Elsevier Editorial System(tm) for Palaeogeography, Palaeoclimatology, Palaeoecology Manuscript Draft

Manuscript Number: PALAE07687R3

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

Article Type: SI: Papers from 17th ISO

Keywords: Ostracoda; morphometrical analyses; geochemical analyses; palaeoenvironmental reconstruction; post-evaporitic Messinian; Sicily (Italy)

Corresponding Author: Dr. Francesco Grossi, Ph.D.

Corresponding Author's Institution: Roma Tre University

First Author: Francesco Grossi, Ph.D.

Order of Authors: Francesco Grossi, Ph.D.; Elsa Gliozzi, Full Professor; Pedro Anadón, CSIC researcher; Francesca Castorina, Associate Professor; Mario Voltaggio, CNR researcher

Abstract: The living euryhaline species Cyprideis torosa (Jones) undergoes morphometric variations in size, noding 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 prevailingly 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 palaeosalinometer for the Quaternary brackish basins. In this paper we attempt to verify whether the ecophenotypical behaviour of the post-evaporitic Messinian species Cyprideis agrigentina Decima was comparable with that of C. torosa. To reach this goal, three morphometric characters have been analysed: 1) size variability; 2) noding and ornamentation; 3) variability of the percentage of the sieve-pore shapes. The palaeoenvironmental 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 C. agrigentina cannot be considered a palaeosalinometer for the Messinian Salinity Crisis. There is a correlation of the 213C with the percentages of sieve-pore shapes, linking them to the oxygen availability at the bottom of the basin.

#### ANSWERS TO REFEREE COMMENTS

## **REFEREE #1 – NEVIO PUGLIESE**

#### **GENERAL OPINION**

Very good paper, well organized and , mainly, original work. Systematics correct. I appreciated the capability to combine different disciplines, mainly micropalaeontology and geochemistry. Thus, I think the work is adequate for the magazine, and worthy of being published with minor corrections. Most of my suggestions are optional. It is not necessary that I revise the text again. My anonymity is not necessary.

#### INTRODUCTION

It is very clear; it properly presents the topic of the paper.

The aim of the work is very clear. However, it is included in the introduction. I suggest instead the Authors to better highlight the purpose of the work putting its sentences in a new paragraph. Basically the lines from 98 to 107 should become a new paragraph well separated from the previous text. The lines from 103 to 105 seem not clear. Are they maybe incomplete?

We have checked the sentence from line 103 to 105 and corrected the English language. We have moved the lines from 98 to 107 to a new paragraph as suggested.

#### CHAPTER 2

Material and methods: very clear. However, I personally prefer the 0,062 mm-mesh, but I understand that for the purpose of the work the 0.126mm sieve used can be good too.

To analyze ostracods we generally use two sediment fractions (0.063 mm 0.125 mm) as suggested by the referee but in this case, being the work devoted only to the analysis of adult valves of C. agrigentina (average sizes around 1 mm in length x....) we considered that the 0.125 mm mesh was more than enough. We have better specified this in the text.

#### CHAPTER 3

It is clear. There is a small mistake in the lines 238 to 240: the authors of the species not in italics: *Livental...Olteanu* become Livental...Olteanu.

All the author names have been written in plain text. Thanks to the referee to have signaled this editing mistake.

#### CHAPTER 4

No observations. It is very good. There is a small mistake in line 372: (**DeDeckker**...) becomes (**De Deckker**...).

We have corrected the misspelled name at line 364.

#### CHAPTER 5

I suggest to change a little the order of the paragraphs:

lines **434-439** concern the ornamentation; lines **440-449** concern the sizes; lines **450-464** concern the sieve-pore canals. Thus, following the aims of the introduction (lines **102-103**) I suggest to report the data in this order: sizes, ornamentation, pore canals.

As suggested, we changed the order of the paragraphs, starting with size followed with ornamentation and pore canals.

#### CHAPTER 6

The discussion is well organized and well articulated.

#### CHAPTER 7

The conclusions are clear and original, even if apparently negative. The authors well underline the role of C. agrigentina as in palaeoenvironmental research, excluding it as marker of palaeosalinity.

#### REFERENCES

Lines 734-735: Graham et al. (1982). I do not find it cited in the text. We have deleted it

## FIGURES

Fig. 2 : I suggest to indicate in the caption the meaning of the numbers 3,4,5,6 reported in the figure We have better specified in the caption the meaning of numbers in Fig. 2 (now fig 3)

## POSSIBLE OPTIONAL SUGGESTIONS

I suggest to insert a photo of *C. agrigentina*. Done

## Referee #2 – Julio Rodriguez Lazaro

I have read the ms and in my opinion it is a very good paper, perfectly planned and written, with several sets of data allowing to reach the important conclusions (though they are "negative" for the use of *C. agrigentina* as palaeosalinometer).

Only couple of comments in the text. In particular:

In Fig. 4, are mentioned levels A, B, E, but these haven't been so far described. In Fig. 5 they are included by the first time (and described in paragraph 4.5). Since they are very used through the text, the units A, B, C, D, E must be added to some other figures, in order to easy the reading.

Done. We have changed the order of Fig. 4 and 5 (now fig 5 and 6), mentioned in the paragraphs 4.1-4.4 the intervals and reported the intervals in Fig. 7 (now fig. 8).

Fig. 7 Interval B. The hydrological interpretation with: "High freshwater and detrital inputs. Possible low salinities that slightly increase again around 222-225 m." is in apparent contradiction with the salinity inferred by pores, in the left of figure. After the latter, there is the maximum of salinity in these levels.

Yes, fig. 7 (now 8) is thought to show the contradiction between the salinity inferred by geochemistry and the salinity inferred by sieve pores. To better clarify it, in Fig. 8 we added to "Palaeohydrology" the sentence "inferred from geochemical analyses". The lack of correspondence between the two dataset is widely discussed in chapter "Discussion" and is the core of the paper.

Intervals D, E. There are marked dysoxic levels coincident with the increase of Shannon diversity. In general, the increase of diversity is indicative of some stabilisation of the environment, which is the opposite of indicated. It must be another factor influencing (you mention the oxygen availability, at the end of discussion). (Please correct disoxyc in D, and hydrochemstry in E). Yes, indeed Shannon-Wiener index and authigenic U curves are negatively correlated. We added a discussion on those results in the paragraph "Discussion" concluding that it is probable that at Eraclea Minoa the causes for the authigenic U accumulation were others than oxygen availability. We have corrected the misspelled words in Fig. 7 (now 8).

In this matter, a "Relatively stable hydrochemical conditions" are indicated in A, but the diversity is very low (monospecific), so some important environmental factor is acting to prevent the "natural trend" of increase of diversity. (oxygen availability, as well?) (have you any proxy for oxygen availability?).

You are right. Some important environmental factor is limiting the colonization by ostracods but....which one? In this paper we have tried to perform different geochemical analyses, but none of them explained us what happened in this close "Lago-Mare" basin after the acme of the Messinian Salinity Crisis. Data show that it was a high suitable environment for *C. agrigentina* alone, but which kind of environment?

Fortunately, the palaeoenviromental interpretation of the Eraclea Minoa succession wasn't the main aim of this paper, which is focussed to the possible use of *C. agrigentina* as palaeosalinometer. Anyway, in no other Lago-Mare section in which ostracod assemblages were studied there is such a long interval in which *C. agrigentina* is so abundant and alone in the assemblage. But Eraclea Minoa is also the only one section in which diagenetic gypsum cristalized from the groundwater, so....

Concerning the oxygen availability, we hoped that authigenic Uranium could be a good proxy to evaluate it. It seems that in the case of Eraclea Minoa it is not true. Anyway, another good proxy could be, as it has been discussed, the  $\delta^{13}$ C and, indeed, it seems that the sieve-pore variability in C. agrigentina could correlate with it.

#### **COMMENTS BY EDITOR IN CHIEF**

As editor in chief, I will be glad to endorse the guest editor's decision to accept this ms for publication in our journal after one minor change. You have to realize that we have an international readership, therefore Figure 1 is not appropriate. Instead of just showing Italy (without even giving the name of the country), you need to provide a larger view of the Mediterranean, with proper country names (Rome and Florence are not needed on such a map).

We modified fig. 2 as requested.

## Highlights

- We study in a palaeoenvironmental perspective a post-evaporitic ostracod assemblage.
- We perform morphometric and geochemical analyses on *Cyprideis agrigentina* valves.
- *C. agrigentina* sizes and ornamentation are not affected by salinity variations.
- Sieve-pore shapes in *C. agrigentina* seem linked to the bottom oxygen availability.
- *C. agrigentina* is not a palaeosalinometer for the Messinian Salinity Crisis.

## \*Revision, changes marked Click here to view linked References

1	Is Cyprideis agrigentina Decima a good palaeosalinometer for the Messinian Salinity Crisis?
2	Morphometrical and geochemical analyses from the Eraclea Minoa section (Sicily)
3	
4	F. Grossi <sup>a,*</sup> , E. Gliozzi <sup>a,b</sup> , P. Anadón <sup>c</sup> , F. Castorina <sup>d</sup> , M. Voltaggio <sup>b</sup>
5	
6	<sup>a</sup> Dipartimento di Scienze, Università Roma Tre, Largo S. Leonardo Murialdo, 1, I-00146, Roma, Italy
7	<sup>b</sup> IGAG, CNR, Area della Ricerca di Roma RM1, Via Salaria km 29,300, CP 10, I-00016, Monterotondo Stazione,
8	Roma, Italy
9	<sup>c</sup> Institut de Ciències de la Terra "Jaume Almera" (CSIC), C. Lluís Solé Sabarís sn, 08028, Barcelona, Spain
10	<sup>d</sup> Dipartimento di Scienze della Terra, Università Roma La Sapienza, P.le A. Moro, 5, I-00185, Roma, Italy
11	
12	
13	
14	
15	* Corresponding author: Present address: Dipartimento di Scienze, Università Roma Tre, Largo S. Leonardo Murialdo,
16	1, I-00146, Rome, Italy
17	e-mail address: <u>francesco.grossi@uniroma3.it</u> (F. Grossi)
18	
19	
20	ABSTRACT
21	
22	The living euryhaline species Cyprideis torosa (Jones) undergoes morphometric variations in size,
23	noding and sieve-pore shape linked to the environmental salinity. In particular it is known that
24	salinity values around 8-9 psu represent the osmoregulation threshold and also the turning point
25	between smaller and greater valve dimensions and prevailingly noded against un-noded valves. The
26	variation of the percentage of round-, elongate- and irregular-shaped sieve-pores on the valves has

27 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 palaeosalinometer for the
Quaternary brackish basins.

30 In this paper we attempt to verify whether the ecophenotypical behaviour of the post-evaporitic 31 Messinian species Cypride agrigentina Decima was comparable with that of C. torosa. To reach 32 this goal, three morphometric characters have been analysed: 1) size variability; 2) noding and 33 ornamentation; 3) variability of the percentage of the sieve-pore shapes. The palaeoenvironmental 34 interpretation was made using synecological and geochemical approaches [stable isotopes, trace 35 elements, Sr-isotopes and natural radioactivity (NRD)]. For this study, the 250 m-thick Messinian 36 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. 37

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 *C. agrigentina* cannot be considered a palaeosalinometer for the Messinian Salinity Crisis.

There is a correlation of the  $\delta^{13}$ C and NRD data with the percentages of sieve-pore shapes, linking them to the <u>behavior of the dissolved inorganic carbon (DIC) and to the oxygen availability at the</u> bottom of the basin.

- 48 KEYWORDS
- 49 <u>Ostracoda; morphometrical analyses; geochemical analyses; palaeoenvironmental reconstruction;</u>
  50 post-evaporitic Messinian; Sicily (Italy).
- 51
- 52 **1. Introduction**

Since the pioneering studies by Schäfer (1953), Sandberg (1964), Vesper (1975) and 53 54 Rosenfeld and Vesper (1977), it is known that the living anomalohaline species Cyprideis torosa 55 (Jones) undergoes morphometrical variations in size, noding and sieve-pore shape linked to 56 environmental physical and chemical parameters - especially salinity - showing a clear 57 environmentally cued polymorphism. The species can withstand and thrive in a very wide range of 58 salinity (0.4 to 150 psu according to Neale, 1988 and Griffiths and Holmes, 2000), thus it is 59 commonly regarded as a valuable palaeosalinometer for the Quaternary marginal marine and athalassic brackish deposits (Marco-Barba, 2010; Pint et al., 2012 with references therein). Its low-60 61 Mg calcite shell represents also a source of biogenic carbonate for the geochemical analyses (trace elements, stable isotopes and <sup>87</sup>Sr/<sup>86</sup>Sr ratios) to infer the chemical composition of past waterbodies, 62 63 because of its high rate of valve calcification. In many studies, morphometrical variations were 64 coupled with the geochemical approach to make more detailed palaeoenvironmental reconstructions 65 of brackish environments (Barbieri et al., 1999; Anadón et al., 2002; Marco-Barba, 2010; Curry et 66 al., 2013; Pint et al., 2013; Rossi et al., 2013).

67 Several studies (Carbonel, 1982; Aladin, 1993; van Harten, 1996; 2000; Keiser and Aladin, 68 2004; Keyser, 2005; Boomer and Frenzel, 2011; Frenzel et al., 2011; 2012 among others) showed 69 that salinity values around 8-9 psu represent the osmoregulation threshold and also the turning point 70 between smaller and greater valve dimensions and prevailingly noded against un-noded valves. 71 Rosenfeld and Vesper (1977) showed an empiric logarithmic correlation between the variation of 72 the percentage of round-, elongate- and irregular-shaped sieve-pores on the valves of C. torosa and 73 the water salinity from 0 to 100 psu. This correlation has been confirmed by subsequent papers 74 (Neale, 1988; Keating et al., 2007; Pint et al., 2012) and Frenzel et al. (2011) elaborated a transfer 75 function based on the percentages of round sieve-pores.

76 In order to decipher the palaeosalinity changes during the end of the Messinian Salinity 77 Crisis (Hsü et al., 1973; CIESM, 2008; Roveri et al., 2014a), Rosenfeld (1977) and Bonaduce and 78 Sgarrella (1999) applied the counting of different sieve-pore shapes to the fossil species Cyprideis 3

*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 this those values reliable for the evaporative
palaeoenvironment that yielded the deposition of the gypsum.

83 C. agrigentina (Fig. 1) is one of the most widespread ostracod that lived in the 84 Palaeomediterranean during the latest Messinian Lago-Mare event (5.53–5.33 Ma, CIESM, 2008; 85 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 Palaeomediterranean after the deposition of the Primary 86 87 Lower Gypsum and the partially desiccation of the basin, and il that been recovered both in the Messinian sediments drilled on the Palaeomediterranean bottoms and in those cropping out along 88 89 the peri-Mediterranean chains, from the most western area (Malaga Basin) to the easternmost Adana Basin (Benson, 1978; Iaccarino and Bossio, 1999; Bonaduce and Sgarrella, 1999; Grossi and 90 91 Gennari, 2008; Guerra-Merchán et al., 2010; Cosentino et al., 2012; Faranda et al., 2013). In their 92 study on the Messinian Lago-Mare palaeoenvironments inferred from the ostracod assemblages, 93 Grossi et al. (2008) showed that C. agrigentina behaved as a very euryhaline species: it was 94 associated a) with the benthic foraminifer Ammonia tepida ("Cyprideis-Ammonia assemblage") in 95 very oligotypic assemblages supposed to be typical of high mesohaline environments; b) with Loxoconcha muelleri (Mehés) and Loxoconcha eichwaldi Livental ("Cyprideis-Loxoconcha 96 97 assemblage") (low mesohaline environment); c) it was also a component, although not dominant, of the "pointed candonids-Leptocytheridae assemblage" and "pointed candonids assemblage", 98 99 supposed to be characteristic of oligohaline to low mesohaline environments.

100 Anyway, despite its apparent capability to withstand different salinities, no noded specimens 101 of *C. agrigentina* have been ever found (Ligios and Gliozzi, 2012) and this could arise some 102 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*.

105	agrigentina from the long section of Eraclea Minoa (Agrigento, Sicily) were investigated and three
106	morphometrical characters have been analysed: 1) size variability; 2) noding and ornamentation; 3)
107	variability of the percentage of the sieve-pore shapes. The palaeoenvironmental framework to
108	which the ecophenotypical characters displayed by C. agrigentina will be compared has been built
109	based on synecological analysis (assemblages taxonomic composition and diversity) (Chapter 3)
110	and geochemical approaches [stable isotopes, trace elements, Sr-isotopes and natural radioactivity
111	(NRD)] (Chapter 4).

112

#### 113 2. Material and methods

114 One hundred fifty-two samples have been soaked in a H<sub>2</sub>O<sub>2</sub> 5%<sub>vol</sub> solution for 24 hours, sieved with 0.063 and 0.125 mm-mesh sieves and dried in oven at 40°C. Total manual picking has 115 been carried out on the 0.125 mm dried sieved samples. When possible, up to 300 valves where 116 hand-picked from each sample. Ostracods have been identified and their frequency counted; the 117 118 obtained values have been normalized to 10 g in order to get comparable figures all along the 119 section to perform a reliable palaeoenvironmental interpretation using the synecological approach 120 proposed by Gliozzi and Grossi, 2008 and Grossi et al., 2008. Shannon-Wiener index has been 121 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.

126

127 2.1 Morphometrical analyses

128 All juvenile and adult valves of *C. agrigentina* were observed under the stereo-microscope 129 to investigate the ornamentation and noding. Formatted: Highlight

130 Over one thousand adult female and male valves of C. agrigentina from fifty-three selected 131 samples were measured under the stereo-microscope, using the Leica Application Suite 2.5.0. Mean 132 values were calculated for each sample. Around 20 adult female and male valves of C. agrigentina from fifty-three samples, chosen 133 134 on the basis of its high frequency, were observed under the Scanning Electron Microscope (LIME 135 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 136 137 calculated. To obtain the inferred salinity value, the following transfer function elaborated by 138 Frenzel et al. (2011), based on the percentage of rounded sieve-pores was used:  $S = e^{-0.06RS+4.7}$ 139 where S = salinity (psu) and RS = percentage of rounded sieve-pores. 140 141 142 2.2 Geochemical analyses 143 144 2.2.1 Stable isotopes Carbon and oxygen stable isotope analyses ( $\delta^{13}$ C and  $\delta^{18}$ O) were performed on fifty-three 145 ostracod samples each consisting of 8-eight C. agrigentina clean adult valves. Two splits of each 146 sample (4 valves each) were reacted with anhydrous phosphoric acid at  $76^{\circ}C \pm 2^{\circ}C$  in a Finnigan 147 MAT Kiel preparation device directly coupled to the inlet of a Finnigan MAT 251 triple collector 148 149 isotope ratio mass spectrometer (Stable Isotope Laboratory, University of Michigan, Ann Arbor, 150 MI, USA). The isotopic results of the mean of the two splits are reported in permil (‰) notation 151 relative to the Pee Dee Belemnite (PDB) standard. The measured precision for the analyses was

- 152 0.04 for  $\delta^{13}$ C and 0.07 for  $\delta^{18}$ O.
- 153
- 154 2.2.2 Trace elements

155	Trace and minor element analyses together with Ca on fifty-three ostracod samples,
156	consisting each in 6 to 10 clean adult valves of C. agrigentina, were performed by inductively
157	coupled plasma atomic emission spectrometry (ICP-AES). The ostracod valves were dissolved in 3
158	ml of ultrapure HNO3 acid (3%). The solutions were analysed for Ca (317.9 nm), Mg (285.2 nm),
159	Na (589.5 nm) and Sr (215.2 nm) in the ICP-AES Thermo Jarrell IRIS Advantage Radial device of
160	the Institute of Environmental Assessment and Water Research (IDAEA-CSIC, Barcelona, Spain).
161	The limits of detection were 0.05 ppm for Ca and Mg, 0.01 ppm for Na and 0.005 ppm for Sr. All
162	the analyses were run against multielemental standards prepared from Johnson Mattey <sup>TM</sup> stock
163	solutions. The obtained results are expressed as metal/calcium ratios of the valves (Me/Ca <sub>v</sub> ).

164

165 2.2.3 Sr isotope analyses

Strontium isotope measurements were obtained from 26 suitable samples of hand-picked valves of *C. 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-X12cation exchange resin. The total procedure blank was 0.5 ng. Sr was collected in 2.9 and 6.3 N HCl and evaporated.

