxy for reducing conditions is common in the chemiography of marine sediments (Pattan and Pearce, 2009), several authors have questioned the real preservation of the authigenic uranium signal by different processes as burn down, fast change of sedimentation rate and oxygen ventilation or bioturbation (Zheng et al., 2002). Therefore any indication of oxygen depletion suggested by the authigenic uranium has to be regarded in a wider fitting context.

U_a from the bulk sediment display values from 0.3 to 9.5 ppm (Table 2). The lowest values are attained in intervals A, B and lower C, with figures generally below 2. In the upper part of interval C, U_a

increases and maintains high values in interval D and E, where some fluctuations occur, similarly to what observed for the stable isotopes and trace elements ratios (Fig. 5). A similar trend is observed for the Th/U ratios, which show values greater than 1 in intervals A, B and C, and values mainly around 1 in intervals D and E (Table 2).

4.5. Palaeoenvironmental episodes inferred from the geochemical proxies

The geochemical analyses performed on the valves of *Cyprideis agrigentina* and bulk sediment samples collected from the 96.5-260 m portion of the post-evaporitic Messinian succession of Eraclea Minoa confirm the frame of a Paleomediterranean waterbody discontinuous and isolated, characterized by diluted waters after the evaporative phase of the Lower Gypsum Unit, the closure of the Atlantic-Paleomediterranean connection and the subsequent global humid climate phase (Griffin, 2002; CIESM, 2008; Grossi et al., 2008). In fact, notwithstanding the well known saline character of the Paleomediterranean waters, testified by the presence of brackish ostracod assemblages, all the geochemical indicators point to a clear differentiation with the Messinian oceanic seawater. On the other hand, the stable isotopes values reported in Figs. 5 and 6 do not show the overall covariant trend that would correspond to a marginal marine environment or a

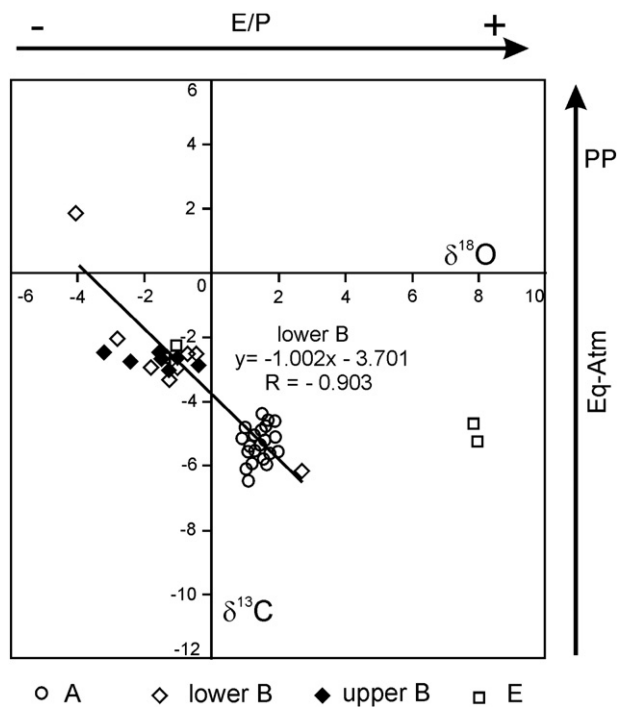


Fig. 6. Stable isotopic composition ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$; PDB notation) of *Cyprideis agrigentina* calcite valves (Table 1). Note the negative correlation and regression line for samples from interval lower B. The larger variation of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ along the regression line corresponds to samples EM 6"-8 (198.2 m) to 6"-20 (216 m) from lower interval B. E/P: Evaporation /Precipitation ratio; PP: Primary productivity; Eq-Atm: Atmospheric CO_2 equilibrium. See also Fig. 4.

closed waterbody (Talbot, 1990; Utrilla et al., 1998; Ligios et al., 2012), and also trace elements behave in a different manner. The Mg/Ca_v values from *C. agrigentina* (0.0052-0.0152) are similar to most of the analyses from *Cyprideis* shells for the Messinian Lago-Mare horizons from DSDP sites (De Deckker et al., 1988). For these Mg/Ca_v values, De Deckker et al. (1988) consider the host water had Mg/Ca values lesser than that of Messinian seawater, and in some cases similar to most of the Mg/Ca shown by freshwaters ($\text{Mg}/\text{Ca} = 1$). The Sr/Ca_v values from *C. agrigentina* at 153-189 m (0.0025-0.0030) are similar to most of the analyses from *Cyprideis* shells from the Messinian Lago-Mare horizons from DSDP sites (De Deckker et al., 1988). For these Sr/Ca_v values, these authors consider the host water had Sr/Ca values lesser than that of Messinian oceanic seawater. On the contrary, the Sr/Ca_v values for most of the samples from 198 to 225 m and 252.8 to 257.8 m (0.0038-0.0054) indicate that the host water frequently had Sr/Ca values greater than that of Messinian oceanic seawater. The values of Sr/Ca_v and Mg/Ca_v indicate that the waters where the Eraclea Minoa ostracods lived were very different than the Messinian seawater and there is no indication of connection with oceanic seawater. Furthermore, the $^{87}\text{Sr}/^{86}\text{Sr}$ range of values obtained from the analyses of *C. agrigentina* valves is consistent with the isotopic values of the Upper Gypsum Unit from Sicily and other localities of the Paleomediterranean (Müller and Mueller, 1991; Keogh and Butler, 1999; Flecker and Ellam, 2006; Roveri et al., 2014b). This range is also similar to the range (0.708600-0.70875) reported from most ostracod valves (*Cyprideis*) from Messinian Lago-Mare deposits from several DSDP sites of the Paleomediterranean studied by McCulloch and De Deckker (1989). On the other hand, the Sr isotopic values from Eraclea Minoa are quite different from the value of the average ocean water during the deposition of the Upper Evaporite: 0.709012 (Howarth and McArthur, 1997; Flecker et al., 2002). The $^{87}\text{Sr}/^{86}\text{Sr}$ values of the Eraclea Minoa *C. agrigentina*, as is the case of materials from other post-evaporitic Messinian localities, confirm to be the result of a large influence of freshwater on the Sr isotopic composition of the desiccating subbasins

