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Enhanced primary productivity and magnetotactic bacterial production in response to middle Eocene warming in the Neo-Tethys Ocean

Jairo F. Savian a,⁎, Luigi Jovane b, Fabrizio Frontalini c, Ricardo I.F. Trindade d, Rodolfo Cocciono e, Steven M. Bohaty f, Paul A. Wilson g, Fabio Florindo h, Andrew P. Roberts i, Rita Catanzariti j, Francesco Iacoviello b

a Departamento de Geología, Instituto de Geociencias, Universidad Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, 91501-970 Porto Alegre, Brazil
b Departamento de Oceanografia Física, Instituto Oceanográfico, Universidade de São Paulo, Praça do Oceanográfico, 191, 05508-120 São Paulo, Brazil
c Dipartimento di Scienze della Terra, della Vita e dell'Ambiente, Università degli Studi di Urbino "Carlo Bo", Campus Scientifico, Località Crocichia, 61029 Urbino, Italy
d Departamento de Geofísica, Instituto de Astronomia, Geofísica e Ciências Atmosféricas, Universidade de São Paulo, Rua do Matão, 1226, 05508-090 São Paulo, Brazil
e Ocean and Earth Science, University of Southampton, National Oceanography Centre, Southampton S04 3ZD, UK
f Istituto Nazionale di Geofisica e Vulcanologia, Via di Vigna Murata 656, 00143 Rome, Italy
g Research School of Earth Sciences, The Australian National University, Canberra ACT 0200, Australia
h Istituto di Geoscienze e Georisorse CNR, 56124 Pisa, Italy
i Dipartimento di Scienze della Terra, dell'Ambiente, dell'Energia, e Vulcanologia, Via di Vigna Murata 605, 00143 Rome, Italy
j Istituto di Geoscienze e Georisorse CNR, 56124 Pisa, Italy

⁎ Corresponding author. Tel.: +55 51 33086364; fax: +55 51 33086337.
E-mail addresses: jairo.savian@ufrgs.br, jairosavian@gmail.com (J.F. Savian).

ABSTRACT

Earth's climate experienced a warming event known as the Middle Eocene Climatic Optimum (MECO) at ~40 Ma, which was an abrupt reversal of a long-term Eocene cooling trend. This event is characterized in the deep Southern, Atlantic, Pacific and Indian Oceans by a distinct negative δ18O excursion over 500 kyr. We report results of high-resolution paleontological, geochemical, and rock magnetic investigations of the Neo-Tethyan Monte Cagnero (MCA) section (northeastern Apennines, Italy), which can be correlated on the basis of magneto- and biostratigraphic results to the MECO event recorded in deep-sea sections. In the MCA section, an interval with a relative increase in eutrophic nannofossil taxa (and decreased abundances of oligotrophic taxa) spans the culmination of the MECO warming and its aftermath and coincides with a positive carbon isotope excursion, and a peak in magnetite and hematite/goethite concentration. The magnetite peak reflects the appearance of putative magnetofossils, while the hematite/goethite apex is attributed to an enhanced detrital mineral contribution, likely as aeolian dust transported from the continent adjacent to the Neo-Tethys Ocean during a drier, more seasonal climate during the peak MECO warming. Based on our new geochemical, paleontological and magnetic records, the MECO warming peak and its immediate aftermath are interpreted as a period of high primary productivity. Sea-surface iron fertilization is inferred to have stimulated high phytoplankton productivity, increasing organic carbon export to the seafloor and promoting enhanced biomineralization of magnetotactic bacteria, which are preserved as putative magnetofossils during the warmest periods of the MECO event in the MCA section. Together with previous studies, our work reinforces the connection between hyperthermal climatic events and the occurrence (or increased abundance) of putative magnetofossils in the sedimentary record.

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1. Introduction

The early part of the Cenozoic Era was characterized by greenhouse conditions through the early Eocene, followed by a ~17 Myr-long cooling trend (e.g. Zachos et al., 2008). This long-term cooling trend was interrupted by the Middle Eocene Climatic Optimum (MECO) – a warming event that peaked at ~40 Ma (base of Chron C18n.2n) (e.g. Bohaty and Zachos, 2003; Jovane et al., 2007; Bohaty et al., 2009). The MECO event has been recognized from multiple sites in the Southern, Atlantic, Pacific, Indian, and Tethyan Oceans (Fig. 1a). It was first identified in foraminiferal stable isotope records from the Atlantic and Indian sectors of the Southern Ocean (Barrera and Huber, 1993; Bohaty and Zachos, 2003) and the hallmark of the event is a distinct negative δ18O excursion that spanned 500 kyr (Bohaty et al., 2009). The end of the event was marked by a prominent negative shift in benthic foraminiferal δ13C of up to ~1‰ (e.g. Bohaty et al., 2009; Edgar et al., 2010). The long-lasting δ18O excursion, with a <100 kyr warming peak (MECO warming), has been interpreted to indicate a ~4–6 °C temperature increase of both surface and intermediate deep waters (Bohaty et al., 2009; Edgar et al., 2010). Organic molecular paleothermometry in the southwest Pacific revealed absolute sea surface temperatures of 24 °C
to 26 °C just below the onset of MECO, and MECO peak temperatures exceeding 28 °C (Bijl et al., 2010). The temperature increase corresponded to a concomitant $pCO_2$ increase by a factor of 2 to 3 (Bijl et al., 2010). An atmospheric $pCO_2$ rise has also been inferred at other sites by changes in deep ocean chemistry as revealed by the net decline in carbonate accumulation that reflects widespread calcite compensation depth (CCD) shoaling (Bohaty et al., 2009). The abrupt $pCO_2$ increase during the MECO event has been tentatively ascribed to massive decarbonation during subduction of Tethyan Ocean pelagic carbonates under Asia as India drifted northward (Bohaty and Zachos, 2003; Bijl et al., 2010).

