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Tempo and duration of short-term environmental perturbations across the Cretaceous-Paleogene boundary

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ABSTRACT: The complex interplay between extraterrestrial events and earth-bound processes that triggered one of the greatest biological crises of the Phanerozoic requires a high resolution timescale. Detailed magnetic susceptibility measurements at the Contessa Highway and Bottaccione sections (Italy) span the Cretaceous-Paleogene boundary and reveal clear orbital signatures in the sedimentary record. Identification of precession and 405 kyr eccentricity cycles allows an estimate of 324 $\pm$ 40 kyr for the duration of the Maastrichtian part of Chron C29r.

We present in the same high resolution time frame sites in Spain and the North and South Atlantic and bio-horizons, biotic changes, stable isotopic excursions and the decrease in Osmium isotopes recorded in these sections. The onset of ¹⁸⁷Os/¹⁸⁸Os decrease coincides with the $\delta^{13}\text{C}$ negative excursion K-PgE1, thus suggesting a first pulse in Deccan volcanism at 66.64 Ma. The K-PgE3 $\delta^{13}\text{C}$ negative excursion is possibly the expression of a second pulse at 66.26 Ma. Late Maastrichtian $\delta^{13}\text{C}$ negative excursions are of low intensity and span durations of one to two eccentricity cycles, whereas early Danian excursions are brief (about 30 kyr) and acute. Biotic response to late Maastrichtian perturbations occurred with a delay of ca. 200 kyr after the beginning of K-PgE1 shortly before K-PgE3. The biotic perturbation could be thus either a delayed response to K-PgE1, or a direct response to K-PgE3, and possibly, a threshold response to the stepwise buildup of CO₂ atmospheric injections. No delay is evident in response to early Danian hyperthermal events. These differences suggest that short-lived, volcanically-derived environmental perturbations were buffered within the stable late Maastrichtian oceanic realm whereas they were amplified by the more sensitive and highly disturbed early Danian oceanic ecosystem.

INTRODUCTION

Resolving the events that triggered and followed the major biological crisis marking the end of the Cretaceous requires a high resolution and well constrained geological timescale. Complex climatic and biotic changes took place during the late Maastrichtian-early Danian transition. The respective roles of Deccan volcanism and the Chicxulub extraterrestrial impact are still debated (Keller et al. 2008; Schulte et al., 2010; Archibald et al. 2010; Courtillot and Fluteau 2010; Keller et al. 2010; Alegret, Thomas and Lohmann 2012; Renne et al. 2013).

During the last decades, the progress in cyclostratigraphic methods and astronomical solutions has allowed the development of a Cenozoic astronomical time scale leading to an unprecedented improvement of precision and accuracy (Dinarell et al 2003; Lourens et

al. 2004; Laskar et al. 2004; Westerhold et al. 2008; Kuiper et al. 2008; Laskar et al. 2010; Hilgen, Lourens and Van Dam 2012). The astronomical calibration of the Geologic Time Scale has been recently extended with success down into the late Cretaceous and correlated to carbon-isotope stratigraphy (Husson et al. 2011; Batenburg et al. 2012; Thibault et al. 2012b). Astronomical calibrations of the early Paleogene and late Cretaceous have mostly been performed independently, not often focusing on the calibration of biotic and environmental changes that occurred across the Cretaceous-Paleogene boundary (K-PgB).

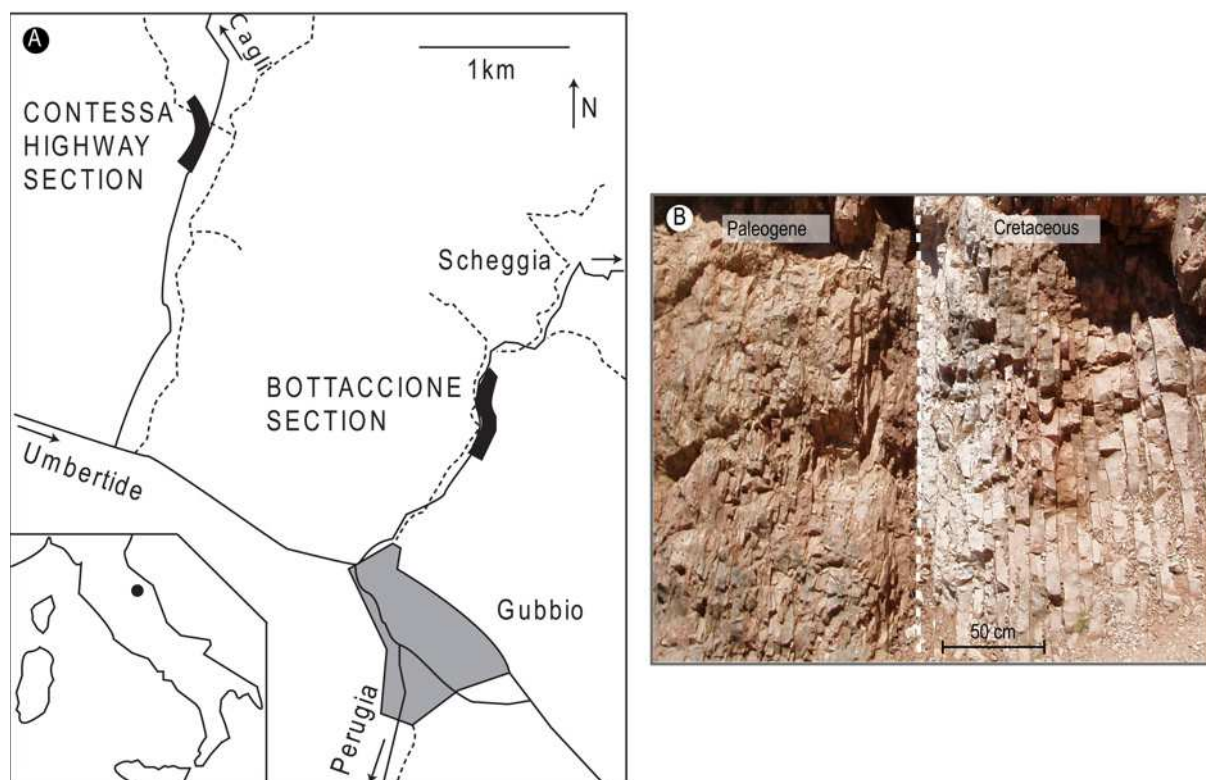


Figure 1: A) Map of the Contessa and Bottaccione sections location (From Monechi et al., 1985) B) Photograph of the Cretaceous-Paleogene boundary at the Bottaccione section highlighting the white limestone layers preceding the boundary.