of the Paleomediterranean (Müller et al., 1990). Finally, it is noteworthy that isotopic ratios anomalously low could result from reworking of older marine evaporites, or diagenetic overprinting. However, according to Keogh and Butler (1999), the reworking of Sr from the older marine evaporites implies mixing in different proportions between Sr deriving from continental run-off and coming from ground water circulating inside the buried evaporites. Such a process likely produces high variability in both salinity and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

Based on the geochemical signature of *Cyprideis agrigentina* valves and bulk sediment samples, five main paleoenvironmental intervals may be differentiated along the studied portion of the Eraclea Minoa succession (Fig. 5):

Interval A (153-189 m), characterized by high $\delta^{18}\text{O}$, Na/Ca_v , Mg/Ca_v and $^{87}\text{Sr}/^{86}\text{Sr}$ values, and low $\delta^{13}\text{C}$, Sr/Ca_v , and U_a . This interval records relatively stable hydrochemical conditions as suggested by the small variation of each geochemical indicator, isotopically concentrated waters and high Na/Ca_v and Mg/Ca_v ratios that were attained after the deposition of the 6th gypsum level. An overall evaporative environment (Fig. 5) with moderate salinity could be inferred for this interval. The high amount of Th and detrital U, the low content of authigenic uranium and the rather high Th/U ratios (Table 2) record possible well oxygenated bottoms.

Interval B (198-225 m), characterized by low $\delta^{18}\text{O}$, Na/Ca_v , Mg/Ca_v , $^{87}\text{Sr}/^{86}\text{Sr}$, and U_a values, and high $\delta^{13}\text{C}$ and Sr/Ca_v . A major change is recorded at the base of this interval (198 m, sample EM 6"-8) where large shifts in all the geochemical indicators appear. A possible explanation for these features is to consider the noticeable detrital and freshwater inputs that increase the Ca dissolution, recorded both by the coarser lithologies, the high values of Th and detrital U and the low $^{87}\text{Sr}/^{86}\text{Sr}$ values for most samples. Those inputs may explain the lowering of $\delta^{18}\text{O}$ in the valves, the increase of Sr/Ca_v (recording Sr inputs from the CaSO_4 -rich subsurface waters) and the lowering in Mg/Ca_v because of the high increase in Ca in the waterbody. The increase in $\delta^{13}\text{C}$ values

Table 2

Summary of natural radioactivity data, with the concentrations of U, Th and K (with relative errors), values of authigenic uranium expressed in ppm and percentage and Th/U ratios.

Height (m)	Sample	U (mean) (ppm)	Th		K		Uaut (ppm)	Uaut (%)	Th/U
			(ppm)	Error (%)	%	Error (%)			
260.4	EM 8-11	6.7	5.3	0.1	0.96	0.03	5.4	81	0.8
259	EM 8-9	11.7	8.7	0.1	1.76	0.03	9.5	81	0.7
257.8	EM 8-7	4.7	9.0	0.1	1.88	0.03	2.5	53	1.9
252.8	EM 8-3	4.0	9.0	0.1	1.99	0.03	1.8	45	2.3
241.8	EM 7-33	8.5	4.4	0.1	0.76	0.02	7.4	87	0.5
240.9	EM 7-31	10.1	7.8	0.1	1.56	0.03	8.2	81	0.8
239.8	EM 7-28	5.0	7.9	0.1	1.66	0.03	3.0	61	1.6
236.2	EM7-24	5.7	6.8	0.1	1.47	0.03	4.0	70	1.2
230.9	EM 7-17	4.4	9.3	0.1	1.91	0.03	2.1	48	2.1
228	EM7-13	2.8	10.1	0.1	1.90	0.03	0.3	11	3.6
225	EM 7-10	4.6	10.0	0.1	2.00	0.03	2.1	46	2.2
220.9	EM 7-5	4.7	10.3	0.1	2.11	0.04	2.1	45	2.2
218.5	EM 7-2	4.5	9.8	0.1	1.80	0.03	2.0	44	2.2
216	EM 6"-20	3.1	9.5	0.1	2.02	0.03	0.7	23	3.1
204.5	EM 6"-14a	3.4	8.8	0.1	1.83	0.03	1.2	35	2.6
199.0	EM 6"-9	2.7	5.8	0.1	0.81	0.03	1.3	48	2.1
198.5	EM 6"-8	3.1	10.2	0.1	1.93	0.03	0.6	19	3.3
189.0	EM 6"-7	4.5	8.3	0.1	1.60	0.03	2.5	56	1.8
185	EM 6"-3	3.1	9.7	0.1	1.83	0.03	0.7	22	3.1
180	EM 6"-27	2.4	8.0	0.1	1.92	0.03	0.4	17	3.3
178	EM 6"-25	3.2	8.6	0.1	2.05	0.03	1.1	34	2.7
172	EM 6"-19	3.3	9.0	0.1	1.89	0.03	1.1	33	2.7
169	EM 6"-16	3.9	9.3	0.1	2.03	0.03	1.6	41	2.4
165	EM 6"-12	2.9	9.1	0.1	2.18	0.04	0.6	22	3.1
159	EM 6"-6	2.9	9.7	0.1	2.02	0.03	0.5	17	3.4
153	EM 6"-1	3.1	9.1	0.1	1.91	0.03	0.8	26	2.9
96.5	EM 4-7	5.9	8.0	0.1	1.62	0.03	3.9	66	1.4

