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Multiproxy Cretaceous-Paleogene boundary event stratigraphy: an Umbria-Marche basin-wide perspective

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ABSTRACT

The complete and well-studied pelagic carbonate successions from the Umbria-Marche Basin (Italy) permit the study of the event-rich stratigraphical interval around the Cretaceous-Paleogene (K-Pg) boundary (e.g. Deccan volcanism, boundary impact, Paleocene recovery and climate). The robustness of various proxy records (bulk carbonate δ^{13}C, δ^{18}O, 87Sr/86Sr and Ca, Fe, Sr and Mn concentrations) inside the same basin (i.e. Umbria-Marche) is tested by investigating several stratigraphically equivalent sections. Besides the classical Gubbio sections of Bottaccione and Contessa, the new Morello section is put forward as an alternative sampling location for this stratigraphical interval. Handheld X-Ray Fluorescence (pXRF) elemental profiles (Ca, Fe, Sr, Mn) simultaneously proof to be efficient regional chemostratigraphical tools and provide paleoenvironmental information. For example, the characteristic pattern of the Sr/Ca profile across the K-Pg boundary is driven by the extinction and recovery of coccolithophores. Cyclostratigraphic analyses show the imprint in the sedimentary record of a 2.4 Myr eccentricity minimum around 66.45-66.25 Ma and suggest that the occurrence of the DAN-C2 hyperthermal event was astronomically paced.

1. INTRODUCTION

The Cretaceous-Paleogene (K-Pg) boundary is one of the major mass extinctions of the Phanerozoic (Raup and Sepkoski, 1982). The K-Pg mass extinction is also one of the most debated ones (e.g. Schulte et al., 2010 and comments by Archibald et al., 2010; Courtillot and Fluteau, 2010; Keller et al., 2010). A large number of K-Pg boundary sections worldwide are characterized by the presence of iridium and other platinum group elements (PGEs), often in combination with ejecta layers which contain shocked minerals, spherules and Ni-rich spinels (Alvarez et al., 1980;
Smit and Hertogen, 1980; Montanari et al., 1983; Claeys et al., 2002; Schulte et al., 2010). Radioisotopic dating (\(^{40}\)Ar/\(^{39}\)Ar) of melt rock from the Chicxulub impact crater (Hildebrand et al., 1991; Swisher et al., 1992) and tektites from several K-Pg boundary sections (Renne et al., 2013) demonstrates their synchrony and favors the hypothesis that a large impact caused the mass extinction. An alternative hypothesis for the K-Pg mass extinction is a causal relationship with the occurrence of a large igneous volcanic province (basaltic Deccan Traps). Radiometric dating of the Deccan basalts (\(^{40}\)K-\(^{40}\)Ar, Chenet et al., 2007) and volcanic deposits (U-Pb, Schoene et al., 2015) shows that the main second stage of Deccan volcanism started a few hundred thousand years before the K-Pg boundary and lasted until at least the earliest Danian –spanning the K-Pg extinction event. Additional arguments brought forward to support the Deccan volcanism hypothesis are based on other proxies which are interpreted as tracers for volcanic activity: e.g. Mercury (Hg) concentration and isotopic signatures, magnetic susceptibility properties and the presence of the mineral akaganéite (Font et al., 2011; Font et al., 2016; Sial et al., 2016; Font et al., 2018; Keller et al., 2018). The stratigraphical interpretation of records used in these studies is, however, subject of debate (e.g. Smit et al., 2016; Mukhopadhyay et al., 2016). Recently, a new hypothesis was presented, which suggests that the impact itself triggered a major increase in the activity of Deccan volcanism (Renne et al., 2015; Richards et al., 2015) and global magmatism, such as, for example, in mid-oceanic ridges (e.g. Byrnes and Karlstrom, 2018).

Complete and well-studied sedimentary successions, like the marine pelagic carbonates from the Umbria-Marche Basin (Italy), are suitable archives to help to dissect this event-rich stratigraphical interval. The K-Pg boundary was biostratigraphically defined for the first time in the classical sections of Gubbio, one of the K-Pg boundary sections in the Umbria-Marche basin (Luterbacher and Premoli Silva, 1964). It is also in the Gubbio sections that Alvarez et al. (1980)
first reported the iridium anomaly that led to the hypothesis of an asteroid impact. Besides the K-Pg boundary itself, the continuous and complete sedimentary records in Gubbio provide the opportunity to investigate the signatures of other events preceding and following the K-Pg boundary. A decline in the marine Osmium isotopes ($^{187}\text{Os}/^{188}\text{Os}$) record a few hundred thousand years before the K-Pg boundary was interpreted as a chemostratigraphical marker for the beginning of the second main phase of Deccan volcanism (Ravizza and Peucker-Ehrenbrink, 2003) and was also identified in the Bottaccione Gorge section at Gubbio (Robinson et al., 2009). The mass extinction itself was followed by an ecological recovery (e.g. D’Hondt et al., 1998; Coxall et al., 2006; Schulte et al., 2010). A typical feature of the post K-Pg boundary climatic system of the Paleogene is the occurrence of numerous hyperthermals events, with the Paleocene-Eocene Thermal Maximum (PETM) as most prominent example (Kennett and Stott, 1991; Zachos et al., 2001). The exact mechanism(s) behind these hyperthermals is still debated (e.g. Dickens et al., 1995; Sluijs et al., 2007; Zeebe et al, 2009), but the timing seems to be astronomically paced (Lourens et al., 2005; Galeotti et al., 2010; Littler et al., 2014; Lauretano et al., 2015; Laurin et al., 2016). The DAN-C2 is the first of these Paleogene hyperthermal events (Quillévére et al., 2008), and was identified just above the K-Pg boundary at Gubbio by Coccioni et al. (2010).

It is common practice to compare different chronologically equivalent records of various geographical locations and sedimentary settings. This is necessary to be able to assess the potential global nature and variability of worldwide climatic events. In this study, the robustness of proxy records inside the same basin (i.e. Umbria-Marche) is tested for the stratigraphical interval encompassing the K-Pg boundary by investigating various stratigraphically equivalent sections of Gubbio. The Gubbio sections encompassing the K-Pg boundary were recently investigated in detail using an integrated multiproxy cyclostratigraphic approach focusing on the sedimentology
and temporal framework (Sinnesael et al., 2016a; Sinnesael et al., 2018, with minor revisions). In addition to the conventional K-Pg sedimentological succession in the Umbria-Marche basin, the application of handheld X-Ray Fluorescence (pXRF) for chemostratigraphical correlations between the several locations in the Umbria-Marche basin (using Fe, Ca, Sr and Mn profiles) was tested in this study. To verify pXRF correlations with the well-established Gubbio stratigraphy, classical stratigraphical tools like bio- and magnetostratigraphy, δ¹³C and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope chemostratigraphy were applied on the continuous K-Pg boundary section of Morello. The new K-Pg section of Morello is stratigraphically complete, easily accessible, seems less affected by diagenesis than Gubbio and offers a good alternative for further studies next to the heavily sampled Gubbio sections. The new data from Gubbio and stratigraphically equivalent sections allow the reconstruction of more robust patterns in this events-rich interval encompassing the K-Pg boundary.

2. GEOLOGICAL AND STRATIGRAPHIC SETTING
The classical sections of Gubbio (Fig. 1B, Bottaccione (BOT) and Contessa (COH)) are known for pioneering work on the K-Pg boundary interval (Luterbacher and Premoli Silva, 1964; Alvarez et al., 1977, 1980). These sections are part of the larger Umbria-Marche Basin succession of pelagic carbonates continuously spanning the early Jurassic to the late Miocene. The Maastrichtian R2 member of the Scaglia Rossa Formation (Montanari et al., 1989) is characterized...
by pink biomicritic limestone made up of planktonic foraminiferal tests suspended in a coccolith matrix with a terrigenous component of silt and clay considered to be of eolian origin (Arthur and Fischer, 1977; Johnsson and Reynols, 1986; Sinnesael et al., 2016a). The Danian R3 member is also part of the Scaglia Rossa Formation but contains more marly intervals which are interbedded with pelagic limestones compared to the Maastrichtian R2 member (Montanari et al., 1989). The Umbria-Marche basin contains multiple other K-Pg boundary sections, from which the following were investigated in this study (Fig. 1): Fornaci East quarry (FOE), Frontale (FRO), Morello (MRL) and the Petriccio Core (PTC).

