Palaeogeography, Palaeoclimatology, Palaeoecology 459 (2016) 348–364

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

journal homepage: www.elsevier.com/locate/palaeo

New insights into the early Pliocene hydrographic dynamics and their relationship to the climatic evolution of the Mediterranean Sea

G. Kontakiotis [a],*, V. Karakitsios [a], P.G. Mortyn [b,c], A. Antonarakou [a], H. Drinia [a], G. Anastasakis [a], K. Agiadi [a], N. Kafousia [a], &, M. De Rafelis [d,e]

[a] Faculty of Geology & Geoenvironment, School of Earth Sciences, Department of Historical Geology-Paleontology, National & Kapodistrian University of Athens, Panepistimiopolis, Zografou 15784, Greece
[b] Institute of Environmental Science and Technology (ICTA), Universitat Autònoma de Barcelona (UAB), Edifici Z - Carrer de les Columnes, Bellaterra 08193, Spain
[c] Department of Geography, Universitat Autònoma de Barcelona (UAB), Spain
[d] Université Pierre et Marie CURIE, Institut des Sciences de la Terre de Paris UMR 7193 CNRS-UPMC, 75005 Paris, France
[e] Géosciences Environnement Toulouse (GET), Univ. Paul Sabatier, UMR CNRS 5563, Toulouse, France

ARTICLE INFO

Article history:
Received 26 February 2016
Received in revised form 22 June 2016
Accepted 19 July 2016
Available online 21 July 2016

Keywords:
"Trubi" formation
Sediment cycles
Stable isotopes
Mg/Ca-SSTs
Sea-level changes
Paleoceanography

ABSTRACT

One of the most enigmatic features of long-term Cenozoic climatic evolution, with some analog potential for present/future global climate change, is the last sustained warm and high-atmospheric CO_2 interval in Earth's history, which started after the end of the Messinian Salinity Crisis (5.971–5.332 Ma) in the Mediterranean Sea. We present high-resolution, astronomically-tuned climate (Mg/Ca, $\delta^{18}O$) and productivity (Ba/Ca, $\delta^{13}C$) proxy records from the planktonic foraminifera *Globigerinoides obliquus* in the Kalamaki section (Zakynthos Island, Greece), which sheds new light on the early Pliocene Mediterranean hydrographic dynamics, and the associated climatic transition from 5.33 to 5.11 Ma. We recognized four distinct climatic phases with variable amplitude changes: (1) very warm climate interval prior to 5.28 Ma characterized by minimum ice volume, large salinity fluctuations, enhanced productivity, and intense river runoff, (2) stable paleoceanographic conditions from 5.28 to 5.23 Ma, which reflect a relatively warm and mesotrophic to eutrophic open-marine environment with improved ventilation, (3) a brief interval (20 ky) characterized by the most pronounced ice growth and intense cooling (~5 °C) coupled with the abrupt decrease of ventilation and primary productivity, and (4) reinstatement of relatively stable conditions (warm and well-ventilated mesotrophic upper water column) in conjunction with relatively stable sea-level after 5.21 Ma. Overall, the succession of these phases provides an explanation for the more variable Mediterranean climate and stronger hydrographic variability with respect to other regions during the early Pliocene.

1. Introduction

The Pliocene Epoch (5.33–2.58 Ma) spans a critical period in Earth history during which global climate underwent a profound transition from relatively warm conditions to the substantially cooler climate that heralded the high magnitude glacial–interglacial (G/I) oscillations of the Pleistocene. The early Pliocene is the most recent period in Earth history when the average global temperature (2.70–4.05 °C or 3–9 °C according to computer modeling (Haywood et al., 2013a, 2013b; Lunt et al., 2010) and multi-proxy (e.g. Mg/Ca, $U^{k'}_{37}$) paleothermometers (Haywood et al., 2005; Lawrence et al., 2009; Dekens et al., 2007, 2008; Medina-Elizalde et al., 2008; Seki et al., 2010; Karas et al., 2011) and sea-level (5–70 m; Miller et al., 2005, 2011; Rohling et al., 2014) were higher than today. Moreover, the atmospheric carbon dioxide concentrations (pCO_2) were close to or slightly above modern values (350–400 ppmv; Pagani et al., 2010; Seki et al., 2010; Bartoli et al., 2011). Although this time period is not an ideal analog for present or future anthropogenic climate change according to Haywood et al. (2011), it does offer an appropriate interval to understand the climatic processes of a warm, high CO_2 world and its response to the changing cryosphere.