could be produced by an increase in the productivity, linked to the detrital and nutrient inputs and a trend to re-equilibration with the atmospheric CO₂ (Fig. 5). As in the previous interval, NRD results (Table 2) testify for possible well oxygenated bottoms.

Interval C (225-240 m). In this interval, only NRD analyses have been performed due to the low frequency of *Cyprideis agrigentina* in the ostracod assemblages that prevented the possibility to reach the suitable amount of biogenic carbonate for the analyses. The content of authigenic uranium in the upper part of this interval, higher than in

the previous one, (Table 2, Fig. 5) points to possibly progressively less oxygenated bottoms.

Interval D (240-242 m). This short interval is characterized by the highest values of authigenic U and low values of the Th/U ratios, suggesting possible dysoxic conditions at the bottom.

Interval E (252.8-259.1 m). In this interval two portions may be differentiated and a main change is recorded from the lower samples to the upper ones. The lower samples are characterized by high δ¹⁸O, Sr/Ca_v, Na/Ca_v, and ⁸⁷Sr/⁸⁶Sr values, and low δ¹³C and Mg/Ca_v values.

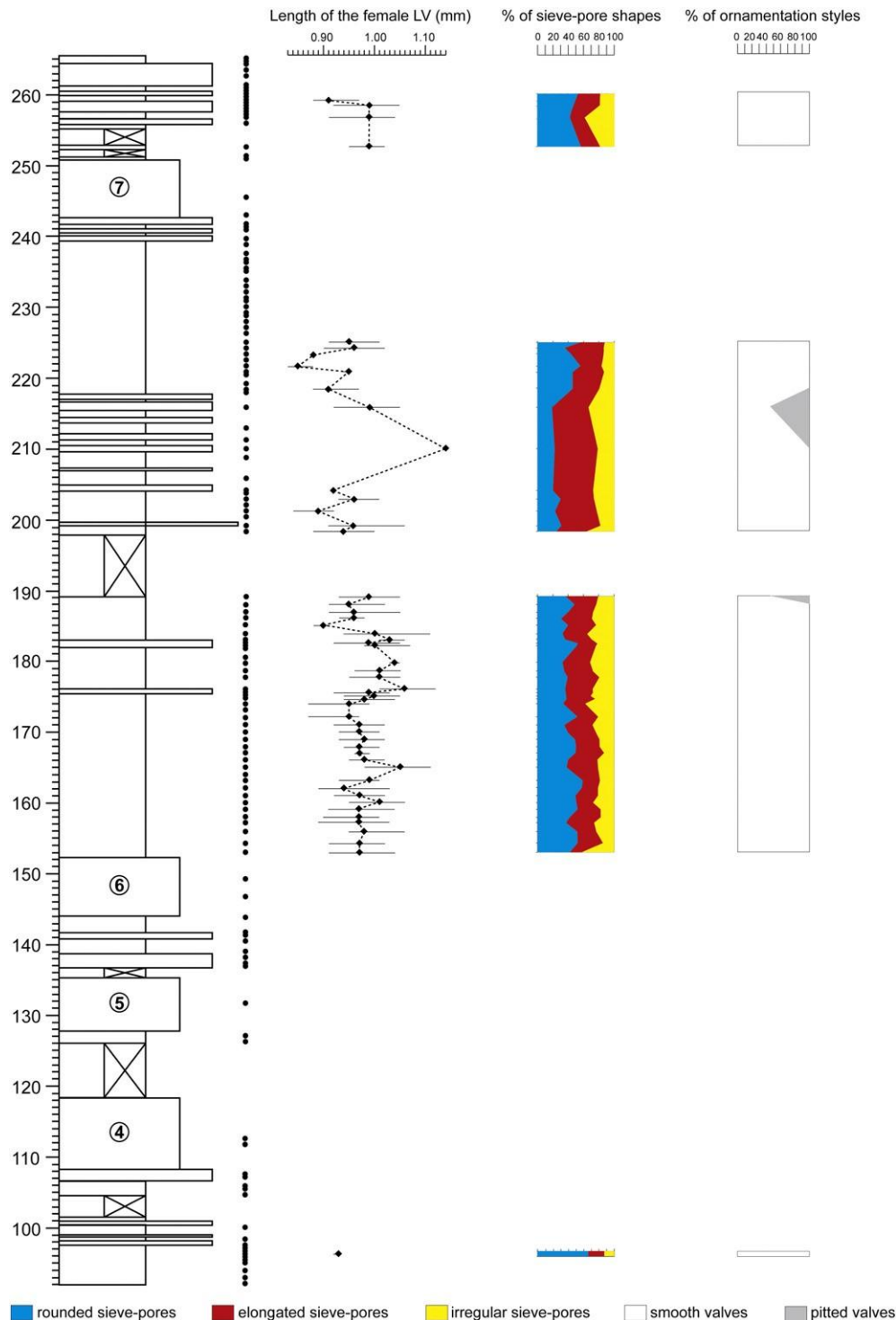


Fig. 7. Results of the morphometrical analyses (mean lengths, percentages of sieve-pore shape and ornamentation/noding) performed on *Cyprideis agrigentina* adult valves, plotted against the stratigraphic log of the Eraclea Minoa section.