3. MATERIALS AND METHODS

Biostratigraphy at Morello

The biostratigraphical study of the Morello section (Fig. 2A) focuses on a 16-m-thick stratigraphic segment across the K-Pg boundary (29 samples from the upper 12 m of the Maastrichtian with an average resolution of ca 0.41 m and 27 samples in the lower 4 m of the Danian with an average resolution of ca. 0.15 m). Samples were treated following the cold acetolysis technique of Lirer (2000) by sieving through a 42 μm mesh and drying at 50 °C. This method enabled extraction of generally easily identifiable foraminifera even from indurated limestones, providing the possibility for accurate taxonomic determination and detailed analysis of foraminiferal specimens. All the studied materials are housed in the laboratory of the Dipartimento di Scienze Pure e Applicate, Università di Urbino, Italy. The planktonic foraminiferal standard zonations of Coccioni and Premoli Silva (2015) for the Cretaceous and of Wade et al. (2011) for the Paleogene were followed.
Magnetostratigraphy at Morello

Oriented core samples were obtained from 19 levels between -9.00 m and +2.20 m in the Morello section (Fig. 2A). They were drilled using an electric corer with a 25-mm-diameter diamond bit barrel. Samples were then segmented with a diamond disk saw at the Geological Observatory of Coldigioco (Italy) to obtain standard cylindrical paleomagnetic samples (i.e. 25-mm-diameter, 22-mm-height) from each level. Natural Remanent Magnetization (NRM) was measured at the Centre Européen de Recherche et d’Enseignement des Géosciences de l’Environnement (CEREGE), Aix-en-Provence, France) using a SQUID magnetometer (model 755R from 2G Enterprises) with a noise level of 10-11 Am². Samples were demagnetized using alternating field (AF). Demagnetization data were evaluated using principal component analyses (Kirschvink, 1980). All paleomagnetic data were processed using PaleoMac software (Cogné, 2003).

Samples for bulk geochemistry

Bulk sampling for geochemical analyses targeted the pink biomicritic limestone which is made up of planktonic foraminiferal tests suspended in a coccolith matrix. Samples from the upper 7.2 m of the Maastrichtian in BOT were sampled by Sinnesael et al. (2016a) at regular 5.0 cm intervals (~40 g powder) using an electric drill (Fig. 2D). The m-levels used in Sinnesael et al. (2016a) were rescaled (K-Pg boundary now at 0 m level instead of 100 m level). In this study negative meter levels will consequently represent Maastrichtian strata and positive meter levels Danian strata. The lowest 4.0 m Danian in COH was sampled at regular 2.5 cm intervals by collecting small hand samples (~30 cm³) with hammer and chisel from the cleaned outcrop. At MRL (Fig. 2C), similar hand samples were taken for the upper 6.0 m of the Maastrichtian (every
At FOE, hand samples were taken for the upper 4.7 m of the Maastrichtian (every 5.0 cm) and lower 0.6 m of the Danian (every 2.5 cm). Analyses of the FRO section with pXRF were done on a single polished slab spanning the upper 0.6 m of the Maastrichtian (every 15.0 cm) and lower 0.15 m of the Danian (every 2.5 cm). Analyses done on the PTC core with pXRF spanned the upper 1.25 m of the Maastrichtian (every 5.0 cm) and lower 1.80 m of the Danian (every 2.5 cm) after cleaning and polishing the core surface. Sampling was done at a higher resolution for the Danian than the Maastrichtian because of the lower sedimentation rate of the Danian strata (e.g. Mukhopadhyay et al., 2001, Sinnesael et al., 2016a).

A larger hand sample (Fig. 9) was acquired from -1.50 m in the BOT section to study the geochemical signature ($\delta^{13}$C, $\delta^{18}$O and concentrations of Ti, K, Fe, Ca and Sr) of calcite veins and styolites (pressure solution surfaces) on a high spatial resolution (Sinnesael et al., 2018, with minor revisions). Six samples were drilled from the hand sample for isotopic analyses ($\delta^{13}$C, $\delta^{18}$O) with varying compositions (Fig. 9). The first type of composition contains pure calcite from a calcite vein, a second is mixed calcite vein with surrounding pink matrix, the third type is mixed styolite with surrounding matrix and the fourth type contained a pure pink micritic matrix.
Figure 2. (A) Overview picture of the Morello section. (B) Overview picture of the Bottaccione section. (C) Detail of the Maastrichtian bedding in Morello showing the 30-40 cm thick bedding (hammer for scale). (D) Detail of the Maastrichtian bedding in Bottaccione showing stylolitisation and less clear bedding compared to Morello (for scale: numbers are in cm).

X-Ray Fluorescence measurements

Portable X-Ray Fluorescence measurements were carried out on polished surfaces of hand or core samples using a Bruker Tracer IV Hand Held portable XRF device (HHpXRF, hereafter: pXRF) equipped with a 2 W Rh anode X-ray tube and a 10 mm² Silicon Drift Detector (SDD) with
a resolution of 145 eV (Mn-Ka). All pXRF measurements were carried out by putting the pXRF nozzle directly on the flat sample surface. All analyses were carried out in duplicate with a measurement time of 30 seconds. This integration time was sufficient for Time of Stable Reproducibility (TSR) and Time of Stable Accuracy (TSA) to be reached for individual point spectra for all elements considered in this study (see de Winter et al., 2017a). Concentrations reported in this study are averages of both measurements. Further technical details on the pXRF measurements and calibration are according to Sinnesael et al. (2018, minor revisions). Calibrated elemental concentrations of the pXRF measurements carried out for Ca, Mn, Fe and Sr are available in the Supplementary Materials (“Table_pXRF”).

Micro-XRF mapping and line scans were carried out at the Vrije Universiteit Brussel (VUB), Brussels, Belgium, using the Bruker M4 Tornado micro XRF (hereafter: μXRF). Technical details on the μXRF measurements are found in de Winter and Claeys (2017), and calibrations were done according to Vansteenberge et al. (in review). These conditions allowed concentrations of major and trace elements to be characterized only semi-quantitatively for the mapping (see de Winter et al., 2017b).

Stable isotopes ($\delta^{13}C$ & $\delta^{18}O$)

Stable carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) isotope measurements of the bulk carbonate rock were carried out at the VUB, using a Nu Perspective isotope ratio mass spectrometer (IRMS, Nu Instruments, UK) interfaced with a Nu Carb automated carbonate device. Acidification of the samples occurred at a temperature of 70 °C. Calibration was carried out using an in-house Carrara marble (MAR) standard (+3.41 ‰ VPDB, -0.13 ‰ VPDB) calibrated against the international NBS-19 standard. All values are expressed relative to the Vienna Pee Dee Belemnite (%o-VPDB)
standard. On the basis of replicated measurements of the MAR standard, reproducibility errors on δ¹³C and δ¹⁸O were determined to be <0.05 ‰ (1 σ) and <0.10 ‰ (1 σ), respectively. Corrected δ¹³C and δ¹⁸O carbonate isotope values are available in the Supplementary Materials ("Table_Stable_Isotopes").

Strontium Isotopes (⁸⁷Sr/⁸⁶Sr)

This study integrates various published and unpublished ⁸⁷Sr/⁸⁶Sr data sets from different sections from the Umbria-Marche basin. The Sr isotope (⁸⁷Sr/⁸⁶Sr) results from the Maastrichtian strata of BOT (N = 12) were published in Sinnesael et al. (2018, with minor revisions). The exact same analysis technique, analyzing the whole rock and carbonate fraction with Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) at the GTime laboratory of the Université Libre de Bruxelles, Belgium, was used in this study to analyze the Danian COH (N = 23) and the lowermost Danian and upper Maastrichtian in MRL (N = 12) samples. These measurements have uncertainties (2σ) of 0.000040 (N = 15 on the NBS987 standard).

Additionally, 32 whole rock limestone samples (and 4 samples only containing the carbonate fraction) from the MRL section were selected for Sr Thermal Ionization Mass Spectrometry (TIMS) isotope analysis. The TIMS Sr isotope measurements were performed at the Laboratory of Geochronology, Department of Lithospheric Research, University of Vienna, Austria. Before chemical treatment, weathering crusts were removed mechanically and the samples were crushed in a disc mill to homogeneous powders (< 63 µm) from which ~ 50 mg were used for analysis. Sample dissolution was performed using 6N HCL (or 0.1N CH₃COOH for a test sequence), and element separation followed conventional procedures, using AG® 50 W-X8 (200-400 mesh, Bio-Rad) resin and 2.5N HCl as elution medium. Total procedural blanks for Sr were < 1 ng. Sr
fractions were loaded as chlorides and evaporated from a Re double filament, using a ThermoFinnigan® Triton TI TIMS. A $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710252 ± 0.000002 (N = 7) was determined for the NBS987 (Sr) international standard during the period of investigation. Within-run mass fractionation was corrected for $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. Uncertainties on the Sr isotope ratios are quoted as 2σ.