The pelagic successions of the Umbria-Marche (Italy) have played a major role in the development of the Cretaceous and Paleogene time scale. These deep water limestones are mostly composed of calcareous plankton, with a very good continuity, allowing the development of a thorough biostratigraphic framework for the Cretaceous (Renz 1936; 1951; Luterbacher and Premoli Silva 1964; Gardin et al. 2012). Multiple bio- and magnetostratigraphic studies of these sections allowed the micropalaeontological calibration and dating of the C-sequence marine magnetic anomalies, the sections also carrying a very good record of Earth magnetic field reversals (Alvarez et al. 1977; Lowrie and Alvarez 1977; Premoli Silva, Paggi and Monechi, 1977; Monechi and Thierstein 1985). The Bottaccione section provided, in particular, the first constraint on the location of the Cretaceous-Paleogene boundary within the Chron C29r (Alvarez et al. 1977). The K-PgB transition interval, which was thought in the 1970s to be marked by a global hiatus (Alvarez et al. 1977), has later proved to be continuous in this section, and the succession of biotic and abiotic events characterizing this interval is complete. A recent Maastrichtian timescale has been developed by Voigt et al. (2012), based on $\delta^{13}\text{C}$ measurements from several sections, including the Bottaccione and Contessa Highway section. A new biostratigraphic timescale based on Gubbio section has also been presented recently (Gardin et al. 2012). Cyclostratigraphic analysis of Magnetic Susceptibility variations (MS) proved to be successful in the lower Maastrichtian of the Contessa Highway section, allowing construction of a relative timescale (Husson et al. 2012). A decline in the late Maastrichtian marine $^{187}\text{Os}/^{188}\text{Os}$

record of the Bottaccione has been related to the second and main phase of Deccan volcanism (Robinson et al. 2009). The Gubbio sections are thus very suitable to investigate the tempo and duration of biotic and environmental changes across the K-PgB event.

We present a new high-resolution cyclostratigraphic time scale for all the bio-horizons, paleoclimatic events and biotic changes spanning the last 450 kyr before the K-PgB and investigate the rates of change and relationships between carbon-isotopic excursions, biotic changes and Deccan volcanism before and after the K-PgB mass extinction.

GEOLOGY AND METHOD

Geological setting

The Upper Cretaceous Scaglia Rossa Formation is located in the central Apennines (Italy), with major outcrops in the Contessa Highway valley and Bottaccione Gorge, near Gubbio. It is composed of hard pelagic limestones, with approximately 10% of foraminifera and 5% of clay in a matrix of calcareous nannofossils (Lowrie et al., 1982). The formation owes its name to its red color, lighter in the Cretaceous than in the Paleogene. An interval approximately 0.50 m thick composed by white limestone occurs in the Cretaceous just before the K-PgB. Magnetite and hematite components, formed during early diagenesis, are responsible for an exceptional record of Earth magnetic field reversals by the Scaglia Rossa Formation limestones (Lowrie and Alvarez 1977).

The differences in continuity and accessibility between the Contessa Highway and Bottaccione sections necessitate using a composite section. This composite section corresponds to the uppermost Cretaceous of the Bottaccione section and the lowermost Paleogene from the Contessa Highway section.

Maastrichtian magnetostratigraphy of the Bottaccione section derived from Roggenthen and Napoleone (1977) places the Chrons C29r/C30n boundary at 369 m (344 m on their scale). A higher resolution study by Rocchia et al. (1990) on the Bottaccione section confirmed the interpretation of Roggenthen and Napoleone (1977), locating the Chrons C29r/C30n boundary between 368.72 and 368.94 m. The magnetostratigraphic interpretation of Lowrie et al. (1982) is used for the Paleogene of the Contessa Highway section.

Biostratigraphy of the Contessa section has been established for this study following the methodology presented by Gardin et al. (2012).

Cyclostratigraphic data and method

Magnetic Susceptibility (MS) measures the capacity of a substance to acquire magnetization when submitted to an external magnetic field. High frequency variations of MS in sedimentary series are correlated to the terrestrial input in the ocean (Ellwood et al. 2000). This property is easily and quickly measurable with a nondestructive tool on samples or directly on sedimentary cores. MS is thus a good paleoclimatic proxy, used frequently in cyclostratigraphic studies (Weedon et al. 1999; Norris and Röhl 1999; Weedon, Coe and Gallois 2004; Boulila et al. 2008, 2010; Guo et al., 2008; Husson et al. 2011; Martinez et al. 2012; Husson et al. 2014). MS was measured on samples from the Contessa Highway and the Bottaccione section every 5 cm using a Kappabridge KLY-2 (data available on Pangea at <http://issues.pangea.de/browse/PDI-7152>). Illite, Montmorillonite, Hematite and Magnetite, minerals found in the Scaglia Rossa bear magnetic susceptibility, and could be affected by reworking (Lowrie and Alvarez, 1977). Nevertheless the important similarities between Hole 1267B and Gubbio section magnetic susceptibility record indicate a good conservation of the sedimentary record. The amount of diagenetic Glaucony, which possess a relatively high magnetic susceptibility, is not significant in the sediments except in the KPgB clay layer (Ellwood et al., 2003). The high magnetic susceptibility values observed at the boundary

result however mainly from the presence of magnetic microspherules and hematite (Verma et al., 2002).

