Orbitally paced phosphogenesis in Mediterranean shallow marine carbonates during the middle Miocene Monterey event

Gerald Auer1, Christoph A. Hauzenberger1, Markus Reuter1, and Werner E. Piller1
1Institute of Earth Sciences, University of Graz, NAWI Graz Geocenter, Graz, Austria

Abstract During the Oligo-Miocene, major phases of phosphogenesis occurred in the Earth’s oceans. However, most phosphate deposits represent condensed or allochthonous hemipelagic deposits, formed by complex physical and chemical enrichment processes, limiting their applicability for the study regarding the temporal pacing of Miocene phosphogenesis. The Oligo-Miocene Decontra section located on the Maiella Platform (central Apennines, Italy) is a widely continuous carbonate succession deposited in a mostly middle to outer neritic setting. Of particular interest are the well-winnowed grain to packstones of the middle Miocene Bryozoan Limestone, where occurrences of authigenic phosphate grains coincide with the prominent carbon isotope excursion of the Monterey event. This unique setting allows the analysis of orbital forcing on phosphogenesis, within a bio, chemo, and cyclostratigraphically constrained age-model. LA-ICP-MS analyses revealed a significant enrichment of uranium in the studied authigenic phosphates compared to the surrounding carbonates, allowing natural gamma-radiation (GR) to be used as a qualitative proxy for authigenous phosphate content. Time series analyses indicate a strong 405 kyr eccentricity forcing of GR in the Bryozoan Limestone. These results link maxima in the GR record and thus phosphate content to orbitally paced increases in the burial of organic carbon, particularly during the carbon isotope maxima of the Monterey event. Thus, phosphogenesis during the middle Miocene in the Mediterranean was controlled by the 405 kyr eccentricity and its influence on large-scale paleoproductivity patterns. Rare earth element data were used as a tool to reconstruct the formation conditions of the investigated phosphates, indicating generally oxic formation conditions, which are consistent with microbiobly mediated phosphogenesis.

1. Introduction

Episodes of globally increased phosphogenesis are widely recognized throughout the Earth’s history [Cook and McElhenny, 1979; Föllem et al., 1992, 1994, 2005, 2008, 2015; Föllem, 1996; Jacobs et al., 1996; John et al., 2002]. These events of phosphogenesis correlate well with episodes of strong climatic shifts and carbon isotope excursions, of which the so called Monterey event (~16.9–13.5 Ma) is a well-known example during the Miocene [Woodruff and Savin, 1991; Flower and Kennett, 1994; Jacobs et al., 1996; Abels et al., 2005; Holf Boum et al., 2007; Mourik et al., 2011; Diester-Haass et al., 2013; Tian et al., 2013]. The middle Miocene climate optimum (MMCO) and the subsequent middle Miocene climate transition (MMCT) associated with the Monterey event are of particular interest to the Earth’s climatic evolution since they represent the beginning shift from the Miocene greenhouse climate to the icehouse climate of the Pleistocene [Woodruff and Savin, 1989; Zachos et al., 2001a, 2001b, 2008; Shevrenell et al., 2008; Tian et al., 2013]. In combination with decreases in global CO2 atmospheric concentrations, the MMCT is often brought into a causal relationship with major changes in the organization of Earth’s ocean-circulation pattern [e.g., Vincent and Berger, 1985; Hannon et al., 2013]. This global oceanographical reorganization resulted from the formation of North Atlantic Deep Water and the gradual establishment of the modern ocean conveyor belt [Woodruff and Savin, 1989, 1991; Tian et al., 2009]. A likely cause for this shift is the closure of the Tethyan Seaway as a direct connection between the Indian and the Atlantic Ocean [Rögl, 2000; Steininger and Wessely, 2000; Harzhaurer et al., 2002, 2007, 2009; Reuter et al., 2009; Karami et al., 2011; Hannon et al., 2013]. In the Mediterranean, episodes of phosphogenesis coincide with these marked climatic and oceanographic changes [e.g., Föllem et al., 2008]. These widespread occurrences of authigenic phosphate are thus of particular interest in terms of their relationship to the paleoenvironmental and paleoclimatic changes in the late Oligocene to early late Miocene.
However, as most phosphorite deposits in deeper marine sections of the Mediterranean are highly condensed or were formed through gravitational enrichment processes (e.g., the hemipelagic phosphate deposits of Malta and Sicily) [see Föllmi et al., 2008], an exact correlation of authigenic phosphate precipitation and recognized shifts in paleoecological conditions has proven difficult, since they lack the needed stratigraphic resolution [Föllmi, 1996; John et al., 2002; Stamatakis, 2004; Föllmi et al., 2008, 2015; Filippelli, 2011].

In order to fully resolve such episodes of phosphogenesis and to understand underlying geological, climatic, and ecological processes, it is necessary to study the accumulation of authigenic phosphates in sections with sufficiently high sedimentation rates and a low content of reworked phosphate. This also presupposes the need for sections with well-established correlations to both global chronostatigraphy as well as global climatic records. Furthermore, phosphogenesis needs to be studied with sufficiently high temporal resolution to estimate changes in the amount of phosphate formed over time, in order to accurately correlate them with established palaeoecological and paleoclimatological records. To that end the Decontra section, which is a well-established shallow-marine reference section, with a robust orbitally tuned stratigraphic framework [Mutti and Bernoulli, 2003; Reuter et al., 2013; Auer et al., 2015], provides an opportunity to study the relationship between the occurrence of phosphates and global climatic events.

Recent studies found that most occurrences of phosphogenesis in the present day and ancient oceans were directly mediated by microbial activity, irrespective of the marine setting in which they formed [Föllmi, 1996; Mutti and Bernoulli, 2003; Hubert et al., 2005; Crosby and Bailey, 2012]. This direct biological control on the creation of one of the primary phosphorous sinks in the Earth’s ocean has far-reaching implications regarding the connection of the global phosphorous with the global carbon cycle as well as local primary productivity variations [Föllmi, 1996; Filippelli, 1997; Delaney, 1998; Schau et al., 2000; Slomp et al., 2002; van der Zee et al., 2002; Paytan and McLaughlin, 2007; Slomp and Van Cappellen, 2007]. Using the established stratigraphic framework of the section, it is possible to relate variations in phosphate accumulation within the section to important palaeoclimatological and paleoenvironmental changes along the Maiella carbonate ramp and the Mediterranean Sea as a whole.