The Contessa Highway (CHW) section in Central Italy represents the first outcrop section of marine sediments in which MECO was documented (Fig. 1a, b; Jovane et al., 2007). More recently, the MECO event has also been recognized at the Alano di Piave section, northeast Italy (Fig. 1a; Luciani et al., 2010). In the Alano section the MECO event is followed by deposition of two organic-rich intervals (ORG1 and ORG2; Spofforth et al., 2010), which are thought to represent rapid organic carbon burial contemporaneous with the global $pCO_2$ drawdown during the post-MECO recovery interval. Significant paleoredox, foraminifera and calcareous nannofossil assemblage changes have been documented in the same section that point to a shift toward more eutrophic waters and a lowering of oxygen availability at the end of MECO during deposition of organic-rich beds (Luciani et al., 2010; Spofforth et al., 2010; Toffanin et al., 2011). Deposition of organic-rich sediments after the transient warming event has been associated
with enhanced delivery of terrestrial material that would have both increased nutrient availability to the sea surface and stimulated primary productivity (Spofforth et al., 2010).

In marine environments, changes in primary productivity are directly related to the distribution and availability of nutrients and can be tracked by several proxies. One proxy is the relative abundance of magnetofossils in pelagic sediments (e.g., Hesse, 1994; Tarduno, 1994; Tarduno and Wilkison, 1996; Lean and McCave, 1998; Yamazaki and Kawahata, 1998; Kopp and Kirschvink, 2008; Yamazaki, 2008; Roberts et al., 2011; Chang et al., 2012; Larrasoña et al., 2012; Yamazaki, 2012). Magnetofossils are the inorganic remains of magnetotactic bacteria, which intracellularly biomine magnetically non-interacting single domain crystals, composed of magnetite, greigite, or both, which are arranged in chains within the cell (Bazylinski and Frankel, 2003; Faivre and Schüler, 2008; Kopp and Kirschvink, 2008; Moskowitz et al., 2008). These chains of nanocrystals (40–300 nm) are used by the magnetotactic bacteria to orient themselves relative to Earth’s magnetic field (Blakemore, 1975) to find optimal living conditions in strongly chemically stratified aquatic environments (Bazylinski and Frankel, 2004). Magnetosomes can be preserved in sediments and in some cases may account for 20–60% of their bulk magnetization (Egli, 2004; Housen and Moskowitz, 2006; Roberts et al., 2011). Although magnetotactic bacteria are found in various marine environments (e.g., Petersen et al., 1986; Vai et al., 1987; McNeill, 1990; Petermann and Bleil, 1993; Hesse, 1994; Housen and Moskowitz, 2006; Jovane et al., 2012), detection of fossil magnetosomes can be complicated by their mixture with other magnetic minerals, or with magnetic particles with different magnetic domain structures. Nevertheless, magnetofossils have been reported from ancient pelagic marine environments of different ages, such as the Cretaceous–Paleogene boundary (e.g., Abrajевич and Kodama, 2009), the Paleocene–Eocene boundary (e.g., Chang et al., 2012; Larrasoña et al., 2012), the Eocene–Oligocene (e.g., Roberts et al., 2011, 2012; Yamazaki et al., 2013), the Oligocene–Miocene (Channell et al., 2013; Florindo et al., 2013; Ohneiser et al., 2013), and the Pliocene (Yamazaki, 2009; Yamazaki and Ikehara, 2012). Magnetosome abundance in sediments is strongly controlled by the availability of particulate iron and organic carbon flux to the seafloor (Roberts et al., 2011), which can be related to climate, including hyperthermal conditions (e.g., Schumann et al., 2008; Chang et al., 2012; Larrasoña et al., 2012).

Here we present a high-resolution environmental magnetic, micropaleontological and stable isotopic investigation of a western Tethyan pelagic marine section at Monte Cagnero (MCA), Italy, which was deposited toward the end of the middle Eocene. Environmental magnetic data are used to detect magnetofossil variations across the MECO event and just after the warming event. These results, combined with paleoecological data from nannofossils and foraminifera, are used to assess paleoenvironmental scenarios associated with the MECO event in the Neo-Tethys realm.

2. Geological setting and magneto- and bio-stratigraphic framework

A continuous Paleogene sedimentary record is preserved in the Scaglia limestone, which includes pelagic limestones and marly limestones of the Umbria–Marche succession, central Italy. The MCA section is exposed on the southeastern slope of Monte Cagnero (Lat. 43°38′50″N, Long. 12°28′05″E, 727 m above sea level) near the town of Urbania, northeastern Apennines, Italy (Fig. 1a, b). Because of its completeness and stratigraphic continuity, the MCA section is an important pelagic sedimentary succession for studying Eocene and Oligocene climatic events (Coccioni et al., 2008; Hyland et al., 2009; Jovane et al., 2013; Fig. 1c). Following Coccioni et al. (2008), the meter system in the MCA section was established with meter level 100 as the stratigraphic equivalent to meter level 0 of the Global Boundary Stratotype Section and Point (GSSP) for the Eocene/Oligocene boundary at Massignano (Premoli Silva and Jenkins, 1993). We focus on the lower part of the section, from 58 to 72 meters stratigraphic level (msl) (Fig. 2). This 14-m-thick interval of the MCA section belongs to the Scaglia Variegata Formation and consists of bundles of limestone-marl couplets. From foraminifera assemblages, a lower bathyal (1000–2000 m) water depth was inferred for the depositional environment of the MCA section during the middle Eocene (Guerrera et al., 1988; Parisi et al., 1988), which gradually shoaled to mid-bathyal (800–1000 m) and upper bathyal (400–600 m) water depths in the late Eocene and early Oligocene, respectively.