172 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 173 174 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 <sup>87</sup>Sr/<sup>86</sup>Sr ratios of the 175 samples were normalized to a <sup>86</sup>Sr/<sup>88</sup>Sr value of 0.1194. The internal precision (<sup>46</sup>within-run<sup>2</sup>) 176 177 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 178 179 > 2.0 V. Repeated analyses of NIST-987 during the period of the analyses gave a mean value  ${}^{87}$ Sr/ ${}^{86}$ Sr = 0.710251±15 (2 $\sigma$ , n = 15). 180

**Formatted:** Indent: First line: 1.27 cm, Don't adjust space between Latin and Asian text, Don't adjust space between Asian text and numbers

182 2.2.4 Natural Radioactivity (NRD)

183	Natural Radioactivity (NRD) was measured on 27 bulk sediment samples. Uranium, thorium and	Formatted: Highlight
184	potassium were determined by high resolution gamma spectrometry using a low background (GEM-	Formatted: Highlight
185	EG&G ORTEC) HPGe coaxial detector in a PopTop capsule including detector element,	
186	preamplifier and high voltage filter at the Institute of Environmental Geology and Geoengineering	
187	(IGAG, CNR, Rome - Italy). The multichannel buffer (16,384 channels, Ethernim-ORTEC 919E),	
188	including ADC with extended live time correction, was connected into an Ethernet environment	
189	under Windows XP and its control and spectral display was achieved by the use of MAESTRO	
190	application software. In particular, $^{232}$ Th and K were estimated from 583 keV ( $^{208}$ Tl) and 1461 keV	
191	$(^{40}K)$ peaks, while $^{238}U$ was estimated -by the weighted average of U1 and U2, -where U1 is the	
192	product of the known $^{238}$ U/ $^{235}$ U natural activity ratio by the $^{235}$ U activity (calculated by the 186 keV	
193	peak corrected by the <sup>226</sup> Ra contribution) and U2 is the <sup>238</sup> U activity -estimated by the 352 keV peak	
194	$(^{214}$ Pb) assuming full equilibrium in the $^{238}$ U radioactive series.	
195	Capo di Bove leucitite (Voltaggio et al., 2004) was used as standard, while counting time and	
196	amount of each sample were, respectively, 86,400 sec and 150 grams.	
197		
198	2.3 Statistical analyses	
199	A raw matrix of data has been was constructed taking into account those samples that have provided	
200	all the results for the considered types of analyses ( $9$ variables): stratigraphic position, lithology,	Formatted: Highlight
201	$\delta^{13}$ C, $\delta^{18}$ O, Mg/Ca <sub>va</sub> , Sr/Ca <sub>v</sub> , Na/Ca <sub>v</sub> , <u>Th/U</u> , assumed salinity after the sieve-pore analysis and the	Formatted: Highlight
202	<sup>87</sup> Sr/ <sup>86</sup> Sr ratio. The statistical software used was STATISTICA 7.0. From the raw matrix, with 9	Formatted: Highlight
203	variables and 20 cases (samples), a correlation matrix was obtained. Moreover from the raw matrix,	Formatted: Highlight
204	a set of multivariate analysis techniques, as cluster and principal-component analysis (PCA) was	Formatted: Highlight
205	applied. Cluster analysis defines groups of more or less related variables and the corresponding	
206	dendrogram (tree clustering) corresponds to the graphic display of the groups. PCA defines 8	

207	eigenvectors showing the position of the variables in the factor plane and revealing the underlying
208	structure of the data set. From the raw matrix, with 8 variables and 26 cases (samples), a correlation
209	matrix is obtained. Moreover from the raw matrix, a set of multivariate analysis techniques, as
210	cluster and principal component analysis (PCA) have been applied. Cluster analysis defines groups
211	of more or less related variables and the corresponding dendrogram (tree clustering) corresponds to
212	the graphic display of the groups. PCA defines eigenvectors showing the position of the variables in
213	the factor plane and revealing the underlying structure of the data set. An additional analysis with 9
214	variables, the 8 ones mentioned above and the Th/U ratio, has been performed. In this case the
215	number of suitable samples is reduced to 10.

216

#### 217 3. The Eraclea Minoa section and its palaeoenvironments inferred from ostracod assemblages The ca. 266 m-thick Messinian Lago-Mare succession of Eraclea Minoa crops out along the 218 south-western coast of Sicily (lat. 37°23'30"N, long. 13°16'50"E) along the cliff which borders the 219 220 village (Fig. 42). The section has been extensively studied since 1971 (Decima and Wezel, 1971) 221 because it is one of the most complete Messinian Lago-Mare section of the Palaeomediterranean 222 where several gypsum levels referred to the Upper Gypsum Unit crop out (among the most recent 223 papers: Schreiber, 1997; Caruso and Rouchy, 2006; Van der Laan et al., 2006; Manzi et al., 2009 224 with references therein), and because it represents the GSSP of the Messinian/Zanclean boundary 225 (Van Couvering et al., 2000 with references therein) (Fig. 23).

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. 34). 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 *C. agrigentina*) up to 13 species mainly made by the typical Lago-Mare ostracod assemblages of Paratethyan origin.

243 In the lowest portion from 88 (sample EM 3-3) to 144 m (sample EM 6-7), C. agrigentina is 244 scarce and the assemblages, made by Loxoconcha muelleri (Méhes), L. kocki Méhes, L. eichwaldi 245 Livental, Loxocorniculina djafarovi (Schneider), Loxocauda limata (Schneider), Camptocypria sp. 246 1, Tyrrhenocythere pontica (Livental), Euxinocythere (Maeotocythere) praebaquana (Livental), 247 Amnicythere propinqua (Livental), A. subcaspia (Livental), A. multituberculata (Livental) and A. 248 accicularia Olteanu, are rather diversified. These assemblages can be referred to the "Cyprideis-249 Loxoconchidae assemblage" (sensu Grossi et al., 2008), suggesting low mesohaline and shallow 250 waterbodies (supposed salinities <10 psu).

251 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 252 abundant and well preserved. In this long interval, C. agrigentina is the only species present in the 253 samples or is accompanied by the euryhaline benthic foraminifer Ammonia tepida (Cushman). 254 255 Grossi and Gennari (2008) defined the "Cyprideis-Ammonia assemblage" for some ostracod and 256 forams associations recovered in the Lago-Mare borehole of Montepetra (northern Apennines, Italy) in which, together with C. agrigentina and A. tepida, also other two-benthic foraminifers, Florilus 257 258 boueanum (d'Orbigny) and Elphidium spp. were seldom present or A. tepida was the dominant 10

species of the assemblage. The authors related such "Cyprideis-Ammonia assemblage" to high 259 mesohaline to hyperhaline shallow waterbody. At Eraclea Minoa no other brackish benthic 260 261 foraminifers have been recovered except A. tepida. Moreover, this latter species is not always 262 present and generally it-is far subordinated to C. agrigentina. Thus, the palaeoenvironmental 263 interpretation of the interval from 153 to 227 m at Eraclea Minoa could be slightly different. At the 264 moment, we can suppose for this new "Cyprideis assemblage" a relatively high salinity waterbody 265 and/or a dysoxic bottom, based on the capability of the living species C. torosa and Ammonia spp. to withstand low oxygen contents (Jahn et al., 1996; Bernhard and Sen Gupta, 2002). Different 266 267 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 268 269 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 *C. agrigentina* is associated with few other species: with *L. 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.

276 Finally, in the uppermost part of the section [from 228 m (sample EM 7-13) to 265.5 m 277 (sample EM 8-20)], C. agrigentina is again accompanied by the Paratethyan assemblage in which 278 Loxoconchidae are slightly less abundant and two more leptocytherid species are included, even if 279 with scarce frequency: Amnicythere litica (Livental) and A. costata (Olteanu). On the whole, this 280 topmost interval seems again to be referable to the "Cyprideis-Loxoconchidae assemblage" (Grossi 281 et al., 2008), pointing to shallow waterbodies with supposed salinities <10 psu). Within this uppermost interval, it is possible to identify three horizons (from 228 m (sample EM 7-13) to 232 282 283 m (sample EM 7-19), at 234 m (sample EM 7-21) and from 235 m (sample EM 7-25) to 238 m 284 (sample EM 7-28) in which C. agrigentina shares its dominance only with two candonids 11 285 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 286 which C. agrigentina is again the only ostracod species of the assemblage. 287

- 288
- 289 4. Geochemical analyses on *Cyprideis agrigentina* from Eraclea Minoa and inferred Formatted: Highlight 290 palaeoenvironmental features
- 291
- 292 4.1 Stable isotopes

293	<u>Ostracod-C. agrigentina</u> calcite val <u>veues</u> display a wide range of stable isotopic values. $\delta^{13}$ C	_	Formatted: Font: Italic
294	ranges from -6.40 to 1.91‰; $\delta^{18}$ O ranges from -4.08 to 7.95‰ (Tab. 1; Figs. <u>45</u> , <u>56</u> ). The $\delta^{13}$ C		Formatted: Strikethrough
295	values of the ostracod valves show a slight increase from 153-189 m (interval A) to 198-225 m	_	Formatted: Highlight
296	(interval B), Significant, rapid variations are shown around 198-204 m and in the upper portion of		Formatted: Highlight
297	the section <u>faround</u> 253-260 m) <u>(interval E).</u>		Formatted: Highlight
298	The $\delta^{18}$ O values of the ostracod valves show a slight increase from 153 to 189 m <u>(interval</u> )		Formatted: Highlight Formatted: Highlight
299	A), a rapid variation around 198-204 m (lower interval B), and lowering in $\delta^{18}$ O values decrease		Formatted: Highlight
300	from <u>198-204</u> to 225 m (upper interval B). In the upper portion of the section, from 257.8 to 258.5		Formatted: Highlight
301	m <u>(interval E)</u> , a significant decrease in $\delta^{18}$ O values, from 8% to -1.4% is observed.		Formatted: Highlight Formatted: Highlight
302	The $\delta^{13}$ C and $\delta^{18}$ O values from 153 to 189 m (interval A) display small fluctuations,		Formatted: Highlight
303	suggesting minor variations in the palaeohydrological conditions. On the contrary, the valves from		
304	198-204 m (interval B) and 253-260 m (interval E) display significant oscillations, both in $\delta^{13}$ C and		Formatted: Highlight
305	$\delta^{18}$ O values suggesting instabilities in the palaeohydrological conditions related to these intervals		Formatted: Highlight
305	In both cases the larger instabilities (major $S^{13}C$ and $S^{18}C$ oscillations) may be linked to significant		
207	In both cases the larger instabilities (major 6°C and 6°C oscinations) may be initied to significant		
307	detrital and treshwater inputs as reflected by the coarse-grained detrital beds at 199 m and 256-		
308	264.5 m.		

309	The distribution in a X-Y plot (Fig. 46) shows that the isotopic values from 153 to 216 m	Formatted: Highlight
310	(interval A and lower B) display a negative covariant trend with a significant correlation ( $R=$	
311	0.894). This is mainly due to the negative correlation of the interval from 198-216 m (lower B, $R=$	
312	0.903) and the almost invariant values in the interval 153-189 m (interval A).	
313		
314	4.2 Trace elements	
315	For <i>ostracod <u>C. agrigentina</u></i> calcite valves, the Mg, Sr and Na content expressed as Mg/Ca <sub>v</sub> ,	Formatted: Font: Italic
316	Sr/Ca <sub>v</sub> and Na/Ca <sub>v</sub> molar ratios are listed in Tab <u>le</u> 1 and represented in Fig. 5. The Mg/Ca <sub>v</sub> values	Formatted: Highlight
317	range from 0.0052 to 0.0158, the Sr/Ca <sub>v</sub> values range from 0.0022 to 0.0054 and the Na/Ca <sub>v</sub> values	
318	range from 0.0032 to 0.0046.	
319	The Mg/Ca <sub>v</sub> values from <i>C. agrigentina</i> valves show a significant drop from 189- <u>to</u> 198.2	Formatted: Highlight
320	m <u>(intervals A and B boundary)</u> towards the upper portion of the succession, with a rapid variation	Formatted: Highlight
321	around 153-156 m (lower interval A). An overall increase trend in Mg/Ca <sub>v</sub> is recorded in the	Formatted: Highlight
322	interval 198.2-225 m (interval B) and a significant increase in Mg/Ca, is observed also in the upper	Formatted: Highlight Formatted: Highlight
323	part of the section <u>(interval E)</u> . This is parallelized with a similar increase in the $\delta^{13}$ C values.	Formatted: Highlight
324	The Na/Ca <sub>v</sub> values from <i>C. agrigentina</i> show a slight decrease from 153-189 m (interval A)	Formatted: Highlight
325	to 198-216 m (interval B), with a rapid variation around 198.2—201 m. A significant decrease of	Formatted: Highlight
326	Na/Ca <sub>v</sub> is observed in the upper portion of the section <u>(interval B)</u> . This is parallelized with the	Formatted: Highlight
327	decrease in Sr/Ca and $\delta^{18}$ O values.	
328		

329 4.3 Sr isotopes

Differently 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 compositions of ostracod shells allow us to

evaluate the connectivity of the basin with the open ocean and <u>the</u> paleoclimatic conditions and
hydrography.

336	The Eraclea Minoa section shows that the ${}^{87}$ Sr/ ${}^{86}$ Sr values from the C. agrigentina valves
337	are comprised between 0.708510 and 0.708729 (Tab- <u>le</u> 1). The range of values is high in the lower
338	analysed interval (153-189 m $\frac{1}{2}$ interval A) and decreases in the portion comprised between 198 to
339	225 m (interval B), reaching the minimum values (0.708510 and 0.708511) in the interval 204.2-
340	210 m (low interval B), in correspondence of low $\delta^{18}$ O, Sr/Ca <sub>v</sub> and Na/Ca <sub>v</sub> values. In the upper
341	portion of the section (253-260 m $\frac{1}{2}$ interval E) the <sup>87</sup> Sr/ <sup>86</sup> Sr values rise again, with a maximum
342	(0.708704) at 253 m (Fig. $\frac{55}{2}$ ). Sr isotopic data of <i>C. agrigentina</i> are markedly different with respect
343	to coeval global ocean values (Henderson et al., 1994; McArthur et al., 2001) being significantly
344	lower than the marine waters at that time, but this is a common feature for -latest Miocene-earliest
345	Pliocene strontium values of the Mediterranean Palaeomediterranean Basin carbonates.

346

#### 347 4.4 Natural Radioactivity

<sup>232</sup>Th and K<u>measured in bulk sediment samples</u> are highly correlated ( $\frac{R}{R}$ =-0.94) suggesting that 348 <sup>232</sup>Th is mainly contained in the detrital fraction. Detrital uranium, in turns, was calculated by the 349 product of measured <sup>232</sup>Th and the average <sup>238</sup>U/<sup>232</sup>Th weight ratio of pelagic sediments, considered 350 close to 0.25 (Mangini et al., 2001). Finally, authigenic uranium,  $-^{238}U_a$ , -was estimated by 351 subtracting the detrital  $^{238}$ U from measured  $^{238}$ U (Tab-<u>le</u> 2). Authigenic uranium as well as the Th/U 352 ratio was proposed by Wignall and Myers (1988) as an index of bottom-water oxygenation= the U<sub>a</sub> 353 values trending to increase in a reducing environment, where uranium is immobile as tetravalent 354 ion, According to Wignall (1994) Ua values comprised between 2 and 10 are indicative of dysoxic 355 environments; similarly for Th/U values, Th/U<<1 indicate anoxic conditions, Th/U>>1 indicate oxic 356 conditions, while values in the range 1<Th/U>1 point to dysoxic conditions, Even if the use of authigenic 357 358 uranium as proxy for reducing conditions -is common in the chemiography of marine sediments 359 (Pattan and Pearce, 2009), several authors have questioned the real preservation of the authigenic 14



Formatted: Highlight
Formatted: Highlight
Formatted: Highlight
Formatted: Highlight
Formatted: Highlight
Formatted: Subscript
Formatted: Highlight
Formatted: Highlight
Formatted: Highlight
Formatted: Highlight
Formatted: English (U.K.), Highlight
Formatted: Highlight
Formatted: English (U.K.), Highlight
Formatted: Highlight
Formatted: English (U.K.), Highlight
Formatted: Highlight
Formatted: English (U.K.), Highlight
Formatted: Highlight

360	uranium signal by different processes as burn down, fast change of sedimentation rate and oxygen
361	ventilation or bioturbation (Zheng et al., 2002). Therefore any indication of oxigen depletion
362	suggested by the authigenic uranium has to be regarded in a wider fitting context.

- Jua 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, Ua 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).
- Formatted: Highlight

   Formatted: Subscript, Highlight

   Formatted: Highlight

#### 370 4.5 Palaeoenvironmental episodes inferred from the geochemical proxies

369

371 The geochemical analyses performed on the valves of C. agrigentina and bulk sediment 372 samples collected from the 96.5-260 m portion of the post-evaporitic Messinian succession of 373 Eraclea Minoa confirm the frame of a Palaeomediterranean waterbody discontinuous and isolated, 374 characterised by diluted waters after the evaporative phase of the Lower Gypsum Unit, the closure 375 of the Atlantic-Palaeomediterranean connection and the subsequent global humid climate phase 376 (Griffin, 2002; CIESM, 2008; Grossi et al., 2008). In fact, notwithstanding the elear-well known 377 saline character of the Palaeomediterranean waters, testified by the presence of brackish ostracod 378 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. 45, 6 does not 379 380 show the overall covariant trend that would correspond to a marginal marine environment or a closed waterbody (Talbot, 1990; Utrilla et al., 1998; Ligios et al., 2012), and also trace elements 381 382 behave in a different manner. The Mg/Ca<sub>v</sub> values from *C. agrigentina* (Mg/Ca<sub>v</sub>=0.0052-0.0152) are 383 similar to most of the analyses from Cyprideis shells for the Messinian Lago-Mare horizons from 384 DSDP sites (De Deckker et al., 1988). For these Mg/Ca<sub>v</sub> values, De Deckker et al. (1988) consider 385 the host water had Mg/Ca values lesser than that of Messinian seawater, and in some cases similar

Formatted: Highlight

to most of the Mg/Ca shown by freshwaters (Mg/Ca=1). The Sr/Ca<sub>y</sub> values from C. agrigentina at 386 153-189 m (Sr/Ca,=0.0025-0.0030) are similar to most of the analyses from Cyprideis shells from 387 the Messinian Lago-Mare horizons from DSDP sites (De Deckker et al., 1988). For these Sr/Ca<sub>v</sub> 388 389 values, these authors consider the host water had Sr/Ca values lesser than that of Messinian oceanic 390 seawater. On the contrary, the Sr/Ca<sub>v</sub> values for most of the samples from 198-225 m and 252.8-391 257.8 m (Sr/Ca,=0.0038-0.0054) indicate that the host water frequently had Sr/Ca values greater 392 than that of Messinian oceanic seawater. The values of Sr/Cav and Mg/Cav indicate that the waters where the Eraclea Minoa ostracods lived were very different than the Messinian seawater and there 393 is no indication of connection with oceanic seawater. Furthermore, the <sup>87</sup>Sr<sup>86</sup>Sr range of values 394 obtained from the analyses of C. agrigentina valves from Eraclea Minoa is consistent with the 395 396 isotopic values of the Upper Gypsum Unit from Sicily and other localities of the Palaeomediterranean (Müller and Mueller, 1991; Keogh and Butler, 1999; Flecker and Ellam, 2006; 397 Roveri et al., 2014b). This range is also similar to the range (0.708600-0.70875) reported from most 398 399 ostracod valves (Cyprideis) from Messinian Lago-Mare deposits from several DSDP sites of the 400 Palaeomediterranean studied by McCullock and De Deckker (1989). On the other hand, the Sr 401 isotopic values from Eraclea Minoa are quite different from the value of the average ocean water 402 during the deposition of the Upper Evaporite: 0.709012 (Howarth and McArthur, 1997; Flecker et 403 al., 2002). The  ${}^{87}$ Sr/ ${}^{86}$ Sr values of the Eraclea Minoa C. agrigentina, as is the case of materials from 404 other post-evaporitic Messinian localities, confirm to be the result of a large influence of freshwater 405 on the Sr isotopic composition of the desiccating subbasins of the Palaeomediterranean (Müller et 406 al., 1990). Finally, it is noteworthy that isotopic ratios anomalously low could result from 407 reworking of older marine evaporites, or diagenetic overprinting. However, according to Keogh and 408 Butler (1999), the reworking of Sr from the older marine evaporites implies mixing in different 409 proportion between Sr deriving from continental run-off and coming from ground water circulating 410 inside the buried -evaporites. Such a process likely produces high variability in both salinity and <sup>87</sup>Sr/<sup>86</sup>Sr ratios. 411

Formatted: Highlight

412	Based on the geochemical signature of C. agrigentina valves and bulk sediment samples,	
413	five main palaeoenvironmental intervals may be differentiated along the studied portion of the	
414	Eraclea Minoa succession (Fig. 5):	
415	Interval A (153-189 m), characterised by high $\delta^{18}$ O, Na/Ca <sub>v</sub> , Mg/Ca <sub>v</sub> and $^{87}$ Sr/ $^{86}$ Sr values,	
416	and low $\delta^{13}C_{\underline{a}}$ and Sr/Ca <sub>ve and Ua</sub> . This interval records relatively stable hydrochemical conditions	Formatted: Not Superscript/ Subscript
417	as suggested by the small variation of each geochemical indicator, isotopically concentrated waters	Formatted: Not Superscript/ Subscript
418	and high Na/Ca <sub>v</sub> and Mg/Ca <sub>v</sub> ratios that were attained after the deposition of the $6^{th}$ gypsum level.	
419	An overall evaporative environment (Fig. 45) with moderate salinity could be inferred for this	
420	interval. The high amount of Th and detrital U, the low content of authigenic uranium and the rather	Formatted: Highlight
421	high Th/U ratios (Table 2) record possible well oxygenated bottoms.	Formatted: Highlight
422	Interval B (198 <u>-to-</u> 225 m), characterised by low $\delta^{18}$ O, Na/Ca <sub>v</sub> , Mg/Ca <sub>v</sub> , and ${}^{87}$ Sr/ ${}^{86}$ Sr, and	Formatted: Highlight
423	<u>U<sub>a</sub></u> values, and high $\delta^{13}$ C and Sr/Ca <sub>v</sub> . A major change is recorded at the base of this interval (198 m,	Formatted: Subscript
424	sample EM 6"-8) where large shifts in all the geochemical indicators appear. A possible explanation	
425	for these features is to consider the noticeable detrital and freshwater inputs that increase the Ca	
426	dissolution, recorded both by the coarser lithologies, the high values of Th and detrital U and the	
427	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,	
428	the increase of $Sr/Ca_v$ (recording Sr inputs from the CaSO <sub>4</sub> -rich subsurface waters) and the lowering	
429	in Mg/Ca <sub>v</sub> because of the high increase in Ca in the waterbody. The increase in $\delta^{13}C$ values could	
430	be produced by an increase in the productivity, linked to the detrital and nutrient inputs and a trend	
431	to re-equilibration with the atmospheric CO <sub>2</sub> (Fig. 4 <u>5</u> ). <u>As in the previous interval, NRD results</u>	Formatted: Highlight
432	(Table 2) testify for possible The high amount of Th and detrital U and the low content of	Formatted: Highlight Formatted: Highlight
433	authigenic uranium (Tab. 2) record well oxygenated bottoms.	Formatted: Highlight
434	Interval C (225-240 m). In this interval, only NRD analyses have been performed due to the	
435	low frequency of <i>C. agrigentina</i> in the ostracod assemblages <del>,</del> that prevented the possibility to reach	
436	the suitable amount of biogenic carbonate for the analyses. The content of authigenic uranium in the	