These recent $^{87}\text{Sr}/^{86}\text{Sr}$ results are integrated with a previously unpublished data set from the early nineties. In total, these data originate from various locations in the Umbria-Marche Basin and span a larger stratigraphic interval (Campanian up to Ypresian) than just the K-Pg boundary interval. Most of the data were taken from BOT and COH on the bulk carbonate fraction. The samples were washed in extremely dilute acetic acid prior to dissolution using 3 ml of distilled water and 20 µl of sub-boiled glacial acetic acid ultrasonically agitated for 30 minutes, following the method outlined by McArthur et al. (1993). The treatment is expected to preferentially dissolve cements and overgrowths and leach radiogenic Sr present on exchangeable sites on clays. About 15 % of the sample is dissolved in this first wash solution. The washed samples were centrifuged, the supernatant discarded and the residue leached in an identical acidic solution for another 30 minutes. After subsequent centrifugation the solution was evaporated to dryness. The impure CaCO$_3$ thus obtained was redissolved in 1.5N HCl and the Sr fraction collected after passing the solution through ion exchange columns. This was again evaporated to dryness. Approximately 10 ng of the Sr from each sample was loaded onto a Re filament with Ta oxide for analysis in a VG Sector 354 multi-collector mass spectrometer in dynamic multi-collection mode. Two standards of NBS-987 and two of modern seawater (MS) were run in each turret of 20 samples. Column blanks averaged 183 ±97 pg Sr, which is negligible for carbonate samples.
It is possible that secondary cements have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios different from that of the original microfossils so that the overall acid soluble fraction contains diagenetically redistributed Sr. To enable some evaluation of diagenetic effects we analyzed several samples of inoceramid bivalves found articulated and presumably in life position in the limestone, as well as fish teeth extracted from the marl layers. Both the phosphate and low-Mg calcite in these samples may be diagenetically modified to some degree, but the magnitude of the Sr isotopic difference between these samples and the bulk carbonate samples gives some indication of the severity of diagenetic modification. All $^{87}\text{Sr}/^{86}\text{Sr}$ data with respective sample sections, stratigraphical levels and measuring techniques are available in the Supplementary Materials (“Table_Strontium_Isotopes”).

$^{40}\text{Ar}/^{39}\text{Ar}$ dating ALE Volcanic Ash

Samples from the volcanic ash “livello Alessandro” (ALE, Odin et al., 1992) were collected both in COH (at stratigraphic level 2.00 m) and MRL (at stratigraphic level 2.45 m). Biotite grains were handpicked after wet sieving using the > 63 µm fraction. Unfortunately the biotite grains from the MRL-ALE sample were too small to date accurately, so only the COH-ALE data are presented in this study. $^{40}\text{Ar}/^{39}\text{Ar}$ analytical methods were largely as described in Kavalieris et al. (2017), with variations noted here. Samples were irradiated for 20 hours. Background measurements were run every 3 analyses; backgrounds were fit with a mean ± standard deviation. Discrimination and detector intercalibration factors were determined via measurements of 3 air pipettes approximately twice per day. The sample was co-irradiated with Fish Canyon sanidine (FCs), and ages were calculated using an age for FCs of 28.201 ± 0.023 (1σ) (Kuiper et al., 2008).
and decay constants from Min et al. (2000) for $^{40}$K. Full raw data are provided in the Supplementary Materials (‘Table_40Ar39Ar_ALE_dating’).

**Time series analysis**

Cyclostratigraphic analyses were carried out using sliding fast Fourier transformations (FFT) in Matlab®. The algorithms were modified from Muller and MacDonald (2000) and are explained in detail by Bice et al. (2012). The data were linearly detrended and padded with zeros prior to analysis. This approach was successfully applied in other cyclostratigraphic studies in the Umbria-Marche basin (e.g. Cleaveland et al., 2002; Sinnesael et al., 2016a; Montanari et al., 2017). The MRL Fe concentrations (pXRF) data were used for the Maastrichtian (5 cm resolution and window size of 2 m) and for the Danian the COH magnetic susceptibility data from Sinnesael et al. (2016a) were used (1 cm resolution and window size of 0.7 m). This is a composite record using two different proxies from two different sections. The motivation for this selection is to use the respective best quality records with the highest available stratigraphical resolution. Cyclostratigraphic analyses of magnetic susceptibility and pXRF Fe data on sediments from the Scaglia Rossa have been shown to be basically interchangeable (Sinnesael et al., 2018, with minor revisions).

4. **RESULTS**

**Planktonic Foraminiferal Biostratigraphy at Morello**

Planktonic foraminifera are continuously present and abundant throughout the study interval, with diverse genera and species typical of late Maastrichtian - early Danian low-latitude pelagic environments. Preservation varied from poor to good, but it was mostly moderate to good
and therefore offered the possibility for accurate taxonomic determinations and detailed analysis of foraminiferal assemblages (not presented here). All the marker species that define the standard planktonic foraminiferal zones of Coccioni and Premoli Silva (2015) for the Cretaceous and of Wade et al. (2011) for the Paleogene occurred in the analyzed material. The common planktonic foraminiferal biozones for this stratigraphic interval were identified, and the locations of the boundaries are reported in Table 1 and Figure 6.

<table>
<thead>
<tr>
<th>Boundaries and Events</th>
<th>Morello (m)</th>
<th>Gubbio (BOT-COH) (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1a-P1b</td>
<td>2.60</td>
<td>2.25</td>
</tr>
<tr>
<td>ALE volcanic ash</td>
<td>2.45</td>
<td>2.00</td>
</tr>
<tr>
<td>C29r-C29n upper potential boundary</td>
<td>1.75</td>
<td>1.20</td>
</tr>
<tr>
<td>C29r-C29n lower potential boundary</td>
<td>1.42</td>
<td>1.20</td>
</tr>
<tr>
<td>DAN-C2 hyperthermal peak dissolution</td>
<td>0.95</td>
<td>0.80</td>
</tr>
<tr>
<td>δ¹³C 'drop'</td>
<td>0.70</td>
<td>0.60</td>
</tr>
<tr>
<td>P0/Pα-P1a</td>
<td>0.70</td>
<td>0.55</td>
</tr>
<tr>
<td>K-Pg Boundary</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td><em>Plummerita hantkeninoides-Pseudotextularia elegans</em></td>
<td>-1.50</td>
<td>-1.41</td>
</tr>
<tr>
<td>local δ¹³C minimum</td>
<td>-1.95</td>
<td>-1.65</td>
</tr>
<tr>
<td>local δ¹³C maximum, also knickpoint in Mn profile</td>
<td>-3.55</td>
<td>-3.15</td>
</tr>
<tr>
<td>C30n-C29r upper potential boundary</td>
<td>-3.70</td>
<td>-3.80</td>
</tr>
<tr>
<td>C30n-C29r lower potential boundary</td>
<td>-4.10</td>
<td>-3.80</td>
</tr>
<tr>
<td><em>Pseudotextularia elegans-Pseudoguembelina hariaensis</em></td>
<td>-5.50</td>
<td>-4.83</td>
</tr>
</tbody>
</table>

**Paleomagnetic results at Morello**

AF demagnetization was efficient to reveal the characteristic remnant magnetization (ChRM) after removal of an overprint up to about 20 mT (Fig. 3). After tilt-correction, there is clear dichotomy between samples up to -3.05 m (normal polarity ChRM, Fig. 3a) and above -2.95 m (reverse polarity ChRM, Fig. 3b). The normal and reverse direction populations yield a positive
reversal test (McFadden and McElhiny, 1990), strongly suggesting that the ChRM is a primary magnetization (Fig. 4). For two of the reverse polarity samples (level -2.00 and -0.20 m), the ChRM direction could not be defined with precision because of spurious demagnetization behavior at high AF. One of the normal polarity samples (level -8.80 m) has a slightly deviating direction and may have been misoriented in the field. These analyses indicate that the magnetostratigraphical boundary in the Morello section between chron C30n and C29r is situated between levels -4.10 and -3.70 m and the C29r-C29n boundary between 1.42 and 1.75 m (Tab. 1).

Figure 3. Orthogonal projection plots of stepwise alternating field (AF) demagnetization data of representative normal- (level 92.00 m = -8.00 m) and reverse- (level 97.05 m = -2.95 m) polarity samples. Open and solid symbols represent projections on the horizontal and vertical plane respectively.
Figure 4. Stereographic projection of the ChRM directions of the seven samples for which a well-defined ChRM could be defined (except outlying direction from level 91.20m). The MAD (Maximum Deviation Angle of Kirschvink, 1980) of each direction is shown.

**Portable X-Ray Fluorescence measurements**

The Gubbio Ca profile oscillates around 35 wt. % for the Maastrichtian strata in the BOT section and decreases towards lower values around 30 wt. % across the K-Pg boundary for the COH Danian (Fig. 5). The boundary clay layer is clearly visible in the profile as the minimum at the 0.00 meter level (Fig. 5). The ALE volcanic ash is also clearly marked by a local minimum at the 2.00 meter level. The Fe profile displays the opposite trends as the Ca profile, as both are respectively proxies for the clay (detrital) versus calcium carbonate content. The Gubbio Sr profile is mainly characterized by a sharp decrease across the K-Pg boundary from Maastrichtian concentrations of 700-800 ppm (with several enrichments up to a 1000 ppm in the upper half of the Maastrichtian) to 200-300 ppm right after the boundary (Fig. 5). Danian Sr concentrations seem to rise steadily, except for a small increase to values of 500-600 ppm between 0.25 and 0.35 m. The variability in the Sr concentration signal increases in the upper half meter (3.50 - 4.00 m).
The Gubbio Mn profile for the Maastrichtian is relatively stable with values of 300 – 400 ppm and shows a sudden increase of 200 ppm after the K-Pg boundary (Fig. 5). The Mn concentration decreases towards the 3.00 m level after which it slowly increases again. Elevated Mn concentrations are also found in the ALE volcanic ash.