High-resolution magneto- and bio-stratigraphic calibration of the MCA section was carried out by Coccioni et al. (2008), Hyland et al. (2009), and Jovane et al. (2013). The studied interval spans from the middle–upper part of Chron C18r to the lowermost part of C18r.1r with an average sedimentation rate of ~8.57 m/Myr following the geomagnetic polarity timescale (GPTS) of Cande and Kent (1995) (confirmed by Ogg, 2012). The primary nannofossil and foraminiferal biostatigraphic events identified are (from bottom to top) the: (1) lowest occurrence (LO) of Orbulinoides beckmanni at 63.2 msl; (2) highest occurrence (HO) of O. beckmanni at 65.5 msl; and (3) HO of Chiasmolithus solitus at 70.0 msl (Jovane et al., 2013). It is worth noting, however, that recognition of the LO of O. beckmanni can be subjective because this taxon originates from Globigerinathela eugenae, and some transitional forms of problematic taxonomic assignment occur from 62.8 to 63.2 msl. Additionally, identification of the HO of O. beckmanni is hampered by its scarce abundance, moderate preservation of planktic (P) and benthic (B) foraminifera and some problematic specimen identifications up to 66.60 msl. Nevertheless, the MCA biostatigraphic record in the 58–72 msl interval is likely continuous and is interpreted to span planktonic foraminiferal Zones P12 to P14 of Berggren et al. (1995) and Zones E11 to E13 of Wade et al. (2011), and calcareous nannofossil Zones NP16 to NP17 of Martini (1971) and CP14a to CP14b of Okada and Bulkey (1980).

3. Materials and methods

Two-hundred-sixty-five bulk rock samples were collected at ~5 cm stratigraphic intervals from the MCA section, corresponding to a temporal spacing of ~6 ky between samples. High-resolution calcium carbonate, stable isotopic, rock magnetic and micropaleontological analyses were performed. Carbonate contents were measured at the National Oceanography Centre, Southampton (NOCS). One-hundred-twenty-five bulk rock samples were reduced to fine powder in an agate mortar and their CaCO3 content was obtained using a Dietrich-Frühling calcimeter that measures the CO2 volume produced by complete dissolution of pre-weighed samples (300 ± 1 mg each) in 10% vol. HCl. Total carbonate contents (wt.% CaCO3) were computed with a precision of 1% taking into account pressure and temperature of the laboratory environment, the amount of bulk sample used, and the volume of CO2 in the calcimeter. Standards of pure calcium carbonate (e.g. Carrara Marble) were measured every ten samples to ensure proper calibration (Appendix A). For coarse-fraction analyses, weighed freeze-dried samples were soaked in deionized distilled water, and were washed through 63 µm sieves. The >63 µm fraction residue was collected, dried, and weighed. The coarse fraction is defined as the weight percent ratio of the >63 µm size fraction to the weight of the bulk sample (~100 g for each sample) (Broecker and Clark, 1999, 2001). This index has been largely used as an indicator of carbonate dissolution (e.g. Hancock and Dickens, 2005; Colosimo et al., 2006; Leon-Rodriguez and Dickens, 2010; Luciani et al., 2010).

Semi-quantitative mineralogy of the bulk fraction was determined on 6 representative samples distributed along the section (58.15, 63.25, 63.50, 64.90, 65.10, and 69.05 msl) using powder X-ray diffraction (XRD) analysis. For bulk analyses, an aliquot of about 1 g was crushed and pulverized in a mortar. About 15 mg was used for XRD analysis made on an automated Olympus® BTX diffractometer, using Co-K radiation, operated at 30 kV and 0.326 mA, over the range
Fig. 2. Changes in CaCO₃ content, coarse fraction, δ¹³C and δ¹⁸O in bulk sediments, low-field magnetic susceptibility (χ), and rock magnetic properties (anhydrous remanent magnetization, ARM; isothermal remanent magnetization, IRM at 900 mT; hard isothermal remanent magnetization, HIRM; S-ratio₃₀₀) across the 14-m-thick studied MCA section. χ, ARM, IRM₉₀₀, and HIRM₉₀₀ were also calculated on a carbonate-free basis (CFB, dashed lines). The magnetobiostratigraphy is from Jovane et al. (2013). Numerical ages (1) are from Cande and Kent (1995) (star) and Ogg (2012) (diamond). Biostratigraphy is based on the planktonic foraminiferal Zones of (2) Berggren et al. (1995) and (3) Wade et al. (2011) and calcareous nannoplankton Zones of (4) Martini (1971) and (5) Okada and Bukry (1980). The areas shaded in yellow, dark yellow and green highlight the intervals (2–4) that represent the MECO, MECO warming peak and the post-MECO periods.
5–55° of 2θ, with a step size of 0.05° and 100 exposures, for an analysis time of 22 min. Mineral identification and analysis was carried out using the XPowder software (Version 2010.01.15 PRO), which uses the PDF-2 International Centre for Diffraction Data (ICDD) database. In order to minimize subjective influences, the baseline was determined automatically with XPowder defaults. X-ray diffraction identification criteria were based on the indications of Biscaye (1965), Brown and Brindley (1980), and Moore and Reynolds (1997). For quantitative analysis, the Reference Intensity Ratio (RIR) method, which is based upon scaling all diffraction data to the diffraction of standard reference materials, was used (Chung, 1974). The XPowder software automatically computes an amorphous phase that is characterized by all the phases not identified by their basal reflection at 3.85 and 3.03 Å (calcite), 4.26 and 3.34 Å (quartz), 15–16 Å (smectite), and 14.2, 7, and 4.72 Å (chlorite).