One period of geological time receiving considerable attention within the early Pliocene is the basal Pliocene, specifically that (5.33–5.00 Ma) immediately following the Messinian Salinity Crisis (MSC). The sedimentary expression of this event is widely recorded, both in land sections and in deep sea cores, showing that the transition from an evaporitic or continental (e.g. Messinian Lago-Mare deposits) to a marine (e.g. Zanclean "Trubi" marls) environment across the Miocene/Pliocene (M/P) boundary was typified by geologically instantaneous and continuous

---

* Corresponding author.
E-mail addresses: gkontak@geol.uoa.gr (G. Kontakiotis), vkarak@geol.uoa.gr (V. Karakitsios), graham.mortyn@uab.es (P.G. Mortyn), aantonar@geol.uoa.gr (A. Antonarakou), cntrinia@geol.uoa.gr (H. Drinia), anastasakis@geol.uoa.gr (G. Anastasakis), kagiadi@geol.uoa.gr (K. Agiadi), nkafousia@geol.uoa.gr (N. Kafousia), marc.derafelis@get.omp.eu (M. De Rafelis).

http://dx.doi.org/10.1016/j.palaeo.2016.07.025
0031-0182/

sedimentation, which was also synchronous throughout the Mediterranean basin. However, this time period is less well studied than other key Pliocene periods, such as the Mid-Piacenzian Warm Period (Dowsett et al., 2009; Drinia et al., 2005; Beltran et al., 2007; Robinson et al., 2008) or the Marine Isotope Stage (MIS) M2 (De Schepper et al., 2009). Unfortunately, the time-equivalent records for this interval are sparse, since most lower Pliocene stratigraphic Mediterranean sequences, especially on land and/or from the deep sea, are marked by a hiatus with the basal Pliocene being absent (Sprovieri, 1976). In the deep sea, several continuous sedimentary sequences in the Pacific and Atlantic Oceans (e.g. Ocean Drilling Project (ODP) Sites 846, 849, 926, 953C, 982, 1085, 1264, and International Ocean Drilling Program (IODP) Site U1338; Shackleton et al., 1995; Mix et al., 1995; Shackleton and Hall, 1997; Hodell et al., 2001; Vidal et al., 2002; Riforgiato, 2013; Bell et al., 2015; Drury et al., 2016) have been recovered across the M/P boundary and tuned astronomically (or present astronomically-based age models). The "basal Pliocene gap" has been partially filled by astronomically tuning of sedimentary cycles in well-exposed land sections in Italy (Hilgen, 1991a, 1991b; Lourens et al., 1996, 2004), and by cyclostratigraphic correlation of deep marine "Trubi" deposits in Italy, Spain and Greece (Iaccarino et al., 1999; Di Stefano et al., 1996; Drinia et al., 2008; Di Stefano and Sturiale, 2010; Riforgiato et al., 2011). However, an equally intriguing and important aspect is that most of these studies have been exclusively focused on biostratigraphic and/or cyclostratigraphic proxies. Although these approaches provide the possibility to improve the biostratigraphic resolution and furthermore supply useful correlation tools between the Mediterranean and broader oceanic areas, we still lack any combination of the evident lithological cyclicity with climate-proxy records to fully evaluate the paleoenvironmental conditions during the earliest Pliocene.

Here we present the first multidisciplinary high-resolution study of the stratigraphic interval encompassing the M/P boundary in Greece. The studied succession, the Kalamaki section (Zakynthos Island), belongs to one of the most impressive outcrops of the upper Messinian-lower Pliocene deposits in the entire central-eastern Mediterranean, both for the peculiar upper Messinian "Lago-Mare" deposits and the well-exposed lower Zanclean "Trubi" marls (Karakitsios et al., 2013, 2016). In combination with magneto- and bio-stratigraphy, an integrated cyclostratigraphic approach based on lithological observations and small-scale fluctuations of the calcium carbonate ($CaCO_3$) content was used to provide a high-resolution chronostratigraphic subdivision of the investigated time interval. The recognized cyclic patterns are also recorded through paleoclimatic proxies, such as stable isotopes ($\delta^{18}O$, $\delta^{13}C$) and elemental ratios (Mg/Ca, Ba/Ca, Cd/Ca, Sr/Ca), both performed on the climate-sensitive surface dwelling (0–50 m) planktonic foraminiferal species of *Globigerinoides obliquus* (Lourens et al., 2004; Sprovieri et al., 2006; Antonarakou et al., 2007). To gain consistency in our results, we further considered the most potentially compromising factors on foraminiferal Late Neogene Mg/Ca, which are the geochemical preservation and changes in seawater Mg/Ca (Mg/Ca_{sw}). Scanning Electron Microscope (SEM) analyses were also performed to better constrain the diagenetic alteration of *G. obliquus* shells that could potentially affect Mg/Ca and Ba/Ca proxies. The combined $\delta^{18}O$ and Mg/Ca ratios are also used to reconstruct changes in the early Pliocene ice volume through the stable oxygen isotope composition of seawater ($\delta^{18}O_{SW}$) and assess the role that the short-lived, episodic glaciation events and accompanying sea-level fluctuations played in the generally warm climate. Issues associated with marine productivity ($\delta^{13}C$, Cd/Ca; Boyle, 1992; Lynch-Stieglitz et al., 1996; Marchitto and Broecker, 2006) and riverine runoff (Ba/Ca; Weldeab et al., 2007; Sprovieri et al., 2008; Hönisch et al., 2011; Antonarakou et al., 2015) are further discussed, as these are fundamental to the reliable interpretation of the $\delta^{18}O$ and Mg/Ca signals, and they enable us to evaluate paleoceanographic evolution of the central Mediterranean during the early Pliocene. Finally, these paleoceanographic and paleoclimatic data are further compared with previously published on-land/deep sea regional (Lourens et al., 1996; Di Stefano et al., 2015) and open ocean (Pacific and Atlantic oceans; Hodell et al., 2001; Shackleton et al., 1995) coeval climate records to understand processes involved in driving and regulating the hydrography within the Mediterranean Sea.