The present work deals with three questions regarding phosphogenesis in the Decontra section during the MMCO and Monterey event: (1) Determine the phosphate contents on a sufficiently high-resolution to correlate them with global climatic records; (2) Apply selected rare earth element (REE) proxies to reconstruct the formation history of the phosphates, in order to put them into relation to the already established paleo-environmental history of the section; (3) Find the dominant uranium-bearing phase using electron microprobe and LA-ICP-MS analyses and understand the proxy-relationship between these phases and existing gamma log data.

2. Setting and Stratigraphy

The late Oligocene to late Miocene Decontra section lies on the northern slope of the Orfento river valley (N 42°09′43.5″, E 014°02′21.6″) southeast of the village Decontra on the Maiella mountains in Central Italy (Figure 1). The ~120 m thick Decontra section is composed of shallow marine carbonates deposited on a gently inclined carbonate ramp along the northern margin of the Apulian Platform [e.g., Vecsei and Sanders, 1999]. The section exposes the Bolognano Formation which represents the last depositional unit on the long-lived Maiella carbonate ramp before the beginning of the Mediterranean salinity crisis [Crescenti et al., 1969; Mutti et al., 1997; Vecsei et al., 1998; Vecsei and Sanders, 1999; Carnevale et al., 2011].

Within the section five lithostratigraphic units are described (Figure 2): (1) The 32 m thick Lepidocyclina Limestone, which is dominated by larger benthic foraminifera; (2) The Cerratina cherty Limestone—a 35 m thick succession of hemipelagic wackestones to packstones dominated by planktic foraminifers containing chert nodules, phosphatized foraminiferal tests, and sponge spicules. The first occurrence of the planktic foraminifer Praeorbulina sp. in the upper part of this unit indicates an age of <16.2 Ma; (3) The 32 m thick Bryozoan Limestone dominated by winnowed bryozoan grainstones with abundant planktonic and benthic foraminifers; (4) The 3 m thick Orbulina Limestone with abundant Orbulina sp.; (5) The Lithothamnium Limestone characterized by abundant red algal fragments overlying the Orbulina Limestone with a sharp contact. The base of the Lithothamnium Limestone is a 1.5 m thick horizon containing abundant Heterostegina fragments [see Reuter et al., 2013]. The Decontra section is dated using bio, chemo, and cyclostratigraphy [Vecsei and Sanders, 1999; Carnevale et al., 2011; Reuter et al., 2013; Auer et al., 2015]. Regional discrepancies
regarding the names of the used informal lithostratigraphic units, still hampers regional correlation of the units [e.g., Vecsei and Sanders, 1999; Cornacchia et al., 2015]. The lithostratigraphy after Reuter et al. [2013] and the current age model of the Decontra section are summarized in Figure 2.

The Decontra section is also well known for occurrences of authigenic phosphate, particularly within the middle Miocene Bryozoan Limestone, where a prominent phosphatic hardground occurs [Mutti and Bernoulli, 2003; Reuter et al., 2013]. This hardground was extensively studied in the past, and interpreted as an example of early lithification caused by microbially mediated phosphogenesis in a eutrophic shallow marine setting [Mutti and Bernoulli, 2003]. While the hardground represents the most prominent example of phosphatisation within the section, the Bryozoan Limestone contains phosphates throughout its well-sorted 32 m thick low-angle planar cross-bedded grainstones dominated by bryozoan and echinoid fragments with frequent occurrences of benthic and planktonic foraminifera in variable quantities. No major observable hiatuses occur throughout the Bryozoan Limestone [Reuter et al., 2013]. Planktonic foraminifera-dominated limestones occur at 72 m, and between 80 and 83 m above the base of the section [Reuter et al., 2013; Auer et al., 2015]. The sharp contact surface with frequent bioturbation at the top of the so-called Orbulina Limestone, is interpreted as the Ser4/Tor1 sequence boundary [Reuter et al., 2013]. Orbital tuning was used to further constrain the age of the Bryozoan Limestone and the overlying Orbulina Limestone to ~15.24—~11.92 Ma, indicating generally low but continuous sedimentation within this part of the section [Auer et al., 2015].

3. Methods

The gamma-ray measurements were carried out in the field in 2012 using a portable “GS-512” gamma-ray spectrometer (SatisGeo; measuring time 20 s), and are reported in total counts (TC) [Reuter et al., 2013; Auer et al., 2015]. Twenty-seven thin sections (5 × 5 cm) were prepared of the Bryozoan Limestone and used for microfacies analysis and a rough estimation of the phosphate content of the grainstones (Figure 5). Ten selected rock samples were analyzed for their bulk geochemical composition using X-ray fluorescence spectrometry (XRF) to characterize their overall P$_2$O$_5$ content and check for impurities in the limestone (mainly the concentrations of K$_2$O and MgO as an indicator of glauconite and other clay minerals. XRF analysis was performed at the Institute for Earth Sciences, NAWI Graz, University of Graz with a Bruker Pioneer S4. The ML-2 standard [Webb et al., 2012] (http://www.geoanalyst.org) as well as JLS-1 (Geological Survey...
of Japan) were measured as unknowns and reproduced within the reported errors for major components including P$_2$O$_5$.

P$_2$O$_5$ was subsequently correlated with the reported gamma-ray values from the field measurements. Comparison was done by averaging the gamma-ray measurements in the vicinity of the sampling spot. The results of this comparison together with the correlation coefficient were plotted in a standard cross plot (Figure 4a). To exclude potassium as a significant gamma-ray source, a similar cross plot was produced for K$_2$O and the averaged gamma ray density (Figure 4b).

Based on thin-section analyses, three representative samples were selected based on the presence of varying amounts of phosphatic grains and phosphatized skeletal material. Polished thick-sections (~150–200 μm thickness) of the samples were prepared and documentation of phosphatic grains was performed by backscattered electron (BSE) imaging, using a Jeol Superprobe JXA-8200 electron microprobe (EMP) at the Eugen F. Stumpfl Electron Microprobe Laboratory, UZAG (University of Leoben, University of Graz, Graz University of Technology). (Figure 6).