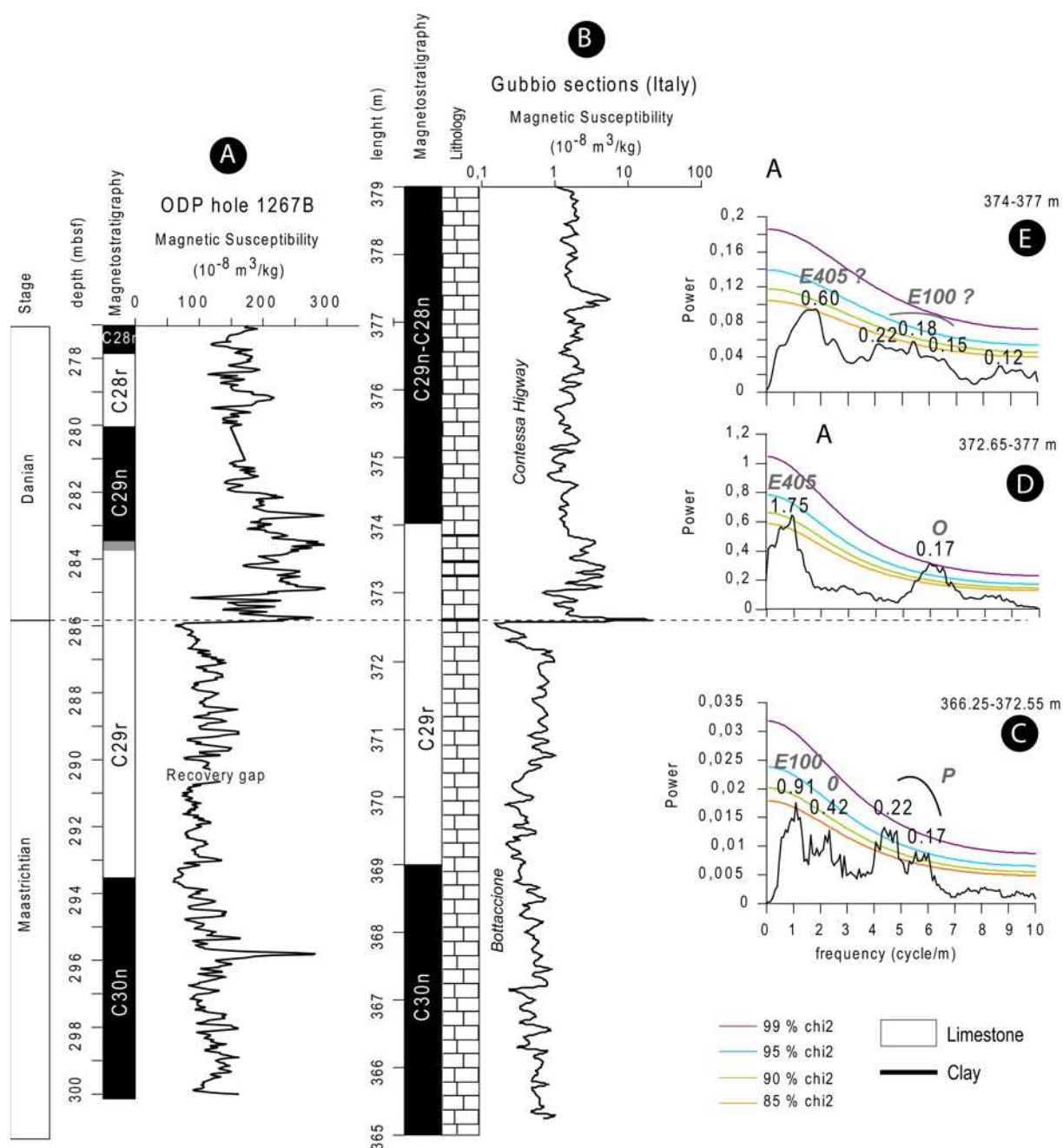


Figure 2: Cyclostratigraphic analysis of Magnetic Susceptibility variations from the Contessa Highway and the Bottaccione sections (Italy) on both sides of the Cretaceous-Paleogene boundary (B). Lithology of the Contessa Highway section for the C29r interval is from Coccioni et al. (2010). The MS signal from ODP Hole 1267B is also presented for comparison (A). The analysis method used was the multitaper method, completed by a Chi2 test to assess the reliability of the cycles detected. Comparison to MS variations from ODP Hole 1267B (South Atlantic) highlight a high similarity between the two signals. Precession and 100 kyr eccentricity variations are well defined in the Cretaceous, as highlighted by the spectral analysis of this interval (C), whereas the perturbations of the sedimentation rate following the K-PgB affect the record of the orbital parameters variations in the Paleogene. Results from the lowermost Paleogene spectral analysis (D) are very different from from analysis results of the C29n-C28n interval (E).

MS measurements covering 6 m across the K-PgB, obtained on the Bottaccione section, have been previously compared to several records in Oman, Caribbean, North Atlantic and South Pacific by Elwood et al. (2003), highlighting very similar features between these sites. According to Elwood et al. (2003), these features could be used to locate the K-Pg boundary interval. This is confirmed by Font et al. (2011), who studied MS variations across the K-PgB in Gubbio and Bidart (France) sections. The K-PgB is characterised by an abrupt positive shift of the MS concomitant with the boundary clays. An anomalous interval with very low MS precedes the boundary, due to an unusual Cl-bearing iron oxide Font et al. (2011). This interval is related by Font et al. (2011) to possible reactions of solid/aqueous aerosols and volcanic gas emitted by the Deccan Traps within atmospheric plume, considering a dry environment. It could be a marker of the Deccan Trap main eruptive phase. A comparison between the MS signal obtained from Gubbio sections and MS variations measured on cores from ODP Hole 1267B highlights very similar features (Fig 2.A). Previous cyclostratigraphic studies of Site 1267 cores (Westerhold et al. 2008; Husson et al. 2011) highlighted orbital control of the sedimentation by 100 kyr and 405 kyr eccentricity cycles, on both sides of the K-PgB. Similar low and high frequency cycles can be observed in the Maastrichtian of the Gubbio sections and Hole 1267B, with a progressive decrease of the MS mean value until the K-PgB (Fig 2.B).

At the Bottaccione section, MS values are lower in the white beds covering the last 50 cm of the Cretaceous before the K-PgB. Values in the Paleogene are significantly higher than in the Cretaceous at both sites (Fig 2.B). The K-PgB is characterised by a very high value, of more than $21.10 \cdot 10^{-8} \text{ kg/m}^{-3}$ in the Bottaccione section. High MS values at the K-PgB are found in several sections, and can be attributed to the presence of multidomain magnetite microspherules (Worm and Banerjee 1987). The K-PgB is immediately followed by a broad cycle of about 1.5 m width divided into higher frequency peaks (Fig 2.B). This particular feature is also observed in Hole 1267B. This feature was linked to a high perturbation of the sedimentation following the K-PgB, supposedly hampering cyclostratigraphic analyses of the lowermost Paleogene (Herbert et al. 1990; Dinares Turell et al. 2003; Westerhold et al. 2008; Kuiper et al. 2008). A short wavelength cycle with very high amplitude can also be observed in the Contessa Highway record between 342.25 and 342.55 m (Fig 2.B).

Cyclostratigraphic analysis has been performed using spectral analysis by multitaper method (MTM) (Thomson, 1982). Prior to the analyses, a linear and a polynomial detrending was applied to suppress long-term trends. Links between the cycles detected in the analyzed time series and known orbital parameter variations are assessed using the frequency ratios method (Mayer and Appel 1999), based on the orbital frequencies estimated for the Cretaceous (Berger and Loutre 1994; Laskar et al. 2004). The red-noise hypothesis is tested using scripts written under Matlab™ (available at <http://www.mathworks.com/matlabcentral/fileexchange/45539-rednoiseconfidencelevels>) based on the work of Mudelsee (2002) and Schulz and Mudelsee (2002).

CYCLOSTRATIGRAPHIC ANALYSIS

The Cretaceous and the Paleogene part of the record are studied separately, considering the very different range of MS values and signal features on either side of the K-PgB. The composite signal is plotted using a log scale to take these discrepancies into account (Fig. 2.B).

Spectral analysis performed on the MS variations of the Cretaceous Bottaccione section (Fig 2.C) highlights cycles with wavelengths ranging from 0.17 to 0.91 m. High frequency cycles with wavelength of 0.17 and 0.22 m possess a high power. Considering a sedimentation rate of 10-15 m/Myr as estimated by Lowrie et al. (1990), the detected cycles are in the orbital band. Two powerful cycles with wavelengths of 0.17 and 0.22 m would correspond to the two modes of the precession, cycles with a wavelength of about 0.42 m are attributed to an obliquity forcing, and cycles with a wavelength of 0.91 m to a short eccentricity forcing (Fig 2.C). This is confirmed by matching of the observed frequency ratios to the predicted orbital parameter frequency ratios.