The low content of authigenic uranium indicates possibly oxygenated bottoms. The upper samples are characterized by the opposite trend. The geochemical features of the ostracod valves from the lower part may be explained by the evaporitic concentration of the waterbody (Figs. 5, 6) leading to high $\delta^{18}\text{O}$, Sr/Ca_v and Na/Ca_v values. A subsequent large input of freshwater produced the lowering of $\delta^{18}\text{O}$, Sr/Ca_v and Na/Ca_v . At present, we have no explanation for the variations of the Mg/Ca_v values in this interval. It is worth to note the high content of authigenic uranium that reaches in one sample the value of 9.5 ppm, possibly indicating dysoxic conditions at the bottom.

5. Morphometrical analyses on *Cyprideis agrigentina* valves

Length and height of one thousand-sixty valves of adult males and females were measured. The obtained values fall within the variability field typical of the species (Decima, 1964; Ligios et al., 2012). The mean values of the length of the female left valve (the most numerous in the measured samples) have been compared. Generally the mean values of the length vary from 0.96 to 1.00 mm, but in few samples the mean values are rather small: at 185 m (sample EM 6"-3, mean value 0.90 mm), 201 m (EM 6"-11, mean value 0.89 mm), 222 m (EM 7-6, mean value 0.85 mm), and 223.5 m (EM 7-8, mean value

0.88 mm) (Fig. 7). Only in four samples the mean values of the length result significantly high: at 165 m (sample EM 6"-12 mean value 1.05 mm), 176.2 m (EM 6"-24, mean value 1.06 mm), 180 m (EM 6"-27, mean value 1.04 mm), and 210 m (EM 6"-17, mean value 1.14 mm).

The several thousands specimens of *Cyprideis agrigentina* investigated for the ornamentation and nodding, showed rather homogeneous ornamentation: no noded specimens have been observed all along the section among both juveniles and adults; almost all valves were smooth (at least some of them showed few small pits in the posterior surface); only two samples (EM 6"-7 at 189.0 m and EM 6"-20 at 216.0 m) showed, respectively, the 54.2% and 54.6% of valves pitted on the entire surface (Fig. 7).

The analysis of the percentage of the sieve-pore shape was carried out on fifty-three samples from the middle and upper portion of the section, where *Cyprideis agrigentina* was more abundant, making both monospecific and diversified assemblages. On average, more than 500 sieve-pores were observed for each sample and counted on the basis of their shape: rounded, elongated, irregular, following the indications by Rosenfeld and Vesper (1977). The results are reported in Fig. 7. In most cases, the percentages of the rounded sieve-pores are comprised between 40 and 50%; in twelve scattered samples they are higher, reaching the maximum value of 65% at 96.5 m (sample EM 4-7) and only in a short interval from 198.5 m (sample EM 6"-8) to 216 m