438progressively less oxygenated bottoms.Formatted: Highlight439Interval D (240-242 m). This short interval is characterised by the highest values ofInterval D (240-242 m). This short interval is characterised by the highest values of440authigenic U and low values of the Th/U ratios, suggesting possble_dysoxic conditions at theInterval D (252.8-259.1 m). In this interval two portions may be differentiated and a main442Interval E (252.8-259.1 m). In this interval two portions may be differentiated and a mainInterval D (252.8-259.1 m).	
<ul> <li>439 Interval D (240-242 m). This short interval is characterised by the highest values of</li> <li>440 authigenic U and low values of the Th/U ratios, suggesting possble_dysoxic conditions at the</li> <li>441 bottom.</li> <li>442 Interval E (252.8-259.1 m). In this interval two portions may be differentiated and a main</li> </ul>	
<ul> <li>440 authigenic U and low values of the Th/U ratios, suggesting possble_dysoxic conditions at the</li> <li>441 bottom.</li> <li>442 Interval E (252.8-259.1 m). In this interval two portions may be differentiated and a main</li> </ul>	
<ul> <li>441 bottom.</li> <li>442 Interval E (252.8-259.1 m). In this interval two portions may be differentiated and a main</li> </ul>	
442 Interval E (252.8-259.1 m). In this interval two portions may be differentiated and a main	
443 change is recorded from the lower samples to the upper ones. The lower samples are characterised	
444 by high $\delta^{18}$ O, Sr/Ca <sub>v</sub> , Na/Ca <sub>v</sub> , and ${}^{87}$ Sr/ ${}^{86}$ Sr values, and low $\delta^{13}$ C and Mg/Ca <sub>v</sub> values, The low Formatted: Highlight	
445 <u>content of authigenic uranium indicates possibly oxygenated bottoms.</u> The upper samples are <b>Formatted:</b> Highlight	
446 characterised by the opposite trends. The geochemical features of the ostracod valves from the	
447 lower part may be explained by the evaporitic concentration of the waterbody (Figs. 5, 46) leading	
448 to high $\delta^{18}$ O, Sr/Ca <sub>v</sub> and Na/Ca <sub>v</sub> values. A subsequent large input of freshwater produced the	
449 lowering of $\delta^{18}$ O, Sr/Ca <sub>v</sub> and Na/Ca <sub>v</sub> . At present, we have no explanation for the variations of the	
450 Mg/Ca <sub>v</sub> values in this interval. <u>It is worth to note the high content of authigenic uranium that</u> Formatted: Highlight	
451 reaches in one sample the value of 9.5 ppm, possibly indicating dysoxic conditions at the bottom. Formatted: Highlight	
452	]
453 <b>5. Morphometrical analyses on</b> <i>Cyprideis agrigentina</i> valves	
454 Length and height of one thousand-sixty valves of adult males and females were measured.	
455 The obtained values fall within the variability field typical of the species (Decima, 1964; Ligios et	
456 al., 2012). The mean values of the length of the female left valve (the most numerous in the	
457 measured samples) have been compared. Generally the mean values of the length vary from 0.96 to	
458 1.00 mm, but in few samples the mean values are rather small: at 185 m ( <u>sample EM 6</u> "-3, mean	
459 value 0.90 mm), 201 m (EM 6"-11, mean value 0.89 mm), 222 m (EM 7-6, mean value 0.85 mm),	
460 and 223.5 m (EM 7-8, mean value 0.88 mm) (Fig. 67). Only in four samples the mean values of the	
461 length result significantly largehigh: at 165 m (sample EM 6'-12 mean value 1.05 mm), 176.2 m	

# 462 (sample <u>EM</u> 6'-24, mean value 1.06 mm), 180 m (EM 6'-27, mean value 1.04 mm), and 210 m (EM 463 6"-17, mean value 1.14 mm).

The several thousands specimens of *C. agrigentina* investigated for the ornamentation and noding, 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. 67).

470 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 C. agrigentina was more abundant, making 471 472 both monospecific and diversified assemblages. On average, more than 500 sieve-pores were 473 observed for each sample and counted on the basis of their shape: rounded, elongated, irregular, 474 following the indications by Rosenfeld and Vesper (1977). The results are reported in Fig. 67. In 475 most cases, the percentages of the rounded sieve-pores are comprised between 40 and 50%; in 476 twelve scattered samples they are higher, reaching the maximum value of 65% at 96.5 m (sample 477 EM 4-7) and only in a short interval from 198.5 m (sample EM 6"-8) to 216 m (sample EM 6"-20) 478 they are lower, comprised between 19 and 30%, reaching their minimum values (19-21%) in the 479 interval 204.5-216 m. Applying the transfer function elaborated by Frenzel et al. (2011) for C. 480 torosa, the resulting salinities expressed in psu shows values included in the mesohaline range (5-18 481 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 482 483 (polyhaline to euhaline ranges, 18-40 psu) are recorded only in a limited portion of the section, from 484 198.5 to 216 m (Fig. 78).

As explained in the introduction, the living species C. torosa is considered to be one of the 488 most valuable tools to detect past salinities in the marginal marine environments, owing to its 489 environmentally cued polymorphism that induces variations in size, noding and sieve-pore shapes 490 depending on salinity. Large sizes, presence of nodes and high percentages (around 40-45%) of 491 rounded sieve-pores point to salinity less than 8-9 psu that is considered an important 492 osmoregulation threshold for the species (Keiser and Aladin, 2004; Keyser, 2005).

493 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 494 495 Cyprideis 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 496 497 Palaeomediterranean area with Cyprideis ruggierii Decima (late Tortonian-early Messinian), 498 including Cyprideis agrigentina Decima (post-evaporitic Messinian) and Cyprideis crotonensis 499 Decima (post-evaporitic Messinian-Late Pliocene). The great morphological similarity of the 500 species of the stem lead some authors to suppose that the same environmentally cued polymorphism 501 displayed by C. torosa could affect also its relatives (Neale, 1988), notwithstanding no noded 502 specimens of the other species had never been recorded. Thus, Rosenfeld (1977) and Bonaduce and 503 Sgarrella (1999) inferred hyperhaline post-evaporitic Messinian environments respectively for the 504 Mavqi'im Formation (Israel) and at Eraclea Minoa, applying on C. agrigentina valves the empirical 505 methods of the percentage of the rounded sieve-pores elaborated by Rosenfeld and Vesper (1977) 506 on C. torosa.

507 As a first step to investigate whether C. agrigentina shared with C. torosa the same ecophenotypical behavior, we have analyzed size, ornamentation and sieve-pore shapes on some 508 509 thousand of specimens from the post-evaporitic Messinian section of Eraclea Minoa. The expected 510 results, in case of a comparable behavior, is a positive correlation between large size, noding (or 511 strongly pitted valve surface), and high percentages of rounded sieve-pores. Fig. 6-7 shows that this 512 correlation lacks: the largest sizes (thus the supposed lowest salinities, below 8-9 psu) are attained 20

513 by specimens recovered in samples bearing smooth valves (supposed high salinities) and 514 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 515 516 percentages of rounded sieve-pores (22,7%); the smallest sizes (supposed high salinities) correlates 517 with smooth valve surfaces (supposed high salinities) but to percentages of rounded sieve-pores 518 greater than 40% except in one case (sample EM 6"-11 at 201 m) in which the percentage is low 519 (23.1%); the only two samples in which C. agrigentina valves are densely pitted (supposed low 520 salinities), corresponds, on average, to intermediate dimensions and high percentage values.

From those comparisons it is possible to conclude that size and ornamentation/noding in *C. agrigentina* are not correlated. In particular, pitted ornamentation and noding 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). Thus, it seems that those characters do not display in *C. agrigentina* the same salinity-dependant polymorphism of *C. torosa*.

A further question is to investigate whether the percentage variations of the sieve-pore shapes are correlated with salinity variations as in *C. 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 palaeohydrological variations inferred by the geochemical analyses (Figs. 78, 89, 910).

531 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 532 (monotypic ostracod assemblages) corresponds to different inferred salinities: oligo-low mesohaline 533 534 in the intervals 153-171, 218-225 and 253-257.8 m; high mesohaline from 174 to 189 m; 535 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, 536 537 according to the salinity curve based on sieve-pore percentage should have deposited in 538 polyhaline/euhaline waters. We should conclude that there is no correspondence between the

salinities inferred by the method of the sieve-pore percentages and the synecological palaeoenvironmental 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 546 547 of C. agrigentina is difficult to assess. Although Na/Ca<sub>v</sub> could be tentatively perceived as a proxy of the salinity (assuming salinity dominated by NaCl solute), the obtained data must be considered 548 549 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 550 551 palaeoenvironmental reconstructions must be taken into account (Gouramanis et al., 2010; 552 Devriendt, 2011). On the other hand, Sr/Ca and Mg/Ca from ostracod valves just may inform about 553 the Sr/Ca and Mg/Ca of the waters (De Deckker et al., 1999; Dettman and Dwyer, 2012; Holmes 554 and De Deckker, 2012; Dettman and Dwyer, 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,  $\delta^{18}$ O 555 556 variations in closed non-marine environments are linked usually to evaporation/precipitation 557 processes (Talbot, 1990), that in some cases are associated to salinity variations. Anyway, the 558 decreasing Na/Ca<sub>v</sub> 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  $\delta^{18}$ O values in B. However, this 559 560 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. 78). 561

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 <u>eight-nine</u> variables is shown in Tab<u>-le</u> 3. Significant correlations 22

Formatted: Highlight
Formatted: Highlight

565 (p<0.01) are displayed only by the pairs  $\delta^{18}$ O and Na/Ca<sub>v</sub>, Na/Ca<sub>v</sub> and Mg/Ca<sub>v</sub>, Sr/Ca<sub>v</sub> and 566 stratigraphic position. Significant negative correlations are shown by  $\delta^{13}$ C and Na/Ca<sub>v</sub>,  $\delta^{13}$ C and 567  $\delta^{18}$ O,  $\delta^{13}$ C and Mg/Ca<sub>v</sub>, Mg/Ca<sub>v</sub> and Sr/Ca<sub>v</sub>. In fact salinity assumed from sieve-pore analysis (N 568 pores), and Sr isotopic ratios of the valves do not show significant correlation with any of the other 569 considered variables.



590	If we add the Th/U ratios in the sediments to the other variables in order to perform a new statistical.
591	analysis (9 variables), the number of available samples for this analysis is reduced to 10. In this new
592	examination, the percentages of rounded sieve pores is associated to Th/U and this pair is linked to
593	$\delta^{43}$ C. The links among these 3 variables reflect the relationship between the number of rounded
594	sieve pores in C. agrigentina and the environmental changes in the bottom of the basin in relation
595	with the cycling of carbon (OM decomposition), oxygen availability and redox conditions.
596	Nevertheless, for this analysis the correlations are low and weak. We need additional data to fully
597	confirm these links with Th/U in the sediments, It is worth to note that, although some authors
598	consider both the Ua and Th/U values as good proxies to detect past oxic/dysoxic conditions
599	(Adams and Weawer, 1958; Wignall and Myers, 1988; Wignall, 1994; Jones and Manning, 1994),
600	Wignall and Meyers (1988) suggest to couple the Uaresults with the Shannon-Weaver dominance-
601	diversity index (H) since, under low-oxygen conditions, assemblages are dominated by a few
602	eurytopic forms, and values of H are typically low. If we compare the H-index curve (Fig. 8) with
603	the oxygen availability at the bottom derived from the U <sub>a</sub> curve of Fig. 5, we notice that they are
604	contradictory: when U <sub>a</sub> values are high (comprised between 2 and 10 and indicate possible dysoxic
605	bottoms) the H-index values are high (rather well diversified assemblages). This negative
606	correlation suggest, as supposed by Zheng et al. (2002) that the accumulation of U <sub>a</sub> in sediments
607	could due also to physico-chemical variables other than the oxygen availability.
608	The results of the statistical analyses underline that there is no significant relationship

between the salinity assumed from the sieve-pore analyses on the values of *C. agrigentina* and the variables linked to the hydrochemical changes ( $\delta^{18}$ O, Na/Ca<sub>v</sub> and Mg/Ca<sub>v</sub>, i.e. the salinity changes). On the other hand, the number of <u>rounded sieve</u> pores in C. *agrigentina* seems to be <u>mainly</u> linked to  $\delta^{13}$ C (OM decomposition, DIC-cycling of C), oxygen availability and redox condition in the bottom. **Formatted:** Indent: First line: 0 cm, Don't adjust space between Latin and Asian text, Don't adjust space between Asian text and numbers

Formatted: Highlight
Formatted: Subscript, Highlight
Formatted: Highlight
Formatted: Subscript, Highlight
Formatted: Highlight
Formatted: Highlight
Formatted: Font: 12 pt, Highlight
Formatted: Font: 12 pt, English (U.K.), Highlight
Formatted: Font: 12 pt, Highlight
Formatted: Font: 12 pt, English (U.K.), Highlight
Formatted: Font: 12 pt, English (U.K.), Highlight
Formatted: Font: 12 pt, Highlight
<b>Formatted:</b> Font: 12 pt, English (U.K.), Highlight
Formatted: Font: 12 pt, Highlight
Formatted: Font: 12 pt, English (U.K.), Highlight
<b>Formatted:</b> Font: 12 pt, Not Italic, English (U.K.), Highlight
<b>Formatted:</b> Font: 12 pt, English (U.K.), Highlight
Formatted: Font: 12 pt, Highlight
<b>Formatted:</b> Font: 12 pt, English (U.K.), Highlight
Formatted: Highlight
Formatted: Highlight
Formatted: Subscript, Highlight
Formatted: Highlight
Formatted: Highlight
Formatted: Subscript, Highlight
Formatted: Highlight
Formatted: Highlight
Formatted: Highlight
Formatted: Subscript, Highlight
Formatted: Highlight

In conclusion, this puzzly set of data does not confirm that the percentages variation of the sieve-pore shapes in *C. 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 deposition-re-sedimentation of the Upper Gypsum Unit and scattered inputs of detrital materials and meteoric waters accounts for a complex palaeohydrological and palaeohydrochemical scenario in which it seems that the factors responsible for the changes in the shape of the pores in the valves of *C. agrigentina* could be the behaviour of the DIC and the oxygen availability.

621 On the other hand, the geochemical data give a negative response to the hypothesis that the 622 "*Cyprideis* assemblage" could be related to dysoxia at the bottom. Data from the percentage of the 623 authigenic U, Th/U ratios indicate that some <u>episodes of oxygen depletionaccumulation of Ua</u> 624 occurred at the bottom of the Eraclea Minoa waterbody, but it seems that they were not so important 625 to affect the benthic ostracod assemblages.

626 Although it is beyond the aim of this paper, in order to try to understand the 627 palaeoenvironmental meaning of the "Cyprideis assemblage" we have tried to extend our 628 investigations comparing other Lago-Mare successions of the Mediterranean area that included 629 monotypic C. agrigentina assemblages. In the first case, such assemblage, represented by very 630 scarce specimens, has been recovered in the lower portion of the Lago-Mare succession of the 631 Adana Basin (Turkey) during the deposition of resedimented evaporites and marls, where a very 632 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 633 input connected with the high subsidence rate that affected the Adana Basin during the Lago-Mare 634 phase. At Eraclea Minoa the "Cyprideis assemblage" is present with high frequencies and 635 636 continuously recovered along the entire interval, but it is rather confined to the thick marly-sandy 637 succession included between gypsum bodies 6 and 7. If we hypothesize that this portion of 638 succession represents one precessional cycle, as supposed by Van der Laan et al. (2006), high 639 sedimentation rates affected both Adana (12.5 mm/yr) (Radeff et al., submitted) and Eraclea Minoa Formatted: Highlight
Formatted: Subscript, Highlight

Formatted: Not Highlight

640  $(4_{7,3} \text{ mm/yr})$  successions. Similar stratigraphical, sedimentological and paleontological conditions 641 have been found also in the lower portion of the Lago-Mare succession cropping out in the Iraklion 642 Basin (central Crete) (unpublished data). Unfortunately, not everywhere high sedimentation rates 643 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 644 645 within the short temporal frame of the Loxocorniculina djafarovi zone (5.40-5.33 Ma), thus a very 646 high sedimentation rate above 13 mm/yr was calculated, but the recovered Lago-Mare ostracod assemblages were highly diversified (Cosentino et al., 2006). 647

648 In conclusion, at the moment no plausible hypothesis can be arised on the palaeoenvironmental meaning of the "Cyprideis assemblage", once again stressing the peculiar and 649 650 complex geological and palaeoenvironmental history of the Eraclea Minoa succession.

651

#### 652 7. Conclusion

653 The ostracod assemblages of the post-evaporitic Messinian section of Eraclea Minoa (Sicily)cm 654 have been studied in a palaeoenvironmental perspective to decipher the environmental changes verified during the deposition of the Upper Gypsum Unit. Rich and diversified assemblages made 655 656 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 657 succession, very abundant monospecific assemblages made only by C. agrigentina, were 658 recognized, suggesting high mesohaline to hyperhaline shallow waterbody with low oxygen 659 content. To test this latter interpretation, morphometric and geochemical analyses (stable, isotopes, 660 trace elements, <sup>87</sup>Sr/<sup>86</sup>Sr, and NRD), have been performed on <u>C. agrigentinaostracod</u> valves and 661 Formatted: Font: Not Italic 662 bulk sediment samples in order to verify if *its-C. agrigentina* ecophenotypical behavior was 663 comparable with that of the living species C. torosa. The results have shown that: 664

665

1) C. agrigentina sizes and ornamentations are not affected by salinity variations;

Formatted: Indent: First line: 1.06

Formatted: Font: Italic

666	2) The percentages of sieve-pore shapes do not depend from the water salinity, as in <i>C. torosa</i> ,	
667	but seem linked to the <u>behavior of the DIC and the</u> oxygen availability at the bottom.	
668	Thus, it is possible to conclude that C. agrigentina cannot be considered as a	
669	palaeosalinometer for the Messinian Salinity Crisis.	
670	Furthermore, the geochemical analyses have shown that the deposition of the Eraclea Minoa	
671	succession occurred in a complex palaeohydrological and palaeohydrochemical scenario.	
672		
673		
674	Acknowledgements	
675		
676	The research of F.G. and E.G. has been founded by the Italian National Research Project PRIN	
677	2009-2010. P.A. work is supported by Project CGL2011-23438. The authors are grateful to Rafael	
678	Bartrolí (ICTJA and IDAEA, CSIC) for the ICP-AES analyses and to Lora Wingate (Stable Isotope	
679	Laboratory, University of Michigan) for the stable isotope analyses on the ostracod valves.	
680		
681	REFERENCES	_
682		F
683	Adams J.A. & Weaver C.E., 1958, Thorium-uranium ratios as indicators of sedimentary processes:	F
684	example of concept of geochemical facies. Bulletin American Association of Petroleum	F <sup>i</sup> N
685	<u>Geologists, 42(2), 387-430.</u>	Fi N
686	Aladin, N.V., 1993. Salinity tolerance, morphology and physiology of the osmoregulation organs in	N F
687	Ostracoda with special reference to Ostracoda from the Aral Sea. In Jones, P. and McKenzie	N (l
688	K. (Eds.), Ostracoda in Earth and Life Sciences, A.A. Balkema, Rotterdam, 387-404.	F
689	Anadón, P., Gliozzi, E., Mazzini, I., 2002. Paleoenvironmental reconstruction of marginal marine	F
690	environments from combined paleoecological and geochemical analyses on Ostracods. In:	(i

Formatted: Highlight Formatted: Highlight Formatted: Indent: Left: 0 cm, Hanging: 1.06 cm Formatted: Font: (Default) Times New Roman, 12 pt, English (U.K.), Formatted: Font: (Default) Times New Roman, 12 pt, Roffault) Times New Roman, 12 pt, Not Italic, Highlight Formatted: Font: (Default) Times New Roman, 12 pt, Not Italic, English (U.K.), Highlight Formatted: Font: (Default) Times New Roman, 12 pt, Highlight Formatted: Font: (Default) Times New Roman, 12 pt, Highlight Formatted: Font: (Default) Times New Roman, 12 pt, Not Bold, English (U.K.), Highlight Formatted: Font: (Default) Times New Roman, 12 pt, Not Bold, English (U.K.), Highlight

Formatted: Font: Italic, English (U.K.)