A spectral analysis performed on the lowermost Paleogene highlights two main cycles with wavelengths of 0.17 and 1.75 m (Fig 2.C). The low frequency peak seems to correspond to the broad, high amplitude cycle covering an interval from 372.6 to 374.1 m (Fig 2.D). The strength of the match for the two cycles frequency to the predicted frequency ratios of 405 kyr eccentricity to obliquity is taken as strong support for the proposed average sedimentation rate. Moreover, considering a sedimentation rate of 2.5-3 m/Myr as estimated by Lowrie et al. (1990) for the lowermost Paleogene, cycles with a wavelength of 1.75 m would characterize a record of the 405 kyr eccentricity, whereas 0.17 m cycles correspond to an obliquity forcing. Two high frequency cycles, located at 373.2 and 373.4 m, could correspond to two hyperthermal events, as observed by Coccionni et al. (2012). The expression of the orbital control within the sedimentary record could have been enhanced by these climatic events, or these two high frequency cycles could be an overprint of these events. Further studies based on different paleoclimatic proxies are thus needed to ascertain the nature of these two high frequency MS cycles. A higher sampling rate allowing the recovery of precession cycles, would help to better assess the orbital control, and better understand the strong perturbations of the sedimentation in the interval following the K-PgB event.

A second spectral analysis is performed on the interval from 374 to 377 m, before a cycle with high MS value that disturbs the spectral analysis (Fig 2.E). Cycles with wavelengths ranging from 0.15 to 0.60 m are detected. Frequency ratios of the high frequency cycles (0.15 m to 0.22 m) and low frequency cycle (0.60 m) are close to the 100 kyr eccentricity to 405 kyr eccentricity frequency ratio. This would suggest an important drop of the sedimentation rate at the beginning of chron C29n, preventing the detection of precession and obliquity cycles.

No other evidence of such an important drop of the sedimentation rate can be observed on this section, and the cycles detected have a low confidence level (below 85%). Uncertainties are thus high on this interval, and a study of a longer Paleogene interval is needed to better constrain cycle attributions.

The spectral analyses illustrate a drop of the sedimentation rate across the K-PgB, characterized on the periodograms by a shift of the recorded cycles toward higher frequencies (Fig 2). This is in accordance with Lowrie et al. (1990), who indicated a drop of the sedimentation rate between the Maastrichtian and the lowermost Danian, interpreted as a strong decrease in carbonate productivity.

The detection of an orbital control of the sedimentation in the Bottaccione allows the construction of a cyclostratigraphic time-scale covering the Maastrichtian. The low resolution of the study in the Paleogene of the Contessa section prevents the development of a cyclostratigraphic timescale. The timescale presented here is based only on the GTS 2012 (Ogg, 2012) estimate of the Paleogene part of Chron C29r duration, considering a constant sedimentation rate during the lowermost Paleogene. It can be noted that the sedimentation rate inferred through this method is similar to the one obtained using the cyclostratigraphic results.

Due to the chaotic behavior of the solar system (Laskar et al. 2004), the 405 kyr component of the eccentricity is the only orbital parameter for which variations remain predictable down to the K-PgB. It is not realistic to perform a direct calibration to the most recent astronomical solutions (Laskar et al. 2011) using the identified 405 kyr eccentricity cycles considering the short length of our signal (ca. 800 kyr). The cycle identification and amplitude variations obtained on Gubbio sections need to be ascertained by the study of other sites before any attempt of a calibration with a precession-scale accuracy.