The Ca, Fe, Sr and Mn profiles for the Morello section show the same trends as the Gubbio elemental profiles (Figs. 5 and 6). The decrease in Ca and corresponding increase in Fe are more pronounced for the Morello data series. There is also a larger difference in amplitude variability for the Morello Ca and Fe data compared to the Gubbio profiles (Figs. 5 and 6). The K-Pg boundary clay itself was not sampled and measured in Morello and the sampling stopped just below the MRL-ALE level (-2.45 m) and therefore both sedimentological features are not visible in the respective profiles. There is a clear local maximum in the Morello Fe profile (Ca minimum) at level 0.95 m (Fig. 6) which is also present in Gubbio at level 0.80 m (Fig. 5). In contrast to the Maastrichtian Sr profile in Gubbio (Fig. 5), the Maastrichtian Morello profile does not show enrichments up to 1000 ppm (Fig. 6). Relative Sr variations in the Danian profiles are similar for both sections, except for ~100 ppm increases for samples at 0.350, 0.375, 0.400 and 0.700 m in Morello (Fig. 6). There is also a difference in the absolute concentrations between both sections, with values up to 100-200 ppm higher for the Gubbio sections. The Morello Mn concentration profile is similar, both in terms of absolute as relative variations, to the one in Gubbio (Figs. 5 and 6).

The smoothed (7-point running average) elemental Ca, Fe, Sr and Mn profiles for all the investigated K-Pg sections (Bottaccione (BOT), Contessa Highway (COH), Morello (MRL), Fornaci East quarry (FOE), Frontale (FRO), Morello (MRL) and the Petriccio Core (PTC).) is shown in Figure 7. As an exception, the dataset from FRO is not averaged because it contains just
14 measurements. All data are plotted in the distance domain, and because of varying sedimentation rates over the basin, certain features occurring before or after the K-Pg boundary (which is the common 0 m reference level) are not positioned at the same stratigraphical levels. The Maastrichtian Ca (wt. %) content varies for the different sections between 30 and 37 wt. %. Right after the K-Pg boundary clay layer the Ca content peaks (i.e. Eugubina limestone) where after all profiles reach a minimum around 1.00 m. The relative variations in the Ca content are mirrored for the Fe (wt. %) profiles. The boundary clay measurement is clearly distinguishable in the FRO data as a peak in Fe and minimum in Ca. The Maastrichtian BOT Fe profile shows more variation compared to the other Maastrichtian data (FOE, MRL, PTC) – which also the case for the BOT Fe curve. Moreover the absolute Fe concentrations for BOT are more elevated compared to its parallel profiles. Besides a common Fe peak around 1.00 m, only the PTC Fe profile shows a second pronounced peak before the 2.00 m level. The Sr (ppm) values of the Maastrichtian BOT section are 200 to 300 ppm higher than FRO, FOE, MRL and PTC - except for a sudden sharp increase in the PTC profile. All sections have an immediate strong decrease in Sr concentrations followed by a gradual increase upwards. Anomalies on this predominantly monotonous increase in Sr concentrations include a small increase between levels 0.25-0.50 m (larger for MRL) and a sudden sharp increase for the PTC data at level 1.275 m to levels comparable to the Sr concentrations at level 3.50 m in COH. Levels of Mn (ppm) are comparable for all profiles for the Maastrichtian with values between 300 and 400 ppm. There is an increase in Mn concentrations from ~350 to ~400 ppm from level -4.00 up to -2.00 m. Across the K-Pg boundary there is a ~200 ppm increase in Mn concentration for all sections, but there is a larger variability in absolute concentrations for the Danian parts compared to the Maastrichtian. The second highest Danian sample in the FRO profile (at 0.14 m) has Maastrichtian values for Sr and Mn.
Figure 5. Stratigraphy and multiproxy records of the Gubbio sections (Maastrichtian Bottaccione and Danian Contessa Highway). The magnetostratigraphy is according to Roggenthen and...
Napoleone (1977) for COH and to Lowrie et al. (1982) for BOT. The biostratigraphy for the COH section is from Coccioni et al. (2013), whereas that for the BOT section is from Coccioni and Premoli Silva (2015). Elemental concentration profiles of Ca, Fe, Sr and Mn were measured with portable X-Ray Fluorescence (pXRF). Bulk stable isotopes ($\delta^{13}$C and $\delta^{18}$O) from BOT are from Sinnesael et al. (2016a), while the COH were measured in this study (full lines) and Coccioni et al. (2012) (dotted lines). All reported $^{87}$Sr/$^{86}$Sr isotope results were measured during this study.
Figure 6. Stratigraphy and multiproxy records of the Morello section (all this study).

Figure 7. Smoothed (7-point running average), except the FRO data, elemental concentration profiles (Ca, Fe, Sr and Mn) measured with portable X-Ray Fluorescence (pXRF) for six different K-Pg sections in the Umbria-Marche basin.

Stable isotopes (δ¹³C & δ¹⁸O)

Oxygen stable isotope (δ¹⁸O) measurements on bulk pelagic limestone material from the Danian COH section (full blue line on Fig. 5) have slightly less negative values compared to the results published in Coccioni et al. (2012) (dotted blue line on Fig. 5). Especially the pronounced negative peaks (> 1 ‰) described by Coccioni et al. (2012) are not present. However, the main trend is still similar: a decrease over the Danian from ~1.5 ‰ down to ~2.5 ‰. Superimposed on this trend the new record has local minima around levels 0.80, 2.00 and 3.80 m. The Maastrichtian MRL δ¹⁸O results vary between -1.79 and -1.28 ‰ around an average value of -1.50 ‰, with a small shift (0.2 ‰) in values around -1.4 ‰ to -1.6 ‰ at level -2.4 m (Fig. 6). These
values are less negative compared to the BOT Maastrichtian data as published and discussed by Sinnesael et al. (2016a). Danian MRL $\delta^{18}$O values start around -1.00 ‰, have a sharp decrease in values for the 0.35-0.40 m interval, have another local minimum around 1.00 m and finally show a decreasing trend in the upper half meter. Compared to the BOT data, do the MRL Maastrichtian data show much less amplitude variations and less negative values (Figs. 5, 6 and 8). Relative variations for both Danian $\delta^{18}$O profiles are similar, but again are the Morello $\delta^{18}$O less negative compared to Gubbio-COH (Figs. 5, 6 and 8).

The difference between the new (this study) and published (Coccioni et al., 2012) $\delta^{13}$C data for the Danian COH are more pronounced compared to the $\delta^{18}$O results (Fig. 5). None of the large (> 1.00 ‰) negative excursions in $\delta^{13}$C occur in the new data set. The profile of the new dataset starts with lowermost Danian values of ~2.15 ‰ which stay stable till level 0.575. Then a significant negative shift (~0.5 ‰) occurs whereafter there is a slight decreasing trend from values of ~1.8 ‰ to ~1.4 ‰ to the top of the record. There is a ~0.3 ‰ negative excursion for samples 3.800, 3.825 and 3.850 m. Also the Danian MRL $\delta^{13}$C data start with stable values of ~2.10 followed by a ~0.5 ‰ shift at level 0.70 m and a slight decrease trend (~1.9 ‰ to ~1.6 ‰) till the top of the measured section. In contrast with the $\delta^{18}$O signals, are the MRL and BOT Maastrichtian $\delta^{13}$C almost identical in terms of relative variations and absolute values (Figs. 5, 6 and 8). Both profiles vary between 2.0 and 2.5 ‰ and have local minima roughly around levels -2.0 and -5.0 m.

A cross-plot of the respective $\delta^{18}$O and $\delta^{13}$C ratios (Fig. 8) confirms some of these observations, but additionally shows a bimodal distribution for the Danian samples. Most of the samples of both the COH and MRL profiles plot on a linear trend with $\delta^{13}$C values between 1.5 and 2.0 ‰. However, some samples plot as a clearly distinguishable cluster with values between
2.0 and 2.5 ‰. For both data sets, these samples correspond to samples from the stratigraphical interval between the K-Pg boundary and the ~0.5 ‰ drop in δ^{13}C values around 0.6 m (COH) and 0.7 m (MRL) (Figs. 5 and 6). The linear trend with decreasing δ^{18}O values for decreasing δ^{13}C values is similar for both records. The three data points with the lowest values for both isotopic systems correspond with the 3.80-3.85 m COH Danian anomaly (Fig. 5). Furthermore, are the anomalous, compared to MRL, negative δ^{18}O values for the Maastrichtian BOT clearly distinguishable. Average Maastrichtian δ^{13}C values for MRL are also slightly lower (0.08 ‰) than for BOT.

Figure 8. Cross-plot of bulk stable carbon and oxygen data from the respective Maastrichtian and Danian sections of Morello and Gubbio (Bottaccione and Contessa Highway).