- Holmes, J., Chivas, A. (Eds), The Ostracoda: Applications in Quaternary Research,
  Geophysical Monograph 131, 227–247.
- Barbieri, M., Carrara, C., Castorina, F., Dai Pra, G., Esu, D., Gliozzi, E., Paganin, G., Sadori, L.,
  1999. Multidisciplinary study of Middle-Upper Pleistocene deposits in a core from the Piana
  Pontina (central Italy). Giornale di Geologia 61, 47–73.
- Benson, R.H., 1978. The paleoecology of the ostracodes of DSDP Leg 42A. In: Initial Reports of
  the Deep Sea Drilling Project 42, 777–787, U.S. Government Printing Office, Washington,
  D.C.
- Bernhard, J.M, Sen Gupta, B.K., 2002. Foraminifera of oxygen-depleted environment. In: Sen
  Gupta, B.K. (Ed.), Modern Foraminifera. Kluwer Academic Publishers, 201-216.
- Bonaduce, G., Sgarrella, F., 1999. Paleoecological interpretation of the latest Messinian sediments
  from southern Sicily (Italy). Memorie della Società Geologica Italiana 54, 83–91.
- Boomer, I., Frenzel, P., 2011. Possible environmental and biological controls on carapace size in
   *Cyprideis torosa* (Jones, 1850). Joannea Geologie und Paläontologie 11, 26–27.
- Bossio, A., Costantini, A., Lazzarotto, A., Liotta, D., Mazzanti, R., Mazzei, R., Salvatorini, G.,
  Sandrelli, F., 1993. Rassegna delle conoscenze sulla stratigrafia del Neoautoctono toscano.
  Memorie della Società Geologica Italiana 49, 17–98.
- Bossio, A., Cerri, R., Mazzei, R., Salvatorini, G., Sandrelli, F., 1996. Geologia dell'area
  Spicchiaiola-Pignano (Settore orientale del Bacino di Volterra). Bollettino della Società
  Geologica Italiana 115, 393-422.
- Carbonel, P., 1982. Les Ostracodes, traceurs des variations hydrologiques dans des systèmes de
  transition eaux douces-eaux salées. Mémoirs de la Societé géologique de France 8(144),
  117–128.
- 714 Caruso, A., Rouchy, J.-M., 2006. The Upper Gypsum Unit. In: Roveri, M., Manzi, V., Lugli, S.,
- 715 Schreiber, B.C., Caruso, A., Rouchy, J.-M., Iaccarino, S.M., Gennari, R., Vitale, F.P., Ricci

- Lucchi, F. (Eds.), Clastic vs. primary precipitated evaporites in the Messinian Sicilian
  basins. Acta Naturalia de "L'Ateneo Parmense" 42(4), 157-159.
- 718 CIESM (Commission Internationale pour l'Exploration de la Mer Méditerranée Mediterranee,
- Monaco), 2008. The Messinian Salinity Crisis from Mega-Deposits to Microbiology: A
  Consensus Report. CIESM Workshop Monograph 33, 1-168.
- Cosentino, D., Bertini, A., Cipollari, P., Florindo, F., Gliozzi, E., Grossi, F., Lo Mastro, S.,
  Sprovieri, M., 2012. Orbitally-forced palaeoenvironmental and palaeoclimate changes in the
  late post-evaporitic Messinian stage of the central Mediterranean Basin. Geological Society
  of America Bulletin 124(3-4), 499-516.
- Cosentino, D., Federici, I., Cipollari, P., Gliozzi, E., 2006. Environments and tectonic instability in
  central Italy (Garigliano Basin) during the late Messinian *Lago-Mare* episode: New data
  from the onshore Mondragone well (Garigliano Plain, central Italy). Sedimentary Geology
  188-189, 293-317.
- Curry, B., Mesquita-Joanes, F., Fanta, S., Sterner, D., Calò, C., Tinner, W., 2013. Two coastal
  sinkhole lakes in SW Sicily (Italy) reveal low-salinity excursion during Greek and Roman
  occupation. Naturalista Siciliano 4, 37(1), 93-95.
- De Deckker, P., Chivas, A.R., Shelley, J.M.G., 1988. Paleoenvironment of the Messinian
  Mediterranean "Lago Mare" from strontium and magnesium in ostracode shells. Palaios, 3,
  352-358.
- De Deckker, P., Chivas, A.R., Shelley, J.M.G., 1999. Uptake of Mg and Sr in the euryhaline
  ostracod *Cyprideis* determined from in vitro experiments. Palaeogeography,
  Palaeoclimatology, Palaeoecology 148, 105–116.
- Decima, A., 1964. Ostracodi del genere *Cyprideis* Jones del Neogene e del Quaternario italiani.
  Palaeontographia Italica, 57(1962), 81-133.
- Decima, A., Wezel, F.C., 1971. Osservazioni sulle evaporiti messiniane della Sicilia centromeridionale. Rivista mineraria siciliana 130-132, 172-187.

Formatted: Highlight

- Dettman, D.L., Dwyer, G.S., 2012. Biological and environmental controls on ostracod shell traceelement chemistry. In: D. J. Horne, J. Holmes, J. Rodriguez-Lazaro and F. Viehberg (Eds.).
  Ostracoda as proxies for Quaternary climate change. Developments in Quaternary Sciences.
  Elsevier, v. 17, -145-163.
- Devriendt, L.S.J., 2011. Late Quaternary environment of paleolake Carpentaria inferred from the
   chemistry of ostracod valves. Master of Sciences Research Thesis, University of
   Wollongong, Australia, 175 pp. <u>http://ro.uow.edu.au/theses/3319/</u>
- Faranda, C., Gliozzi, E., Cipollari, P., Grossi, F., Darbaş, G., Gürbüz, K., Nazik, A., Gennari, R.,
  Cosentino, D., 2013. Messinian paleoenvironmental changes in the easternmost
  Mediterranean Basin: Adana Basin, southern Turkey. Turkish J Earth Sci 22, 839-863.
- 752 Faure, G., Powell, J.L., 1972. Strontium Isotope Geology. Springer-Verlag, Berlin, 1-188.
- Flecker, R., de Villiers, S., Ellam, R.M., 2002. Modelling the effect of evaporation on the salinity–
   <sup>87</sup>Sr/<sup>86</sup>Sr relationship in modern and ancient marginal–marine systems: the Mediterranean
   Messinian Salinity Crisis. Earth Planet. Sci. Lett. 203 (1), 221–233.
- Flecker, R., Ellam, R.M., 2006. Identifying Late Miocene episodes of connection and isolation in
   the Mediterranean–Paratethyan realm using Sr isotopes. Sediment. Geol. 188–189, 189–203.
- Frenzel, P., Schulze, I., Pint, A., 2011. Salinity dependant morphological variation in *Cyprideis torosa*. Joannea Geologie und Paläontologie 11, 59–61.
- Frenzel, P., Schulze, I., Pint, A., 2012. Noding of *Cyprideis torosa* valves (Ostracoda) a proxy for
  salinity? New data from field observations and a long-term microcosm experiment.
  International Review of Hydrobiology 97(4), 314–329.
- Gliozzi, E., Grossi, F., 2008. Late Messinian Lago-mare ostracod palaeoecology: a correspondence
   analysis approach. Palaeogeography, Palaeoclimatology, Palaeoecology 264, 288-295.
- Gouramanis, C., Wilkins, D., De Deckker, P., 2010. 6000 years of environmental changes recorded
   in Blue Lake, South Australia, based on ostracod ecology and valve chemistry.
- 767 Palaeogeography, Palaeoecology, Palaeoclimatology 297, 223-237.

- 768 Graham, D.W., Bender, M.L., Williams, D.F., Keigwin, L.D., 1982. Strontium calcium ratios in the
   769 Cenozoic planktonic foraminifera. Geochim. Cosmochim. Acta 46, 1281–1292.
- Griffin, D.L., 2002. Aridity and humidity: Two aspects of the late Miocene climate of North Africa
  and the Mediterranean. Palaeogeography, Palaeoclimatology, Palaeoecology 182, 65–91.
- Griffiths, H.I., Holmes, J.A., 2000. Non-marine ostracods & Quaternary palaeoenvironments.
  Quaternary Research Association, Technical Guide 8, 1-179.
- Grossi, F., Gennari, R., 2008. Palaeoenvironmental reconstruction across the Messinian/Zanclean
  boundary by means of ostracods and foraminifers: the Montepetra borehole (Northern
  Apennine, Italy). Atti del Museo Civico di Storia Naturale di Trieste 53(suppl), 67-88.
- Grossi, F., Cosentino, D., Gliozzi, E., 2008. Palaeoenvironmental reconstruction of the late
  Messinian lago-mare successions in central and eastern Mediterranean using ostracod
  assemblages. Bollettino della Società Paleontologica Italiana 47(2), 131–146.
- Guerra-Merchán, A., Serrano, F., Garcés, M., Gofas, S., Esu, D., Gliozzi, E., Grossi, F., 2010.
  Messinian Lago-Mare deposits near the Strait of Gibraltar (Malaga Basin, S Spain).
  Palaeogeography, Palaeoclimatology, Palaeoecology 285, 264–276.

783 Henderson, G. M., Martel, D. J., O'Nions, R. K., Shackleton, N. J., 1994. Evolution of seawater

- <sup>87</sup>Sr/<sup>86</sup>Sr over the last 400 ka: the absence of glacial/interglacial cycles. Earth Planetary
  Sciences and Letetrs 128, 643–651.
- Holmes, J., De Deckker, P., 2012. Introduction to ostracod shell chemistry and its application to
  Quaternary palaeoclimate studies. In: D. J. Horne, J. Holmes, -J. Rodriguez-Lazaro and F.
  Viehberg (Eds.). Ostracoda as proxies for Quaternary climate change. Developments in
  Quaternary Sciences. Elsevier, v. 17, 131-144.
- Howarth, R., McArthur, J.M., 1997. Statistics for Strontium Isotope Stratigraphy: a robust
  LOWESS fit to the marine Sr-isotope curve for 0 to 206 Ma, with look-up table for
  derivation of numeric age. J. Geol. 105, 441–456.
- Hsü, K.J., Ryan, W.F.B., Cita, M.B., 1973. Late Miocene desiccation of the Mediterranean. Nature
  242, 240–244.
- Iaccarino, S., Bossio, A., 1999. Paleoenvironment of uppermost Messinian sequences in the
  Western Mediterranean (sites 974, 975 and 978). In: Zahn, R., Comas, M.C., Klaus, A., et
  al. (Eds.), Proceedings of Ocean Drilling Program, Scientific Results 161, 529–541, College
  Station, Texas.
- Jahn, A., Gamenick, I., Theede, H., 1996. Physiological adaptations of *Cyprideis torosa* (Crustacea,
  Ostracoda) to hydrogen sulphide. Marine Ecology Progress Series 142, 215–223.
- Jones, B. and Manning, D.A.C., 1994. Comparison of geochemical indices used for the interpretation of paleoredox conditions in ancient mudstones. Chemical Geology, 111, 111–
   129.
- Keating, K.W., Hawkes, I., Holmes, J.A., Flower, R.J., Leng, M.J., Abu-Zied, R.H., Lord, A.R.,
  2007. Evaluation of ostracod-based palaeoenvironmental reconstruction with instrumental
  data from the arid Faiyum Depression. Egyptian Journal of Paleolimnology 38, 261–283.
- Keogh, S.M., Butler, R.W.H., 1999. The Mediterranean water body in the late Messinian:
  interpreting the record from marginal basins on Sicily. J. Geol. Soc. (Lond.) 156, 837–846.
- Keyser, D., 2005. Histological peculiarities of the noding process in *Cyprideis torosa* (Jones)
  (Crustacea, Ostracoda). Hydrobiologia 538, 95–106.
- Keyser, D., Aladin, N., 2004. Noding in *Cyprideis torosa* and its causes. Studia Quaternaria 2, 19–
  24.
- Ligios, S., Anadón, P., Castorina, F., D'Amico, C., Esu, D., Gliozzi, E., Gramigna, P., Mola, M.,
  Monegato, G., 2012. Ostracoda and Mollusca biodiversity and hydrochemical features of
  Late Miocene brackish basins of Italy. Geobios 45, 351-367.
- Ligios, S., Gliozzi, E., 2012. The genus *Cyprideis* Jones, 1857 (Crustacea, Ostracoda) in the
  Neogene of Italy: A geometric morphometric approach. Revue de micropaléontologie 55,
  171–207.

Formatted: Font: (Default) Times New Roman, 12 pt, English (U.K.),
Formatted: Font: (Default) Times New Roman, 12 pt, English (U.K.),
Formatted: Justified
Formatted: Font: (Default) Times New Roman, 12 pt, Highlight
Formatted: Font: (Default) Times New Roman, 12 pt, Highlight
Formatted: Font: (Default) Times New Roman, 12 pt, English (U.K.),
Formatted: Font: (Default) Times New Roman, 12 pt, Highlight
Formatted: Font: (Default) Times New Roman, 12 pt, English (U.K.),
Formatted: Font: (Default) Times New Roman, 12 pt, Highlight
Formatted: Font: (Default) Times New Roman, 12 pt, English (U.K.),
Formatted: Font: (Default) Times New Roman, 12 pt, English (U.K.),
Formatted: English (U.K.)

819 Mangini, A., Jung, M., Laukenmann, S., 2001. What do we learn from peaks of uranium and of

-	Form	hotte	No	underl	ine

Manzi, V., Lugli, S., Roveri, M., Schreiber, C., 2009. A new facies model for the Upper Gypsum of
Sicily (Italy): chronological and palaeoenvironmental constraints for the Messinian salinity
crisis in the Mediterranean. Sedimentology 56, 1937-1960.

manganese in deep sea sediments? Marine Geology 177(1), 63-78.

- Manzi, V., Gennari, R., Lugli, S., Roveri, M., Scafetta, N., Schreiber, B.C., 2012. High-frequency
  cyclicity in the Mediterranean Messinian evaporites: evidence for solar–lunar climate
  forcing. Journal of Sedimentary Research- 82, 991–1005.
- Manzi, V., Gennari, R., Hilgen, F., Krijgsman, W., Lugli, S., Roveri, M., Sierro F.J., 2013. Age
  refinement of the Messinian salinity crisis onset in the Mediterranean. Terra Nova, doi:
  10.1111/ter.12038
- Marco-Barba, J., 2010. Freshwater ostracods ecology and geochemistry as paleoenvironmental
  indicators in marginal marine ecosystems: a case of study the Albufera of Valencia. Ph. D.
  thesis, Univ. of Valencia.
- 833 McArthur, J.M., Howarth, R.J., Bailey T.R., 2001. Strontium isotope stratigraphy: LOWESS
- version 3: Best fit to the marine Sr-isotope curve for 0–509 Ma and accompanying look-up
  table for deriving numerical age. Journal of Geology 109, 155–170.
- McCulloch, M.T., De Deckker, P., 1989. Sr-isotope constraints on the Mediterranean environment
  at the end of the Messinian salinity crisis. Nature 342, 63–65.
- Müller, D.W., Mueller, P.A., 1991. Origin and age of the Mediterranean Messinian evaporites:
  implications from Sr isotopes. Earth Planet. Sci. Lett. 107, 1 –12.
- Müller, D.W., Mueller, P.A., McKenzie, J.A., 1990. Strontium isotopic ratios as fluid tracers in
  Messinian evaporites of the Tyrrhenian sea (western Mediterranean sea). Proc. ODP Sci.
  Res. 107, 603–614.

- Neale, J.V., 1988. Ostracods and paleosalinity reconstruction. In: De Deckker, P., Colin, J.-P.,
  Peypouquet, J.-P. (Eds.), Ostracoda in the Earth Sciences. Elsevier, Amsterdam, pp. 125–
  155.
- Pattan, J.N., Pearce, N.J.G., 2009. Bottom water oxygenation history in southeastern Arabian Sea
  during the past 140 ka: Results from redox-sensitive elements. Palaeogeography,
  Palaeoclimatology, Palaeoecology 280(3-4), 396-405.
- Pint, A., Frenzel, P., Fuhrmann, R., Scharf, B., Wennrich, V., 2012. Distribution of *Cyprideis torosa* (Ostracoda) in Quaternary athalassic sediments in Germany and its application for
  palaeoecological reconstructions. International Review of Hydrobiology 97(4), 330-335.
- Pint, A., Melzer, S., Frenzel, P., Engel, M., Brückner, H., 2013. Monospecific occurrence of *Cyprideis torosa* associated with micro- and macrofauna of marine origin in sabkha
  sediments of the Northern Arabian Peninsula. Naturalista Siciliano 4, 37(1), 277-278.
- Radeff, G., Schildgen, T.F., Cosentino, D., Strecker, M.R., Cipollari, P., Darbaş, G., Gürbüz, K.,
  (submitted). Sedimentary evidence for late Miocene uplift of the SE margin of the central
  Anatolian Plateau: Adana Basin, Southern Turkey. Geological Society of America Bulletin.
- Rosenfeld, A, Vesper, B., 1977. The variability of the sieve-pores in recent and fossil species of *Cyprideis torosa* (Jones, 1850) as an indicator for salinity and paleosalinity. In: Löffler, H.,
  Danielopol, D. (Eds.), Aspects of ecology and zoogeography of recent and fossil Ostracoda.
  Junk Publishers, The Hague, 55–67.
- Rosenfeld, A., 1977. The Sieve-pores of *Cyprideis torosa* (Jones, 1850) from the Messinian
  Mavqi'im Formation in the Coastal Plain and Continental Shelf of Israel as an Indicator of
  Paleoenvironment. Israel Journal of Earth-Sciences 26, 89-93.
- Rossi, V., Amorosi, A., Sammartino, I., Sarti, G., 2013. Environmental changes in the lacustrine
  ancient harbour of Magdala (Kinneret Lake, Israel) inferred from ostracod, geochemical and
  sedimentological analyses. Naturalista Siciliano 4, 37(1), 331-332.

Formatted: Font: Times New Roman, Font color: Auto, English (U.K.)

**Formatted:** Line spacing: single, Don't adjust space between Latin and Asian text, Don't adjust space between Asian text and numbers

869	Roveri, M., Flecker, R., Krijgsman, W., Lofi, J., Lugli, S., Manzi, V., Sierro, F.J., Bertini, A.,	Formatted: Italian (Italy)
870	Camerlenghi, A., De Lange, G., Govers, R., Hilgen, F.J., Hübscher, C., Meijer, P.Th.,	
871	Stoica, M., 2014a, The Messinian Salinity Crisis: Past and future of a great challenge for	Formatted: Italian (Italy)
872	marine sciences. Marine Geology 352, 25-58.	
873	Roveri, M., Lugli, S., Manzi, V., Gennari, R., Schreiber, B.C., 2014b. High-resolution strontium	
874	isotope stratigraphy of the Messinian deep Mediterranean basins: Implications for marginal	
875	to central basins correlation, Marine Geology, doi: 10.1016/j.margeo.2014.01.002	
876	Sampalmieri, G., Iadanza, A., Cipollari, P., Cosentino, D., Lo Mastro, S., 2010.	
877	Palaeoenvironments of the Mediterranean Basin at the Messinian hypersaline/hyposaline	
878	transition: evidence from natural radioactivity and microfacies of post-evaporitic	
879	successions of the Adriatic sub-basin. Terra Nova 22, 239-250.	
880	Sandberg, P., 1964. The ostracod genus Cyprideis in the Americas. Stockholm Contributions in	
881	Geology 12, 1-178.	
882	Schäfer, H.W., 1953. Über Meeres- und Brackwasserostracoden aus dem Deutschen Küstengebiet	
883	mit 2. Mitteilung über die Ostracodenfauna Griechenlands. Hydrobiologia 5(4), 351-389.	
884	Schreiber, B.C., 1997. Field trip to Eraclea Minoa: Upper Messinian. "Neogene Mediterronean	
885	Paleoceanography". Excursion Guide Book Palermo-Caltanissetta Agrigento. Erice (Sicily),	
886	24-27 September 1997, 72-80.	
887	Talbot, M.R., 1990. A review of the palaeohydrological interpretation of carbon and oxygen	
888	isotopic ratios in primary lacustrine carbonates. Chemical Geology (Isot. Geosci. Sect.) 80,	
889	261–279.	
890	Testa, G., 1995. Upper Miocene extensional tectonics and synrift sedimentation in the western	
891	sector of the Volterra Basin (Tuscany, Italy). Studi Geologici Camerti vol. spec. 1, 617-630.	
892	Utrilla, R., Vazquez, A., Anadón, P., 1998. Paleohydrology of the Upper Miocene Bicorb Lake (E	
893	Spain) as inferred from stable isotopic data from inorganic carbonates. Sedimentary	
894	Geology 121, 191-206.	

- Van Couvering, J.A., Castradori, D., Cita, M.B., Hilgen, F.J., Rio, D., 2000. The base of the
  Zanclean Stage and of the Pliocene Series. Episodes 23(3), 179-187.
- Van der Laan, E., Snel, E., de Kaenel, E., Hilgen, F.J., Krijgsman, W., 2006. No major deglaciation
  across the Miocene-Pliocene boundary: integrated stratigraphy and astronomical tuning of
  the Loulja sections (Bou Regreg area, NW Morocco). Paleoceanography 21, PA3011,
  doi:10.1029/2005PA001193.
- Van Harten, D., 1996. *Cyprideis torosa* (Ostracoda) revisited. Of salinity, nodes and shell size. In:
   Keen, C. (Ed.), Proceedings of the second European Ostracodologists Meeting. British
   Micropalaeontological Society, London, pp. 191–194.
- Van Harten, D., 2000. Variable noding in *Cyprideis torosa* (Ostracoda, Crustacea): an overview,
  experimental results and a model from Catastrophe Theory. Hydrobiologia 419, 131–139.