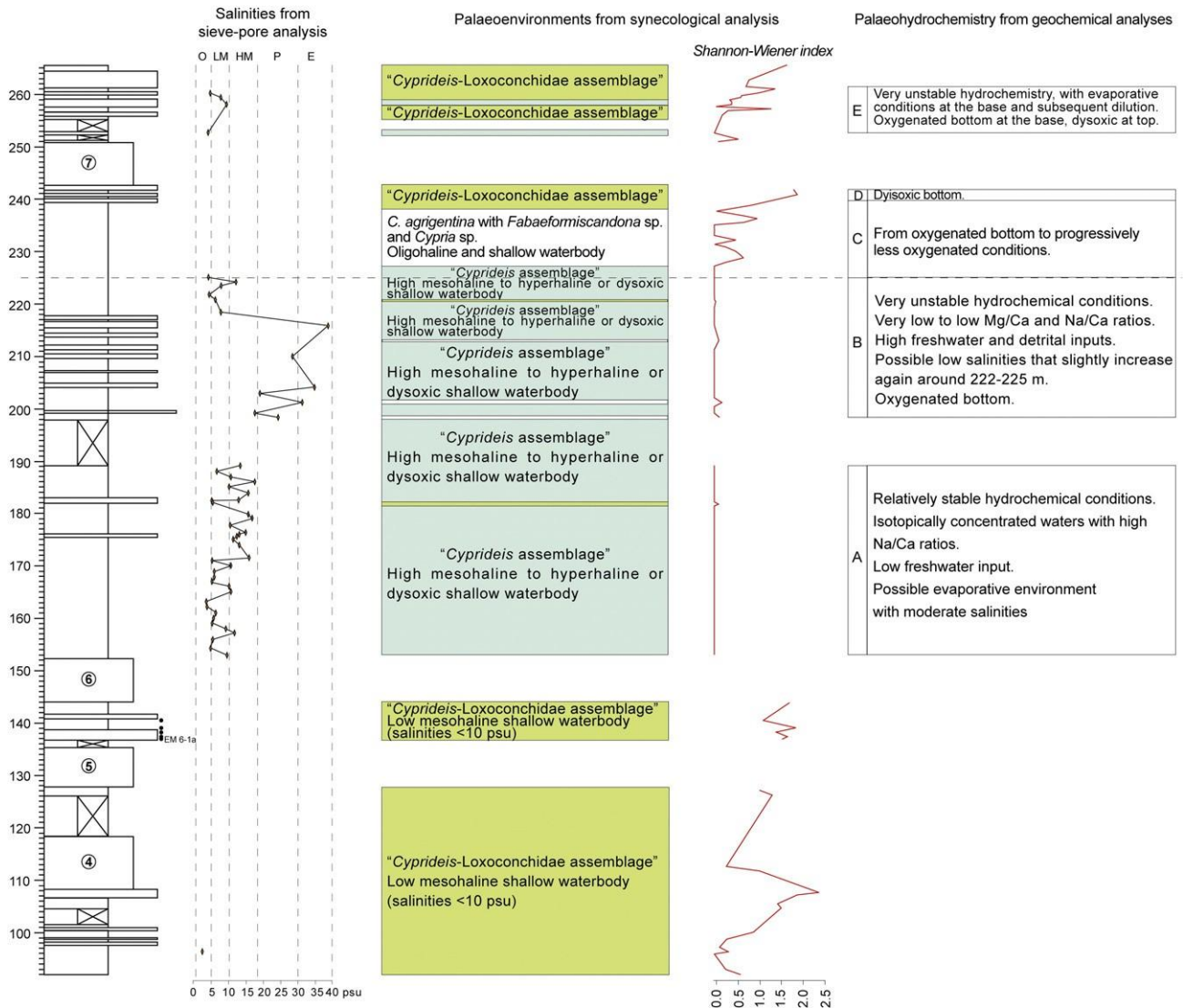


Fig. 8. Comparisons among the paleosalinity curve inferred by the analysis of the percentages of the sieve-pore shape on *Cyprideis agrigentina* and the paleoenvironmental and paleohydrochemistry changes inferred from synecological and Shannon-Wiener and geochemical proxies.

(sample EM 6"-20) they are lower, comprised between 19 and 30%, reaching their minimum values (19–21%) in the interval 204.5–216 m. Applying the transfer function elaborated by Frenzel et al. (2011) for *Cyprideis torosa*, the resulting salinities expressed in psu shows values included in the mesohaline range (5–18 psu, Venice Symposium, 1958) for most samples. Only few scattered samples in the lower and upper portions of the section point to the oligohaline range (0.5–5 psu), while higher salinities (polyhaline to euhaline ranges, 18–40 psu) are recorded only in a limited portion of the section, from 198.5 to 216 m (Fig. 8).

6. Discussion

As explained in the introduction, the living species *Cyprideis torosa* is considered to be one of the most valuable tools to detect past salinities in the marginal marine environments, owing to its environmentally cued polymorphism that induces variations in size, nodding and sieve-pore shapes depending on salinity. Large sizes, presence of nodes and high percentages (around 40–45%) of rounded sieve-pores point to salinity less than 8–9 psu that is considered an important osmoregulation threshold for the species (Keiser and Aladin, 2004; Keyser, 2005).

It is not clear when *Cyprideis torosa* appeared for the first time, owing to the difficulty to identify the species. Often in the Neogene sediments *Cyprideis* remains have been recorded as *C. gr. torosa* or *Cyprideis* sp. (Bossio et al., 1993, 1996; Testa, 1995). According to Decima (1964) and Ligios and Gliozzi (2012) the species is the only survivor of a stem that started in the Paleomediterranean area with *Cyprideis ruggierii* Decima (late Tortonian-early Messinian), including *Cyprideis agrigentina* Decima (post-evaporitic Messinian) and *Cyprideis crotonensis* Decima (post-evaporitic Messinian-Late Pliocene). The great morphological similarity of the species of the stem leads some authors to suppose that the same environmentally cued polymorphism displayed by *C. torosa* could affect also its relatives (Neale, 1988), notwithstanding no noded specimens of the other species had never been recorded. Thus, Rosenfeld (1977) and Bonaduce and Sgarrella (1999) inferred hyperhaline post-evaporitic Messinian environments respectively for the Mavqi'im Formation (Israel) and at Eraclea Minoa, applying on *C. agrigentina* valves the empirical methods of the percentage of the rounded sieve-pores elaborated by Rosenfeld and Vesper (1977) on *C. torosa*.

As a first step to investigate whether *Cyprideis agrigentina* shared with *Cyprideis torosa* the same ecophenotypical behavior, we have analyzed size, ornamentation and sieve-pore shapes on some thousand of specimens from the post-evaporitic Messinian section of Eraclea Minoa. The expected results, in case of a comparable behavior, is a positive correlation between large size, nodding (or strongly pitted valve surface), and high percentages of rounded sieve-pores. Fig. 7 shows that this correlation lacks: the largest sizes (thus the supposed lowest salinities, below 8–9 psu) are attained by specimens recovered in samples bearing smooth valves (supposed high salinities) and percentages of rounded sieve-pores less than 40% (above the 8–9 psu threshold). In particular, in sample EM 6"-17 (at 210 m) the largest *C. agrigentina* valves matches with one of the lowest percentages of rounded sieve-pores (22.7%); the smallest sizes (supposed high salinities) correlate with smooth valve surfaces (supposed high salinities) but to percentages of rounded sieve-pores greater than 40% except in one case (sample EM 6"-11 at 201 m) in which the percentage is low (23.1%); the only two samples in which *C. agrigentina* valves are densely pitted (supposed low salinities), corresponds, on average, to intermediate dimensions and high percentage values.