Figure 2. Lithology and orbitally tuned age model shown together with stratigraphic tie-points of the Decontra section and the Bryozoan Limestone (yellow) with occurrences of intervals rich in planktonic foraminifera (olive) [Auer et al., 2015; Reuter et al., 2013]. Natural gamma-radiation is shown as total counts per second, with a Gaussian band-pass filter applied to the frequency peak corresponding to the orbital 405 kyr eccentricity cycle (see Fig. 3) used as a proxy for long-term phosphate accumulation in the sediment. Maxima in the gamma-ray data were correlated to the carbon isotope maxima (CM-) events [see Holbourn et al., 2007], occurring during the Monterey event (highlighted in pink) TOC (black) and carbon isotope (red) curves are plotted adjacent to the gamma-ray signal. The benthic carbon isotope stack of Zachos et al. [2008] is shown for comparison.
| Table 1. Results of the LA-ICP MS Measurements of the Analyzed Phosphates and Carbonates as well as the Calculated REE Ratios |
|---------------------------------------------------------------|
| **Sample** | **Th (ppm)** | **U (ppm)** | **La (ppm)** | **Ce (ppm)** | **Pr (ppm)** | **Nd (ppm)** | **Sm (ppm)** | **Yb (ppm)** | **ΣREE (ppm)** | **Ce/Ce*** | **Pr/Pr*** | **Ce Anomaly** | **La/Sm** | **La/Yb** |
|---------------------------------------------------------------|
| **Phosphate** | | | | | | | | | | | | | | |
| AP01 | 0.01 | 0.63 | 28.8 | 11.9 | 4.79 | 21.3 | 4.52 | 5.5 | 104 | 0.23 | 1.4 | −0.68 | 0.93 | 0.39 |
| AP04 | 1.73 | 51.3 | 119 | 74.2 | 18.4 | 81.7 | 18.6 | 15.2 | 410 | 0.36 | 1.25 | −0.49 | 0.93 | 0.58 |
| AP05 | 14.8 | 69.8 | 596 | 374 | 128 | 565 | 120 | 84 | 2390 | 0.31 | 1.35 | −0.53 | 0.72 | 0.53 |
| AP06 | 0.24 | 57.5 | 30.5 | 18.5 | 4.93 | 21.3 | 3.88 | 3.7 | 103 | 0.34 | 1.3 | −0.51 | 1.14 | 0.61 |
| AP07 | 3.19 | 25.6 | 1346 | 668 | 371 | 1706 | 438 | 15.2 | 6252 | 0.22 | 1.43 | −0.68 | 0.45 | 0.61 |
| AP08 | 2.47 | 40.3 | 253 | 127 | 40.6 | 181 | 37 | 42 | 879 | 0.28 | 1.33 | −0.59 | 1 | 0.45 |
| AP10 | 3.4 | 37 | 237 | 177 | 64.7 | 284 | 67.9 | 31.6 | 1129 | 0.33 | 1.38 | −0.49 | 0.51 | 0.56 |
| AP12 | 6.49 | 132 | 602 | 344 | 119 | 494 | 108 | 84 | 2390 | 0.31 | 1.35 | −0.53 | 0.72 | 0.53 |
| AP13 | 0.57 | 29.5 | 59.7 | 31 | 13.8 | 65.5 | 16.2 | 7.97 | 257 | 0.25 | 1.42 | −0.55 | 0.81 | 0.45 |
| AP14 | 6.94 | 34.7 | 1051 | 446 | 215 | 992 | 438 | 173 | 4233 | 0.22 | 1.4 | −0.7 | 0.65 | 0.45 |
| AP15 | 19.9 | 30.5 | 1076 | 475 | 241 | 1161 | 286 | 168 | 4634 | 0.22 | 1.36 | −0.7 | 0.55 | 0.47 |
| AP16 | 0.31 | 35.1 | 248 | 105 | 43.8 | 195 | 47.8 | 38.2 | 905 | 0.23 | 1.4 | −0.67 | 0.75 | 0.48 |
| AP18 | 2.14 | 66.6 | 375 | 248 | 71.8 | 335 | 71.4 | 58.1 | 1504 | 0.35 | 1.25 | −0.5 | 0.77 | 0.48 |
| AP23 | 5.33 | 14.8 | 46.2 | 23.1 | 12.7 | 57 | 14.5 | 6.39 | 213 | 0.22 | 1.46 | −0.67 | 0.47 | 0.53 |
| AP24 | 5.14 | 40.2 | 199 | 85.5 | 29.7 | 138 | 30.7 | 38 | 694 | 0.25 | 1.31 | −0.65 | 0.95 | 0.39 |
| AP26 | 8.97 | 60 | 408 | 190 | 70.4 | 313 | 64.1 | 60.3 | 1427 | 0.26 | 1.37 | −0.63 | 0.93 | 0.5 |
| AP27 | 8.85 | 43.5 | 253 | 157 | 61.5 | 286 | 66.9 | 44 | 1169 | 0.29 | 1.34 | −0.57 | 0.55 | 0.43 |
| AP28 | 39.9 | 58.4 | 1497 | 933 | 360 | 1694 | 419 | 220 | 6811 | 0.29 | 1.32 | −0.56 | 0.52 | 0.5 |
| AP29 | 14.9 | 96.1 | 1290 | 874 | 305 | 1287 | 298 | 158 | 5402 | 0.32 | 1.41 | −0.51 | 0.63 | 0.6 |
| AP33 | 3.23 | 13.5 | 75.2 | 48.4 | 21.5 | 87.3 | 18.8 | 7.29 | 322 | 0.28 | 1.53 | −0.55 | 0.58 | 0.76 |
| AP34 | 32.4 | 51.6 | 923 | 856 | 259 | 1073 | 254 | 137 | 4488 | 0.4 | 1.38 | −0.39 | 0.53 | 0.5 |
| AP35 | 4.11 | 57.4 | 179 | 134 | 46.1 | 160 | 33.6 | 19.6 | 693 | 0.34 | 1.63 | −0.45 | 0.78 | 0.68 |
| AP37 | 0.75 | 14.2 | 866 | 443 | 18.9 | 77.5 | 18.2 | 8.23 | 320 | 0.25 | 1.5 | −0.61 | 0.69 | 0.78 |
| **Carbonate** | | | | | | | | | | | | | | |
| AP19 | 0.11 | 0.49 | 7.82 | 3.68 | 1.78 | 8.1 | 1.73 | 1.55 | 32.6 | 0.23 | 1.41 | −0.67 | 0.66 | 0.37 |
| AP20 | 0.02 | 0.28 | 3.66 | 1.39 | 0.56 | 2.48 | 0.51 | 0.57 | 3.26 | 0.2 | 1.4 | −0.68 | 0.88 | 0.62 |
| AP21 | 0.27 | 0.17 | 4.79 | 1.85 | 0.96 | 4.05 | 0.8 | 0.57 | 12.2 | 0.22 | 1.4 | −0.71 | 1.05 | 0.43 |
| AP22 | 0.69 | 0.4 | 7.07 | 3.31 | 1.33 | 5.72 | 1.23 | 0.83 | 24 | 0.25 | 1.43 | −0.64 | 0.84 | 0.63 |
| AP25 | 1.03 | 0.38 | 7.63 | 4.34 | 1.65 | 7.3 | 1.55 | 1.11 | 29.8 | 0.28 | 1.38 | −0.58 | 0.72 | 0.51 |
| AP30 | 0.42 | 0.23 | 8.05 | 3.66 | 1.41 | 6.17 | 1.25 | 0.93 | 26.2 | 0.25 | 1.4 | −0.64 | 0.94 | 0.64 |
| AP31 | 0.7 | 0.38 | 6.35 | 3.34 | 1.35 | 5.86 | 1.2 | 0.99 | 24.1 | 0.26 | 1.42 | −0.6 | 0.77 | 0.48 |
| AP32 | 0.34 | 0.18 | 7.05 | 3.42 | 1.28 | 5.49 | 1.2 | 0.81 | 23.7 | 0.26 | 1.42 | −0.62 | 0.86 | 0.64 |
| AP38 | 0.52 | 0.99 | 6.34 | 3.13 | 1.32 | 5.62 | 1 | 0.67 | 21.7 | 0.25 | 1.45 | −0.63 | 0.92 | 0.7 |
Using the BSE images, suitable phosphates were selected for LA-ICP-MS analyses. LA-ICP-MS analyses were performed at the NAWI Graz Central Lab “Water, Minerals and Rocks” (University of Graz and Graz University of Technology), in order to obtain concentrations for U, Th, and selected rare earth element (REE; see Table 1 for measured elements). A total 29 phosphatic aggregates and nine carbonate reference spots were measured (AP01–AP38; Table 1). Spots were measured using a 193 nm laser with a 75 μm spot pulse at 10 Hz, for very small grains of particular interest (AP7, AP11, AP37) a 50 μm spot was used instead. Dwell time was set at 60 s for each spot, preceded by a 30 s gas blank. Fractionation of elements may have an influence on analytical precision, especially when using nonmatrix-matched standards. However, as shown by Williams et al., [2014] fractionation is generally lower when using a 193 nm wavelength laser system and fractionation of lithophile elements is also generally much smaller compared to siderophile elements, resulting in only small or no fractionation effects for U, Th, and REEs in the analyzed material [Fryer et al., 1995].