2. Material and methods

2.1. Description of the section, age model and sedimentation rates

The studied sedimentary interval represents the upper part of the Kalamaki section, from the southeastern part of Zakynthos Island (Greece, central Mediterranean) (Fig. 1A). It covers a ~7 meter-thick complete and relatively undisturbed succession of carbonate cycles corresponding to the "Trubi" Formation (Fig. 1B,D), which overlies the Lago-Mare (Fig. 1C) and thereafter the uppermost Messinian deposits through a low-angle angular unconformity corresponding to the Messinian Erosional Surface (MES; Cornée et al., 2006, 2008, 2016; Roveri et al., 2008; Karakitsios et al., 2013, 2016; Manzi et al., 2015; Fig. 2). The "Trubi" Formation begins with 3 m of massive marly limestones, which are overlain by an alternation of decimetric carbonate and laminated marl beds. The recognized cyclic patterns display a distinct grey-white to beige-white color layering with the grey and beige layers being less indurated and $CaCO_3$-poor.

The age model for the study interval is based on six planktonic foraminiferal bioevents supplemented by one magnetostratigraphic control point (the magnetic polarity reversal C3r/C3n.4n) (Karakitsios et al., 2016), and is established by linear interpolation between them. Although additional benthic foraminiferal bioevents were detectable in the lowermost Zanclean sediments (Table 1), consistent with other Mediterranean successions (Di Stefano et al., 1996, 1999; Iaccarino et al., 1999), they were not used in the paleoenvironmental reconstruction. Accordingly, the sediment levels used here span the stratigraphic interval from the M/P boundary through the base of the MPL2 biozone between 5.33 and 5.11 Ma. The sedimentation rate is characterized by mean values of 3.29 cm/ky for the study interval, which is in agreement with those (3.20 cm/ky at Site 975B, 5.52 cm/ky at Site 969B) calculated in western and eastern Mediterranean respectively (Di Stefano et al., 2015). Among the cycles, we recognized an almost constant sedimentation rate of about 3.32 cm/ky, with the only exception of cycle 6 (mean values of 4.77 and 3.62 cm/ky for sub-cycles 6a and 6b respectively) and cycle 4 (mean value of 1.83 cm/ky). The increase/decrease in thickness of the above cycles has been interpreted as a change in the sedimentation rate.

2.2. Sample preparation and analytical methods

Ninety-four samples were collected in the first 10 lithological cycles at 5–20-centimeter intervals corresponding to a thickness of about 7 m, and processed following standard procedures (Lourens et al., 1996; Sprovieri et al., 2006, 2008; Barker et al., 2003; Rosenthal et al., 2004). The dried bulk samples were weighed, washed over a 63-μm sieve, oven-dried at 40 °C, and subsequently dry sieved into sub-fractions. The entire residue from each sample was analyzed for biostratigraphy. Biostratigraphic events were used as reference points in order to check the correct sequence of the identified cycles, with reference to the works of Hilgen (1991a, 1991b). The $CaCO_3$ content for each sample corresponding to the recognized lithological cycles was measured at the National and Kapodistrian University of Athens through a De Astis Calcimeter (Correns, 1968).

Stable oxygen and carbon isotope measurements ($\delta^{18}O$, $\delta^{13}C$) were determined on 94 samples comprising ~30 *G. obliquus* specimens from the 250–350 μm size fraction. This size fraction limitation was used to minimize ontogenetic, growth rate and size effects on shell geochemistry (Lea et al., 2000; Elderfield et al., 2002). The choice of the shallow-dwelling species *G. obliquus* for isotopic and trace element analyses is based on 4 factors: a) it is abundant in the Mediterranean Pliocene sediments, b) it has similar ecological characteristics and food requirements