From those comparisons it is possible to conclude that size and ornamentation/nodding in *Cyprideis agrigentina* are not correlated. In particular, pitted ornamentation and nodding seem to be, respectively, very rare and totally absent in *C. agrigentina*, despite the species seems to be strongly euryhaline as it is its living relative (Ligios and Gliozzi, 2012).

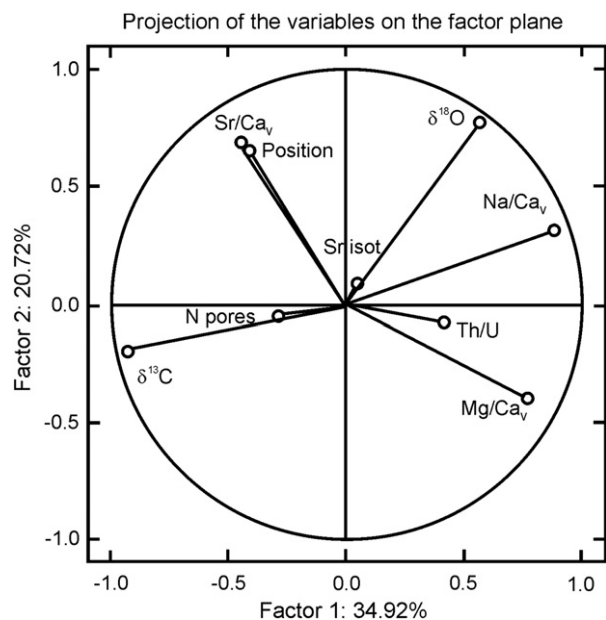


Fig. 9. Principal Component Analysis (PCA) plot of the scores of the eigenvectors for the variables listed in Table 3. Abbreviations: N pores: variability of percentage of sieve pores (rounded sieve pores assumed as a proxy of salinity), Position: stratigraphic position of the samples, Sr isot: ⁸⁷Sr/⁸⁶Sr values. See the text for discussion.

Thus, it seems that those characters do not display in *C. agrigentina* the same salinity-dependant polymorphism of *Cyprideis torosa*.

A further question is to investigate whether the percentage variations of the sieve-pore shapes are correlated with salinity variations as in *Cyprideis torosa*. To test this hypothesis we have based the comparisons of the salinity curve obtained applying the transfer function elaborated by Frenzel et al. (2011) with the salinity inferred by the synecological analysis and with the paleohydrological variations inferred by the geochemical analyses (Figs. 8, 9, 10).

Based on the synecological analysis and the Shannon-Wiener diversity curve, it is possible to observe that the "*Cyprideis* assemblage", correlatable with the minimum diversity values (monotypic ostracod assemblages) corresponds to different inferred salinities: oligo-low mesohaline in the intervals 153–171, 218–225 and 253–257.8 m; high mesohaline from 174 to 189 m; polyhaline-euhaline from 198.5 to 216.5 m. Moreover, it is worth to note that the two oligohaline levels with *Cyprideis* and *Ilyocypris*, included in the "*Cyprideis*" long interval at 198.5 and 201 m, according to the salinity curve based on sieve-pore percentage should have deposited in polyhaline/euhaline waters. We should conclude that there is no correspondence between the

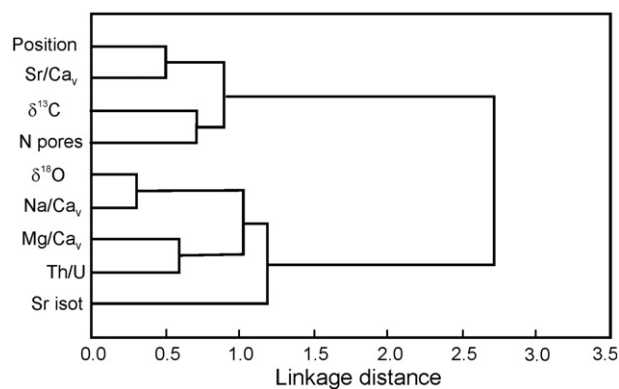


Fig. 10. Tree diagram for the considered variables defining the relationships between the groups of variables. Ward's method, 1-Pearson r. Abbreviations as in Fig. 8. See the text for discussion.

salinities inferred by the method of the sieve-pore percentages and the synecological paleoenvironmental interpretation. This conclusion contradicts the statement by Bonaduce and Sgarrella (1999) who, on the basis of the percentage of sieve-pore shapes, inferred for the Eraclea Minoa portion of succession with monospecific *Cyprideis* assemblage hyperhaline environments (50-70 psu). Probably their conclusions are affected by the very few analyzed samples along the succession (only two) and the scarcity of counted sieve-pores for each sample (respectively 74 and 161).

The calculation of past salinities from the results of the geochemical analyses on the valves of *Cyprideis agrigentina* is difficult to assess. Although Na/Ca_v could be tentatively perceived as a proxy of the salinity (assuming salinity dominated by NaCl solute), the obtained data must be considered with caution because of the poor knowledge of the Na uptake in the ostracod calcite shell (Holmes and De Deckker, 2012). However, recent attempts to use Na/Ca ratios from ostracod valves for paleoenvironmental reconstructions must be taken into account (Gouramanis et al., 2010; Devriendt, 2011). On the other hand, Sr/Ca and Mg/Ca from ostracod valves just may inform about the Sr/Ca and Mg/Ca of the waters (De Deckker et al., 1999; Dettman and Dwyer, 2012; Holmes and De Deckker, 2012), and only in some cases (i.e. some estuarine environments) these ratios could correlate with the salinity of the waters. On the other hand, δ¹⁸O variations in closed non-marine environments are linked usually to evaporation/precipitation processes (Talbot, 1990), that in some cases are associated to salinity variations. Anyway, the decreasing Na/Ca_v ratios from Interval A to Interval B (Fig. 5) is consistent with the interpretation of more diluted waters in this latter interval, as pointed by the low δ¹⁸O values in B. However, this is in contradiction with the higher salinity assumed for interval B than for interval A based on the sieve-pore analysis of *C. agrigentina* (Fig. 8).