906 Venice Symposium on the Classification of Brackish Waters, Venice 8-14 April 1958 in Remane,

- 907 A., Schlieper, C. (eds.), Die Biologie der Brackwassers. Schweizerbartsche Verlag,
  908 Stuttgart, 1-348.
- Vesper, B., 1975. To the problem of noding on *Cyprideis torosa* (Jones, 1850). In: Swain, F.,
  Kornicker, L.S., Lundin, R.F. (Eds.), Biology and Paleobiology of Ostracoda. Bulletin of
  American Paleontology 65(282), 205-216.
- Voltaggio, M., Branca, M., Tedesco, D., Tuccimei, P., Di Pietro, L., 2004. <sup>226</sup>Ra-excess during the
  1631-1944 activity period of -Vesuvius (Italy): a model of alpha recoil enrichment in a
- 914 metasomatized mantle and implications on the current state of the magmatic system.
- 915 Geochimica et Cosmochimica Acta 68, 167-181.
- 916 Wignall, P.B., 1994. Black Shales. Claredon Press, Oxford, 127 pp.
- Wignall, P.B., Myers, K.J., 1988. Interpreting benthic oxygen levels in mudrocks: anew approach.
  Geology 16, 452-455.

**Formatted:** Font: (Default) Times New Roman, 12 pt, English (U.K.),

**Formatted:** Normal, Don't adjust space between Latin and Asian text, Don't adjust space between Asian text and numbers

Formatted: Highlight

Formatted: Font: 8 pt, Italian (Italy)

919	Zheng, Y., Anderson, R.F., Van Geen, A., Fleisher, M.Q., 2002. Remobilization of authigenic
920	uranium in marine sediments by bioturbation. Geochimica et Cosmochimica Acta 66 (10),
921	1759–1772.
922	

925			
926	Fig. 1 – SEM pictures of Cyprideis agrigentina, Decima. a, male left valve, sample EM 8-3; b, male		Formatted: English (U.K.), Highlight
927	right value, sample EM 7.2; o female left value, sample EM 7.2; d, female right value, sample EM		Formatted: Font: Italic, English (U.K.), Highlight
)21	inght varve, sample Ewi 7 2, e. temate ieit varve, sample Ewi 7 2, u. temate right varve, sample Ewi		Formatted: English (U.K.), Highlight
928	8-3. White bar corresponds to 0.1 mm.		Formatted: Highlight
			Formatted: English (U.K.), Highlight
929			Formatted: Highlight
			Formatted: English (U.K.), Highlight
930	Fig. $\frac{1}{2}$ – Geographical location of the Eraclea Minoa section.		Formatted: Highlight
021			Formatted: English (U.K.)
951			
932	Fig. 2-3 – Panoramic view of the Eraclea Minoa section. In evidence the gypsum levels of the		
933	Upper Gypsum Unit from gypsum body 3 to gypsum body 6 (marked by numbers) and the		
934	Messinian/Zanclean boundary.		
935			
936	Fig. <u>3-4</u> – Simplified stratigraphic log of the Eraclea Minoa section (modified from Manzi et al.,		
937	2009). Legend: 1. sapropels; 2. clays; 3. sandstones/sandy levels; 4. microconglomerate levels; 5.		
938	marls; 6. gypsum bodies (Upper Gypsum Unit); 7. samples for paleontological analyses; 8. samples		
939	for morphometrical analyses (ornamentation, dimensions and percentage of sieve-pore shapes) on		
940	C. agrigentina valves; 9. samples for stable isotopes analyses on C. agrigentina valves; 10. samples		
941	for trace elements analyses on C. agrigentina valves; 11. samples for Sr-isotopes analyses on C.		
942	agrigentina valves; 12. samples for NRD analyses on marls.		
943			
944	Fig. 5 – Stable isotopes, trace and minor elements, <sup>87</sup> Sr/ <sup>86</sup> Sr, and authigenic uranium curves plotted		
945	against the stratigraphic log of the Eraclea Minoa section. For the descriptions of the intervals, see		
946	the text.		
947			
948	Fig. <u>4-6</u> - Stable isotopic composition ( $\delta^{13}$ C and $\delta^{18}$ O; PDB notation) of <i>Cyprideis agrigentina</i>	_	Formatted: Highlight
949	calcite valves (Table 1). Note the negative correlation and regression line for samples from interval 38		

950lower B. The larger variation of  $\delta^{13}$ C and  $\delta^{18}$ O along the regression line corresponds to samples EM9516"-8 (198.2 m) to 6"-20 (216 m) from lower interval B. E/P: Evaporation /Precipitation ratio; PP:952Primary productivity; Eq-Atm: Atmospheric CO<sub>2</sub> equilibrium. See also Fig. <u>54</u>.

953

Fig. 5 Stable isotopes, trace and minor elements, <sup>87</sup>Sr/<sup>86</sup>Sr, and authigenic uranium curves plotted
 against the stratigraphic log of the Eraclea Minoa section. For the descriptions of the intervals, see

956 the text.

957

Fig. 6-7 – 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.

961

962 Fig. 78 — Comparisons among the palaeosalinity curve inferred by the analysis of the percentages
963 of the sieve-pore shape on *Cyprideis agrigentina* and the palaeoenvironmental and
964 palaeohydrochemistry changes inferred from synecological and Shannon-Wiener and geochemical
965 proxies.

966

967 Fig. 8-9 - 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:
87 Sr/<sup>86</sup>Sr values. See the text for discussion.

971

972 Fig. 9-10 - Tree diagram for the considered variables defining the relationships between the groups
973 of variables. Ward's method, 1-Pearson r. Abbreviations as in Fig. 8. See the text for discussion.

974

Formatted: Highlight

0	_	~
ч	1	٦.
/	1	~

# 977

978

## TABLE CAPTIONS

979 Tab.-<u>le</u> 1 – Stratigraphic position and lithology of the samples, and geochemical analytical results 980 from *C. agrigentina* valves: stable isotope data ( $\delta^{13}$ C and  $\delta^{18}$ O; PDB notation), Mg/Ca<sub>v</sub>, Sr/Ca<sub>v</sub>, and 981 Na/Ca<sub>v</sub> in molar ratios, and <sup>87</sup>Sr/<sup>86</sup>Sr ratios.

982

Tab.-<u>le</u> 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.

985

Table 3 – 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</li>
(rounded sieve pores assumed as a proxy of salinity), Position: stratigraphic position of the samples,
Sr isot: <sup>87</sup>Sr/<sup>86</sup>Sr values.

- 992
- 993
- 994
- 995

## Formatted: Highlight

1	Is Cyprideis agrigentina Decima a good palaeosalinometer for the Messinian Salinity Crisis?
2	Morphometrical and geochemical analyses from the Eraclea Minoa section (Sicily)
3	
4	F. Grossi <sup>a,*</sup> , E. Gliozzi <sup>a,b</sup> , P. Anadón <sup>c</sup> , F. Castorina <sup>d</sup> , M. Voltaggio <sup>b</sup>
5	
6	<sup>a</sup> Dipartimento di Scienze, Università Roma Tre, Largo S. Leonardo Murialdo, 1, I-00146, Roma, Italy
7	<sup>b</sup> IGAG, CNR, Area della Ricerca di Roma RM1, Via Salaria km 29,300, CP 10, I-00016, Monterotondo Stazione,
8	Roma, Italy
9	<sup>c</sup> Institut de Ciències de la Terra "Jaume Almera" (CSIC), C. Lluís Solé Sabarís sn, 08028, Barcelona, Spain
10	<sup>d</sup> Dipartimento di Scienze della Terra, Università Roma La Sapienza, P.le A. Moro, 5, I-00185, Roma, Italy
11	
12	
13	
14	
15	* Corresponding author: Present address: Dipartimento di Scienze, Università Roma Tre, Largo S. Leonardo Murialdo,
16	1, I-00146, Rome, Italy
17	e-mail address: <u>francesco.grossi@uniroma3.it</u> (F. Grossi)
18	
19	
20	ABSTRACT
21	
22	The living euryhaline species Cyprideis torosa (Jones) undergoes morphometric variations in size,
23	noding and sieve-pore shape linked to the environmental salinity. In particular it is known that
24	salinity values around 8-9 psu represent the osmoregulation threshold and also the turning point
25	between smaller and greater valve dimensions and prevailingly noded against un-noded valves. The
26	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 palaeosalinometer for the
Quaternary brackish basins.

30 In this paper we attempt to verify whether the ecophenotypical behaviour of the post-evaporitic 31 Messinian species Cypride agrigentina Decima was comparable with that of C. torosa. To reach 32 this goal, three morphometric characters have been analysed: 1) size variability; 2) noding and 33 ornamentation; 3) variability of the percentage of the sieve-pore shapes. The palaeoenvironmental 34 interpretation was made using synecological and geochemical approaches [stable isotopes, trace 35 elements, Sr-isotopes and natural radioactivity (NRD)]. For this study, the 250 m-thick Messinian 36 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. 37

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 *C. agrigentina* cannot be considered a palaeosalinometer for the Messinian Salinity Crisis.

44 There is a correlation of the  $\delta^{13}$ C with the percentages of sieve-pore shapes, linking them to the 45 behavior of the dissolved inorganic carbon (DIC) and to the oxygen availability at the bottom of the 46 basin.

47

48 KEYWORDS

49 Ostracoda; morphometrical analyses; geochemical analyses; palaeoenvironmental reconstruction;
50 post-evaporitic Messinian; Sicily (Italy).

51

52 1. Introduction

Since the pioneering studies by Schäfer (1953), Sandberg (1964), Vesper (1975) and 53 54 Rosenfeld and Vesper (1977), it is known that the living anomalohaline species Cyprideis torosa 55 (Jones) undergoes morphometrical variations in size, noding and sieve-pore shape linked to 56 environmental physical and chemical parameters - especially salinity - showing a clear 57 environmentally cued polymorphism. The species can withstand and thrive in a very wide range of 58 salinity (0.4 to 150 psu according to Neale, 1988 and Griffiths and Holmes, 2000), thus it is 59 commonly regarded as a valuable palaeosalinometer for the Quaternary marginal marine and athalassic brackish deposits (Marco-Barba, 2010; Pint et al., 2012 with references therein). Its low-60 61 Mg calcite shell represents also a source of biogenic carbonate for the geochemical analyses (trace elements, stable isotopes and <sup>87</sup>Sr/<sup>86</sup>Sr ratios) to infer the chemical composition of past waterbodies, 62 63 because of its high rate of valve calcification. In many studies, morphometrical variations were 64 coupled with the geochemical approach to make more detailed palaeoenvironmental reconstructions 65 of brackish environments (Barbieri et al., 1999; Anadón et al., 2002; Marco-Barba, 2010; Curry et 66 al., 2013; Pint et al., 2013; Rossi et al., 2013).

67 Several studies (Carbonel, 1982; Aladin, 1993; van Harten, 1996; 2000; Keiser and Aladin, 68 2004; Keyser, 2005; Boomer and Frenzel, 2011; Frenzel et al., 2011; 2012 among others) showed 69 that salinity values around 8-9 psu represent the osmoregulation threshold and also the turning point 70 between smaller and greater valve dimensions and prevailingly noded against un-noded valves. 71 Rosenfeld and Vesper (1977) showed an empiric logarithmic correlation between the variation of 72 the percentage of round-, elongate- and irregular-shaped sieve-pores on the valves of C. torosa and 73 the water salinity from 0 to 100 psu. This correlation has been confirmed by subsequent papers 74 (Neale, 1988; Keating et al., 2007; Pint et al., 2012) and Frenzel et al. (2011) elaborated a transfer 75 function based on the percentages of round sieve-pores.

In order to decipher the palaeosalinity 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
palaeoenvironment that yielded the deposition of the gypsum.

83 C. agrigentina (Fig. 1) is one of the most widespread ostracod that lived in the 84 Palaeomediterranean during the latest Messinian Lago-Mare event (5.53–5.33 Ma, CIESM, 2008; 85 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 Palaeomediterranean after the deposition of the Primary 86 87 Lower Gypsum and the partially desiccation of the basin. It has been recovered both in the Messinian sediments drilled on the Palaeomediterranean bottoms and in those cropping out along 88 89 the peri-Mediterranean chains, from the most western area (Malaga Basin) to the easternmost 90 Adana Basin (Benson, 1978; Iaccarino and Bossio, 1999; Bonaduce and Sgarrella, 1999; Grossi and 91 Gennari, 2008; Guerra-Merchán et al., 2010; Cosentino et al., 2012; Faranda et al., 2013). In their 92 study on the Messinian Lago-Mare palaeoenvironments inferred from the ostracod assemblages, 93 Grossi et al. (2008) showed that C. agrigentina behaved as a very euryhaline species: it was 94 associated a) with the benthic foraminifer Ammonia tepida ("Cyprideis-Ammonia assemblage") in 95 very oligotypic assemblages supposed to be typical of high mesohaline environments; b) with Loxoconcha muelleri (Mehés) and Loxoconcha eichwaldi Livental ("Cyprideis-Loxoconcha 96 97 assemblage") (low mesohaline environment); c) it was also a component, although not dominant, of the "pointed candonids-Leptocytheridae assemblage" and "pointed candonids assemblage", 98 99 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.

103In this paper we attempt to verify whether the ecophenotypical behavior of *C. agrigentina*104was comparable with that of *C. torosa*. To reach this goal, adult male and female valves of *C.* 

Formatted: Not Highlight

*agrigentina* from the long section of Eraclea Minoa (Agrigento, Sicily) were investigated and three
morphometrical characters have been analysed: 1) size variability; 2) noding and ornamentation; 3)
variability of the percentage of the sieve-pore shapes. The palaeoenvironmental 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).

112

### 113 2. Material and methods

One hundred fifty-two samples have been soaked in a H<sub>2</sub>O<sub>2</sub> 5% vol solution for 24 hours, 114 115 sieved with 0.063 and 0.125 mm-mesh sieves and dried in oven at  $40^{\circ}$ C. Total manual picking has been carried out on the 0.125 mm dried sieved samples. When possible, up to 300 valves where 116 117 hand-picked from each sample. Ostracods have been identified and their frequency counted; the 118 obtained values have been normalized to 10 g in order to get comparable figures all along the 119 section to perform a reliable palaeoenvironmental interpretation using the synecological approach 120 proposed by Gliozzi and Grossi, 2008 and Grossi et al., 2008. Shannon-Wiener index has been 121 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.

126

### 127 2.1 Morphometrical analyses

All juvenile and adult valves of *C. agrigentina* were observed under the stereo-microscope
to investigate the ornamentation and noding. Over one thousand adult female and male valves of *C.*

Formatted: Not Highlight
Formatted: Not Highlight
Formatted: Not Highlight

agrigentina from fifty-three selected samples were measured under the stereo-microscope, using the 130 131 Leica Application Suite 2.5.0. Mean values were calculated for each sample. 132 Around 20 adult female and male valves of C. agrigentina from fifty-three samples, chosen on the basis of its high frequency, were observed under the Scanning Electron Microscope (LIME 133 134 Laboratory, Roma Tre University). Following the methodology proposed by Rosenfeld and Vesper 135 (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 136 137 Frenzel et al. (2011), based on the percentage of rounded sieve-pores was used:  $S = e^{-0.06RS+4.7}$ 138 where S = salinity (psu) and RS = percentage of rounded sieve-pores. 139 140 141 2.2 Geochemical analyses 142 143 2.2.1 Stable isotopes Carbon and oxygen stable isotope analyses ( $\delta^{13}$ C and  $\delta^{18}$ O) were performed on fifty-three 144 ostracod samples each consisting of eight C. agrigentina clean adult valves. Two splits of each 145 146 sample (4 valves each) were reacted with anhydrous phosphoric acid at  $76^{\circ}C \pm 2^{\circ}C$  in a Finnigan MAT Kiel preparation device directly coupled to the inlet of a Finnigan MAT 251 triple collector 147 isotope ratio mass spectrometer (Stable Isotope Laboratory, University of Michigan, Ann Arbor, 148 149 MI, USA). The isotopic results of the mean of the two splits are reported in permil (‰) notation 150 relative to the Pee Dee Belemnite (PDB) standard. The measured precision for the analyses was 0.04 for  $\delta^{13}$ C and 0.07 for  $\delta^{18}$ O. 151 152 153 2.2.2 Trace elements 154 Trace and minor element analyses together with Ca on fifty-three ostracod samples,

155 consisting each in 6 to 10 clean adult valves of *C. agrigentina*, were performed by inductively

coupled plasma atomic emission spectrometry (ICP-AES). The ostracod valves were dissolved in 3
ml of ultrapure HNO<sub>3</sub> acid (3%). The solutions were analysed 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 Mattey<sup>TM</sup> stock
solutions. The obtained results are expressed as metal/calcium ratios of the valves (Me/Ca<sub>v</sub>).

163

### 164 2.2.3 Sr isotope analyses

Strontium isotope measurements were obtained from 26 suitable samples of hand-picked 165 valves of C. agrigentina, perfectly preserved. About 10 mg of each sample was subjected to the 166 167 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; 168 169 centrifugation; loading onto standard BIO-RAD AG50-X12cation exchange resin. The total 170 procedure blank was 0.5 ng. Sr was collected in 2.9 and 6.3 N HCl and evaporated. Isotopic 171 analyses were carried out at IGAG-CNR c/o Department of Earth Sciences, University of Rome -172 La Sapienza using a FINNIGAN MAT 262RPQ multicollector mass spectrometer with Re double 173 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 <sup>87</sup>Sr/<sup>86</sup>Sr ratios of the samples were normalized to a 174 <sup>86</sup>Sr/<sup>88</sup>Sr value of 0.1194. The internal precision (within-run' precision) of a single analytical result 175 is reported as 2 standard errors of the mean (2SE) and is obtained as the mean of more than 800-176 177 1000 ratios collected in each sample with a stable beam of > 2.0 V. Repeated analyses of NIST-987 during the period of the analyses gave a mean value  ${}^{87}$ Sr/ ${}^{86}$ Sr = 0.710251±15 (2 $\sigma$ , n = 15). 178

179

180 2.2.4 Natural Radioactivity (NRD)

181	Natural Radioactivity (NRD) was measured on 27 bulk sediment samples. Uranium, thorium and
182	potassium were determined by high resolution gamma spectrometry using a low background (GEM-
183	EG&G ORTEC) HPGe coaxial detector in a PopTop capsule including detector element,
184	preamplifier and high voltage filter at the Institute of Environmental Geology and Geoengineering
185	(IGAG, CNR, Rome - Italy). The multichannel buffer (16,384 channels, Ethernim-ORTEC 919E),
186	including ADC with extended live time correction, was connected into an Ethernet environment
187	under Windows XP and its control and spectral display was achieved by the use of MAESTRO
188	application software. In particular, <sup>232</sup> Th and K were estimated from 583 keV ( <sup>208</sup> Tl) and 1461 keV
189	$(^{40}K)$ peaks, while $^{238}U$ was estimated by the weighted average of U1 and U2, where U1 is the
190	product of the known $^{238}$ U/ $^{235}$ U natural activity ratio by the $^{235}$ U activity (calculated by the 186 keV
191	peak corrected by the <sup>226</sup> Ra contribution) and U2 is the <sup>238</sup> U activity estimated by the 352 keV peak
192	( <sup>214</sup> Pb) assuming full equilibrium in the <sup>238</sup> U radioactive series. Capo di Bove leucitite (Voltaggio et
193	al., 2004) was used as standard, while counting time and amount of each sample were, respectively,
194	86,400 sec and 150 grams.

206

### 196 2.3 Statistical analyses

197 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,  $\delta^{13}$ C,  $\delta^{18}$ O, Mg/Ca<sub>v</sub>, 198 Sr/Ca<sub>v</sub>, Na/Ca<sub>v</sub>, Th/U, assumed salinity after the sieve-pore analysis and the <sup>87</sup>Sr/<sup>86</sup>Sr ratio. The 199 statistical software used was STATISTICA 7.0. From the raw matrix, with 9 variables and 20 cases 200 201 (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 202 203 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 204 205 position of the variables in the factor plane and revealing the underlying structure of the data set.

Formatted: Not Highlight

#### Formatted: Not Highlight

Formatted: Not Highlight

. . . . . . . .

Formatted: Not Highlight

Formatted: Not Highlight

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

The ca. 266 m-thick Messinian Lago-Mare succession of Eraclea Minoa crops out along the 208 209 south-western coast of Sicily (lat. 37°23'30"N, long. 13°16'50"E) along the cliff which borders the 210 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 Palaeomediterranean 211 212 where several gypsum levels referred to the Upper Gypsum Unit crop out (among the most recent 213 papers: Schreiber, 1997; Caruso and Rouchy, 2006; Van der Laan et al., 2006; Manzi et al., 2009 214 with references therein), and because it represents the GSSP of the Messinian/Zanclean boundary 215 (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 216 217 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 218 219 section is different according to several authors. As stated by Caruso and Rouchy (2006), six 220 sedimentary cycles covered by the Arenazzolo Fm. up to the Messinian/Zanclean boundary are 221 recognizable, with a possible seventh basal cycle represented by an intensively deformed gypsum 222 deposit located along the fault contact at the base of the succession. Van der Laan et al. (2006) 223 consider the presence of seven cycles and a half, including the Arenazzolo Fm. They are linked to 224 the precessional cyclicity and date the deposition of the Eraclea Minoa succession between 5.508 225 Ma to 5.332 Ma. Finally, Manzi et al. (2009; 2012) hypothesize the presence of nine to ten 226 sedimentary cycles, including the Arenazzolo Fm., bracketing the depositional age between 5.53 227 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 *C. 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), C. agrigentina is 234 scarce and the assemblages, made by Loxoconcha muelleri (Méhes), L. kocki Méhes, L. eichwaldi 235 Livental, Loxocorniculina djafarovi (Schneider), Loxocauda limata (Schneider), Camptocypria sp. 236 1, Tyrrhenocythere pontica (Livental), Euxinocythere (Maeotocythere) praebaquana (Livental), 237 Amnicythere propinqua (Livental), A. subcaspia (Livental), A. multituberculata (Livental) and A. 238 accicularia Olteanu, are rather diversified. These assemblages can be referred to the "Cyprideis-239 Loxoconchidae assemblage" (sensu Grossi et al., 2008), suggesting low mesohaline and shallow 240 waterbodies (supposed salinities <10 psu).