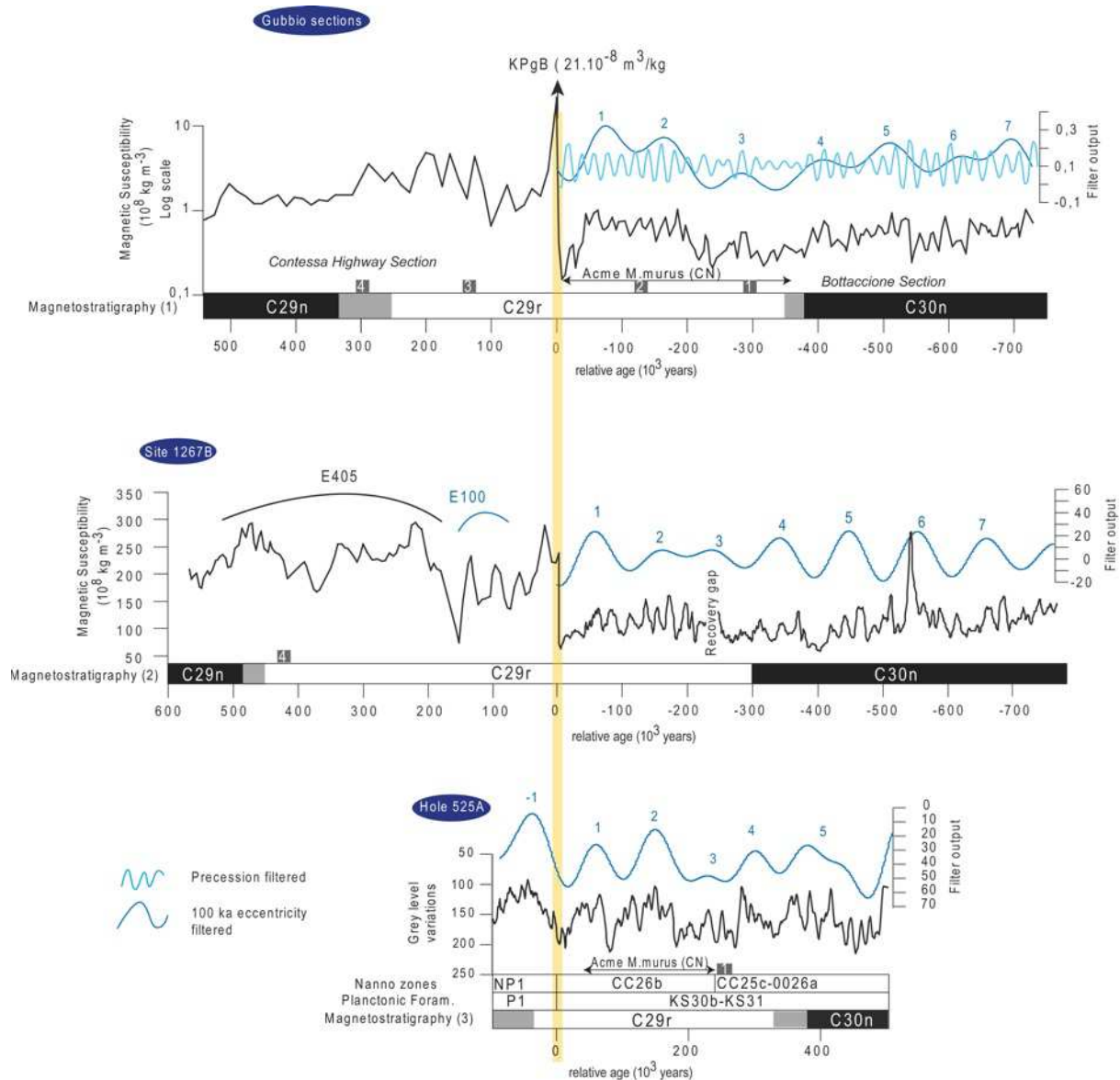


Figure 3: Cyclostratigraphic framework covering the Maastrichtian part of Chron C29r on Gubbio sections, ODP Site 1267B and DSDP Site 525A. The temporal frame for Gubbio sections is based on the identification of the precession cycles for the Cretaceous part of the MS variations. The temporal frame for the Paleogene C29r part is based on the GTS 2012 (Ogg 2012) estimate for the duration of the Paleogene C29r part. The very good Cretaceous record of the Bottaccione allowed a filtering highlighting the evolution of 100 kyr cycles and precession. Numbers in gray squares indicate the bio-horizons from Gardin et al. (2012) and this study, and Coccioni et al. (2012b): 1= FO *M. prinsii*, 2=FO *P. hantkeninoides*, 3= FO *P. eugubina*, 4= FO *C. intermedius*. Magnetostratigraphy 1) from Lowrie et al. (1982) for the Paleogene and Rocchia et al. (1990) for the Maastrichtian 2) from Westerhold et al. (2008) for the Paleogene and Zachos et al. (2004) 3) from Chave (1984).

The cyclostratigraphic time-frame has thus been created based on the identification of precession cycles in the Maastrichtian. The K-PgB is defined as zero in this time scale, and a value in time has been attributed to each cycle boundary based on its period and cycle counts on both sides of the K-PgB (Fig. 3). The relative age of each point between the boundaries has then been interpolated. Time is negative in the Cretaceous, and positive in the Paleogene. The duration of the precession is based on an average of the two modes of the precession for the Late Cretaceous (Laskar et al. 2004). The 100 kyr eccentricity and precession are filtered using a Taner filter (Taner 2000) to highlight their evolution in the Cretaceous (Fig 3). Building this relative timescale allows correcting the sedimentation rate variations and comparing the events on both sides of the Cretaceous-Paleogene boundary.

DISCUSSION

Duration of Chron C29r Maastrichtian

As previously observed on other sedimentary records (Herbert et al. 1995; Westerhold et al. 2008; Kuiper et al. 2008; Husson et al. 2011; Batenburg et al. 2012), the K-PgB of the Gubbio area is situated in a minimum of the 405 kyr eccentricity variations in the MS signal.

Herbert and d'Hondt (1990) first estimated the duration of Chron C29r based on DSDP Sites from the South Atlantic. This work was later pursued by Herbert et al. (1995), who identified 18.5 precession cycles in the Maastrichtian part of C29r (M-C29r), equivalent to 377 ± 0.2 kyr (Table 1). Based on an astronomical calibration of ODP sedimentary records, Westerhold et al. (2008) estimated the duration of M-C29r between 345 ± 11 kyr (calibration option 1) and 327 ± 11 kyr (calibration option 2). Astronomical calibration of ODP Hole 1267B by Husson et al. (2011) provided an M-C29r estimate of 300 ± 20 kyr, corresponding to 15 precession cycles, slightly less than the previous estimates. A recent cyclostratigraphic study based on limestone-marl alternations in the Zumaia (Spain) section resulted in an estimation of 17.5 precession cycles, equivalent to a duration of 350 ± 11 (option 1) or 340 ± 11 (option 2), respectively considering a K-PgB dated to 65.56 ± 0.02 Ma or 65.97 Ma (Batenburg et al. 2012) (Table 1). However, the magnetostratigraphy of the Zumaia section bears large uncertainties due to remagnetization. Therefore, the Chrons C30n/C29r boundary location was not defined directly on the section but by correlating the Zumaia record to ODP Sites 1262 and 1267 (Batenburg et al. 2012).

Duration of the M-C29r is estimate here based on the time scale inferred through precession cycles counting, considering a constant sedimentation rate between each cycles boundary. The duration uncertainty takes into account the error margin on the location of the C29r-C30n boundary. Our results for the location for the Chrons C29r/C30n boundary at 369 m from the Bottaccione section (Figs. 2) are in good agreement with previous estimations (Roggenthien and Napoleone 1977; Rocchia et al. 1990). The Cretaceous part of the C29r covers 18 precession cycles, equivalent to a duration of 357 ± 40 kyr (Table 1). A smaller estimation of 300 ± 20 kyr obtained from ODP Hole 1267B study by Husson et al. (2011) may be explained by the recovery gap at 290.3–290.65 mbsf (Fig. 2).

Age estimations of bio-horizons and isotopic event

Many important bio-horizons, as well as biotic and environmental changes in the K-PgB of the Gubbio reference sections have been discussed in the literature over the years (Coccioni et al. 2010; Coccioni et al. 2012a; Coccioni et al. 2012b; Gardin et al. 2012 and references therein). The newly constructed cyclostratigraphic time-frame, covering Chron C29r and anchored to the K-PgB at 66.04 Ma (Renne et al. 2013), can thus be used to provide ages and/or durations of these signals (Fig. 4). In addition, some of these results can be compared to Hole 525A, which has recently been calibrated to the astronomical solution (Husson et al. 2011).

The first occurrence (FO) of nannofossil *Micula prinsii*, which approximates the base of Chron C29r (Gardin et al. 2012), is situated at 66.3 Ma in the Bottaccione section and at Site 525 (Table 2, Fig. 4). The acme of nannofossil *Micula murus*, considered as a good marker of Deccan-induced intense warming in sea-surface waters of the late Maastrichtian (Thibault and Gardin 2007; 2010), starts in the Bottaccione section at 66.36 Ma and ends 33 kyr prior to the K-PgB. This is entirely consistent with estimations obtained at Site 525A, where the acme of *M. murus* occurs in coincidence with the negative excursion in benthic foraminiferal $\delta^{18}\text{O}$ (Fig. 4). The FO of *Crucioplacolithus intermedius*, marker of the base of nannofossil zones NP2 and CP1b, and considered as a proxy for the Chrons C29r/C29n boundary, is situated at 65.67 Ma (Fig. 4).

Voigt et al. (2012) identified and named a number of carbon isotopic excursions in the latest Maastrichtian with similar amplitudes across a wide range of shelf and oceanic sections from the Boreal realm, the Tethys, and the Atlantic and Pacific oceans. The slight negative $\delta^{13}\text{C}$ excursions K-PgE1 and K-PgE3 bracket the longer stable interval K-PgE2 at the Bottaccione section (Voigt et al. 2012). K-PgE1 and K-PgE3 span 140 kyr (from ca. 66.65 to ca. 66.51 Ma) and 200 kyr (from ca. 66.32 to ca. 66.12 Ma) respectively (Fig. 4, Table 3).

The DAN-C2 early Paleogene hyperthermal event identified by Coccioni et al. (2010) in the Contessa Highway section would start at about 65.8 Ma. This event is characterized by two sharp concomitant negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ excursions with short durations, perhaps <50 kyr, named here Dan-C2a and Dan-C2b (Fig. 4, Table 3). The lower C29n hyperthermal event would last only a few kyr and occurs at about 65.73 Ma. This last event, though only defined by one data point, is mirrored in the lithology of the Contessa section by a thin layer of clay, and corresponds to a peak of opportunistic taxa in the benthic foraminifer assemblage, similarly to the layers marking the DAN-C2 events (Coccioni et al. 2010).