Oxygen and carbon isotope analyses were conducted using VG Optima and VG Prism dual-inlet isotope ratio mass spectrometers at NOCS. One-hundred-twenty-five samples were reacted in a common acid bath at 90 °C using an automated carbonate preparation system with a carousel device. NBS-19, Atlantis II, and an in-house Carrara Marble standard were included in all sample runs. All values are reported in standard delta notation (‰) in parts per mil (‰) relative to VPDB (Vienna Pee Dee Belemnite), and analytical precision is estimated at 0.06‰ (1σ) for δ13C and 0.08‰ (1σ) for δ18O (Appendix A).

Paleomagnetic and environmental magnetic measurements were carried out at NOCS and at the University of São Paulo (USP). The magnetic remanence of 253 unoriented block samples (5-cm resolution) was measured using a three-axis 2-G Enterprises cryogenicagnetometer (model 755R), housed in a magnetically shielded room at NOCS.

Low-field magnetic susceptibility (χ) was measured with a Kappabridge KLY-3 (AGICO) magnetic susceptibility meter. All data were normalized by mass, due to the irregular sample volumes. An anhysteretic remanent magnetization (ARM) was imparted in a 100 mT alternating field (AF) with a direct current bias field of 0.05 mT. An isothermal remanent magnetization (IRM) was imparted in a direct field of 900 mT (IRM900mT) and was demagnetized in backfields of 100 mT (–IRM100mT) and 300 mT (–IRM300mT). From these measurements, we calculated the S-ratio (S300mT = (–IRM300mT / IRM900mT)) and “hard” isothermal remanent magnetization (HIRM300mT = |IRM300mT + IRM200mT| / 2), in order to investigate the coercivity of magnetic minerals. Hysteresis loops and first-order reversal curve (FORC) diagrams were analyzed for eight samples from the MCA section spanning the MECO interval and from intervals immediately before and after the warming event. FORC measurements were performed with an averaging time of 200 ms, a smoothing factor (SF) of 4, and using the input parameters of Egli et al. (2010) (HIRM300mT = 0 mT; HIRM900mT = 110 mT; HIRM100mT = 0 mT; HIRM200mT = 0 mT; HIRM300mT = 0 mT).

Magnetic mineralogy was further investigated at USP for selected samples through the acquisition of an IRM and measurement of thermomagnetic curves. IRM acquisition curves were obtained for six samples with a 2-G Enterprises pulse magnetizer and a cryogenic magnetometer (model 755UC). IRM acquisition curves were analyzed with cumulative log-Gaussian (CLG) functions using the software of Kruiver et al. (2001). The CLG function is described by three parameters (SIRM, B1/2, and dispersion parameter, DP) that characterize magnetic minerals (Robertson and France, 1994; Kruiver et al., 2001). Thermomagnetic curves up to 700 °C were obtained using a KLY-4S AGICO magnetic susceptibility meter with high-temperature attachment at USP to determine the Curie or Néel temperatures of magnetic minerals.

For calcareous nanofossil analyses, samples were prepared from unprocessed material as simple smear slides using standard preparation methods (Bown and Young, 1998) at the Istituto di Geoscienze e Georisorse CNR di Pisa (Italy). Smear slides were studied under a Leitz Laborlux 12 Pol light microscope both under crossed nicols and transmitted light at a magnification of 1250×. Most nanoplankton species were identified according to the taxonomy of Perch — Nielsen (1985) except for sphenoliths and Dictyococci that were classified following Fornaciari et al. (2010) and Reticolofenestra umbilicus that was defined following the taxonomic criteria adopted by Backman and Hermelin (1986), ascribing to this species all specimens >14 μm and grouping as Reticolofenestra spp. all specimens <14 μm. Assemblages were studied following quantitative counting methods based on at least 300 specimens (Appendix B). Following Toffanin et al. (2011), the relative abundances of species belonging to the genus Sphenolithus were determined by counting 100 specimens. Rare taxa, such as the genus Chiasmolithus and species belonging to the genus Chiasmolithus were counted in a prefixed area of 10 mm² (three–four transects). The standard calcareous nanofossil zonations of Martini (1971) and Okada and Bukry (1980) are widely used for low– and middle-latitude Eocene–Oligocene (E–O) biostratigraphic studies, and were used in this paper. To infer probable temperature and trophic variations of surface waters, most calcareous nanofossils were, when possible, allocated into groups of environmental affinities, largely following Haq and Lohmann (1976), Aubry (1992), Gardin and Monèche (1998), Bralower (2002a,b), Tremolada and Bralower (2004), Persico and Villa (2004), Gibbs et al. (2006), Villa et al. (2008), Raffi et al. (2009) and Agnini et al. (2011). Based on this literature, the following environmental groups were used: eutrophic taxa (Dictyococci bicus tus, Dictyococci scrippsi, Reticulofenestra daviesii), and oligotrophic taxa (Cribrocentrum retuculum, Ericsonia spp., Sphenolithus spp., Zygrhablithus bifusus) (Appendix B).