Standardization of the LA-ICP-MS analyses was performed using the NIST standard reference material (SRM) 610 of the National Institute of Standards and Technology, Gaithersburg, MD, USA. Values for the SRMs reported by Jochum et al. [2011] were applied for quantification of results. The NIST SRM 612 standard was measured as an unknown to check for accuracy and reproducibility of the LA-ICP-MS analyses. Reproducibility of the NIST SRM 612 standard was within <5% relative concentration of U, Th, and the selected REE elements.

While the NIST SRM glasses are not matrix-matched to the analyzed carbonate and phosphate material, they offer distinct benefits compared to various matrix-matched standards (i.e., the MACS-3 carbonate and MAPS-4 phosphate reference material). Several analytical studies using biogenic carbonates and authigenic apatite found that the analytical advantages offered by the NIST SRM glasses outweigh the disadvantages of standardization using an unmatched matrix, which is largely based on the much better known trace element concentration of the NIST reference glasses compared to other standards [Jochum et al., 2012; Evans and Müller, 2013; Caragnano et al., 2014; Williams et al., 2014]. Time-averaged concentration values of the LA-ICP-MS analyses were obtained using GLITTER (ver. 4.0) (Macquarie University, Sydney). Nevertheless, the MAPS-4 standard was measured as an unknown to check for accuracy and reproducibility of the LA-ICP-MS analyses. Reproducibility of the MAPS-4 standard was measured as an unknown to check for accuracy and reproducibility of the LA-ICP-MS analyses. Reproducibility of the MAPS-4 standard was within <5% relative concentration of U, Th, and the selected REEs.

Electron microprobe (EMP) analyses were subsequently carried out in close proximity to the LA-ICP-MS craters, after repolishing the samples. Since the grains are complex and often highly porous mineral aggregates of calcium fluor apatite and calcium carbonate, EMP analysis did not yield results close to the theoretical value of fluor apatite and calcite. Thus, all calculations of analyzed phosphates as well as calcium carbonates utilize a consistent CaO concentration of 55 wt. % as the internal standard value [e.g., Koenig et al., 2009].

### 3.1. Data Analysis

Prior to interpretation, the measurements were evaluated for mixed signals of phosphate grains and surrounding carbonate rock based on their major elements (Ca, P, Al, Si). This preevaluation excluded several spots from the subsequent data analyses (AP3, AP09, AP11, AP17, and AP36).

REE concentrations for each spot were transformed into shale-normalized REE concentrations using the Post Archean Australian Sedimentary Rocks (PAAS) standard [McLennan, 1989]. The PAAS standard was chosen for normalization, as it represents a widely used reliable normalization standard for the analysis of REE concentrations in marine environments [Alibo and Nozaki, 1999; Shields and Stille, 2001; Haley et al., 2004; Garnit et al., 2012].