**Hand sample Micro X-Ray Fluorescence and stable isotopes (δ^{13}C & δ^{18}O) measurements**
Four different subsamples (pure calcite vein, mixed calcite vein with matrix, mixed styolite with matrix and pure matrix) were taken from a hand sample containing clear calcite veins and styolites (Fig. 9). The $\delta^{13}$C ratios are statistically inseparable for all samples while the samples containing calcite vein material have lower $\delta^{18}$O values. The pure calcite vein sample (-14.2 ‰) is ~12 ‰ more depleted than the surrounding pink matrix (-2.5 ‰). The mixed sample with some calcite vein material shows a value between these two end-members which suggest mixing, while the mixed sample containing styolite material overlaps within the error with the pink matrix (Fig. 9). Micro XRF mapping and line scanning across several styolite sections shows clear enrichments in detrital elements like K, Fe and Ti – and a reduction in Ca concentrations (Fig. 9). The exact opposite pattern is observable for the same measurements done on the calcite vein. While the Sr concentrations are distinctly more elevated in the calcite veins, the Sr distribution for the styolites is more complicated. In the calcite veins, the Sr enrichments coincide with the decreases in K, Fe and Ti. However, the XRF mapping and line scanning shows an asymmetrical distribution of the Sr concentrations relative to the position of the detrital elements (Fig. 9).
Figure 9. Micro X-Ray Fluorescence mapping (heat maps), line scanning (quantified) and stable isotopes ($\delta^{13}$C and $\delta^{18}$O) analyses of a hand sample containing clear calcite veins and styolites. This sample was taken around level -1.50 m from the Bottaccione section. In contrast to the pressure solution styolites, are the calcite veins enriched in Ca and Sr, and depleted in Fe, K and Ti. The $\delta^{13}$C signal overlaps within the error for all samples (pure calcite vein, mixed calcite vein with matrix, mixed styolite with matrix and pure matrix). The samples containing calcite vein material have lower $\delta^{18}$O values.
Strontium Isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$)

All strontium isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) measurements for the Gubbio sections (BOT+COH) were
done on the bulk carbonate fraction (Fig. 5). Both TIMS and MC-ICP-MS results overlap with
larger variations for the latter ones (full range = 0.707899 – 0.707756). The average MC-ICP-MS
$^{87}\text{Sr}/^{86}\text{Sr}$ value for this interval is 0.707834 and is in line with the GTS 2012 compilation
(McArthur et al., 2012). For this stratigraphical interval in Gubbio, there is no increasing or
decreasing trend on the $^{87}\text{Sr}/^{86}\text{Sr}$ measured on the carbonate fraction (Fig. 5). $^{87}\text{Sr}/^{86}\text{Sr}$
measurements on the MRL carbonate fraction overlap again between TIMS and MC-ICP-MS
measurements and have an indistinguishable (within the MC-ICP-MS 2σ error of 0.00004) average
value of 0.707834 compared to Gubbio (0.707857) but a larger range (0.707797 – 0.707997) (Fig.
6). Whole rock TIMS and MC-ICP-MS $^{87}\text{Sr}/^{86}\text{Sr}$ results for the Maastrichtian MRL section are in
agreement with each other (except for two higher MC-ICP-MS values at levels -5.00 and 6.00 m)
and are ~0.0001 higher than the measurements done on the carbonate fraction (Fig. 6). The Danian
MRL whole rock $^{87}\text{Sr}/^{86}\text{Sr}$ TIMS profile is characterized by a sharp increase at level 0.80 m which
is followed by a hyperbolic decrease to ‘pre-increase’ whole rock isotopic values at ~2.00m (Fig.
6). The sample with a high $^{87}\text{Sr}/^{86}\text{Sr}$ value at MRL level 2.50 m was taken just above the ALE
volcanic ash layer and might have been slightly contaminated with more radiogenic material. An
$^{87}\text{Sr}/^{86}\text{Sr}$ isotope profile in the Umbria-Marche basin for the middle Campanian up to the early
Ypresian as measured in the Gubbio sections (Bottaccione and Contessa Highway) on the bulk
carbonate fraction (TIMS) is shown in Figure 10. The fish teeth $^{87}\text{Sr}/^{86}\text{Sr}$ values generally fall
within error of the associated bulk carbonate samples which suggests that $^{87}\text{Sr}/^{86}\text{Sr}$ values of bulk
carbonate samples are close to the original paleoceanographic value (Supplementary Materials
“Table_Strontium_Isotopes”). Values rise from the middle of the Campanian magnetochron C33n
(0.70765) to maximum in the Danian C29n (0.70783), and then decrease again to the youngest sample in the Ypresian C24r (0.70774). This profile is analogous to the GTS 2012 compilation by McArthur et al. (2012). The early Danian maximum value is in accordance with the Gubbio MC-ICP-MS average value (0.70783) for the latest Maastrichtian – early Danian interval. Measurements close to the K-Pg boundary show more scatter compared to the ones more farther away from the boundary. The Supplementary Material “Table_Strontium_Isotopes” contains other fragmentary $^{87}\text{Sr}/^{86}\text{Sr}$ data from other K-Pg sections in the Umbria-Marche basin which are in close agreement with the profile shown in Figure 10.

Figure 10. $^{87}\text{Sr}/^{86}\text{Sr}$ isotope profile in the Umbria-Marche basin for the middle Campanian up to the early Ypresian as measured in the Gubbio sections (Bottaccione and Contessa Highway) on the bulk carbonate fraction.
The analyzed COH-ALE biotite grains were quite small, and resulting data have multiple possible interpretations. However, given the paucity of available geochronology from this section, the data collected here does provide some constraint on the timing of sedimentation. After removing obvious xenocrysts, and grains that were significantly younger than the main population, the remaining population yields an inverse variance weighted mean age of 64.7 ± 1.6 Ma (Fig. 11) that is younger than the age of the K-Pg boundary (66.043 ± 0.043 Ma according to Renne et al., 2013). This is consistent with the sampling location relative to the K-Pg boundary at Morello (+2.00 m). It should be noted that different recent calibrations of the $^{40}$Ar/$^{39}$Ar system would slightly affect the ages obtained. An alternative is the FC's age and decay constants from (Renne et al., 2011), which would results in a ~0.2 Ma older (well within the relatively large uncertainties). Given the small size of the biotite grains analyzed, it is possible that some of the anomalously young grains were affected by recoil (e.g. Paine et al., 2006), or possibly by outcrop contamination (Montanari, 1986).
Figure 11. Results from the $^{40}$Ar/$^{39}$Ar dating of biotite grains from the ALE volcanic ash layer from the Contessa section.

5. DISCUSSION

Sedimentology and Geochemistry: Basin-wide robust patterns

The sedimentological and geochemical analysis of several stratigraphically equivalent sections from the same Umbria-Marche basin allows us to evaluate which features are basin-wide
robust and which features would only occur in single or certain specific records. A pronounced
difference in bedding style between the BOT (Fig. 2 B and D) and MRL (Fig. 2 A and C) is due
to pseudobedding (*sensu* Alvarez et al., 1985). While the Maastrichtian average bedding thickness
in MRL is ~30-40 cm, the apparent bedding in the BOT section (i.e. the pseudobedding) is much
thinner than that (~5-10 cm) because of the presence of numerous bedding-parallel pressure
solution planes, i.e. styolites (e.g. as discussed in Sinnesael et al., 2016a). In comparison with all
other measured sections in this study, the BOT section shows more elevated concentrations of Sr
and Fe (Fig. 7). These are most probably the effect of accidental sampling calcite veins (enriched
in Sr, Fig. 9) and styolites (enriched in Fe, Fig. 9) in the BOT section while using a drill to collect
sample powder (Fig. 2D and Sinnesael et al. (2018, with minor revisions)). The effect of sampling
calcite veins is also reflected in the negative excursions in the bulk δ¹⁸O signal from BOT (Figs.
4, 8 and 9). Independently of the negative bulk δ¹⁸O excursions in BOT, are the base δ¹⁸O values
for both the Maastrichtian and Danian samples less negative for Morello compared to the COH
and BOT Gubbio sections (Fig. 8). Combining the geochemical observations, the fact that the
Morello section is stratigraphically thicker than the Gubbio one (Tab. 1), the presence of the
pressure solution features and less horizontal bedding angle in Gubbio, suggest that the Gubbio
sections were more affected by burial diagenesis that the Morello section. Robust features for the
Maastrichtian records are the bulk carbonate δ¹³C and Mn concentration profiles (Figs. 5-7). Most
investigated K-Pg boundary intervals are also characterized by the terminal Maastrichtian 20-30-
cm-thick bleached white horizon, which contrasts with the typical pink color of the surrounding
Maastrichtian and Danian pelagic limestones. The bleached horizon is not evident in the FOE
section at Monte Conero (see Fig. 1B for location), because this area of the paleobasin was located
in the immediate proximity of a carbonate platform, a deep marine environment that was
characterized by relatively reducing conditions compared to more oxidizing conditions in deeper and more distal areas of the paleobasin. Practically, the Maastrichtian and Danian Scaglia Rossa limestones in the whole area of Monte Conero are not typically pink like in the rest of the paleobasin, but whitish or pale beige (Montanari et al., 1989; Montanari and Koeberl, 2000), and the actual K-Pg boundary clay typically red in color with a thin reduced green sole (Montanari et al., 1983; Lowrie et al., 1990; Montanari, 1991), exhibits here a homogeneous ochre color, and does not contain authigenic goethite like any other K-Pg boundary clay in the rest of the basin (Montanari, 1991). This probably also explains why the Maastrichtian pelagic limestones in the FOE section have the lowest Fe and highest Ca concentrations off all the other measured sections in the distal Scaglia Rossa basin (Fig. 7). Elevated Ca values for the BOT section might reflect a sampling bias – i.e. sampling of calcite veins which are enriched in CaCO₃ (Fig. 7 and 9). Consistent geochemical features across the K-Pg boundary for all records are the decrease in Sr and Ca concentrations, and increase in Mn and Fe concentrations (Fig. 7). In the Danian profiles is the Eugubina limestone (~0.00 – 0.40 m) typically visible as a maximum in Ca concentration (Fig. 7). Also the marly interval (~0.60 – 1.10 m) corresponding with the DAN-C2 hyperthermal event is a reoccurring feature expressed a local minima in Ca and maxima of Fe (Coccioni et al., 2010; Fig. 7).