Evolution of $^{187}\text{Os}/^{188}\text{Os}$ ratios through the Maastrichtian is characterized by to decrease phases. Our age model shows that the onset of the first $^{187}\text{Os}/^{188}\text{Os}$ decline started at about 66.6 Ma, within the top of Chron C30n, with a shift from 0.6 to 0.42 (Fig. 4, Table3). This decline spanned 240 kyr, in agreement with Robinson et al. (2009) rough duration approximation. A stable interval without variations followed from 66.28 to 66.13 Ma. A second sharp $^{187}\text{Os}/^{188}\text{Os}$ decrease marked the end of Chron C29r Cretaceous part, covering 90 kyr in the Bottaccione section, with a decline from 0.42 to 0.25 (Fig. 4 and Table 3).

Paleoenvironmental changes across the Cretaceous-Paleogene boundary

Although it has been argued that Deccan volcanism was initiated slightly before the K-PgB (Courtillot et al. 2003; Keller et al. 2008; Robinson et al. 2009), there is still doubt on the precise timing of the main volcanic phases and their relationship with the K-PgB mass extinction (Chenet et al. 2007; Keller et al., 2008; Schulte et al. 2010).

It has been shown that $^{187}\text{Os}/^{188}\text{Os}$ variations prior to the KPg-B may be related to weathering of the fresh basalts of the Deccan traps (Ravizza and Peucker-Ehrenbrink 2003; Robinson et al. 2009). The mantle rocks $^{187}\text{Os}/^{188}\text{OS}$ ratio is about 0.13, an order of magnitude lower than the 1.3 ratio obtained from continental erosion input (Ravizza and Peucker-Ehrenbrink, 2003). The residence time of Osmium in the ocean is short, about 10 kyrs (Peucker-Ehrenbrink and Ravizza, 2000). An important decrease in $^{187}\text{Os}/^{188}\text{OS}$ ratio is thus likely to reflect the weathering of the late Maastrichtian large igneous provinces. The second $^{187}\text{Os}/^{188}\text{Os}$ decreased observed in Gubbio sections has been related to a possible second phase of Deccan volcanism or alternatively, it has been attributed to the addition of extraterrestrial Os from the K-Pg impactor by bioturbation mixing in the sediments beneath the K-PgB (Robinson et al. 2009; Ravizza and VonderHaar 2012). This second decrease began 47 kyr before an interval of lower MS values (Table 3) preceding the K-PgB and linked by Font et al. (2011) to possible reactions between aqueous-solid aerosols and volcanic gases in a dry climatic context.

K-PgE1 and K-PgE3 negative isotopic excursions are only ca. 0.25 per mil in the Gubbio area and the South Atlantic (Fig. 4). Although of a small amplitude, these events are reliably recorded in other oceanic basins (Sites 305 and 1210B, central Pacific, Stevns-1 and Hemmoor, Chalk Sea Basin) where their magnitude can reach up to 0.5 per mil (Thibault et al. 2012a, Voigt et al. 2012). Major shifts towards lower $\delta^{13}\text{C}$ values in marine organic matter and carbonate have been linked to an increase of atmospheric pCO_2 fed by volcanism (Kump and Arthur, 1999).

K-PgE1 occurred simultaneously with the onset of the first decrease in $^{187}\text{Os}/^{188}\text{Os}$ (~66.6 Ma), which suggests a direct relationship between the two geochemical events and the onset of a pulse in Deccan volcanism. Moreover, we note here that the onset of the second decrease in $^{187}\text{Os}/^{188}\text{Os}$ occurred during the K-PgE3 negative $\delta^{13}\text{C}$ excursion (Fig. 4). Apart from the boundary clay sharp $\delta^{13}\text{C}$ excursion which can be explained by a drop of primary

productivity (Hsu and McKenzie 1985; Schulte et al. 2010, cum biblio) or as a reduced export production (D'Hondt et al. 1998), we propose that most of the short-lived negative $\delta^{13}\text{C}$ excursions occurring in the late Maastrichtian and early Danian were actually the expression of Deccan CO_2 out-gassing. Chenet et al. (2009) have dated Deccan volcanic events based on radiogenic dating and biostratigraphy. Two major volcanic pulses would take place around 65 $\pm$ 1 Ma, the first one just before the KPgB and the second one approximately covering the C29r/C29n boundary. The $\delta^{13}\text{C}$ excursion timing proposed here based on cyclostratigraphy is thus in agreement with the Deccan volcanic episode occurring within the C29r Cretaceous part.

The amplitudes of $\delta^{13}\text{C}$ excursions observed here are smaller than the amplitude of other excursions related to volcanism, such as the Permo-Triassic boundary events (Kamo et al 2003), the Triassic-Jurassic boundary event (Hesselbo et al., 2002), the Toarcian ocean anoxic event (Suan et al, 2008; Boulila et al, 2014), where a reinforcement of the excursion by methane degassing has been proposed (Hesselbo et al, 2000), and the Paleocene-Eocene thermal maximum (Zachos et al., 2003). However, the rapidity of these events as demonstrated here does not preclude the possibility that some of these excursions may actually be due to clathrate destabilization. Several studies have shown that massive flood volcanism does not only possibly participate to a raise in atmospheric CO_2 by direct injections but also increases the chances to destabilize methane fields by contact metamorphism of sills and dyke intrusions (Svensen et al., 2004; Retallack and Jahren, 2007; Aarnes et al., 2010, 2011).

A major environmental perturbation started at ca. 66.35 Ma, as expressed in bottom waters by the decrease in benthic foraminiferal $\delta^{18}\text{O}$ and in surface waters by the dwarfing of planktic foraminifers, the acme of the tropical nannofossil species *Micula murus*, and a slight decrease in nannofossil species richness (Abramovich and Keller 2003, Thibault and Gardin 2010). Also, this perturbation possibly correlated with a prominent extinction level of benthic faunas at southern high latitudes within the Cretaceous part of Chron C29r (Tobin et al. 2012). The absence of Lilliput effect in Cheilostome Bryozoans colony following the K-Pg boundary highlights the biotic system complexity, and the importance of the information provided by each organism responses to environmental changes (Sogot, Harper and Taylor, 2014). No causes of environmental perturbation independent from volcanism influence have been detected so far in the uppermost Maastrichtian. Only the last 100 kyrs of the Cretaceous are characterized by a short cooling episode (Wilf et al, 2003), postdating the beginning of foraminifer dwarfism, which is itself very well correlated to the greenhouse warming. Perturbation of the biota began ca. 200 kyr after the first volcanic pulse expressed by KPgE1 and nearly simultaneously to K-PgE3 event. The biotic response could be thus a delayed response to K-PgE1, or a direct response to K-PgE3.