PAAS normalized REE concentrations were then used to calculate the Ce anomaly, a useful tool for the characterization of paleoredox conditions [German and Elderfield, 1990; Bau and Dulski, 1996; Morad and Felitsyn, 2001; Shields and Stille, 2001; Garnit et al., 2012]. German and Elderfield [1990] defined the Ce anomaly (Ce/Ce*) as

$$Ce/Ce^* = 3(Ce_{sample}/Ce_{shale})/\{2(\text{La}_{sample}/\text{La}_{shale})+(\text{Nd}_{sample}/\text{Nd}_{shale})\}$$

after De Baar et al. [1985]. (Table 1 and Figure 7).

Furthermore, the plot Ce/Ce* against Pr/Pr* [Bau and Dulski, 1996] can be applied as another way to characterize redox conditions using shale normalized REE concentrations (Table 1 and Figure 8). The Ce/Ce* versus
Pr/Pr* plot allows to evaluate the Ce anomaly for possible spurious results caused by anomalous enrichment of La [Bau and Dulski, 1996; Shields and Stille, 2001; Garnit et al., 2012]. For the Ce/Ce* versus Pr/Pr* plot, the anomalies were calculated according to Bau and Dulski [1996] as:

\[
\text{Ce/Ce}* = \left( \frac{C_{\text{sample}}}{C_{\text{shale}}} \right) / \left( \left\{ 0.5 \left( \frac{La_{\text{sample}}}{La_{\text{shale}}} \right) + 0.5 \left( \frac{Pr_{\text{sample}}}{Pr_{\text{shale}}} \right) \right\} \right)
\]

and

\[
\text{Pr/Pr}* = \left( \frac{Pr_{\text{sample}}}{Pr_{\text{shale}}} \right) / \left( \left\{ 0.5 \left( \frac{Ce_{\text{sample}}}{Ce_{\text{shale}}} \right) + 0.5 \left( \frac{Nd_{\text{sample}}}{Nd_{\text{shale}}} \right) \right\} \right)
\]

Additionally, the La/Sm ratio was calculated to account for the possibility that anomalous Nd enrichment may cause a false negative Ce anomaly [Morad and Felitsyn, 2001]. A combination of these methods was used to account for possible errors or false positives in either one these methods.

A cross plot of the La/Sm versus La/Yb ratios was used to compare the investigated phosphates to the reported ratio of modern seawater to test for the effect of diagenesis on our samples as proposed by Reynard et al. [1999].

The REDFIT power spectrum for the Bryozoan Limestone shown in Figure 3 was calculated from the GR data by Auer et al. [2015] and used for the orbital tuning of the section. The analyses were carried out using the software PAST (version 3.0; http://folk.uio.no/ohammer/past/) [Hammer et al., 2001] and are discussed in the aforementioned work.

4. Results

4.1. Facies and Bulk Sediment Analyses

Thin section analysis of the 27 samples taken within the Bryozoan Limestone reveals well-winnowed carbonatic grainstones, predominantly composed of bryozoan and echinoid derived skeletal fragments containing a variable amount of planktonic and benthic foraminifera. In the lowermost 2 m of the unit below, the microbially formed phosphatic hardground, notable occurrences of benthic foraminifera (Amphistegina, Elphidium, and miliolids) and corallinaceans are common [Reuter et al., 2013]. Microbial micrite occurs in the sediment pores just below the hardground [Mutti and Bernoulli, 2003; Reuter et al., 2013].

Within the Bryozoan Limestone, frequent phosphatisation is observed. Variations in the total amount of phosphatisation are present throughout the investigated interval (Figure 5). The phosphates predominantly occur as diffuse clusters or thin (~10 μm) filaments throughout the carbonatic sediment. They correspond to the diffuse aggregates and accumulations along grain boundaries observed in thin sections (Figure 5). The phosphate along grain boundaries is mostly oriented parallel to the direction of sedimentation. Phosphatized planktonic and benthic foraminiferal tests, as well as infillings of both bryozoan and echinoid skeletal fragments are also common. Clearly delimited well-rounded and thus likely transported phosphatic grains are rare. Glauconitic grains, easily identifiable by their distinctive bright green color, are also rare (Figure 5).

Gamma-ray counts measured in the Bryozoan Limestone unit vary between 1.8 and 7.8 counts per second, with a median of 3.4 and an average of 3.5, the standard deviation is 0.85. Analysis of the gamma-ray records reveals a clear cyclic variation, which is well-resolved in the REDFIT power spectrum.
The results of the spectral analysis reveal a significant peak at 2.94 m with some additional peaks of lower significance, that were confirmed by Wavelet analysis [Auer et al., 2015]. Using the available age model of the section [Reuter et al., 2013], the 2.94 m peak closely fits the 405 kyr long eccentricity, showing that the GR-signal was strongly influenced by orbital parameters. The cyclic pattern matching the 405 kyr eccentricity is well reflected in the Gaussian band-pass filters applied to the data. Interestingly, the amplitudes of the 2.94 m periodicity show a marked decrease in the middle part of the investigated Bryozoan Limestone unit, corresponding to the end of the Monterey event (Figure 2).

Results of the XRF analysis show that all samples are very pure carbonates, with only race amounts of SiO₂, Fe₂O₃, and Al₂O₃ contained in the sample. The samples have an average P₂O₅ content of 0.1 wt. %. Results range from 0.04 to 0.18 wt.% and correlate well with the gamma-ray intensity obtained in the field (r = 0.83) (Figure 4a). K₂O is highly accessory with concentrations ranging between ≤0.02 and 0.08 wt.% and is only weakly correlated (r = 0.57), showing that potassium is not a major gamma-ray source for the sediment (Figure 4b). The correlation between gamma-ray intensity and Al₂O₃, a proxy for phyllosilicates and other terrigenous material, is also weak (r = 0.45; not figured).