Besides these large scale overall observations, other interesting small scale features occur from this high-resolution geochemical study. One of the pXRF measurements of the FRO section was taken from a large bioturbation burrow filled with Maastrichtian pelagic sediment, within the Eugubina Limestone, ~10 cm abobe the K-Pg boundary (see Fig. 5.7.6.10b at p. 235 in Montanari and Koeberl, 2000). In this case, the Sr and Mn correspond exactly with the Maastrichtian bulk values – which are significantly different before and after the K-Pg boundary – and so this
convincingly demonstrates that bioturbation crossed the K-Pg boundary causing some degree of vertical mixing (Fig. 7). Another anomalous feature, compared to the other parallel sections, is the sharp and sudden increase in Sr concentrations at level 1.275 m for the PTC core (Fig. 7). The absolute values of this Sr anomaly correspond with the peak concentrations around level 3.50 m in COH. Putting all elemental pXRF analyses together, it seems that there is a Danian hiatus of about 2 m in the PTC core, which before was not recognized. Samples 0.350, 0.375, 0.400 and 0.700 m in MRL are characterized by clear geochemical anomalies: lower $\delta^{13}$C and $\delta^{18}$O values and higher Sr concentrations (Fig. 5). Interestingly these anomalies do not show up significantly in the Mn data, hinting towards the potential diagenetic signature of the Mn signal. Field inspection of these levels with the hand lens already suggested a potential turbiditic origin of these intervals (e.g. Bice et al., 2007). Small turbidites around similar levels are also visible in the FOE section, but were not analyzed in this study with the pXRF exactly because they were clearly turbiditic. The geochemical anomalies for the MRL samples now confirmed their turbiditic origin. These are illustrations on how the relative fast and cheap chemostratigraphical application of pXRF measurements can be of added value. In summary, the most robust observations for this stratigraphical interval in the Umbria-Marche basin are: 1) The changes across the K-Pg boundary, 2) The occurrence of the K-Pg boundary clay layer, Eugubina limestone and DAN-C2 marly interval and 3) the difference diagenetic history between the Morello and Gubbio sections.

**Event stratigraphy**

**Deccan Volcanism**

Establishing robust basin-wide sedimentological and geochemical observations allows for in-depth evaluation of the global events in this stratigraphical interval: Deccan volcanism, the K-
Pg boundary and recovery, and the DAN-C2 hyperthermal event. One of the most compelling geochemical tracers of Deccan volcanism in the sedimentary archive is a drop in the $^{187}\text{Os}/^{188}\text{Os}$ isotopic ratio a few hundred thousand years predating the K-Pg boundary (Ravizza and Peucker-Ehrenbrink, 2003; Ravizza and Vonderhaar, 2012). This drop has also been measured 5-6 m below (~300-400 kyr before) the K-Pg boundary in the BOT section (Robinson et al., 2009). Foraminiferal $\delta^{18}\text{O}$ values (Li & Keller, 1998; Barnet et al., 2017) and to some extent bulk carbonate $\delta^{18}\text{O}$ records (Thibault et al., 2016), show a global clear warming episode also a few hundred kyr before the K-Pg boundary. The bulk carbonate $\delta^{18}\text{O}$ record from BOT (Fig. 5) which was hypothesized by Sinnesael et al. (2016a) to potentially reflect Deccan global warming is shown to be heavily affected by the sampling of diagenetic calcite veins and is therefore not supporting such an interpretation (Fig. 9). Bulk carbonate $\delta^{18}\text{O}$ values for MRL shift to slightly lower values (0.20 ‰, Fig. 6) around -2.5 m, but this shift is small compared to the measurement error (1 $\sigma$ = 0.10 ‰) and the $\delta^{18}\text{O}$ shift in other bulk records (e.g. Thibault et al., 2016). A basin-wide increase in bulk Mn concentrations ~300 kyr prior to the K-Pg boundary (Figs. 5, 6 and 7) might indicate a global increase in hydrothermal activity (e.g. Le Callonnec et al., 2014). Elevated Hg/TOC ratios at certain stratigraphical levels in BOT have also been suggested to be useful identifiers of the differences pulses of Deccan volcanism (Sial et al., 2016). However, the suggested stratigraphical correlations of these Hg/TOC peaks are debated (e.g. Smit et al., 2016; Mukhopadhyay et al., 2016). All things considered, the $^{187}\text{Os}/^{188}\text{Os}$ record is still the only convincing geochemical record of Deccan volcanism in the Umbria-Marche basin sedimentary succession.

*Extinction and Recovery*
The drop and following increase in bulk Sr concentrations across the K-Pg boundary is a robust pattern in all investigated sections in the Umbria-Marche Basin (Figs. 5-7). The fact that the Sr profile does not correlate with the terrigenous components (e.g. Fe concentrations) suggests that Sr concentrations mainly reflecting the Sr content of the CaCO₃ (calcite) components of the bulk sediments (Figs. 5-7). This is also indicated by the similarity of records of Sr concentration and Sr/Ca ratios (see Supplementary Materials “Table_pXRF”; Sinnesael et al. (2018, with minor revisions)). The sudden decrease in Sr concentrations across the K-Pg boundary was observed earlier in the BOT section by Alzeni et al. (1981) and Renard et al. (1982). Several mechanisms were proposed to potentially explain this shift: changes in relative local sea level, a change in the source area of clastic supply, different diagenetic alteration of clay minerals due to different sedimentation rates, variations in the Sr/Ca ratio of seawater, variations in sea water salinity and/or temperature and metabolic effects on biochemical fractionation of strontium by calcifying microorganisms (foraminifera and nannoplankton) (Alzeni et al.; 1981; Renard et al., 1982). However, none of these hypotheses was supported by conclusive evidence. Interestingly, a similar Sr/Ca profile has been measured in the Scaglia Rossa Formation of the Forada section in the Southern Alps of northern Italy (Fornaciari et al., 2007). Fornaciari et al. (2007) demonstrated that the Sr/Ca decrease coincides with a drastic decrease in coccolithophorid production after the K-Pg mass extinction and that the increase in Sr/Ca goes hand in hand with the recovery of these biogenic carbonate producers (as measured in total abundance as well as taxonomic diversity). This observation is in line with the hypothesis that the coccolith Sr/Ca ratio may be a proxy for coccolithophorid productivity (Stoll and Schrag, 2000). Other factors could also have an influence on coccolithophore Sr/Ca ratios: temperature, dissolution and growth rate (Stoll and Schrag, 2000; Rickaby et al., 2002; DePaolo, 2011). The studied DAN-C2 hyperthermal (potential warming and
carbonate dissolution) marly intervals in the Umbria-Marche show a small decrease in total Sr concentrations, but not in the Sr/Ca ratios – suggesting that temperature and dissolution indeed have a minor influence on the Sr/Ca ratio as stated by Stoll and Schrag (2000) (Figs. 5-7 and Supplementary Materials “Table_pXRF”). Assessing the actual growth rate of these organisms across the K-Pg boundary is difficult because of large variations in taxonomy, ecology, etc. Nevertheless, the fact that early Danian foraminifera and coccolithophores are much smaller than Maastrichtian ones may indicate such a decrease of growth rate, although small test sizes do not necessarily have to correspond with slow growth rates (e.g. Gardin and Monechi, 1998; Bernaolo and Monechi, 2007; Fornacieri et al., 2007).