For foraminiferal analyses, samples were treated at the Università degli Studi di Urbino, following the cold acetylene technique of Lirer (2000), by sieving through a 63 μm mesh and drying at 50 °C. The cold acetylene method enabled extraction of generally easily identifiable foraminifera even from indurated limestones. This technique offered the possibility of accurate taxonomic determination and detailed foraminiferal assemblage analysis. For planktonic foraminifera, all samples were studied for biostratigraphy and quantitative analysis was performed on a subset of 101 samples. The residues were studied with a binocular stereomicroscope to characterize assemblages and to identify biostratigraphic marker species. A representative split of at least 300 specimens was picked from the >63 μm fraction, mounted on micro-slides for permanent record and identification purposes, and classified following the taxonomic criteria of Berggren and Pearson (2005). The planktonic foraminiferal zonations of Berggren et al. (1995) and Wade et al. (2011) were followed. Following Hancock and Dickens (2005), the fragmentation index (FI) was calculated using at least 300 specimens and including the whole test, fragments and dissolved tests to estimate carbonate dissolution effects (Appendix C). For benthic foraminifera, a quantitative study of sixty-four selected samples was performed. A representative split of the >90 μm fraction was used to pick approximately 300 specimens. The sample–split weight used to pick benthic foraminifera was determined so that the foraminiferal density (FD), expressed as the number of foraminifera per gram of dry sediment, could be calculated. The planktonic to planktonic and benthic (P/P + B) ratio, expressed as a percentage, and the percentages of agglutinants were also calculated (Appendices C and D).
4. Results

4.1. Micropaleontology

Benthic foraminiferal assemblages are generally diverse and well-preserved throughout the studied MCA section, except at 63.2–64.0 msl where evidence of partial dissolution is observed (Fig. 3). The assemblages are dominated by calcareous-hyaline forms with variable percentages of agglutinants that are more abundant at the base of the section and at 63.2–64 msl (Fig. 3). The P/(P + B) ratio fluctuates throughout the sequence, with the lowest values at 63.2–64 msl where both the highest FD value and percentage fragmentation are documented (Fig. 3). The 63.2–65.5 msl interval is therefore characterized by pronounced paleoecological and paleoenvironmental changes. The increase of benthic to planktonic foraminifera and of agglutinated forms that are less prone to dissolution might reflect shallowing of the lysocline. In addition, increased FD values might suggest greater nutrient availability at the sea floor probably related to increased detrital mineral influx associated with intensified hydrological and weathering cycles. In two intervals eutrophic taxa increase in abundance relative to oligotrophic taxa: 63.5–65.5 msl and 67.0–70.2 msl (Appendix B). Eutrophic and oligotrophic percentages vary throughout the section, but within the background level of variation.

4.2. Stable isotopes

Bulk δ13C and δ18O values average 1.8% and −1.4‰, respectively, through the studied MCA section (Figs. 2c, d). δ18O data have background values of −1.8‰ and are characterized by an increase from −1.6 to 2.1‰ at 63.2–65.5 msl (−40.2–40.1 Ma) (Fig. 2c). The peak value is followed by a slowly decreasing trend up to 66.34 msl (~39.8 Ma). Bulk δ13C varies from −0.2‰ to −3.3‰ and is noisy (Fig. 2d). Similarly noisy δ18O in the correlative CHW section was interpreted as resulting from burial diagenesis and/or meteoric water diagenesis (Jovane et al., 2007). It is well known that bulk carbonate δ13C is more robust to diagenetic alteration than δ18O because the carbon content of fluids is often too low compared to that of carbonate rocks to modify significantly the carbonate carbon isotopic composition (e.g. Veizer and Hoefs, 1976).

4.3. Environmental magnetism

Low-field magnetic susceptibility (χ) along the studied MCA section varies between 0.57 × 10⁻⁸ and 6.42 × 10⁻⁸ m³/kg (Fig. 2e), whereas CaCO₃ contents vary between 47% and 93% (Fig. 2a). Two narrow intervals (63.30–63.90 msl and 64.15–65.30 msl) have lower CaCO₃ contents and higher χ values (Fig. 2a, e). CaCO₃ and χ have a significant negative correlation (r = −0.72), i.e. lower CaCO₃ is related to higher χ values, which correspond to peak abundances of paramagnetic (e.g. clays) and ferrimagnetic minerals. Six representative samples from depths of 58.15, 63.25, 63.50, 64.90, 65.10, and 69.05 msl have similar XRD patterns, with slight differences between samples. The main phases present, in order of abundance, are: calcite (Cal), quartz (Qtz), smectite (Sm) and chlorite (Chl) (Fig. 4). Calcite contents vary between a minimum of 61.3% (63.50 msl; Fig. 4c) and 77.2% (58.15 msl; Fig. 4a); samples from 58.15 to 69.05 msl (Fig. 4a, f) have relatively higher amounts of calcite (77.2% and 71.8, respectively) compared to samples from 63.25, 63.50, 64.90 and 65.10 msl (61.5%, 61.3%, 65.9% and 66.1%, respectively, Fig. 4b, c, d, e). These results are compatible with the smaller amounts of CaCO₃ in the same interval (Fig. 2a). Quartz values have an opposite trend, with higher values (4.6%) in sample 63.50 msl, and lower amounts (2.7%) in sample 58.15 msl. Smectite and chlorite have similar trends, with lower values (8.3%, 10.3% and 5.7%, 7.9%, respectively) in samples 58.15 msl and 69.05 msl. In contrast, higher percentages of smectite and chlorite are found in samples 63.25, 63.50, 64.90 and 65.10 msl. The amorphous phase also has a comparable trend to that of quartz, smectite and chlorite, with higher contents in samples from 63.25, 63.50, 64.90 and 65.10 msl.