4.2. Trace Element Analysis
LA-ICP-MS and EMP analyses reveal that most investigated phosphatic grains likely represent complex microcrystalline aggregates of phosphate and calcium carbonate, making accurate analysis of the mineral composition difficult. This was further corroborated by the performed electron microprobe analysis of the samples. Nevertheless, matrix standardized results reveal a significant U enrichment of phosphate containing grains in gamma-ray sources compared to the surrounding purely carbonatic host material. Results of the LA-ICP-MS analyses show that the uranium content in the investigated phosphate grains is consistently elevated ranging between 13.5 and 131 ppm, with an average of 48.4 ppm and a median of 43.5 ppm. By comparison, the uranium concentration in the carbonate matrix ranges between 0.17 and 1 ppm, with an average of 0.44 ppm and a median of 0.39 ppm. The standard deviation of the U concentration in the biogenic carbonates is 0.25 ppm. These values result in an average enrichment of roughly 1:111 of uranium in the phosphatic grains compared to the carbonate matrix. Thorium content is comparably low in most analyzed grains, with only three grains showing significantly elevated Th content, in the range of ~30 ppm (Table 1). Th content in the carbonates is consistently low with ~0.44 ppm (Table 1). Total REE concentrations (La + Ce + Pr + Nd + Sm + Eu + Gd + Tb + Dy + Ho + Er + Tm + Yb + Lu) in the studied phosphatic grains vary between 104 and 6811 ppm. By comparison, the total REE concentrations of the carbonate range between 4.05 and 33.2 ppm (Table 1).

Calculation of the Ce anomaly following the methods of German and Elderfield [1990] and Morad and Felitsyn [2001] show a negative anomaly in all samples (Table 1). In the phosphatic grains, the average value of the Ce anomaly is −0.58. The carbonates are comparably similar with an average Ce anomaly of −0.64. Plotting

Figure 4. Cross plots showing the relationship between 60 cm average of natural gamma-radiation field data given in counts per seconds (CPS) and the P₂O₅ (a) and K₂O (b) content of corresponding bulk samples. Correlation coefficient (r) for the respective data sets are shown in the lower right of the plots. High correlation and more inclined regression line indicate a stronger dependency of gamma-ray intensity on P₂O₅ compared to K₂O. This indicates that U bearing phosphates and not K bearing clays (i.e., glauconite) are the dominant gamma-ray source.
Ce/\text{Ce}^* against \text{Pr}/\text{Pr}^* enrichment values [Bau and Dulski, 1996] further supports the observed negative Ce anomaly as true in all investigated grains. The Ce values can thus be used as an indicator for paleoredox conditions [Shields and Stille, 2001; Garnit et al., 2012]. The negative Ce anomaly is further confirmed by the La/Sm ratio, which should always be $>0.3$, in order to rule out that the result an artefact of artificial Nd enrichment [e.g., Morad and Felitsyn, 2001]. For our samples, the ratio has consistent values well above the threshold of $>0.3$ (Table 1).

### 5. Discussion

#### 5.1. Natural Gamma-Radiation as a Proxy for OM Fluxes

Previous studies used a close relationship between the preservation and transport of primary productivity derived organic matter (OM) and both large and small-scale patterns occur within the gamma-ray (GR) record of the Decontra section [Reuter et al., 2013; Auer et al., 2015]. This relationship is of particular importance in the well-winnowed nearly exclusively carbonatic Bryozoan Limestone. Winnowing by bottom currents effectively removed the small clay and silt-sized fraction from the sediment leaving a porous grainstone of sand-sized bryozoan and echinoid fragments, as well as planktonic and benthic foraminifera. Therefore, classical interpretations of variations in the GR record (i.e., content of terrigenous material) are not directly applicable [Auer et al., 2015]. The absence of riverine input and a significant amount of aeolian dust within the sediment leads to the need of a conceptual model explaining the observed orbitally paced variations within the Bryozoan Limestone [Auer et al., 2015]. The absence of potassium bearing minerals (i.e., clays) in the sediment only leaves uranium and thorium as significant gamma-ray sources within the sediment. Gamma-ray probe measurements in the field indicated uranium as the major source of the two. Subsequent laboratory analysis of bulk samples using XRF confirmed these field results and show that K\text{2O} is only repent in accessory amounts (on average 0.06 wt. %), indicating overall weak contribution of 40K to the total gamma ray counts. K\text{2O} is furthermore only weakly correlated with gamma-ray intensity (Figure 4b).

The dominance of uranium as GR-source was further confirmed by the LA-ICP-MS data, which indicate consistently higher U than Th concentrations in the phosphate grains, with low concentrations for both elements in the bulk carbonates (Table 1 and supporting information). The intercept of the regression line above zero in the correlation between \text{P}_2\text{O}_5 and total gamma radiation counts (Figure 4a), is thus a results of a minor but overall negligible contribution of K and Th to the overall signal. However, the analytical error of the gamma-ray spectroscope may also contribute to the offset. Large-scale trends in the signal should nevertheless be unaffected by stochastic analytical noise.

The comparably long residence time of uranium in the ocean of $\sim200–400$ kyr renders U concentrations in the ocean water very stable over geological times [Veeh, 1967; Veeh et al., 1974; Ku et al., 1977; Anderson, 1982]. The isolated position of the Maiella carbonate ramp during the Miocene (Figure 1) also excludes changes in fluvialite input derived variations of dissolved U concentrations as a cause for the observed variations. Changes in U caused by the deposition of different biogenic carbonates (i.e., varying portions of different skeletal fragments) can also be excluded, since all biogenic carbonates are known to incorporate uranium only during their formation and always in equilibrium with seawater [Veizer, 1983; Ter Kuile and Erez, 1987, 1988; Russell et al., 1994; Dunk et al., 2002]. This assumption is also supported by our LA-ICP-MS measurements of the carbonate matrix, where even spots placed in close proximity to other mineral grains (i.e., phosphates and iron oxides) exhibit generally low U and Th ($\sim0.44$ ppm) concentrations (Table 1).

Excluding the above mechanisms, variations in POM transport to the ocean floor serve as an effective way to enrich uranium concentrations within the sediment. This assumption is based on the fact, that dissolved uranium ions are preferentially bound to POM in the water column [Cochran et al., 1986; Klinkhammer and Palmer, 1991; Spirakis, 1996; McManus et al., 2005]. Together with microbiologically mediated dissolution of U enriched POM, this creates a primary productivity controlled process of U enrichment within pure carbonate sediments [Klinkhammer and Palmer, 1991; McManus et al., 2005].