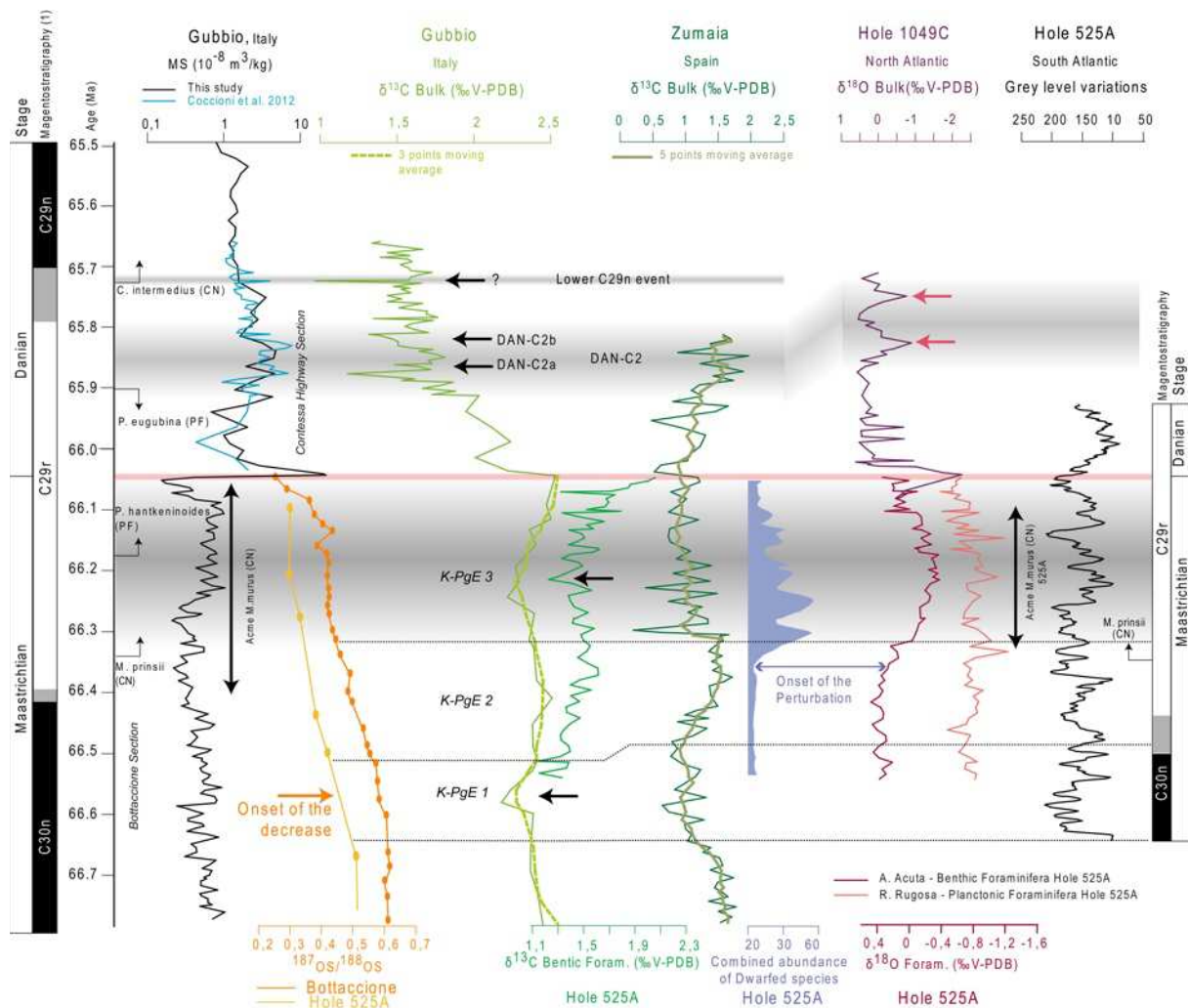


Figure 4: Correlation between the Gubbio sections, DSDP Hole 525A, Zumaia section and ODP Hole 1049C. The relative time scale for the Bottaccione section has been tied to a K-PgB dated to 66.04 Ma, in agreement with Renne et al. (2013) most recent radiogenic dating. The Paleogene timescale is based on the GTS 2012 (Ogg 2012) estimation for the duration of the Paleogene part of Chron C29r, considering a constant sedimentation rate during this interval. Age model of Hole 525A comes from the astronomical calibration of this site by Husson et al. (2011). Bottaccione section: magnetostratigraphy from Rocchia et al. (1990), biostratigraphy from Gardin et al. (2012) and this study, Osmium data from Robinson et al. (2009), and $\delta^{13}\text{C}$ from benthic foraminifers data from Voigt et al. (2012). Contessa section: magnetostratigraphy from Lowrie et al. (1982), biostratigraphy from Coccioni et al. (2012b) and this study, magnetic susceptibility from Coccioni et al. (2012b) and this study, and $\delta^{13}\text{C}$ from bulk data from Coccioni et al. (2012b). Zumaia section: $\delta^{13}\text{C}$ from bulk data from Batenburg et al. (2012). Hole 1049C: $\delta^{18}\text{O}$ from bulk data from Coccioni et al. (2012b). Hole 525A: magnetostratigraphy from Chave (1984), biostratigraphic data from Thibault and Gardin (2007), Osmium data from Robinson et al. (2009), $\delta^{18}\text{O}$ data from Li and Keller (1998a; 1998b), combined abundance of planktonic foraminifers dwarfed species from Abramovitch and Keller (2003), and grey level variations from Husson et al. (2012). Numbers in italic indicate the isotopic events identified and named by Voigt et al. (2012). These events are separated by discontinuous lines. Black arrows indicate short-lived negative $\delta^{13}\text{C}$ excursions that possibly mark volcanic pulses, as defined by Coccioni et al. (2010). Red arrows indicate early Danian hyperthermal events associated to $\delta^{13}\text{C}$ excursions. CN= Calcareous Nannofossils, PF= Planktonic Foraminifers.

The absence of a direct biotic and climatic response to the first excursion in $\delta^{13}\text{C}$ and coincident decrease in Os isotopes suggest buffering of environmental perturbations in the late Maastrichtian oceanic realm. In addition to these extreme volcanic pulses, continuous minor eruptions probably contributed to increase atmospheric CO_2 levels and other greenhouse gases, resulting in intense warming of surface and bottom waters. Although no warming is expressed in planktic foraminifer $\delta^{18}\text{O}$ at Site 525A, nannofossil cool-water taxa

show a marked decrease at this Site within the top of Chron C30n, prior to the acme of *Micula murus* (Thibault and Gardin 2007). In the tropical Pacific, the relative abundance of *Micula murus* actually started to increase slightly in the top of Chron C30n (Thibault and Gardin 2010). In addition, atmospheric temperatures estimated through leaf-margin analysis of terrestrial plants in North Dakota suggest an onset of warming ca. 150 kyr before the C30n/C29r reversal (Wilf et al. 2003). These results suggest that warming in the atmosphere and oceanic surface waters occurred before the intense warming of bottom waters, possibly in coincidence with K-PgE1 and the onset of the $^{187}\text{Os}/^{188}\text{Os}$ decline. The delayed biotic changes in the calcareous plankton regarding the beginning of the volcanic pulses thus evoke a threshold response to a maximum temperature increase in sea-surface waters within Chron C29r.