233

Formatted: Not Highlight Formatted: Not Highlight

241 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 242 243 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). 244 245 Grossi and Gennari (2008) defined the "Cyprideis-Ammonia assemblage" for some ostracod and 246 forams associations recovered in the Lago-Mare borehole of Montepetra (northern Apennines, Italy) 247 in which, together with C. agrigentina and A. tepida, also other benthic foraminifers, Florilus 248 boueanum (d'Orbigny) and Elphidium spp. were seldom present or A. tepida was the dominant 249 species of the assemblage. The authors related such "Cyprideis-Ammonia assemblage" to high 250 mesohaline to hyperhaline shallow waterbody. At Eraclea Minoa no other brackish benthic 251 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 palaeoenvironmental 252 interpretation of the interval from 153 to 227 m at Eraclea Minoa could be slightly different. At the 253 moment, we can suppose for this new "Cyprideis assemblage" a relatively high salinity waterbody 254 255 and/or a dysoxic bottom, based on the capability of the living species C. torosa and Ammonia spp. 256 to withstand low oxygen contents (Jahn et al., 1996; Bernhard and Sen Gupta, 2002). Different 257 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 *C. agrigentina* is associated with few other species: with *L. 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 266 (sample EM 8-20)], C. agrigentina is again accompanied by the Paratethyan assemblage in which 267 268 Loxoconchidae are slightly less abundant and two more leptocytherid species are included, even if with scarce frequency: Amnicythere litica (Livental) and A. costata (Olteanu). On the whole, this 269 topmost interval seems again to be referable to the "Cyprideis-Loxoconchidae assemblage" (Grossi 270 271 et al., 2008), pointing to shallow waterbodies with supposed salinities <10 psu. Within this uppermost interval, it is possible to identify three horizons [from 228 m (sample EM 7-13) to 232 m 272 273 (sample EM 7-19), at 234 m (sample EM 7-21) and from 235 m (sample EM 7-25) to 238 m 274 (sample EM 7-28)] in which C. agrigentina shares its dominance only with two candonids species, 275 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. 276 agrigentina is again the only ostracod species of the assemblage. 277

278

### 279 **4.** Geochemical analyses and inferred palaeoenvironmental features

280

281 4.1 Stable isotopes

282 *C. agrigentina* calcite valves display a wide range of stable isotopic values.  $\delta^{13}$ C ranges 283 from -6.40 to 1.91‰;  $\delta^{18}$ O ranges from -4.08 to 7.95‰ (Tab. 1; Figs. 5, 6). The  $\delta^{13}$ C values of the 11 Formatted: Not Highlight

ostracod valves show a slight increase from 153-189 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  $\delta^{18}$ 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  $\delta^{18}$ O values, from 8‰ to -1.4‰ is observed.

The  $\delta^{13}$ C and  $\delta^{18}$ O values from 153 to 189 m (interval A) display small fluctuations, suggesting minor variations in the palaeohydrological conditions. On the contrary, the valves from 198-204 m (interval B) and 253-260 m (interval E) display significant oscillations, both in  $\delta^{13}$ C and  $\delta^{18}$ O values, suggesting instabilities in the palaeohydrological conditions related to these intervals. In both cases the larger instabilities (major  $\delta^{13}$ C and  $\delta^{18}$ 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).

303 *4.2 Trace elements* 

302

For *C. agrigentina* calcite valves, the Mg, Sr and Na content expressed as Mg/Ca<sub>v</sub>, Sr/Ca<sub>v</sub> and Na/Ca<sub>v</sub> molar ratios are listed in Table 1 and represented in Fig. 5. The Mg/Ca<sub>v</sub> values range from 0.0052 to 0.0158, the Sr/Ca<sub>v</sub> range from 0.0022 to 0.0054 and the Na/Ca<sub>v</sub> from 0.0032 to 0.0046. Formatted: Not Highlight
Formatted: Not Highlight

Formatted: Not Highlight
Formatted: Not Highlight
Formatted: Not Highlight

Formatted: Not Highlight
Formatted: Not Highlight
Formatted: Not Highlight
Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight
Formatted: Not Highlight

The Mg/Ca<sub>v</sub> 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<sub>v</sub> 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  $\delta^{13}$ C values.

The Na/Ca<sub>v</sub> 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<sub>v</sub> is observed in the upper portion of the section (interval B). This is parallelized with the decrease in Sr/Ca and  $\delta^{18}$ O values. Formatted: Not Highlight Formatted: Not Highlight

Formatted: Not Highlight
Formatted: Not Highlight
Formatted: Not Highlight
Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

318 *4.3 Sr isotopes* 

317

Differently 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 allow 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  ${}^{87}$ Sr/ ${}^{86}$ Sr values from the *C. agrigentina* valves 325 are comprised between 0.708510 and 0.708729 (Table 1). The range of values is high in the lower 326 327 analysed interval (153-189 m - interval A) and decreases in the portion comprised between 198 to 328 225 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  $\delta^{18}$ O, Sr/Ca<sub>v</sub> and Na/Ca<sub>v</sub> values. In the upper 329 portion of the section (253-260 m \_ interval E) the <sup>87</sup>Sr/<sup>86</sup>Sr values rise again, with a maximum 330 331 (0.708704) at 253 m (Fig. 5). Sr isotopic data of C. agrigentina are markedly different with respect 332 to coeval global ocean values (Henderson et al., 1994; McArthur et al., 2001) being significantly

Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

lower than the marine waters at that time, but this is a common feature for latest Miocene–earliest Pliocene strontium values of the Palaeomediterranean Basin carbonates.

335

### 336 *4.4 Natural Radioactivity*

<sup>232</sup>Th and K measured in bulk sediment samples are highly correlated (R=0.94) suggesting that 337 <sup>232</sup>Th is mainly contained in the detrital fraction. Detrital uranium, in turns, was calculated by the 338 product of measured <sup>232</sup>Th and the average <sup>238</sup>U/<sup>232</sup>Th weight ratio of pelagic sediments, considered 339 close to 0.25 (Mangini et al., 2001). Finally, authigenic uranium, 238Ua, was estimated by 340 subtracting the detrital <sup>238</sup>U from measured <sup>238</sup>U (Table 2). Authigenic uranium as well as the Th/U 341 ratio was proposed by Wignall and Myers (1988) as an index of bottom-water oxygenation; the Ua 342 343 values trend to increase in a reducing environment, where uranium is immobile as tetravalent ion. 344 According to Wignall (1994) U<sub>a</sub> values comprised between 2 and 10 are indicative of dysoxic 345 environments; similarly for Th/U values, Th/U<<1 indicate anoxic conditions, Th/U>>1 indicate oxic 346 conditions, while values in the range 1<Th/U>1 point to dysoxic conditions. Even if the use of authigenic 347 uranium as proxy for reducing conditions is common in the chemiography of marine sediments 348 (Pattan and Pearce, 2009), several authors have questioned the real preservation of the authigenic 349 uranium signal by different processes as burn down, fast change of sedimentation rate and oxygen 350 ventilation or bioturbation (Zheng et al., 2002). Therefore any indication of oxigen depletion 351 suggested by the authigenic uranium has to be regarded in a wider fitting context.

352  $U_a$  from the bulk sediment display values from 0.3 to 9.5 ppm (Table 2). The lowest values are 353 attained in intervals A, B and lower C, with figures generally below 2. In the upper part of interval 354 C,  $U_a$  increases and maintains high values in interval D and E, where some fluctuations occur, 355 similarly to what observed for the stable isotopes and trace elements ratios (Fig. 5). A similar trend 356 is observed for the Th/U ratios, which show values greater than 1 in intervals A, B and C, and 357 values mainly around 1 in intervals D and E (Table 2).

358



Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

359 4.5 Palaeoenvironmental episodes inferred from the geochemical proxies

The geochemical analyses performed on the valves of C. agrigentina and bulk sediment 360 361 samples collected from the 96.5-260 m portion of the post-evaporitic Messinian succession of 362 Eraclea Minoa confirm the frame of a Palaeomediterranean waterbody discontinuous and isolated, characterised by diluted waters after the evaporative phase of the Lower Gypsum Unit, the closure 363 364 of the Atlantic-Palaeomediterranean connection and the subsequent global humid climate phase 365 (Griffin, 2002; CIESM, 2008; Grossi et al., 2008). In fact, notwithstanding the well known saline character of the Palaeomediterranean waters, testified by the presence of brackish ostracod 366 367 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, 6 do not show 368 369 the overall covariant trend that would correspond to a marginal marine environment or a closed 370 waterbody (Talbot, 1990; Utrilla et al., 1998; Ligios et al., 2012), and also trace elements behave in 371 a different manner. The Mg/Ca<sub>v</sub> values from C. agrigentina (0.0052-0.0152) are similar to most of 372 the analyses from Cyprideis shells for the Messinian Lago-Mare horizons from DSDP sites (De 373 Deckker et al., 1988). For these Mg/Ca<sub>v</sub> values, De Deckker et al. (1988) consider the host water 374 had Mg/Ca values lesser than that of Messinian seawater, and in some cases similar to most of the 375 Mg/Ca shown by freshwaters (Mg/Ca=1). The Sr/Ca<sub>v</sub> values from C. agrigentina at 153-189 m 376 (0.0025-0.0030) are similar to most of the analyses from Cyprideis shells from the Messinian Lago-377 Mare horizons from DSDP sites (De Deckker et al., 1988). For these Sr/Ca<sub>v</sub> values, these authors 378 consider the host water had Sr/Ca values lesser than that of Messinian oceanic seawater. On the 379 contrary, the Sr/Ca<sub>v</sub> values for most of the samples from 198-225 m and 252.8-257.8 m (0.0038-380 0.0054) indicate that the host water frequently had Sr/Ca values greater than that of Messinian 381 oceanic seawater. The values of Sr/Ca<sub>v</sub> and Mg/Ca<sub>v</sub> indicate that the waters where the Eraclea Minoa ostracods lived were very different than the Messinian seawater and there is no indication of 382 connection with oceanic seawater. Furthermore, the <sup>87</sup>Sr/<sup>86</sup>Sr range of values obtained from the 383 analyses of C. agrigentina valves is consistent with the isotopic values of the Upper Gypsum Unit 384

Formatted: Not Highlight Formatted: Not Highlight

Formatted: Not Highlight

from Sicily and other localities of the Palaeomediterranean (Müller and Mueller, 1991; Keogh and 385 386 Butler, 1999; Flecker and Ellam, 2006; Roveri et al., 2014b). This range is also similar to the range 387 (0.708600-0.70875) reported from most ostracod valves (Cyprideis) from Messinian Lago-Mare 388 deposits from several DSDP sites of the Palaeomediterranean studied by McCullock and De Deckker (1989). On the other hand, the Sr isotopic values from Eraclea Minoa are quite different 389 390 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 <sup>87</sup>Sr/<sup>86</sup>Sr values of the Eraclea Minoa C. 391 392 agrigentina, as is the case of materials from other post-evaporitic Messinian localities, confirm to 393 be the result of a large influence of freshwater on the Sr isotopic composition of the desiccating subbasins of the Palaeomediterranean (Müller et al., 1990). Finally, it is noteworthy that isotopic 394 395 ratios anomalously low could result from reworking of older marine evaporites, or diagenetic 396 overprinting. However, according to Keogh and Butler (1999), the reworking of Sr from the older 397 marine evaporites implies mixing in different proportion between Sr deriving from continental run-398 off and coming from ground water circulating inside the buried evaporites. Such a process likely produces high variability in both salinity and <sup>87</sup>Sr/<sup>86</sup>Sr ratios. 399

400

Based on the geochemical signature of C. agrigentina valves and bulk sediment samples, 401 five main palaeoenvironmental intervals may be differentiated along the studied portion of the 402 Eraclea Minoa succession (Fig. 5):

Interval A (153-189 m), characterised by high  $\delta^{18}$ O, Na/Ca<sub>v</sub>, Mg/Ca<sub>v</sub> and  $^{87}$ Sr/ $^{86}$ Sr values, 403 and low  $\delta^{13}$ C, Sr/Ca<sub>v</sub>, and U<sub>a</sub>. This interval records relatively stable hydrochemical conditions as 404 405 suggested by the small variation of each geochemical indicator, isotopically concentrated waters and high Na/Ca<sub>v</sub> and Mg/Ca<sub>v</sub> ratios that were attained after the deposition of the 6<sup>th</sup> gypsum level. 406 407 An overall evaporative environment (Fig. 5) with moderate salinity could be inferred for this 408 interval. The high amount of Th and detrital U, the low content of authigenic uranium and the rather 409 high Th/U ratios (Table 2) record possible well oxygenated bottoms.

Formatted: Not Highlight

Formatted: Not Highlight

410	Interval B (198-225 m), characterised by low $\delta^{18}O,$ Na/Ca_v, Mg/Ca_v, $^{87}Sr/^{86}Sr,$ and $U_a$	
411	values, and high $\delta^{13}C$ and Sr/Ca <sub>v</sub> . A major change is recorded at the base of this interval (198 m,	
412	sample EM 6"-8) where large shifts in all the geochemical indicators appear. A possible explanation	
413	for these features is to consider the noticeable detrital and freshwater inputs that increase the Ca	
414	dissolution, recorded both by the coarser lithologies, the high values of Th and detrital U and the	
415	low ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ values for most samples. Those inputs may explain the lowering of $\delta^{18}\text{O}$ in the values,	
416	the increase of $Sr/Ca_v$ (recording Sr inputs from the $CaSO_4$ -rich subsurface waters) and the lowering	
417	in Mg/Ca <sub>v</sub> because of the high increase in Ca in the waterbody. The increase in $\delta^{13}C$ values could	
418	be produced by an increase in the productivity, linked to the detrital and nutrient inputs and a trend	
419	to re-equilibration with the atmospheric CO <sub>2</sub> (Fig. 5). As in the previous interval, NRD results	Formatted: Not Highlight
420	(Table 2) testify for possible well oxygenated bottoms.	Formatted: Not Highlight
421	Interval C (225-240 m). In this interval, only NRD analyses have been performed due to the	
422	low frequency of C. agrigentina in the ostracod assemblages that prevented the possibility to reach	
423	the suitable amount of biogenic carbonate for the analyses. The content of authigenic uranium in the	
424	upper part of this interval, higher than in the previous one, (Table 2, Fig. 5) points to possibly	Formatted: Not Highlight
425	progressively less oxygenated bottoms.	Formatted: Not Highlight
426	Interval D (240-242 m). This short interval is characterised by the highest values of	
427	authigenic U and low values of the Th/U ratios, suggesting possble dysoxic conditions at the	
428	bottom.	
429	Interval E (252.8-259.1 m). In this interval two portions may be differentiated and a main	
430	change is recorded from the lower samples to the upper ones. The lower samples are characterised	
431	by high $\delta^{18}O$ , Sr/Ca <sub>v</sub> , Na/Ca <sub>v</sub> , and ${}^{87}Sr/{}^{86}Sr$ values, and low $\delta^{13}C$ and Mg/Ca <sub>v</sub> values. The low	Formatted: Not Highlight
432	content of authigenic uranium indicates possibly oxygenated bottoms. The upper samples are	
433	characterised by the opposite trend. The geochemical features of the ostracod valves from the lower	
434	part may be explained by the evaporitic concentration of the waterbody (Figs. 5, 6) leading to high	

 $\delta^{18}$ O, Sr/Ca<sub>v</sub> and Na/Ca<sub>v</sub> values. A subsequent large input of freshwater produced the lowering of 435  $\delta^{18}$ O, Sr/Ca<sub>v</sub> and Na/Ca<sub>v</sub>. At present, we have no explanation for the variations of the Mg/Ca<sub>v</sub> 436 437 values in this interval. It is worth to note the high content of authigenic uranium that reaches in one 438 sample the value of 9.5 ppm, possibly indicating dysoxic conditions at the bottom.

439

#### 440 5. Morphometrical analyses on Cyprideis agrigentina valves

441 Length and height of one thousand-sixty valves of adult males and females were measured. 442 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 443 444 measured samples) have been compared. Generally the mean values of the length vary from 0.96 to 445 1.00 mm, but in few samples the mean values are rather small: at 185 m (sample EM 6"-3, mean 446 value 0.90 mm), 201 m (EM 6"-11, mean value 0.89 mm), 222 m (EM 7-6, mean value 0.85 mm), 447 and 223.5 m (EM 7-8, mean value 0.88 mm) (Fig. 7). Only in four samples the mean values of the 448 length result significantly high: at 165 m (sample EM 6'-12 mean value 1.05 mm), 176.2 m (EM 6'-449 24, mean value 1.06 mm), 180 m (EM 6'-27, mean value 1.04 mm), and 210 m (EM 6''-17, mean 450 value 1.14 mm).

The several thousands specimens of C. agrigentina investigated for the ornamentation and 451 452 noding, showed rather homogeneous ornamentation: no noded specimens have been observed all 453 along the section among both juveniles and adults; almost all valves were smooth (at least some of 454 them showed few small pits in the posterior surface); only two samples (EM 6"-7 at 189.0 m and 455 EM 6"-20 at 216.0 m) showed, respectively, the 54.2% and 54.6% of valves pitted on the entire 456 surface (Fig. 7).

457 The analysis of the percentage of the sieve-pore shape was carried out on fifty-three samples 458 from the middle and upper portion of the section, where C. agrigentina was more abundant, making both monospecific and diversified assemblages. On average, more than 500 sieve-pores were 459 460 observed for each sample and counted on the basis of their shape: rounded, elongated, irregular, 18 Formatted: Not Highlight

Formatted: Not Highlight

following the indications by Rosenfeld and Vesper (1977). The results are reported in Fig. 7. In 461 462 most cases, the percentages of the rounded sieve-pores are comprised between 40 and 50%; in 463 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 (sample EM 6"-20) 464 they are lower, comprised between 19 and 30%, reaching their minimum values (19-21%) in the 465 interval 204.5-216 m. Applying the transfer function elaborated by Frenzel et al. (2011) for C. 466 467 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 468 469 upper portions of the section point to the oligohaline range (0.5-5 psu), while higher salinities 470 (polyhaline to euhaline ranges, 18-40 psu) are recorded only in a limited portion of the section, from 471 198.5 to 216 m (Fig. 8).

### 473 6. Discussion

472

As explained in the introduction, the living species *C. 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, noding 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 *Cyprideis* 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 Palaeomediterranean 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 487 species of the stem lead some authors to suppose that the same environmentally cued polymorphism 488 displayed by *C. torosa* could affect also its relatives (Neale, 1988), notwithstanding no noded 489 specimens of the other species had never been recorded. Thus, Rosenfeld (1977) and Bonaduce and 490 Sgarrella (1999) inferred hyperhaline post-evaporitic Messinian environments respectively for the 491 Mavqi'im Formation (Israel) and at Eraclea Minoa, applying on *C. agrigentina* valves the empirical 492 methods of the percentage of the rounded sieve-pores elaborated by Rosenfeld and Vesper (1977) 493 on *C. torosa*.

494 As a first step to investigate whether C. agrigentina shared with C. torosa the same 495 ecophenotypical behavior, we have analyzed size, ornamentation and sieve-pore shapes on some 496 thousand of specimens from the post-evaporitic Messinian section of Eraclea Minoa. The expected 497 results, in case of a comparable behavior, is a positive correlation between large size, noding (or 498 strongly pitted valve surface), and high percentages of rounded sieve-pores. Fig. 7 shows that this 499 correlation lacks: the largest sizes (thus the supposed lowest salinities, below 8-9 psu) are attained 500 by specimens recovered in samples bearing smooth valves (supposed high salinities) and 501 percentages of rounded sieve-pores less than 40% (above the 8-9 psu threshold). In particular, in 502 sample EM 6"-17 (at 210 m) the largest C. agrigentina valves matches with one of the lowest 503 percentages of rounded sieve-pores (22,7%); the smallest sizes (supposed high salinities) correlates 504 with smooth valve surfaces (supposed high salinities) but to percentages of rounded sieve-pores 505 greater than 40% except in one case (sample EM 6"-11 at 201 m) in which the percentage is low 506 (23.1%); the only two samples in which C. agrigentina valves are densely pitted (supposed low 507 salinities), corresponds, on average, to intermediate dimensions and high percentage values.

508 From those comparisons it is possible to conclude that size and ornamentation/noding in *C*. 509 *agrigentina* are not correlated. In particular, pitted ornamentation and noding seem to be, 510 respectively, very rare and totally absent in *C. agrigentina*, despite the species seems to be strongly 511 euryhaline as it is its living relative (Ligios and Gliozzi, 2012). Thus, it seems that those characters 512 do not display in *C. agrigentina* the same salinity-dependant polymorphism of *C. torosa*.

513 A further question is to investigate whether the percentage variations of the sieve-pore 514 shapes are correlated with salinity variations as in C. torosa. To test this hypothesis we have based 515 the comparisons of the salinity curve obtained applying the transfer function elaborated by Frenzel 516 et al. (2011) with the salinity inferred by the synecological analysis and with the palaeohydrological 517 variations inferred by the geochemical analyses (Figs. 8, 9, 10).