To conclude, the combination of winnowing, U sequestration in the water column by OM and subsequent release of U in the sediment by OM degradation and direct incorporation into microbiologically formed phosphates [O’Brien et al., 1981; Crosby and Bailey, 2012] creates an independent primary productivity controlled
sink for uranium in the sediment, which circumvents problems with subsequent dissolution and remobilization of U in changing redox conditions [e.g., Piper and Calvert, 2009], since these occur contemporary within the sediment water interface, leading to both U and P enrichment, in an environment were microbes are known to be active [Crosby and Bailey, 2012] (Figure 9).

This coupling of microbial and redox processes makes uranium a more accurate proxy for relative primary productivity variations in oxic environments, than direct measurements of total organic carbon (TOC). TOC is generally lost in the sedimentary record, as it is quickly dissolved and refracted by biological processes in most settings. This also explains the comparably low organic carbon content of the investigated grainstones (Figure 2). TOC values are nevertheless slightly raised during the Monterey event, and show a prominent peak that can be correlated to CM6 (Figure 2).

### 5.2. Uranium as a Proxy for Relative Phosphate Concentrations

The aforementioned model does, however, not account for the stable mineral phase, binding U within the lithified sediment. Calcium fluor apatite (CFA) is assumed to be the predominant U bearing mineral phase within the sediment [Auer et al., 2015]. In light of the existing thin-section analyses, SEM and EMP BSE micrographs, as well as subsequent LA-ICP-MS analysis, we can now confirm this hypothesis. Average U concentrations of the CFA aggregates are \( \sim 48.4 \text{ ppm} \) compared to \( \sim 0.44 \text{ ppm} \) in carbonates (Table 1). Phosphatic grains thus show a \( \sim 110 \)-fold uranium enrichment compared to pure carbonates. This analysis is supported by the strong correlation between field gamma-ray intensity and \( P_2O_5 \) content of the XRF measurements of discrete rock samples (Figure 4a).

The fact that no other significant U sources occur within the sediment, and U concentrations of the carbonates remained relatively constant (see section 5.1 for discussion) allows the use of variations within the GR record of the Bryozoan Limestone as a proxy for the relative concentration of phosphate within the section. Similarly, a positive correlation between GR records and phosphorous concentration were also reported for phosphate deposits along the Florida platform [Compton et al., 1993].

Furthermore, the abundant diffuse phosphate observed in thin sections as well as the BSE images indicate a predominantly authigenic nature of the phosphates within the Decontra section, creating a link between phosphogenesis and the GR record (Figures 4–6). These results offer evidence that variations in GR are a useful tool for the relative estimation of the phosphate content within pure carbonates. Variations in phosphogenesis can consequently be reconstructed in unprecedented high resolution within the Decontra section (Table 1; Figure 2). In combination with the existing orbitally tuned age model [see Auer et al., 2015], it becomes possible to reconstruct the processes involved in phosphate formation on the Maiella ramp during the middle Miocene and to relate authigenic phosphate accumulation rates to global paleoclimatological records.

### 5.3. Conceptual Model of Phosphogenesis on the Maiella Ramp

Primary phosphogenesis circumscribes the formation of authigenic phosphate minerals, which predominantly occurs as calcium fluor apatite (CFA) in the marine realm [Ruttenberg and Berner, 1993; Föllmi, 1996; van der Zee et al., 2002; Filippelli, 2011]. The processes of phosphogenesis occur in a wide range of settings and, over the past decades, evidence for the constant and widespread occurrence of phosphogenesis on the Earth’s ocean floors was found, making the formation of authigenic phosphates a global phenomenon [Ruttenberg and Berner, 1993; Föllmi, 1996; Filippelli, 1997; van der Zee et al., 2002; Föllmi et al., 2005; Arning et al., 2009; Crosby and Bailey, 2012]. Current models of CFA formation vary for different settings and are orchestrated by a complex interplay of different processes [e.g., Föllmi, 1996]:

1. Precipitation of phosphate through redox-dependent absorption/desorption processes on Fe-Mn hydroxides.
2. Formation of phosphates in areas of high primary productivity and high net organic matter accumulation.
3. Seawater-derived phosphogenesis in settings with reduced sedimentation rates, early lithification, or impermeable substrates. Recent studies furthermore underscored the importance of microbial mats for the occurrence of phosphogenesis in the marine realm [Arning et al., 2009; Filippelli, 2011; Crosby and Bailey, 2012].