Reference	Duration (kyr)
This study	365 +/-40
GTS 2012	~0.355
Batenburg et al. (2012)	350 +/-11 (option 1) 340 +/- 11 (option 2)
Thibault et al. (2012)	397+/-22
Husson et al. (2011)	300+/-20
Westerhold et al. (2008)	345+/-11 (option 1) 327+/-11 (option 2)
Herbert et al. (1995)	377 +/- 20 (18,5 pc)
Herbert and D'Hondt (1990)	340 (17 +/- 2 pc)

Table 1: Available cyclostratigraphic estimations of the duration of the Chron C29r Maastrichtian in kyr. Pc = precession cycles identified. For this study, uncertainties are based on the uncertainties on the positions of the Chron boundaries and on the cycle identifications (+/- 1 precession cycle).

Planktonic foraminiferal and calcareous nannofossil horizons, Chron boundaries.	Depth (m)	Age (Ma)
KPgB	372.6	66.04 +/- 0.02
Top acme <i>Micula murus</i> (CN)	372.4 +/- 0,05	66.05 +/- 0,07
FO <i>Plummerita hantkeninoides</i> (PF)	371.15 +/- 0,05	66.18 +/- 0,07
FO <i>Micula prinsii</i> (CN)	369.45 +/- 0,3	66.34 +/- 0,32
Base acme <i>Micula murus</i> (CN)	368.9 +/- 0,025	66.40 +/- 0,045
C30n/C29r	368.83+/-0.11	66.41+/-0.1

Table 2: Age estimations of Chron C29r boundaries, Maastrichtian and Paleogene bio-horizons considering an age of 66.04 for the Cretaceous-Paleogene boundary according to the most recent radiogenic dating (Renne et al. 2013). Biostratigraphic data are from Gardin et al. (2012).

Comparing the Maastrichtian $\delta^{13}\text{C}$ excursions to those of the Danian, we observe that short-lived environmental perturbations and their associated time response are different before and after the impact event. In contrast with late Maastrichtian perturbations, early Danian isotopic excursions at the Contessa section are larger (>0.5 per mil) and seems to span shorter durations (<50 kyr for the two sharp negative peaks of the DAN-C2 event and a few kyr only

for the lower C29n event). A longer record is needed on Zumaia section to highlight these events. In addition, the biotic response, as expressed by the increase of opportunistic forms of benthic foraminifers and calcareous nannofossils coincided exactly with the timing of these events (Coccioni et al. 2010). Biotic recovery in the early Paleogene varied between the South Atlantic and Indian Ocean, and the Pacific and neritic Atlantic, and ranged from 350 kyr to 2 Myr after the K-PgB mass extinction (Hull and Norris 2011). Moreover, it has been hypothesized that the transition from the early recovery communities to later communities has been enabled by local short-term environmental perturbations (Hull et al. 2011). For example, such perturbations were coincident with assemblage turnover in the North Pacific (Hull et al. 2011). During the recovery, heterogeneous Danian paleoecosystems were very sensitive and reacted rapidly to short environmental perturbations (D'Hondt et al 1998; D'Hondt 2005).

Age (Ma) (+/- 0,03)	Relative age (Ma) (+/- 0,02)	Event
66.04	0	Cretaceous-Paleogene Boundary
66.08	-0.04	End of planktonic foram dwarfism high abundance
66.084	-0.044	Onset of the MS decrease
66.12	-0.08	End of K-Pg E3
66.131	-0.091	Onset of the second $^{187}\text{Os}/^{188}\text{Os}$ decrease
66.32	-0.28	Onset of K-Pg E3
66.32	-0.28	Onset of $\delta^{18}\text{O}$ decrease
66.348	-0.308	Onset of planktonic foram dwarfism high abundance
66.509	-0.469	End of K-Pg E1
66.578	-0.538	Onset of the first $^{187}\text{Os}/^{188}\text{Os}$ decrease
66.651	-0.611	Onset of K-Pg E1

Table 3: Age estimations of Maastrichtian events considering an age of 66.04 for the Cretaceous-Paleogene boundary according to the most recent radiogenic dating (Renne et al. 2013).

If all the short-lived negative $\delta^{13}\text{C}$ excursions occurring in the late Maastrichtian and early Danian ~~are~~ were the expression of volcanic pulses, then the contrast in their amplitude and durations on both sides of the boundary must be discussed. This contrast may suggest a difference in the intensity of volcanic pulses across the K-Pg that is not indicated in the study of the pile of Deccan lavas across the K-PgB (Chenet et al. 2007; Chenet et al. 2009). More likely, this contrast actually reflects the expression of a different response of oceanic ecosystems to similar perturbations across the K-PgB. The stable oceanic ecosystem of the late Maastrichtian could buffer environmental perturbations through a series of complex feedbacks whereas the fragile and highly disturbed early Danian oceanic ecosystem likely amplified any additional environmental perturbations that occurred after the extraterrestrial impact.

CONCLUSIONS

Cyclostratigraphic study performed on MS variations from the Contessa Highway and Bottaccione sections (Gubbio, Italy) has allowed the construction of a precise relative timescale of Chron C29r Maastrichtian part. Our results provide an estimation of Chron C29r Maastrichtian duration (365 +/-40 kyr), which agrees with previous estimations. Ascertaining more precisely the duration of the Paleogene part of the C29r would benefit from a study with an even higher sampling rate, considering the remaining uncertainties on two high frequency cycles.

The temporal framework based on this timescale brings forward precise dating of bio-horizons, biotic changes, stable isotopic excursions and changes in Osmium isotope composition recorded in the Gubbio sections and in the astronomically calibrated Site 525A (South Atlantic). This comparison highlights the synchronicity of Maastrichtian K-PgE1 and K-PgE3 $\delta^{13}\text{C}$ negative excursions with the two-step decrease in Osmium isotopes, previously interpreted as a marker for the main Cretaceous phase of Deccan volcanism.

This study highlights that the durations and magnitude of these $\delta^{13}\text{C}$ short-lived excursions are different across the KPg-B. Danian isotopic excursions are larger in magnitude and span shorter durations (ca. 30 kyr for each peak of the DAN-C2 event, a few kyr for the lower C29n event vs. 130 and 140 kyr for K-PgE1 and K-PgE3).

The biotic response to Danian perturbations is nearly instantaneous whereas a 200 kyr delayed response of the late Maastrichtian biota to environmental perturbations related to the first volcanic pulse, suggests a threshold reaction to the atmospheric CO₂ buildup.

These differences reflect different sensitivities in the late Maastrichtian and early Danian carbon cycle and ecosystems. The stable late Maastrichtian oceanic ecosystem could buffer environmental perturbations by complex feedbacks. In contrast, the Danian ecosystem, greatly weakened after the extraterrestrial impact, have amplified additional Deccan-induced environmental perturbations.

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