To account for dilution effects by the carbonate matrix, we calculated magnetic parameters (χ, ARM, IRM₀₀₀₀₀ and HIRM₀₀₀₀₀) on a carbonate-free basis (CFB, dashed lines in Fig. 2e–h). To achieve this,
we normalized the magnetic parameters by (100 wt.% CaCO₃). All magnetic parameters that depend on the concentration of ferrimagnetic minerals are well correlated before and after this normalization (Fig. 2e–h). For example, the ARM and ARM CFB, IRM₉₀₀mT and IRM₉₀₀mT CFB, and HIRM₃₀₀mT and HIRM₃₀₀mT CFB have coherent peaks at 63.30–63.90 msl and 64.15–65.30 msl, as mentioned above, but also a less pronounced peak at 66.6–68.8 msl.

The relative concentration of different magnetic minerals across the studied interval can be inferred from the S-ratio₃₀₀mT and HIRM₃₀₀mT (Bloemendal et al., 1992; Liu et al., 2007). The large IRM₃₀₀mT and S-ratio₃₀₀mT fluctuations indicate variable proportions of low and high-coercivity magnetic minerals, i.e. magnetite (predominant when S-ratio is near 1) and hematite/goethite (present in significant concentrations when HIRM is high and S-ratio is close to 0). The presence of mixtures of magnetic minerals with contrasting coercivities is corroborated by stepwise IRM acquisition curves. IRM acquisition curves were measured at fields up to 1 T for six representative samples along the MCA section (Fig. 5a; Table 1) and components due to different magnetic minerals were fitted using CLG functions (Fig. 5b–d) (Kruiver et al., 2001; Heslop et al., 2002). Three magnetic components were identified (Table 1). They correspond to a low-coercivity component (B₁/₂ = 16 mT, DP = 0.40–0.45), a medium-coercivity component (B₁/₂ = 50–70 mT, DP = 0.30–0.40) and a high-coercivity component (B₁/₂ = 250–479 mT, DP = 0.24–0.30). Following Roberts et al. (2011, 2012), component 1 (lowest coercivity component in Table 1) is interpreted as related to relatively coarse-grained magnetite of detrital origin. However, we cannot discount that component 1 represents the coarse end of a distribution of fine-grained, largely superparamagnetic particles, perhaps produced in situ by dissimilatory iron-reducing bacteria (e.g. Egli, 2004). The magnetofossil component is correlated to the medium-coercivity component 2 (Table 1) with coercivity values around 40 mT and a small DP (≈0.3), similar to the IRM signal of magnetotactic bacteria found in other studies (e.g. Egli, 2004; Chen et al., 2007; Jovane et al., 2012; Roberts et al., 2012). Component 3 is interpreted to represent a high coercivity hematite fraction, but can also include some fraction of goethite. Inside the magnetic mineral concentration peaks, the medium-coercivity component usually dominates the IRM signal, with contributions varying between 31%
The low-coercivity component varies from 5% to 17%. It occurs inside the magnetic concentration peaks but is absent (or below the detection level) outside these stratigraphic levels. In these samples (MCA-67.55, MCA-68.60), the high-coercivity component can reach up to 82% of the total IRM.

Hysteresis data (Fig. 6; Table 2), including the ratio of saturation remanence to saturation magnetization ($M_r/M_s$) and the coercivity of remanence to coercive force ($B_{cr}/B_c$), from MCA samples lie within the pseudo-single domain (PSD) field of Day et al. (1977). The presence of hematite mixed with fine-grained magnetite is indicated by the wasp-waisted shape of the loops (Roberts et al., 1995). The mixture of low- and high-coercivity phases does not affect significantly the Day plot because SD hematite has similar hysteresis ratios to those of SD magnetite (Roberts et al., 1995). The significant departure of bulk hysteresis parameters from values expected for uniaxial SD magnetite for both the MCA and CHW samples (Fig. 6) can be related to significant mixtures of non-SD detrital magnetite grains (superparamagnetic, PSD and multi-domain grains) in the studied samples (Dunlop, 2002; Roberts et al., 2012) as suggested by the IRM acquisition curves.