518 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 519 520 (monotypic ostracod assemblages) corresponds to different inferred salinities: oligo-low mesohaline 521 in the intervals 153-171, 218-225 and 253-257.8 m; high mesohaline from 174 to 189 m; 522 polyhaline-euhaline from 198.5 to 216.5 m. Moreover, it is worth to note that the two oligohaline 523 levels with Cyprideis and Ilyocypris, included in the "Cyprideis" long interval at 198.5 and 201 m, 524 according to the salinity curve based on sieve-pore percentage should have deposited in 525 polyhaline/euhaline waters. We should conclude that there is no correspondence between the 526 salinities inferred by the method of the sieve-pore percentages and the synecological palaeoenvironmental interpretation. This conclusion contradicts the statement by Bonaduce and 527 528 Sgarrella (1999) who, on the basis of the percentage of sieve-pore shapes, inferred for the Eraclea 529 Minoa portion of succession with monospecific Cyprideis assemblage hyperhaline environments 530 (50-70 psu). Probably their conclusions are affected by the very few analyzed samples along the 531 succession (only two) and the scarcity of counted sieve-pores for each sample (respectively 74 and 532 161).

533 The calculation of past salinities from the results of the geochemical analyses on the valves 534 of C. agrigentina is difficult to assess. Although Na/Cav could be tentatively perceived as a proxy of 535 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 536 537 and De Deckker, 2012). However, recent attempts to use Na/Ca ratios from ostracod valves for 538 palaeoenvironmental reconstructions must be taken into account (Gouramanis et al., 2010; 21

Devriendt, 2011). On the other hand, Sr/Ca and Mg/Ca from ostracod valves just may inform about 539 540 the Sr/Ca and Mg/Ca of the waters (De Deckker et al., 1999; Dettman and Dwyer, 2012; Holmes 541 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,  $\delta^{18}$ O variations in closed non-542 marine environments are linked usually to evaporation/precipitation processes (Talbot, 1990), that 543 in some cases are associated to salinity variations. Anyway, the decreasing Na/Ca<sub>v</sub> ratios from 544 545 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  $\delta^{18}$ O values in B. However, this is in contradiction with the 546 547 higher salinity assumed for interval B than for interval A based on the sieve-pore analysis of C. 548 agrigentina (Fig. 8).

549 We have tried to test the correlation between the geochemical results and the salinities 550 assumed from the analysis of the sieve-pore percentages using a multivariate approach. The 551 correlation matrix obtained for nine variables is shown in Table 3. Significant correlations (p<0.01) are displayed only by the pairs  $\delta^{18}$ O and Na/Ca<sub>v</sub>, Na/Ca<sub>v</sub> and Mg/Ca<sub>v</sub>, Sr/Ca<sub>v</sub> and stratigraphic 552 position. Significant negative correlations are shown by  $\delta^{13}$ C and Na/Ca<sub>y</sub>,  $\delta^{13}$ C and  $\delta^{18}$ O,  $\delta^{13}$ C and 553 Mg/Ca<sub>v</sub>, Mg/Ca<sub>v</sub> and Sr/Ca<sub>v</sub>. In fact salinity assumed from sieve-pore analysis (N pores), and Sr 554 isotopic ratios of the valves do not show significant correlation with any of the other considered 555 556 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  $\delta^{18}$ O, Na/Ca<sub>v</sub>, Mg/Ca<sub>v</sub>, Th/U and <sup>87</sup>Sr/<sup>86</sup>Sr 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, SO<sub>4</sub>-rich solutions would lead to lowering of  $\delta^{18}$ O, Na/Ca<sub>v</sub>, Mg/Ca<sub>v</sub> and <sup>87</sup>Sr/<sup>86</sup>Sr. On the negative field, the variables are Sr/Ca<sub>v</sub>, the stratigraphic position and the percentages of rounded sieve-pores that are linked to DIC



Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

564 (Dissolved Inorganic Carbon) changes. On the other hand, factor 2 that accounts for 20.72% of the 565 variance, in the positive area contains a group formed by  $\delta^{18}$ O, Sr/Ca<sub>v</sub>, stratigraphic position and 566 NaCa<sub>v</sub>, whereas in the negative area a group formed by N pores,  $\delta^{13}$ C<sub>2</sub> Th/U and Mg/Ca<sub>v</sub> exists. 567 Factor 2 probably is linked to detrital, freshwater and nutrient inputs related to the environmental 568 evolution.

Results from the cluster analysis reveal several groups (Fig. 10). One of the groups shown by the dendrogram reflects the relationship between  $\delta^{18}O$  and Na/Ca<sub>v</sub> revealing the control of the Na/Ca<sub>v</sub> exerted by the P/E balance ( $\delta^{18}O$ ). They are associated with Mg/Ca<sub>v</sub> 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<sub>v</sub>-position of the sample is associated to the pair  $\delta^{13}C$ -percentage of rounded sievepores. This pair reveals the link between DIC changes and the changes in sieve-pore shapes.

575 It is worth to note that, although some authors consider both the Ua and Th/U values as good 576 proxies to detect past oxic/dysoxic conditions (Adams and Weawer, 1958; Wignall and Myers, 577 1988; Wignall, 1994; Jones and Manning, 1994), Wignall and Meyers (1988) suggest to couple the U<sub>a</sub> results with the Shannon-Weaver dominance-diversity index (H) since, under low-oxygen 578 579 conditions, assemblages are dominated by a few eurytopic forms, and values of H are typically low. 580 If we compare the H-index curve (Fig. 8) with the oxygen availability at the bottom derived from 581 the  $U_a$  curve of Fig. 5, we notice that they are contradictory: when  $U_a$  values are high (comprised 582 between 2 and 10 and indicate possible dysoxic bottoms) the H-index values are high (rather well 583 diversified assemblages). This negative correlation suggest, as supposed by Zheng et al. (2002) that the accumulation of Ua in sediments could due also to physico-chemical variables other than the 584 585 oxygen availability.

586 The results of the statistical analyses underline that there is no significant relationship 587 between the salinity assumed from the sieve-pore analyses on the valves of *C. agrigentina* and the 588 variables linked to the hydrochemical changes ( $\delta^{18}$ O, Na/Ca<sub>v</sub> and Mg/Ca<sub>v</sub>, i.e. the salinity changes). Formatted: Not Highlight Formatted: Not Highlight Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

Formatted: Not Highlight

589 On the other hand, the number of rounded sieve pores in C. *agrigentina* seems to be mainly linked 590 to  $\delta^{13}$ 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 *C. 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 palaeohydrological and palaeohydrochemical 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 behaviour of the DIC and the oxygen availability.

598 On the other hand, the geochemical data give a negative response to the hypothesis that the 599 "*Cyprideis* assemblage" could be related to dysoxia at the bottom. Data from the percentage of the 600 authigenic U, Th/U ratios indicate that some accumulation of  $U_a$  occurred at the bottom of the 601 Eraclea Minoa waterbody, but it seems that they were not so important to affect the benthic 602 ostracod assemblages.

603 Although it is beyond the aim of this paper, in order to try to understand the 604 palaeoenvironmental meaning of the "Cyprideis assemblage" we have tried to extend our 605 investigations comparing other Lago-Mare successions of the Mediterranean area that included 606 monotypic C. agrigentina assemblages. In the first case, such assemblage, represented by very 607 scarce specimens, has been recovered in the lower portion of the Lago-Mare succession of the 608 Adana Basin (Turkey) during the deposition of resedimented evaporites and marls, where a very 609 high sedimentation rate was recorded (Faranda et al., 2013). The authors linked the low diversity 610 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 611 phase. At Eraclea Minoa the "Cyprideis assemblage" is present with high frequencies and 612 continuously recovered along the entire interval, but it is rather confined to the thick marly-sandy 613 614 succession included between gypsum bodies 6 and 7. If we hypothesize that this portion of 24

Formatted: Not Highlight

succession represents one precessional cycle, as supposed by Van der Laan et al. (2006), high 615 616 sedimentation rates affected both Adana (12.5 mm/yr) (Radeff et al., submitted) and Eraclea Minoa 617 (4.3 mm/yr) successions. Similar stratigraphical, sedimentological and paleontological conditions 618 have been found also in the lower portion of the Lago-Mare succession cropping out in the Iraklion 619 Basin (central Crete) (unpublished data). Unfortunately, not everywhere high sedimentation rates 620 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 621 622 within the short temporal frame of the Loxocorniculina djafarovi zone (5.40-5.33 Ma), thus a very 623 high sedimentation rate above 13 mm/yr was calculated, but the recovered Lago-Mare ostracod assemblages were highly diversified (Cosentino et al., 2006). 624

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

### 629 7. Conclusion

628

630 The ostracod assemblages of the post-evaporitic Messinian section of Eraclea Minoa (Sicily) 631 have been studied in a palaeoenvironmental perspective to decipher the environmental changes 632 verified during the deposition of the Upper Gypsum Unit. Rich and diversified assemblages made 633 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 634 succession, very abundant monospecific assemblages made only by C. agrigentina were 635 recognized, suggesting high mesohaline to hyperhaline shallow waterbody with low oxygen 636 637 content. To test this latter interpretation, morphometric and geochemical analyses (stable isotopes, trace elements, <sup>87</sup>Sr/<sup>86</sup>Sr, and NRD) have been performed on ostracod valves and bulk sediment 638 639 samples in order to verify if C. agrigentina ecophenotypical behavior was comparable with that of 640 the living species C. torosa.

The results have shown that: 641 642 1) C. agrigentina sizes and ornamentations are not affected by salinity variations; 643 2) The percentages of sieve-pore shapes do not depend from the water salinity, as in C. torosa, but seem linked to the behavior of the DIC and the oxygen availability at the bottom. 644 Thus, it is possible to conclude that C. agrigentina cannot be considered as a 645 palaeosalinometer for the Messinian Salinity Crisis. 646 647 Furthermore, the geochemical analyses have shown that the deposition of the Eraclea Minoa succession occurred in a complex palaeohydrological and palaeohydrochemical scenario. 648 649 650 651 Acknowledgements 652 653 The research of F.G. and E.G. has been founded by the Italian National Research Project PRIN 654 2009-2010. P.A. work is supported by Project CGL2011-23438. The authors are grateful to Rafael 655 Bartrolí (ICTJA and IDAEA, CSIC) for the ICP-AES analyses and to Lora Wingate (Stable Isotope 656 Laboratory, University of Michigan) for the stable isotope analyses on the ostracod valves. 657 658 REFERENCES 659 Adams J.A. & Weaver C.E., 1958. Thorium-uranium ratios as indicators of sedimentary processes: 660 example of concept of geochemical facies. Bulletin American Association of Petroleum 661 Geologists 42(2), 387-430. 662 663 Aladin, N.V., 1993. Salinity tolerance, morphology and physiology of the osmoregulation organs in Ostracoda with special reference to Ostracoda from the Aral Sea. In Jones, P. and McKenzie 664 K. (Eds.), Ostracoda in Earth and Life Sciences, A.A. Balkema, Rotterdam, 387-404. 665

Formatted: Not Highlight

667	environments from combined paleoecological and geochemical analyses on Ostracods. In:
668	Holmes, J., Chivas, A. (Eds), The Ostracoda: Applications in Quaternary Research,
669	Geophysical Monograph 131, 227–247.
670	Barbieri, M., Carrara, C., Castorina, F., Dai Pra, G., Esu, D., Gliozzi, E., Paganin, G., Sadori, L.,
671	1999. Multidisciplinary study of Middle-Upper Pleistocene deposits in a core from the Piana
672	Pontina (central Italy). Giornale di Geologia 61, 47-73.
673	Benson, R.H., 1978. The paleoecology of the ostracodes of DSDP Leg 42A. In: Initial Reports of
674	the Deep Sea Drilling Project 42, 777-787, U.S. Government Printing Office, Washington,
675	D.C.
676	Bernhard, J.M, Sen Gupta, B.K., 2002. Foraminifera of oxygen-depleted environment. In: Sen
677	Gupta, B.K. (Ed.), Modern Foraminifera. Kluwer Academic Publishers, 201-216.
678	Bonaduce, G., Sgarrella, F., 1999. Paleoecological interpretation of the latest Messinian sediments
679	from southern Sicily (Italy). Memorie della Società Geologica Italiana 54, 83-91.
680	Boomer, I., Frenzel, P., 2011. Possible environmental and biological controls on carapace size in
681	Cyprideis torosa (Jones, 1850). Joannea Geologie und Paläontologie 11, 26–27.
682	Bossio, A., Costantini, A., Lazzarotto, A., Liotta, D., Mazzanti, R., Mazzei, R., Salvatorini, G.,
683	Sandrelli, F., 1993. Rassegna delle conoscenze sulla stratigrafia del Neoautoctono toscano.
684	Memorie della Società Geologica Italiana 49, 17–98.
685	Bossio, A., Cerri, R., Mazzei, R., Salvatorini, G., Sandrelli, F., 1996. Geologia dell'area
686	Spicchiaiola-Pignano (Settore orientale del Bacino di Volterra). Bollettino della Società
687	Geologica Italiana 115, 393-422.
688	Carbonel, P., 1982. Les Ostracodes, traceurs des variations hydrologiques dans des systèmes de
689	transition eaux douces-eaux salées. Mémoirs de la Societé géologique de France 8(144),

Anadón, P., Gliozzi, E., Mazzini, I., 2002. Paleoenvironmental reconstruction of marginal marine

690 117–128.

666
- 691 Caruso, A., Rouchy, J.-M., 2006. The Upper Gypsum Unit. In: Roveri, M., Manzi, V., Lugli, S.,
  692 Schreiber, B.C., Caruso, A., Rouchy, J.-M., Iaccarino, S.M., Gennari, R., Vitale, F.P., Ricci
  693 Lucchi, F. (Eds.), Clastic vs. primary precipitated evaporites in the Messinian Sicilian
  694 basins. Acta Naturalia de "L'Ateneo Parmense" 42(4), 157-159.
- CIESM (Commission Internationale pour l'Exploration de la Mer Méditerranée, Monaco), 2008.
   The Messinian Salinity Crisis from Mega-Deposits to Microbiology: A Consensus Report.
   CIESM Workshop Monograph 33, 1-168.
- Cosentino, D., Bertini, A., Cipollari, P., Florindo, F., Gliozzi, E., Grossi, F., Lo Mastro, S.,
  Sprovieri, M., 2012. Orbitally-forced palaeoenvironmental and palaeoclimate changes in the
  late post-evaporitic Messinian stage of the central Mediterranean Basin. Geological Society
  of America Bulletin 124(3-4), 499-516.
- Cosentino, D., Federici, I., Cipollari, P., Gliozzi, E., 2006. Environments and tectonic instability in
  central Italy (Garigliano Basin) during the late Messinian *Lago-Mare* episode: New data
  from the onshore Mondragone well (Garigliano Plain, central Italy). Sedimentary Geology
  188-189, 293-317.
- Curry, B., Mesquita-Joanes, F., Fanta, S., Sterner, D., Calò, C., Tinner, W., 2013. Two coastal
   sinkhole lakes in SW Sicily (Italy) reveal low-salinity excursion during Greek and Roman
   occupation. Naturalista Siciliano 4, 37(1), 93-95.
- De Deckker, P., Chivas, A.R., Shelley, J.M.G., 1988. Paleoenvironment of the Messinian Mediterranean "Lago Mare" from strontium and magnesium in ostracode shells. Palaios, 3, 352-358.
- De Deckker, P., Chivas, A.R., Shelley, J.M.G., 1999. Uptake of Mg and Sr in the euryhaline
  ostracod *Cyprideis* determined from in vitro experiments. Palaeogeography,
  Palaeoclimatology, Palaeoecology 148, 105–116.
- 715 Decima, A., 1964. Ostracodi del genere *Cyprideis* Jones del Neogene e del Quaternario italiani.
  716 Palaeontographia Italica, 57(1962), 81-133.

Formatted: Not Highlight

- Decima, A., Wezel, F.C., 1971. Osservazioni sulle evaporiti messiniane della Sicilia centro meridionale. Rivista mineraria siciliana 130-132, 172-187.
- Dettman, D.L., Dwyer, G.S., 2012. Biological and environmental controls on ostracod shell traceelement chemistry. In: D. J. Horne, J. Holmes, J. Rodriguez-Lazaro and F. Viehberg (Eds.).
  Ostracoda as proxies for Quaternary climate change. Developments in Quaternary Sciences.
  Elsevier, v. 17, 145-163.
- Devriendt, L.S.J., 2011. Late Quaternary environment of paleolake Carpentaria inferred from the
   chemistry of ostracod valves. Master of Sciences Research Thesis, University of
   Wollongong, Australia, 175 pp. <u>http://ro.uow.edu.au/theses/3319/</u>

Field Code Changed

- Faranda, C., Gliozzi, E., Cipollari, P., Grossi, F., Darbaş, G., Gürbüz, K., Nazik, A., Gennari, R.,
   Cosentino, D., 2013. Messinian paleoenvironmental changes in the easternmost
   Mediterranean Basin: Adana Basin, southern Turkey. Turkish J Earth Sci 22, 839-863.
- 729 Faure, G., Powell, J.L., 1972. Strontium Isotope Geology. Springer-Verlag, Berlin, 1-188.
- Flecker, R., de Villiers, S., Ellam, R.M., 2002. Modelling the effect of evaporation on the salinity–
   <sup>87</sup>Sr/<sup>86</sup>Sr relationship in modern and ancient marginal–marine systems: the Mediterranean
   Messinian Salinity Crisis. Earth Planet. Sci. Lett. 203 (1), 221–233.
- Flecker, R., Ellam, R.M., 2006. Identifying Late Miocene episodes of connection and isolation in
  the Mediterranean–Paratethyan realm using Sr isotopes. Sediment. Geol. 188–189, 189–203.
- Frenzel, P., Schulze, I., Pint, A., 2011. Salinity dependant morphological variation in *Cyprideis torosa*. Joannea Geologie und Paläontologie 11, 59–61.
- Frenzel, P., Schulze, I., Pint, A., 2012. Noding of *Cyprideis torosa* valves (Ostracoda) a proxy for
  salinity? New data from field observations and a long-term microcosm experiment.
  International Review of Hydrobiology 97(4), 314–329.
- Gliozzi, E., Grossi, F., 2008. Late Messinian Lago-mare ostracod palaeoecology: a correspondence
  analysis approach. Palaeogeography, Palaeoclimatology, Palaeoecology 264, 288-295.

- Gouramanis, C., Wilkins, D., De Deckker, P., 2010. 6000 years of environmental changes recorded 742 743 in Blue Lake, South Australia, based on ostracod ecology and valve chemistry. 744 Palaeogeography, Palaeoecology, Palaeoclimatology 297, 223-237. 745 Griffin, D.L., 2002. Aridity and humidity: Two aspects of the late Miocene climate of North Africa and the Mediterranean. Palaeogeography, Palaeoclimatology, Palaeoecology 182, 65-91. 746 747 Griffiths, H.I., Holmes, J.A., 2000. Non-marine ostracods & Quaternary palaeoenvironments. 748 Quaternary Research Association, Technical Guide 8, 1-179. Grossi, F., Gennari, R., 2008. Palaeoenvironmental reconstruction across the Messinian/Zanclean 749
- boundary by means of ostracods and foraminifers: the Montepetra borehole (Northern
  Apennine, Italy). Atti del Museo Civico di Storia Naturale di Trieste 53(suppl), 67-88.
- Grossi, F., Cosentino, D., Gliozzi, E., 2008. Palaeoenvironmental reconstruction of the late
  Messinian lago-mare successions in central and eastern Mediterranean using ostracod
  assemblages. Bollettino della Società Paleontologica Italiana 47(2), 131–146.
- Guerra-Merchán, A., Serrano, F., Garcés, M., Gofas, S., Esu, D., Gliozzi, E., Grossi, F., 2010.
  Messinian Lago-Mare deposits near the Strait of Gibraltar (Malaga Basin, S Spain).
  Palaeogeography, Palaeoclimatology, Palaeoecology 285, 264–276.
- Henderson, G. M., Martel, D. J., O'Nions, R. K., Shackleton, N. J., 1994. Evolution of seawater
   <sup>87</sup>Sr/<sup>86</sup>Sr over the last 400 ka: the absence of glacial/interglacial cycles. Earth Planetary
   Sciences and Letetrs 128, 643–651.
- Holmes, J., De Deckker, P., 2012. Introduction to ostracod shell chemistry and its application to
  Quaternary palaeoclimate studies. In: D. J. Horne, J. Holmes, J. Rodriguez-Lazaro and F.
  Viehberg (Eds.). Ostracoda as proxies for Quaternary climate change. Developments in
  Quaternary Sciences. Elsevier, v. 17, 131-144.
- Howarth, R., McArthur, J.M., 1997. Statistics for Strontium Isotope Stratigraphy: a robust
  LOWESS fit to the marine Sr-isotope curve for 0 to 206 Ma, with look-up table for
  derivation of numeric age. J. Geol. 105, 441–456.