We have tried to test the correlation between the geochemical results and the salinities assumed from the analysis of the sieve-pore percentages using a multivariate approach. The correlation matrix obtained for nine variables is shown in Table 3. Significant correlations (p < 0.01) are displayed only by the pairs δ¹⁸O and Na/Ca_v, Na/Ca_v and Mg/Ca_v, Sr/Ca_v and stratigraphic position. Significant negative correlations are shown by δ¹³C and Na/Ca_v, δ¹³C and δ¹⁸O, δ¹³C and Mg/Ca_v, Mg/Ca_v and Sr/Ca_v. In fact salinity assumed from sieve-pore analysis (N pores), and Sr isotopic ratios of the valves do not show significant correlation with any of the other considered variables.

Principal Component Analysis (PCA) delineates similar patterns. About 34.92% of the total variance is explained by the first eigenvector

(Fig. 9), which is tied to concentration-evaporation processes, indicated by the relations among δ¹⁸O, Na/Ca_v, Mg/Ca_v, Th/U and ⁸⁷Sr/⁸⁶Sr in the positive field. This factor is related to the precipitation/evaporation balance and residence time and probably to the resedimentation of evaporites. Inputs of oxygenated, SO₄-rich solutions would lead to lowering of δ¹⁸O, Na/Ca_v, Mg/Ca_v and ⁸⁷Sr/⁸⁶Sr. On the negative field, the variables are Sr/Ca_v, the stratigraphic position and the percentages of rounded sieve-pores that are linked to DIC (Dissolved Inorganic Carbon) changes. On the other hand, factor 2 that accounts for 20.72% of the variance, in the positive area contains a group formed by δ¹⁸O, Sr/Ca_v, stratigraphic position and NaCa_v, whereas in the negative area a group formed by N pores, δ¹³C, Th/U and Mg/Ca_v exists. Factor 2 probably is linked to detrital, freshwater and nutrient inputs related to the environmental evolution.

Results from the cluster analysis reveal several groups (Fig. 10). One of the groups shown by the dendrogram reflects the relationship between δ¹⁸O and Na/Ca_v revealing the control of the Na/Ca_v exerted by the P/E balance (δ¹⁸O). They are associated with Mg/Ca_v, Th/U, and Sr isotopic ratios in the ostracod valve that, into a lesser extent, seem also to be influenced by the P/E balance. The pair Sr/Ca_v-position of the sample is associated to the pair δ¹³C-percentage of rounded sieve-pores. This pair reveals the link between DIC changes and the changes in sieve-pore shapes.

It is worth to note that, although some authors consider both the U_a and Th/U values as good proxies to detect past oxic/dysoxic conditions (Adams and Weaver, 1958; Wignall and Myers, 1988; Jones and Manning, 1994; Wignall, 1994), Wignall and Myers (1988) suggest to couple the U_a results with the Shannon-Weaver dominance-diversity index (H) since, under low-oxygen conditions, assemblages are dominated by a few eurytopic forms, and values of H are typically low. If we compare the H-index curve (Fig. 8) with the oxygen availability at the bottom derived from the U_a curve of Fig. 5, we notice that they are contradictory: when U_a values are high (comprised between 2 and 10 and indicate possible dysoxic bottoms) the H-index values are high (rather well diversified assemblages). This negative correlation suggests, as supposed by Zheng et al. (2002) that the accumulation of U_a in sediments could due also to physico-chemical variables other than the oxygen availability.

The results of the statistical analyses underline that there is no significant relationship between the salinity assumed from the sieve-pore analyses on the valves of *Cyprideis agrigentina* and the variables linked to the hydrochemical changes (δ¹⁸O, Na/Ca_v and Mg/Ca_v, i.e. the salinity changes). On the other hand, the number of

Table
Correlation matrix for the data in Table 1 and Th/U ratios (9 variables, 20 samples). The correlation coefficient r between the diverse variables is shown in the upper part of each division. The p value is indicated in the lower part of each division. The r values are in bold when the correlation is significant p < 0.01. Abbreviations: N pores: variability of percentage of sieve pores (rounded sieve pores assumed as a proxy of salinity), Position: stratigraphic position of the samples, Sr isot: ⁸⁷Sr/⁸⁶Sr values.