This major drop in biogenic carbonate productivity can also explain the slower accumulation rates for the Danian compared to the Maastrichtian (e.g. Arthur and Fischer, 1977; Smit, 1982; Mukhopadhyay et al., 2001; Fornacieri et al., 2007; Gardin et al., 2012; Coccioni et al., 2013; Sinnesael et al., 2016a). Assuming this mechanism is correct; one might expect to see a comparable Sr/Ca signal in sedimentary and stratigraphically equivalent sections (of which the carbonate fraction is dominated by the nannofossil component). However, many other K-Pg boundary sections consist of different types of sediments and often have pronounced lithological differences before and after the K-Pg boundary – complicating the comparison of bulk measurements. The Spanish Zumaia section, for instance, has a documented Sr/Ca drop across the K-Pg boundary, but in contrast with the Umbria-Marche sections, the basal Danian P0-Pa Zone in this section is marly (Margolis et al., 1987) whereas in the Umbria-Marche basin this stratigraphic interval is represented by the hard, 96-97 wt.% CaCO₃ Eugubina Limestone (e.g., Sinnesael et al., 2016a). A sudden drop in bulk Sr/Ca and a rise over the lower Danian is also found for the Spanish Caravaca K-Pg boundary section (Kaiho et al., 1999; Jan Smit, personal communication 2017).
Although the stratigraphical resolution does not allow evaluating the presence of a smooth increase in Sr values, the bulk measurements of upper Maastrichtian and lower Paleocene samples from the European Biarritz, Caravaca, Gubbio, Zumaya (Smit and ten Kate, 1982) and the Sr concentrations of several, mainly North-Atlantic, Deep Sea Drilling Project (DSDP) Sites (Renard et al., 1986) show lower Sr values following the K-Pg boundary compared to upper Maastrichtian concentrations. All these studies reporting a significant change in Sr/Ca over the K-Pg boundary were located in the paleo- Tethys and North-Atlantic Ocean. To our knowledge, no similar Sr profiles have been documented outside the Tethys and North-Atlantic Ocean yet (e.g. Zachos and Arthur, 1986; Schulte et al., 2006). This might be explained by the non-homogenous distribution in time and space of the K-Pg nannoplankton extinction patterns and recovery rates (e.g. Jiang et al., 2010; Hull et al., 2011). Jiang et al. (2010) for example state that extinction rates in the Northern Hemisphere were higher compared to the Southern hemisphere and population recoveries were much faster for the latter one. In this scenario, it is not necessarily the case that all worldwide K-Pg boundary sections with similar pelagic carbonate sedimentology as in the Umbria-Marche basin have a comparable change in Sr/Ca over the K-Pg boundary and during the earliest Paleocene.

**DAN-C2 hyperthermal event**

After Quillévére et al. (2008) suggested for the first time the existence of the first Paleogene DAN-C2 hyperthermal event (top of magnetochron C29r in ODP Site 1049, Coccioni et al. (2010) identified it also in the COH section. The DAN-C2 in COH manifests itself as a ~30 cm thick (0.6-0.9 m levels) marly interval with respective bulk δ^{13}C and δ^{18}O negative shifts accompanied with changes in calcareous nannofossils and foraminiferal fauna (Coccioni et al., 2010). The elevated
He\textsuperscript{3} concentrations for this same interval suggest condensation – for example by carbonate dissolution as is common for hyperthermal events (Fig. 12, Mukhopadhyay et al., 2001) as well as the more radiogenic \textsuperscript{87}Sr/\textsuperscript{86}Sr signature of the whole rock MRL measurements (Fig. 6). In contrast with the previous bulk $\delta^{13}$C record for COH (Coccioni et al., 2012), the new COH record shows a clear drop in $\delta^{13}$C values at the start of this marly interval (Fig. 5). The same pattern is also observed in the MRL section (Fig. 6). The bulk stable carbon and oxygen cross-plot from the Danian MRL and COH data also illustrate that this transition towards the DAN-C2 marls is the splitting point between two clusters (for both sections) in the data (Fig. 8). The first cluster has $\delta^{13}$C values higher than 2.00 \textperthousand and does not show any trend in the $\delta^{18}$O-$\delta^{13}$C space. The second cluster has $\delta^{13}$C values lower than 2.00 \textperthousand with a linear trend of decreasing $\delta^{13}$C values with decreasing $\delta^{18}$O. A first explanation could be differential diagenesis between both intervals as we are still dealing with isotopic measurements on bulk material. An alternative clarification could be that the covariation between $\delta^{13}$C and $\delta^{18}$O represents a true climatic signal. Stable isotope analyses ($\delta^{13}$C and $\delta^{18}$O) on benthic foraminifera for Eocene hyperthermals have shown these linear trends between $\delta^{13}$C and $\delta^{18}$O as well (Stap et al., 2010; Lauretano et al., 2015). These studies suggest that simultaneous warming (hyperthermals, reflected in $\delta^{18}$O signal) might go hand in hand with perturbations of the carbon cycles (e.g. negative $\delta^{13}$C peaks because of the release of isotopically light carbon – events which might be associated with carbonate dissolution (e.g. Zachos et al., 2010; Littler et al., 2014). Stable isotope measurements in this study are however done on bulk material with a probable diagenetic imprint which prevents direct comparison with the previous studies done on foraminifera. Nevertheless, this multiproxy study does support the hypothesis that this marly interval (~0.60-1.00 m) represents the Dan-C2 hyperthermal event in this basin. The exact (global?) nature, severity and extent of this event can only be evaluated by further studies.
Temporal framework and astronomical climate forcing

The sedimentology of the lowest Danian in the Umbria-Marche basin is highly variable in facies on a short stratigraphical interval, making the precise and accurate construction of its temporal framework challenging (e.g. as discussed in Sinnesael et al., 2016a). The strata before the K-Pg boundary clay layer are bleached and geochemically altered but do not show different (rates of) sedimentation compared to the underlying typically pink Maastrichtian limestones of the R2 member Scaglia Rossa (Montanari et al., 1989; Lowrie et al., 1990, Sinnesael et al., 2016a). With the impact at the K-Pg boundary this pelagic carbonate sedimentation was abruptly interrupted, and the K-Pg boundary clay was deposited (Alvarez et al., 1980). The amount of time represented in the K-Pg boundary clay is estimated to be in the order of 10 kyr (e.g. Mukhopadhyay et al., 2001). On top of the boundary clay there is the ~45-cm-thick, hard and fine grained Eugubina Limestone. This limestone interval is followed by a marly interval some ~50-60 cm thick, which then again is followed by a pink limestone interval that becomes more marly again towards the 3-4 m interval. In the middle of this complex interval, there is the ALE volcanic ash layer (2.00 m above the K-Pg boundary in the COH section, 2.45 m in the MRL section). Earlier fission track analysis on 18 selected apatite crystals gave a rough and unrealistic age for the ALE of ~90 Ma (Odin et al., 1992). The same study reports the extraction of small zircons, which were deemed unsuitable for dating, and recovered biotite flakes which, although euhedral, sometime in booklets, seemingly fresh and with no signs of alteration, were believed to be too small for further separation and utilization for radioisotopic dating. In this study, the new $^{40}\text{Ar}/^{39}\text{Ar}$ age of the small biotite flakes of 64.7 ± 1.6 Ma appears more accurate considering its position relative of the K-Pg boundary ($^{40}\text{Ar}/^{39}\text{Ar}$ dated at 66.043 ± 0.043Ma according to Renne et al., 2013), but is
unfortunately not precise enough to be useful to entangle the precise timeline (~10^4 kyr on orbital time scales) of the complex post-K-Pg sedimentary successions.

Classical magneto- and biostratigraphy are the backbone of the temporal calibration of this stratigraphical interval (Roggenthen and Napoleone, 1977; Lowrie et al., 1982; Gardin et al., 2012; Coccioni et al., 2013; Coccioni and Premoli Silva, 2015), but cyclostratigraphical analyses have the additional advantage of providing time information between discrete (boundary) events (Husson et al., 2014; Galeotti et al., 2015; Sinnesael et al., 2016a; Sinnesael et al., 2016b).

Assuming no major sudden changes in the sedimentation rate, for which there are no sedimentological indications, Sinnesael et al. (2016a) documented in the Maastrichtian BOT section a shift from a strong obliquity signal for the ~7.2 - 4.0 interval towards a predominant precession and eccentricity imprint for the latest Maastrichtian interval (~4.0 - 0 m). The sliding FFT off the Maastrichtian pXRF MRL Fe data shows the same pattern (Fig. 12): an obliquity component (~0.6 m period, 1.7 m^-1 frequency) for the ~6.00 - 3.00 m interval which transitions towards a coupled precession (~0.3 m period, 3.0 m^-1 frequency) and eccentricity (~1.6 m period, 0.7 m^-1 frequency) imprint for the upper half of the Maastrichtian section. The ratios between these periodicities match well with the ratios of the estimated durations of precession and obliquity for 66.0 Ma (18.7, 22.5 kyr, and 39.5 kyr respectively, Berger et al., 1992). This interpretation implies an average upper Maastrichtian sedimentation rate for the MRL section of ~15 m Myr^-1, which is considerably higher than the one used for the parallel interval in BOT by Sinnesael et al. (2016a); i.e. 10.7 m Myr^-1. One explanation is that the Gubbio sections are generally more condensed than the Morello section (Tab. 1), but this ~1.15 factor difference does not explain the full discrepancy. An additional explanation is the accidental sampling of styolite material in the BOT series which causes some deviations in the analyzed signal of the detrital proxies like Fe and magnetic
susceptibility (see earlier discussion). However, the general pattern of the shift from an obliquity dominated pattern towards precession-eccentricity is robust.