Formatted: Not Highlight

770	Iaccarino, S., Bossio, A., 1999. Paleoenvironment of uppermost Messinian sequences in the	
771	Western Mediterranean (sites 974, 975 and 978). In: Zahn, R., Comas, M.C., Klaus, A., et	
772	al. (Eds.), Proceedings of Ocean Drilling Program, Scientific Results 161, 529-541, College	
773	Station, Texas.	
774	Jahn, A., Gamenick, I., Theede, H., 1996. Physiological adaptations of Cyprideis torosa (Crustacea,	
775	Ostracoda) to hydrogen sulphide. Marine Ecology Progress Series 142, 215-223.	
776	Jones, B. and Manning, D.A.C., 1994. Comparison of geochemical indices used for the	Formatted: Not Highlight
777	interpretation of paleoredox conditions in ancient mudstones. Chemical Geology 111, 111-	
778	129.	
779	Keating, K.W., Hawkes, I., Holmes, J.A., Flower, R.J., Leng, M.J., Abu-Zied, R.H., Lord, A.R.,	
780	2007. Evaluation of ostracod-based palaeoenvironmental reconstruction with instrumental	
781	data from the arid Faiyum Depression. Egyptian Journal of Paleolimnology 38, 261–283.	
782	Keogh, S.M., Butler, R.W.H., 1999. The Mediterranean water body in the late Messinian:	
783	interpreting the record from marginal basins on Sicily. J. Geol. Soc. (Lond.) 156, 837-846.	
784	Keyser, D., 2005. Histological peculiarities of the noding process in Cyprideis torosa (Jones)	
785	(Crustacea, Ostracoda). Hydrobiologia 538, 95-106.	
786	Keyser, D., Aladin, N., 2004. Noding in Cyprideis torosa and its causes. Studia Quaternaria 2, 19-	
787	24.	
788	Ligios, S., Anadón, P., Castorina, F., D'Amico, C., Esu, D., Gliozzi, E., Gramigna, P., Mola, M.,	
789	Monegato, G., 2012. Ostracoda and Mollusca biodiversity and hydrochemical features of	
790	Late Miocene brackish basins of Italy. Geobios 45, 351-367.	
791	Ligios, S., Gliozzi, E., 2012. The genus Cyprideis Jones, 1857 (Crustacea, Ostracoda) in the	

Hsü, K.J., Ryan, W.F.B., Cita, M.B., 1973. Late Miocene desiccation of the Mediterranean. Nature

768

769

242, 240–244.

Ligios, S., Gliozzi, E., 2012. The genus *Cyprideis* Jones, 1857 (Crustacea, Ostracoda) in the
Neogene of Italy: A geometric morphometric approach. Revue de micropaléontologie 55,
171–207.

Mangini, A., Jung, M., Laukenmann, S., 2001. What do we learn from peaks of uranium and of
manganese in deep sea sediments? Marine Geology 177(1), 63-78.

Field Code Changed

- Manzi, V., Lugli, S., Roveri, M., Schreiber, C., 2009. A new facies model for the Upper Gypsum of
  Sicily (Italy): chronological and palaeoenvironmental constraints for the Messinian salinity
  crisis in the Mediterranean. Sedimentology 56, 1937-1960.
- Manzi, V., Gennari, R., Lugli, S., Roveri, M., Scafetta, N., Schreiber, B.C., 2012. High-frequency
  cyclicity in the Mediterranean Messinian evaporites: evidence for solar–lunar climate
  forcing. Journal of Sedimentary Research 82, 991–1005.
- Manzi, V., Gennari, R., Hilgen, F., Krijgsman, W., Lugli, S., Roveri, M., Sierro F.J., 2013. Age
  refinement of the Messinian salinity crisis onset in the Mediterranean. Terra Nova, doi:
  10.1111/ter.12038
- Marco-Barba, J., 2010. Freshwater ostracods ecology and geochemistry as paleoenvironmental
  indicators in marginal marine ecosystems: a case of study the Albufera of Valencia. Ph. D.
  thesis, Univ. of Valencia.
- McArthur, J.M., Howarth, R.J., Bailey T.R., 2001. Strontium isotope stratigraphy: LOWESS
  version 3: Best fit to the marine Sr-isotope curve for 0–509 Ma and accompanying look-up
  table for deriving numerical age. Journal of Geology 109, 155–170.
- McCulloch, M.T., De Deckker, P., 1989. Sr-isotope constraints on the Mediterranean environment
  at the end of the Messinian salinity crisis. Nature 342, 63–65.
- Müller, D.W., Mueller, P.A., 1991. Origin and age of the Mediterranean Messinian evaporites:
  implications from Sr isotopes. Earth Planet. Sci. Lett. 107, 1 –12.
- Müller, D.W., Mueller, P.A., McKenzie, J.A., 1990. Strontium isotopic ratios as fluid tracers in
  Messinian evaporites of the Tyrrhenian sea (western Mediterranean sea). Proc. ODP Sci.
  Res. 107, 603–614.

- Neale, J.V., 1988. Ostracods and paleosalinity reconstruction. In: De Deckker, P., Colin, J.-P.,
  Peypouquet, J.-P. (Eds.), Ostracoda in the Earth Sciences. Elsevier, Amsterdam, pp. 125–
  155.
- Pattan, J.N., Pearce, N.J.G., 2009. Bottom water oxygenation history in southeastern Arabian Sea
  during the past 140 ka: Results from redox-sensitive elements. Palaeogeography,
  Palaeoclimatology, Palaeoecology 280(3-4), 396-405.
- Pint, A., Frenzel, P., Fuhrmann, R., Scharf, B., Wennrich, V., 2012. Distribution of *Cyprideis torosa* (Ostracoda) in Quaternary athalassic sediments in Germany and its application for
   palaeoecological reconstructions. International Review of Hydrobiology 97(4), 330-335.
- Pint, A., Melzer, S., Frenzel, P., Engel, M., Brückner, H., 2013. Monospecific occurrence of *Cyprideis torosa* associated with micro- and macrofauna of marine origin in sabkha
  sediments of the Northern Arabian Peninsula. Naturalista Siciliano 4, 37(1), 277-278.
- Radeff, G., Schildgen, T.F., Cosentino, D., Strecker, M.R., Cipollari, P., Darbaş, G., Gürbüz, K.,
  (submitted). Sedimentary evidence for late Miocene uplift of the SE margin of the central
  Anatolian Plateau: Adana Basin, Southern Turkey. Geological Society of America Bulletin.
- Rosenfeld, A, Vesper, B., 1977. The variability of the sieve-pores in recent and fossil species of *Cyprideis torosa* (Jones, 1850) as an indicator for salinity and paleosalinity. In: Löffler, H.,
  Danielopol, D. (Eds.), Aspects of ecology and zoogeography of recent and fossil Ostracoda.
  Junk Publishers, The Hague, 55–67.
- Rosenfeld, A., 1977. The Sieve-pores of *Cyprideis torosa* (Jones, 1850) from the Messinian
  Mavqi'im Formation in the Coastal Plain and Continental Shelf of Israel as an Indicator of
  Paleoenvironment. Israel Journal of Earth-Sciences 26, 89-93.
- Rossi, V., Amorosi, A., Sammartino, I., Sarti, G., 2013. Environmental changes in the lacustrine
  ancient harbour of Magdala (Kinneret Lake, Israel) inferred from ostracod, geochemical and
  sedimentological analyses. Naturalista Siciliano 4, 37(1), 331-332.

844	Camerlenghi, A., De Lange, G., Govers, R., Hilgen, F.J., Hübscher, C., Meijer, P.Th.,	
845	Stoica, M., 2014a. The Messinian Salinity Crisis: Past and future of a great challenge for	
846	marine sciences. Marine Geology 352, 25-58.	
847	Roveri, M., Lugli, S., Manzi, V., Gennari, R., Schreiber, B.C., 2014b. High-resolution strontium	
848	isotope stratigraphy of the Messinian deep Mediterranean basins: Implications for marginal	
849	to central basins correlation, Marine Geology, doi: 10.1016/j.margeo.2014.01.002	
850	Sampalmieri, G., Iadanza, A., Cipollari, P., Cosentino, D., Lo Mastro, S., 2010.	
851	Palaeoenvironments of the Mediterranean Basin at the Messinian hypersaline/hyposaline	
852	transition: evidence from natural radioactivity and microfacies of post-evaporitic	
853	successions of the Adriatic sub-basin. Terra Nova 22, 239-250.	
854	Sandberg, P., 1964. The ostracod genus Cyprideis in the Americas. Stockholm Contributions in	
855	Geology 12, 1-178.	
856	Schäfer, H.W., 1953. Über Meeres- und Brackwasserostracoden aus dem Deutschen Küstengebiet	
857	mit 2. Mitteilung über die Ostracodenfauna Griechenlands. Hydrobiologia 5(4), 351-389.	
858	Schreiber, B.C., 1997. Field trip to Eraclea Minoa: Upper Messinian. "Neogene Mediterronean	
859	Paleoceanography". Excursion Guide Book Palermo-Caltanissetta Agrigento. Erice (Sicily),	
860	24-27 September 1997, 72-80.	
861	Talbot, M.R., 1990. A review of the palaeohydrological interpretation of carbon and oxygen	
862	isotopic ratios in primary lacustrine carbonates. Chemical Geology (Isot. Geosci. Sect.) 80,	
863	261–279.	
864	Testa, G., 1995. Upper Miocene extensional tectonics and synrift sedimentation in the western	
865	sector of the Volterra Basin (Tuscany, Italy). Studi Geologici Camerti vol. spec. 1, 617-630.	
866	Utrilla, R., Vazquez, A., Anadón, P., 1998. Paleohydrology of the Upper Miocene Bicorb Lake (E	
867	Spain) as inferred from stable isotopic data from inorganic carbonates. Sedimentary	

Geology 121, 191-206.

843 Roveri, M., Flecker, R., Krijgsman, W., Lofi, J., Lugli, S., Manzi, V., Sierro, F.J., Bertini, A.,

Formatted: Not Highlight

869	Van Couvering, J.A., Castradori, D., Cita, M.B., Hilgen, F.J., Rio, D., 2000. The base of the	
870	Zanclean Stage and of the Pliocene Series. Episodes 23(3), 179-187.	
871	Van der Laan, E., Snel, E., de Kaenel, E., Hilgen, F.J., Krijgsman, W., 2006. No major deglaciation	
872	across the Miocene-Pliocene boundary: integrated stratigraphy and astronomical tuning of	
873	the Loulja sections (Bou Regreg area, NW Morocco). Paleoceanography 21, PA3011,	
874	doi:10.1029/2005PA001193.	
875	Van Harten, D., 1996. Cyprideis torosa (Ostracoda) revisited. Of salinity, nodes and shell size. In:	
876	Keen, C. (Ed.), Proceedings of the second European Ostracodologists Meeting. British	
877	Micropalaeontological Society, London, pp. 191–194.	
878	Van Harten, D., 2000. Variable noding in Cyprideis torosa (Ostracoda, Crustacea): an overview,	
879	experimental results and a model from Catastrophe Theory. Hydrobiologia 419, 131-139.	
880	Venice Symposium on the Classification of Brackish Waters, Venice 8-14 April 1958 in Remane,	
881	A., Schlieper, C. (eds.), Die Biologie der Brackwassers. Schweizerbartsche Verlag,	
882	Stuttgart, 1-348.	
883	Vesper, B., 1975. To the problem of noding on Cyprideis torosa (Jones, 1850). In: Swain, F.,	
884	Kornicker, L.S., Lundin, R.F. (Eds.), Biology and Paleobiology of Ostracoda. Bulletin of	
885	American Paleontology 65(282), 205-216.	
886	Voltaggio, M., Branca, M., Tedesco, D., Tuccimei, P., Di Pietro, L., 2004. <sup>226</sup> Ra-excess during the	
887	1631-1944 activity period of Vesuvius (Italy): a model of alpha recoil enrichment in a	
888	metasomatized mantle and implications on the current state of the magmatic system.	
889	Geochimica et Cosmochimica Acta 68, 167-181.	
890	Wignall, P.B., 1994. Black Shales. Claredon Press, Oxford, 127 pp.	
891	Wignall, P.B., Myers, K.J., 1988. Interpreting benthic oxygen levels in mudrocks: anew approach.	
892	Geology 16, 452-455.	

Formatted: Not Highlight

893	Zheng, Y., Anderson, R.F., Van Geen, A., Fleisher, M.Q., 2002. Remobilization of authigenic
894	uranium in marine sediments by bioturbation. Geochimica et Cosmochimica Acta 66 (10),
895	1759–1772.
896	

898	FIGURE CAPTIONS	
899		
900	Fig. 1 – SEM pictures of Cyprideis agrigentina Decima. a. male left valve, sample EM 8-3; b. male	Formatted: Not Highlight
901	right valve, sample EM 7-2; c. female left valve, sample EM 7-2; d. female right valve, sample EM	
902	8-3. White bar corresponds to 0.1 mm.	
903		
904	Fig. 2 – Geographical location of the Eraclea Minoa section.	
905		
906	Fig. 3 – Panoramic view of the Eraclea Minoa section. In evidence the gypsum levels of the Upper	
907	Gypsum Unit from gypsum body 3 to gypsum body 6 (marked by numbers) and the	Formatted: Not Highlight
908	Messinian/Zanclean boundary.	
909		
910	Fig. 4 - Simplified stratigraphic log of the Eraclea Minoa section (modified from Manzi et al.,	
911	2009). Legend: 1. sapropels; 2. clays; 3. sandstones/sandy levels; 4. microconglomerate levels; 5.	
912	marls; 6. gypsum bodies (Upper Gypsum Unit); 7. samples for paleontological analyses; 8. samples	
913	for morphometrical analyses (ornamentation, dimensions and percentage of sieve-pore shapes) on	
914	C. agrigentina valves; 9. samples for stable isotopes analyses on C. agrigentina valves; 10. samples	
915	for trace elements analyses on C. agrigentina valves; 11. samples for Sr-isotopes analyses on C.	
916	agrigentina valves; 12. samples for NRD analyses on marls.	
917		
918	Fig. 5 – Stable isotopes, trace and minor elements, <sup>87</sup> Sr/ <sup>86</sup> Sr, and authigenic uranium curves plotted	
919	against the stratigraphic log of the Eraclea Minoa section. For the descriptions of the intervals, see	
920	the text.	
921		
922	Fig. 6 - Stable isotopic composition ( $\delta^{13}$ C and $\delta^{18}$ O; PDB notation) of <i>Cyprideis agrigentina</i> calcite	
923	valves (Table 1). Note the negative correlation and regression line for samples from interval lower 37	

B. The larger variation of δ<sup>13</sup>C and δ<sup>18</sup>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<sub>2</sub> equilibrium. See also Fig. 4.

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.

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

937

927

928

932

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:
<sup>87</sup>Sr/<sup>86</sup>Sr values. See the text for discussion.

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.

945

946		
947		
948	TABLE CAPTIONS	
949		
950	Table 1 – Stratigraphic position and lithology of the samples, and geochemical analytical results	
951	from <i>C. agrigentina</i> values: stable isotope data ( $\delta^{13}$ C and $\delta^{18}$ O; PDB notation), Mg/Ca <sub>v</sub> , Sr/Ca <sub>v</sub> , and	
952	Na/Ca <sub>v</sub> in molar ratios, and ${}^{87}$ Sr/ ${}^{86}$ Sr ratios.	
953		
954	Table 2 - Summary of natural radioactivity data, with the concentrations of U, Th and K (with	
955	relative errors), values of authigenic uranium expressed in ppm and percentage and Th/U ratios.	
956		
957	Table 3 – Correlation matrix for the data in Table 1 and Th/U ratios (9 variables, 20 samples). The	Formatted: Not Highlight
958	correlation coefficient r between the diverse variables is shown in the upper part of each division.	
959	The p value is indicated in the lower part of each division. The r values are in bold when the	
960	correlation is significant p<0.01. Abbreviations: N pores: variability of percentage of sieve pores	
961	(rounded sieve pores assumed as a proxy of salinity), Position: stratigraphic position of the samples,	
962	Sr isot: <sup>87</sup> Sr/ <sup>86</sup> Sr values.	
963		
964		
965		







# Figure 4 Click here to download high resolution image



Figure 5 Click here to download high resolution image





# Figure 7 Click here to download high resolution image



pitted valves

## Figure 8 Click here to download high resolution image



Palaeoenvironments from synecological analysis

Palaeohydrochemistry from geochemical analyses

#### Shannon-Wiener index

Very unstable hydrochemistry, with evaporative conditions at the base and subsequent dilution.

- E Oxygenated bottom at the base, dysoxic at top.

### Cypride/s-Loxoconchidae assemblage

Cypride/s-Loxoconchidae assemblage'

Cypride/s-Loxoconchidae assemblage

C. agrigentina with Fabaeformiscandona sp. and Cypria sp. Oligohaline and shallow waterbody

"Cypridels assemblage" High meschaline to hyperhaline or dysoxic shallow waterbody

"Cypridevic assemblage" High mesohabine to hyperhaline or dysoxic shallow waterbody

"Cyprideis assemblage" High mesohaline to hyperhaline or dysoxic shallow waterbody

"Cyprideis assemblage" High mesohaline to hyperhaline or dysoxic shallow waterbody

"Cyprideis assemblage" High mesohaline to hyperhaline or dysoxic shallow waterbody

Cyprideis-Loxoconchidae assemblage Low mesohaline shallow waterbody (salinities <10 psu)

Cyprideis-Loxoconchidae assemblage\* Low mesohaline shallow waterbody (salinities <10 psu)





Possible low salinities that slightly increase again around 222-225 m. Oxygenated bottom.

Relatively stable hydrochemical conditions. Isotopically concentrated waters with high Na/Ca ratios. Low freshwater input.

Possible evaporative environment

with moderate salinities





# Table 1

Height (m)	Sample	mple Lithology	Stable Isotopes (n.	d <sup>13</sup> C	d <sup>18</sup> O	Trace elements		Me/Ca molar			Sr ±se*
			of valves)	(VPDB)	(VPDB)	(n. of valves)	Mg/Cav	Sr/Cav	Na/Cav		
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	$\pm 8$
257.8	EM 8-7	sandstone	8	-4.70	7.83	10	0.0060	0.0051	0.0041	0.708647	$\pm 10$
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	$\pm 11$
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	$\pm 6$
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	$\pm 11$
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 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	0.0029	0.0043	0.700722	±10
175.5	EM 6'-23	sandstone	8	-4.82	1.55	7	0.0137	0.0028	0.0046		
175.1	EM 6'-22h	sandstone	8	-4.83	1.00	8	0.0130	0.0028	0.0039	0 708619	+6
174.6	EM 6'-220	marl	8	-5.08	1.38	8	0.0127	0.0028	0.0039	0.700017	±0
173.0	EM 6' 21	marl	8	5.00	1.50	7	0.0127	0.0028	0.0035		
173.9	EM 6' 10	marl	8	-5.25	1.40	7	0.0131	0.0028	0.0040	0 708671	+6
172.0	EM 6' 18	marl	8	-5.55	1.30	7	0.0123	0.0029	0.0043	0.708071	$\pm 0$
160.0	EM 6' 17	marl	8	-5.27	1.39	0	0.0122	0.0029	0.0042		
169.9	EM 6' 16	marl	8	-5.15	1.29	8	0.0120	0.0029	0.0044	0.708602	+7
169.0	EM 6' 15	marl	0	-5.87	1.21	8	0.0132	0.0027	0.0044	0.708002	±/
167.0	EM 6' 14	marl	0	-0.03	1.05	0	0.0134	0.0029	0.0040		
166.0	EM 6' 12	marl	0	-5.02	0.04	8	0.0123	0.0027	0.0043		
165.0	EM 6' 12	marl	0	-5.15	1.57	0	0.0129	0.0028	0.0044	0 708658	+0
162.0	EM 6' 10	mail	0	-5.17	1.37	0	0.0130	0.0020	0.0041	0.708038	±9
162.0	EM 6' 0	marl	0	-5.00	1.70	0	0.0120	0.0020	0.0043	0 709614	. 6
102.0	ENIO-9	111211	ð	-3.74	1.30	ð	0.0122	0.0027	0.0044	0.708014	±υ
101.0	EN 6'7	mari	ð	-3.32	1.28	9	0.0152	0.0028	0.0043		
160.0	ENIO-/	mari	ð	-5.48	1.17	/	0.0128	0.0027	0.0043	0.700/07	. 5
159.1	EM 0-0	mari	ð	-5.55	1.12	8	0.0131	0.0027	0.0045	0.708685	±Σ
158.0	EM 6-5	mari	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	0.700/77	. 10
156.0	EM 6-3	mari	8	-6.40	1.12	8	0.0133	0.0028	0.0046	0.708675	$\pm 10$
154.3	EM 6'-2	mari	8	-5.00	1.30	1	0.0158	0.0025	0.0044	0.700 (12	. 1 4
153.0	EM 6'-1	mari	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

Та	b	le	2
----	---	----	---

			T	h	k	K		Uaut (%)	
Height (m)	Sample	U (mean) (ppm)	(ppm)	error (%)	%	error (%)	Uaut (ppm)		Th/U
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

# Table 3 Click here to download Table: Table 3 bis last.xls

	Position	$\delta^{13}$ C	$\delta^{18}O$	Mg/Ca <sub>v</sub>	Sr/Ca <sub>v</sub>	Na/Ca <sub>v</sub>	N pores	Sr isot	Th/U
Position	1.000								
р									
δ <sup>13</sup> C	0.192	1.000							
р	p=0.418			_					
δ <sup>18</sup> Ο	0.238	-0.690	1.000						
р	p=0.311	p=0.001							
Mg/Ca <sub>v</sub>	-0.331	-0.628	0.039	1.000					
р	p=0.154	p=0.003	p=0.872						
Sr/Ca <sub>v</sub>	0.506	0.376	0.216	-0.562	1.000				
р	p=0.023	p=0.102	p=0.360	p=0.010			_		
Na/Ca <sub>v</sub>	-0.173	-0.823	0.693	0.516	-0.095	1.000			
р	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		
р	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	
р	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
р	p=0.079	p=0.353	p=0.738	p=0.072	p=0.372	p=0.065	p=0.087	p=0.725	