FORC diagrams provide detailed information about magnetic interactions and microcoercivity distributions (Roberts et al., 2000). High-resolution FORC measurements following the specifications of

Fig. 5. (a) IRM acquisition curves for six representative samples from the MCA section. (b–d) IRM unmixing analyses (Kruiver et al., 2001; Heslop et al., 2002) for three representative samples; (b) and (c) represent samples collected inside the magnetic mineral concentration peaks and (d) from outside the peaks. Raw data (circles) and calculated IRM acquisition curves are shown for two and three fitted components after fitting of a spline function.
Egli et al. (2010) can be used to infer the presence of biogenic magnetite (e.g. Egli et al., 2010; Roberts et al., 2011, 2012; Jovane et al., 2012; Larrasoaña et al., 2012; Yamazaki, 2012; Yamazaki and Ikehara, 2012). FORC distributions are nearly identical in the high-magnetization intervals between 63.2 and 65.5 msl (Figs. 2, 7). These FORC diagrams have a sharp horizontal ridge at $H_b = 0$ that indicate negligible magnetic interactions and a dominance of non-interacting SD particles (Roberts et al., 2000) that is characteristic of intact magnetosome chains (e.g. Egli et al., 2010; Roberts et al., 2011; Jovane et al., 2012; Larrasoaña et al., 2012; Roberts et al., 2012; Yamazaki, 2012; Yamazaki and Ikehara, 2012). The coercivity distribution has a broad peak between 3 and 25 mT, with a maximum at 15–20 mT (Fig. 7) that falls within the range expected for magnetite magnetosomes (Egli, 2004; Kopp and Kirschvink, 2008; Egli et al., 2010). Outside the 63.2–65.5 msl interval, the magnetic signal of the samples is much weaker and no meaningful FORC distribution could be obtained from these samples (Fig. 7a, h).

Multiple runs were then performed for intervals with low magnetization and also within the 66.6–68.8 msl peak. Intervals with low magnetization have no meaningful FORC distributions even after stacking of nine runs (Fig. 7j). On the other hand, statistically significant FORC results are estimated for the 66.6–68.8 msl interval after stacking of nine measurement runs; resulting distributions are similar to those observed within the major magnetic peaks (Fig. 7k).

To compare our results with those from a nearby section, we also performed FORC analyses on samples from the MECO interval at the CHW section, between 135 and 139 msl, as defined by Jovane et al. (2007). This interval is characterized by a peak in magnetic concentration-dependent parameters (e.g. $\chi$, ARM, IRM). A horizontal ridge due to non-interacting SD magnetite with coercivities between 10 and 50 mT is also evident in these samples (Fig. 7i).

5. Discussion

5.1. The MECO event in the Neo-Tethys

Benthic and planktonic foraminiferal and calcareous nannofossil assemblages in the MCA section across the Chron C18r/C18n boundary are affected by important faunal turnovers. Together with rock magnetic, geochemical and stable isotope data, they enable subdivision of the studied 14-m-thick section into five discrete intervals (Figs. 2, 3, 8):
Thus, observed changes in paleoenvironmental proxies provide clues (Luciani et al., 2010). Dissolution during this interval is also supported by increased values of the planktonic foraminiferal FI, greater relative abundances of agglutinated foraminifera that are less prone to dissolution, and a clear decrease of the P/P + B ratio (Fig. 3). The increase in dissolution likely contributes to the higher concentrations of magnetic particles in this interval indicated by magnetic susceptibility, ARM (and ARM CFB), IRM$_{900mT}$ (and IRM$_{900mT}$ CFB), and HIRM$_{900mT}$ (and HIRM$_{900mT}$ CFB) (Fig. 2). In contrast, there is no evidence for carbonate dissolution upsection in Intervals 4 and 5. Interval 3 falls within the lowermost part of Chron C18n, therefore, it can be magnetostratigraphically correlated with peak MECO warming in marine sediment cores (Bohaty et al., 2009), and in the Tethyan CHW (Jovane et al., 2007) and Alano sections (Luciani et al., 2010; Spofforth et al., 2010; Toffanin et al., 2011). Thus, observed changes in paleoenvironmental proxies provide clues that point to seafloor CaCO$_3$ dissolution and lysocline shallowing at the MCA site during the MECO warming. Interval 3 is immediately followed by an interval with lower CaCO$_3$ contents associated with higher magnetic susceptibility values. On the basis of available magneto- and biostratigraphic results, Interval 4 correlates well with the organic-rich ORG1 unit identified at the Alano section (Luciani et al., 2010; Spofforth et al., 2010). These organic-rich layers are thought to represent rapid organic carbon burial events at the end of the MECO event, probably induced by enhanced delivery of terrestrial material to the ocean (Spofforth et al., 2010).

5.2. Ocean iron fertilization and magnetotactic bacterial abundance during the MECO event

Detrital magnetic minerals can be delivered to the deep sea through different transportation pathways, including ice-rafting, mass flows, hemipelagic sediment plumes or wind (e.g. Evans and Heller, 2003; Liu et al., 2012). Fine-grained terrigenous inputs that reached the deep, carbonate-dominated MCA site were most likely transported by suspended plumes or wind. Both processes result in similar grain-size distributions and mineralogy (Rea, 1994). Hemipelagic sediment has been reported in modern environments to distances of 500 km from the coast and possibly as far as 900 km (Rea, 1994 and references therein). Such distances are within the expected range of the MCA section from the paleoshoreline of the Neo-Tethys. Nevertheless, processes that control hemipelagic and aeolian inputs to the deep sea tend to be out of phase; wet conditions (and enhanced runoff) in the source region would favour hemipelagic fluxes, whereas drier source region climates would enhance aeolian dust fluxes. Enhanced aeolian supply relative to detrital fluxes into the Neo-Tethys has been reported on the southern Tethyan margin (central Egypt) as a result of drier, likely more seasonal, climatic conditions during the Paleocene–Eocene Thermal Maximum (PETM) (Schulte et al., 2011). Similar observations have been made for the PETM in the Bighorn Basin, Wyoming (Wing et al., 2005; Kraus and Riggins, 2007; Smith et al., 2009), East Africa (Handley et al., 2012) and the southern Kerguelen Plateau, Indian Ocean, on the Antarctic margin (Larrasoana et al., 2012).