	Position	δ ¹³ C	δ ¹⁸ O	Mg/Ca _v	Sr/Ca _v	Na/Ca _v	N pores	Sr isot	Th/U
Position	1.000								
p									
δ ¹³ C	0.192	1.000							
p	p = 0.418								
δ ¹⁸ O	0.238	-0.690	1.000						
p	p = 0.311	p = 0.001							
Mg/Ca _v	-0.331	-0.628	0.039	1.000					
p	p = 0.154	p = 0.003	p = 0.872						
Sr/Ca _v	0.506	0.376	0.216	-0.562	1.000				
p	p = 0.023	p = 0.102	p = 0.360	p = 0.010					
Na/Ca _v	-0.173	-0.823	0.693	0.516	-0.095	1.000			
p	p = 0.466	p = 0.000	p = 0.001	p = 0.020	p = 0.692				
N pores	0.078	0.286	-0.231	-0.030	0.349	-0.188	1.000		
p	p = 0.743	p = 0.221	p = 0.328	p = 0.901	p = 0.131	p = 0.428			
Sr isot	-0.244	0.035	0.192	-0.166	0.068	-0.035	0.275	1.000	
p	p = 0.299	p = 0.882	p = 0.418	p = 0.484	p = 0.777	p = 0.884	p = 0.240		
Th/U	-0.403	-0.219	0.080	0.410	0.211	0.420	0.392	0.084	1.000
p	p = 0.079	p = 0.353	p = 0.738	p = 0.072	p = 0.372	p = 0.065	p = 0.087	p = 0.725	

rounded sieve pores in *C. agrigentina* seems to be mainly linked to $\delta^{13}\text{C}$ (DIC-cycling of C).

In conclusion, this puzzly set of data does not confirm that the percentages variation of the sieve-pore shapes in *Cyprideis agrigentina* is a reliable salinity indicator for the Lago-Mare episode of the Messinian Salinity Crisis. On the other hand, the complexity of the hydrochemical evolution due to the re-sedimentation of the Upper Gypsum Unit and scattered inputs of detrital materials and meteoric waters accounts for a complex paleohydrological and paleohydrochemical scenario in which it seems that the factor responsible for the changes in the shape of the pores in the valves of *C. agrigentina* could be the behavior of the DIC and the oxygen availability.

On the other hand, the geochemical data give a negative response to the hypothesis that the “*Cyprideis* assemblage” could be related to dysoxia at the bottom. Data from the percentage of the authigenic U, Th/U ratios indicate that some accumulation of U_a occurred at the bottom of the Eraclea Minoa waterbody, but it seems that they were not so important to affect the benthic ostracod assemblages.

Although it is beyond the aim of this paper, in order to try to understand the paleoenvironmental meaning of the “*Cyprideis* assemblage” we have tried to extend our investigations comparing other Lago-Mare successions of the Mediterranean area that included monotypic *Cyprideis agrigentina* assemblages. In the first case, such assemblage, represented by very scarce specimens, has been recovered in the lower portion of the Lago-Mare succession of the Adana Basin (Turkey) during the deposition of resedimented evaporites and marls, where a very high sedimentation rate was recorded (Faranda et al., 2013). The authors linked the low diversity and the scattered distribution of the ostracod assemblage of the Adana Basin to the high siliciclastic input connected with the high subsidence rate that affected the Adana Basin during the Lago-Mare phase. At Eraclea Minoa the “*Cyprideis* assemblage” is present with high frequencies and continuously recovered along the entire interval, but it is rather confined to the thick marly-sandy succession included between gypsum bodies 6 and 7. If we hypothesize that this portion of succession represents one precessional cycle, as supposed by Van der Laan et al. (2006), high sedimentation rates affected both Adana (12.5 mm/yr) (Radeff, 2014) and Eraclea Minoa (4.3 mm/yr) successions. Similar stratigraphical, sedimentological and paleontological conditions have been found also in the lower portion of the Lago-Mare succession cropping out in the Iraklion Basin (central Crete) (unpublished data). Unfortunately, not everywhere high sedimentation rates and siliciclastic inputs support only the “*Cyprideis* assemblage”: in the Mondragone 1 well (Garigliano Plain, Campania, southern Italy) around one-thousand meters of sediments deposited within the short temporal frame of the *Loxocorniculina djafarovi* zone (5.40-5.33 Ma), thus a very high sedimentation rate above 13 mm/yr was calculated, but the recovered Lago-Mare ostracod assemblages were highly diversified (Cosentino et al., 2006).

In conclusion, at the moment no plausible hypothesis can be arised on the paleoenvironmental meaning of the “*Cyprideis* assemblage”, once again stressing the peculiar and complex geological and paleoenvironmental history of the Eraclea Minoa succession.

7. Conclusion

The ostracod assemblages of the post-evaporitic Messinian section of Eraclea Minoa (Sicily) have been studied in a paleoenvironmental perspective to decipher the environmental changes verified during the deposition of the Upper Gypsum Unit. Rich and diversified assemblages made mainly by Paratethyan species, have been recovered in the lower and upper portion of the succession, pointing to shallow and low mesohaline waterbodies. In the central portion of the succession, very abundant monospecific assemblages made only by *Cyprideis agrigentina* were recognized, suggesting high mesohaline to hyperhaline shallow waterbody with low oxygen content. To test this latter interpretation, morphometric and geochemical analyses (stable isotopes, trace

elements, $^{87}\text{Sr}/^{86}\text{Sr}$, and NRD) have been performed on ostracod valves and bulk sediment samples in order to verify if *C. agrigentina* ecophenotypical behavior was comparable with that of the living species *Cyprideis torosa*.

The results have shown that:

- 1) *Cyprideis agrigentina* sizes and ornamentations are not affected by salinity variations;
- 2) The percentages of sieve-pore shapes do not depend from the water salinity, as in *Cyprideis torosa*, but seem linked to the behavior of the DIC and the oxygen availability at the bottom.

Thus, it is possible to conclude that *Cyprideis agrigentina* cannot be considered as a paleosalinometer for the Messinian Salinity Crisis.

Furthermore, the geochemical analyses have shown that the deposition of the Eraclea Minoa succession occurred in a complex paleohydrological and paleohydrochemical scenario.

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