Cyclostratigraphic work on several sections worldwide (Zumaia, Sopelana, Shatsky Rise and Walvis Ridge) suggests that the La2011 eccentricity solution is the one matching best the data for the Danian (Dinarès-Turell et al., 2014). This solution has a 405 kyr eccentricity minimum coinciding with a 2.4 Myr eccentricity minimum between 66.45 and 66.25 Ma. Using the 66.043 \(^{40}\text{Ar}/^{39}\text{Ar}\) age from Renne et al. (2013) and taking the 3 m interval with a sedimentation rate of 15 m Myr\(^{-1}\) (3 m divided by 15 m Myr\(^{-1}\) = 0.2 Myr duration) gives an age for the obliquity-precession transition of 66.243 Ma – so coinciding with 2.4 Myr eccentricity interval of the La2011 eccentricity solution within the error. This interpretation supports the Dinarès-Turell et al. (2014) interpretation concerning the locations of 2.4 Myr eccentricity minima for this stratigraphical interval. Such minimal eccentricity configuration can be a good explanation for the dominant obliquity cycle for this interval. This understanding complements the initial hypothesis by Sinnesael et al. (2016a) that this transition would have been caused by changing climate sensitivity caused by a coinciding global warming caused by Deccan volcanism. Amplified carbon cycle sensitivity to orbital precession during the Deccan greenhouse warming was also suggested by Barnet et al. (2017). One proxy to establish this amplified sensitivity used in this study is the Fe intensity data from Ocean Drilling Program (ODP) Site1262 (Walvis Ridge, South Atlantic) which was originally published in Westerhold et al. (2008). In contrast with the available data from the Umbria-Marche basin this data set spans a longer stratigraphical interval which allows testing if this obliquity-precession also occurs for this section and additionally test the extent of the obliquity dominated interval (assuming precession is dominant once not in the 2.4 Myr eccentricity minimum). The sliding FFT off these Fe intensity data for the uppermost Maastrichtian (not shown
in this paper) indeed shows a transitional increase in obliquity power for this interval (223-225 m
mcd interval using a window size of 4 m). Time series analysis of the same data according to the
age model of Barnet et al. (2017) shows no power in the eccentricity frequency range for its 66.2
-66.4 Ma interval which fits with the hypothesis of a 2.4 Myr eccentricity minimum location.
However, no clear obliquity is visible in this interval according to this age model and there is a
shift to higher frequencies in the precession band which suggests potential tuning of actual
obliquity cycles as precession cycles. The same analysis approach was applied on the magnetic
susceptibility data from the upper Maastrichtian in Zumaia (data from Batenburg et al., 2012,
2014) and also in this case a similar pattern is visible (interpreted obliquity component imprint in
the 5-10 m interval below the K-Pg boundary interval). When analyzing large stretches of time
(e.g. almost the entire Maastrichtian in Batenburg et al., 2012, 2014) such small scale difference
are more difficult to detect because of several reasons (e.g. the focus is on the integrated spectrum
of the whole signal, relative larger window sizes in moving window approach will smooth out
small scale variations). In conclusion does the integration of these data and interpretation from
different sections suggest that there is a 2.4 Myr eccentricity minimum interval, which has the
dominant expression of obliquity signals – unless in the unlikely case that in all different sites there
would be coinciding changes in sedimentation rate – that last for about ~200 kyr (ages ~ 66.25-
66.45, assuming a K-Pg boundary age of 66.043 Ma). With the same assumptions, this interval
includes for all sections the C30n/C29r magnetostratigraphic boundary which is
cyclostratigraphically dated in Morello at an age of 66.32 Ma.

Current cyclostratigraphical interpretations for the earliest Danian are debated in the
Gubbio sections (Husson et al., 2014; Galeotti et al., 2015; Sinnesael et al., 2016a, 2016b) and
elsewhere (e.g. the post-K-Pg boundary “Strange Interval” in Westerhold et al., 2008 and Hilgen
et al., 2015). Can a cyclostratigraphical interpretation for the Maastrichtian and location of the K-Pg boundary intertwined with an eccentricity solution (i.e. La2011) help to resolve the complex lowermost Danian chronology? Therefore the 1 cm resolution magnetic susceptibility record from COH (published in Sinnesael et al., 2016a) is reinvestigated in detail using the sliding FFT technique (Fig. 12). The lower part of the stratigraphical interval (0.0 – 0.8 m) shows a stronger imprint of a ~ 0.18 m thick periodicity (5.5 m\(^{-1}\)) and the upper part (0.8 – 2.0 m) of a ~0.44 m thick periodicity (2.3 m\(^{-1}\)). Admittedly, the changing sedimentology makes robust interpretations difficult, but the current best interpretation (respecting the detailed bio- and magnetostratigraphy) is the association of the ~ 0.18 m periodicity with obliquity and ~0.44 period with short (100 kyr) eccentricity (Fig. 12). Husson et al. (2014) similarly identified a 0.17 m obliquity component and 1.75 m 405-kyr eccentricity component for the lowermost Danian in COH for the whole interval, but did not specify the spatial distribution of the relative occurrence of these components. Again could a potential obliquity imprint be explained by the relative position of being in a 405 kyr eccentricity minimum close to a 2.4 Myr eccentricity minimum. This interpretation results in an average sedimentation rate of ~4.5 m Myr\(^{-1}\) which is in agreement with previous studies (e.g. Sinnesael et al., 2016a, 2016b). Opposed to the Maastrichtian part of the section, the sedimentology is however variable and relatively high changes in sedimentation rate over the stratigraphical interval cannot be totally excluded. The large change in sedimentation rate across the K-Pg boundary is well documented (e.g. see above, Arthur and Fischer, 1977; Smit, 1982; Mukhopadhyay et al., 2001; Gardin et al., 2012; Coccioni et al., 2013; Sinnesael et al., 2016a).

Following the cyclostratigraphical interpretations presented in this study for both the Maastrichtian and Danian in the Umbria-March basin, the stratigraphical location of the DAN-C2 hyperthermal event coincides with the first pronounced short eccentricity maximum in a 405 kyr
maximum after a 2.4 Myr eccentricity minimum (Fig. 12). This is the same orbital setting for the occurrence of the PETM and Elmo hyperthermal events (Lourens et al., 2005). The identical events and corresponding astronomical imprint were identified in the Contessa Road section of the Umbria-Marche basin (Galeotti et al., 2010; Laurin et al., 2016). Although the DAN-C2 event is less large in terms of global climatic perturbation compared to the Elmo and PETM, the astronomical imprint could be a hint that it is an actual hyperthermal event, and that eventually the occurrence of other intervals characterized by marly intervals and negative δ¹³C excursions is astronomically paced. Examples could be the Top-C27n event or Latest Danian Event (LDE) and the Low-C27r which are recognized as well as in the Umbria Marche basin (e.g. Coccioni et al., 2012 and Galeotti et al., 2015) as elsewhere (e.g. Dinarès-Turell et al., 2014; Hilgen et al., 2015).
Figure 12. Cyclostratigraphic interpretation of the Cretaceous-Paleogene (K-Pg) boundary event stratigraphical interval. The La2011 eccentricity solution is shown in the time domain with 20 kyr missing at the K-Pg clay layer (Mukhopadhyay et al., 2001; Laskar et al., 2011a, 2011b; Renne et al., 2013; Dinarès-Turell et al., 2014). Proxies for detrital input with the highest available spatial resolution (every 5 cm Fe pXRF data from the Morello Maastrichtian (this study) and every 1 cm magnetic susceptibility data from COH (Sinnesael at el., 2016a) were selected for evolutionary fast Fourier transformation analysis. Plotted He$^3$ data come are from Mukhopadhyay et al. (2001).

6. CONCLUSIONS

This basin-wide multiproxy study of the K-Pg boundary event stratigraphy in the Umbria-March basin demonstrates the successful application of pXRF measurements as a regional
stratigraphical correlation tool. The pXRF elemental profiles (e.g. Ca, Fe, Sr, Mn) of the new Morello section and the well-studied Gubbio sections can easily be correlated. This correlation was verified with the classical stratigraphical applications such as biostratigraphy and magnetostratigraphy. Furthermore, the first bulk carbonate Campanian to Ypresian $^{87}\text{Sr}/^{86}\text{Sr}$ record from the Gubbio sections provides a chemostratigraphical reference for the Umbria-Marche basin stratigraphy. The Morello section seems less altered by burial diagenesis than the classical Gubbio sections and is put forward as an alternative location for sampling the interval around the K-Pg boundary event. The inclusion of four additional K-Pg sections from the basin allowed a robust inter-basin comparison of the expression of the K-Pg boundary event in the various proxy records. Major extinction and decrease in productivity from coccolithophora at the K-Pg boundary causes a drop in the bulk Sr/Ca ratio across the boundary, while its recovery is expressed in a steady increase in Sr/Ca values. A time interval of ~200 kyr (66.45 - 66.25 Ma) dominated by an obliquity imprint marks a 2.4 Myr eccentricity minimum and fits best with the La2011 eccentricity solution. This cyclostratigraphical interpretation also suggests that the first Paleogene hyperthermal event, the DAN-C2, has a similar astronomical configuration as the PETM (short eccentricity maximum after a 2.4 Myr eccentricity minimum). This is further evidence for the hypothesis that the Paleogene hyperthermals were astronomical paced.

**APPENDIX**

Deposit (new) data in an online database or in supplementary materials.

Table_pXRF

Table_Stable_Isotopes

Table_Strontium_Isotopes
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At the end by Matthias.