Environmental magnetic parameters can serve as sensitive aeolian dust proxies, given that hematite forms in oxidizing, dehydrating desert environments (Larrasoana et al., 2003; Liu et al., 2012 and references therein). Hematite concentrations can be easily tracked using the “hard” IRM on a carbonate free basis (Liu et al., 2009; Liu et al., 2012). The onset of continental aridity and obliquity-dominated climate cyclicity coincides with the MECO peak and continues afterward into the post-MECO cooling.

Aeolian dust is a potential source for iron fertilization of the ocean (e.g. Maher et al., 2010; Roberts et al., 2011; Larrasoana et al., 2012; Liu et al., 2012). Roberts et al. (2011) reported increased iron supply by aeolian dust in Eocene sediments (ODP Hole 738B) of the southern Kerguelen Plateau (Indian Ocean), where a marked increase in hematite concentrations coincided with a switch from oligotrophic to eutrophic conditions. The interval with higher hematite concentrations is also coincident with increased magnetofossil abundances. Roberts et al. (2011) argued that iron input and increased organic carbon delivery to the seafloor were the main factors that controlled the abundance of magnetotactic bacterial populations. Likewise, in the MCA section the magnetic proxies classically used to trace low-coercivity magnetite (ARM CFB) and high-coercivity hematite/goethite (HIRM$_{900mT}$ CFB) co-vary, which indicates a concomitant increase in concentration of both magnetic minerals in Intervals 3 and 4 (Figs. 2c and 8b, c). A significant fraction of the magnetite in these intervals is due to non-interacting SD particles, as indicated by a FORC central ridge signature (Fig. 7), which we attribute to putative magnetofossils. The same intervals are characterized by a relative increase in eutrophic calcareous nanofossil taxa (Fig. 8d). Eutrophication could have been stimulated by sea surface iron fertilization produced by addition of iron-rich aeolian dust to surface waters. This promoted enhanced organic carbon export to deeper waters and burial on the seafloor, which stimulated increased magnetotactic biominalization (e.g. Villa et al., 2014). The iron needed for biominalization by magnetotactic bacteria is likely to have been provided by diagenetic iron reduction that released Fe$^{3+}$ from the most reactive iron-bearing minerals, including hydrous ferric oxide and lepidocrocite (Poulton et al., 2004). Magnetite and hematite are more resistant to dissolution (Yamazaki et al., 2003; Poulton et al., 2004; Garming et al., 2005; Roberts et al., 2011) and, therefore, survived this mild iron reduction that occurred under iron-reducing but not anoxic conditions. Thus, simultaneous delivery of enhanced organic carbon, reactive iron-bearing aeolian dust particles and non-reactive aeolian hematite particles to the seafloor would have released the existing limitation on key nutrients (carbon and iron) for an existing, but small, population of magnetotactic bacteria to produce the observed magnetic signatures. An increase in ARM CFB and HIRM$_{900mT}$ CFB is also observed outside the MECO interval, but with lower intensity, at the

<table>
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<tr>
<th>Sample ID</th>
<th>Depth (m)</th>
<th>M$_c$ (Am$^2$/kg)</th>
<th>M$_s$ (Am$^2$/kg)</th>
<th>M$_c$/M$_s$</th>
<th>B$_{max}$ (mT)</th>
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66.6–68.8 msl peak. FORC distributions for this interval are similar to those observed across the MECO (Fig. 7) and also coincide with an increase in eutrophic taxa (Fig. 8d). In this case, the same mechanism can be advocated for the coeval increase in magnetofossils and high-coercivity phases (Fig. 8b, c) and suggests the presence of a magnetotactic bacteria assemblage throughout the whole studied interval that bloomed with increased supply of limiting nutrients during episodic warming events.

6. Conclusions

An integrated high-resolution stable isotope, geochemical, micropaleontological and environmental magnetic analysis has been carried out over a 14-m-thick interval of the Monte Cagnero section (Umbria-Marche Basin), Italy, which corresponds to the 40.8–39.1 Ma period around the Middle Eocene Climatic Optimum (MECO). Magnetic parameters indicate a concomitant increase of aeolian iron supply in the form of hematite, and a higher abundance of magnetite magnetofossils produced by magnetotactic bacteria as indicated by FORC diagrams that are typical of non-interacting SD particles (Roberts et al., 2000; Egli et al., 2010). Samples 58.15 and 66.30 do not have the same behaviour. FORC diagrams in (a) to (i) were measured with a single run in a VSM, whereas those in (j) and (k) were obtained after stacking nine measurement runs using a more sensitive AGM instrument. FORC diagrams obtained with multiple runs were stacked and calculated using the MATLAB routine of Heslop and Roberts (2012). The smoothing factor (Roberts et al., 2000) is 4 in all cases.

Increased aeolian supply of iron to surface ocean waters. Such a scenario has been recently envisaged for the PETM event (e.g. Chang et al., 2012; Larrasoana et al., 2012), and we now confirm a similar connection between putative magnetofossil abundance and paleoproductivity through the MECO event. It reinforces the connection between hyperthermal climatic events and the occurrence (or increased abundance) of putative magnetofossils. Further work is needed to assess whether the preserved inorganic remains of magnetotactic bacteria can provide a useful paleoproductivity proxy in ancient carbonate sediments.

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