The comparably low sedimentation rates for the Bryozoan Limestone (\( \sim 9 \text{ mm yr}^{-1} \)) [Auer et al., 2015] create a setting that was conducive to the formation of microbiually precipitated authigenic phosphates (Figure 5) similar to recent examples from the east coast of Australia [O’Brien et al., 1981]. Incidentally evidence for this microbial activity was also reported for the prominent hardground \( \sim 2 \text{ m} \) above the base of the Bryozoan...
Figure 5. Transmitted (a–c, e, f) and reflected (d) light micrographs of thin sections from the Bryozoan Limestone, Scale bar = 200 μm. (a) Sample DC3-20B. Arrow shows minor phosphatisation of the chambers of Amphistegina sp.; sample has generally low phosphate contents corresponding to the gamma-ray trough before CM 4b (cf. Figure 2). (b) Diffuse authigenic phosphate coating grains in a sample dominated by planktonic foraminifers (some phosphatized). Sample shows generally high phosphate contents, corresponding to a peak in the gamma-ray data (Figure 2; DC3-21J). Black arrow indicates a phosphatized peloidal coprolite surrounded by diffuse phosphate (c) Transmitted light image of a plankton rich bryozoan fragment grainstone; sample DC3-21C. Phosphates occur as diffuse clusters within the sample; white arrow indicates a phosphatized hyaline foraminiferal test. (d) Corresponding reflected light image to Figure 5c; black arrow indicates iron oxide located in the center of a dense phosphate cluster. (e) Bryozoan fragment and planktonic foraminifers (e.g., Orbulina sp.) dominated grainstone with diffuse phosphates associated with microbial micrite. Black arrow: well-rounded detrital phosphate grain. Sample DC3-21H. (f) Bryozoan fragment dominated grainstone, with microbial micrite and diffuse authigenic phosphorite in diffuse aggregates that are following grain boundaries (white arrowhead) or are emplaced in micrite; black arrow indicates a reworked glauconite grain; sample DC3-21H (see Figure 6 for BSE images showing a similar features).
Figure 6. (a) Thick filamentous phosphate (Sample DC3-21B); (b) fine filamentous phosphate aggregate (Sample DC3-21H). This phosphate type is associated with the thin diffuse layers shown in Figure 5f. BSE image of a thick section prepared for LA-ICP-MS analyses (sample: DC3-21D; see Figure 2). Light grey areas in the BSE image correspond to phosphate grains (CFA), bright white areas correspond to iron oxides (OX), and darker grey areas correspond to minor occurrences of glauconites (Glt) within the carbonates (medium gray area) of the Bryozoan Limestone. White square in the BSE image represents the area shown in the EPMA elemental distribution maps of Phosphorous (P); note the diffuse authigenic phosphate in upper left associated with a phosphatized benthic foraminiferal test, Iron (Fe) was used to trace iron oxides; together with Aluminum (Al) and Silica (Si) indicates silicates like authigenic glauconite. The black spot represents an ablation crater left by the LA-ICP-MS analysis.
Grains using the Ce/Ce* versus Pr/Pr* plot [Garnit et al., 2012] described the fields of the plot as follows: Field I: no anomaly; Field IIa: positive La anomaly causes apparent negative Ce anomaly; Field IIb: negative La anomaly causes apparent positive Ce anomaly; Field IIIa: real positive Ce anomaly; Field IIIb: real negative Ce anomaly; Field IV: positive La anomaly disguises positive Ce anomaly. Using this interpretation, all analyzed phosphates as well as biogenic carbonates plot in the IIIb field, indicating the presence of a real negative Ce anomaly, indicative of oxic formation conditions.

This section and geochemical evidence (see section 5.2) support that phosphogenesis on the Maiella ramp occurred as a microbiologically mediated process in a dynamic current-energy-regime. Microbial activity in turn was largely guided by variable nutrient supply caused by changes in organic matter flux from the ocean surface via primary productivity controlled marine snow [Föllmi, 1996; Mutti and Bernoulli, 2003; Arning et al., 2009; Filippelli, 2011; Crosby and Bailey, 2012] (Figure 9). Here P and U are incorporated into the synchronously precipitating authigenic phosphates. Since the intensity of phosphate precipitation is consequently directly controlled by the amount of OM delivered to the ocean floor, this process follows large-scale productivity patterns and preserves the observed orbital trends in the uranium signal, that are only rarely preserved in TOC records, since most of it is lost to this refraction processes (Figures 6a, 6b, and 9).

Redox cycling only occurred in a limited area at the oxic/anoxic transition zone (OATZ) within the sediment, without significant mixing or enrichment from the overlying ocean water and in conjunction with the activity of magnetotactic bacteria [Aissaoui et al., 1990; McNeill, 1990; Frankel and Bazylinski, 1994; Fortin and Langley, 2005; Maloof et al., 2007; Kopp and Kirschvink, 2008]. This is supported by the investigated REE signatures of the phosphates as well as the biogenic carbonates, which both point towards well-oxygenated formation conditions (Table 1 and Figures 7–9).

REE signatures show a negative Ce anomaly in both the carbonate matrix and all investigated phosphatic grains using the Ce/Ce* versus Pr/Pr* plot [Bau and Dulski, 1996]. The plot is supported by the calculated Ce anomaly [German and Elderfield, 1990] (Figure 7; Table 1). Combined with the available REE signatures of modern pore waters, as well as biogenic, authigenic, and detrital phosphates from the literature indicates
that all investigated phosphates were formed in a well-oxygenated environment [German and Elderfield, 1990; Bau and Dulski, 1996; Alibo and Nozaki, 1999; Morad and Felitsyn, 2001; Haley et al., 2004; Shields and Stille, 2001; Garnit et al., 2012; Emsbo et al., 2015]. Furthermore, the La/Sm and La/Yb ratios from our data plot remarkably close to or within the reported values for modern seawater (Figure 8).

A slight trend toward more negative La/Sm values as well as enriched La/Yb values occurs in our data. This suggests that both phosphates and carbonates in the Decontra section were affected by substitution processes as well as adsorption processes during early diagenesis [Reynard et al., 1999; Shields and Stille, 2001; Garnit et al., 2012]. In general, however, our results indicate that both carbonates and phosphates were only slightly affected by early diagenesis and that any related alteration most likely occurred at the same time after final deposition. Interestingly Quaternary fish debris shows similar values to the investigated phosphates of the Bryozoan Limestone [see Reynard et al., 1999]. Although some contribution of reworked phosphate grains is likely, our results show that all measured phosphates formed in oxic conditions in connection with microbial activity and that their Uranium signal is not a product of subsequent alteration during diagenesis.

This creates a good explanation for the largely in-phase variability of both the magnetic susceptibility and GR records of the Decontra section [Auer et al., 2015], since the formation of microbially derived iron oxides and phosphates predominantly occurred during organic matter decomposition at a microbially controlled OATZ within the sediment. Combining these assumptions with our results allows the construction of a simple box model for the processes involved in phosphogenesis on the Maiella ramp (Figure 9).

5.4. Orbitally Paced Phosphogenesis and Its Implications for the Global Phosphorous Cycle

Economically viable phosphorites are generally deposited as lag deposits or hardgrounds formed during episodes of nondeposition or even active sediment removal. Thus, virtually all global phosphorite deposits are generally unrelated to primary P accumulation within the sediment and subsequent phosphogenesis [Filippelli, 2011]. Therefore, the Decontra section represents a unique opportunity since the formation history of shallow marine phosphates can be analyzed in the context of an orbitally tuned age model. While the continued occurrence of phosphogenesis throughout the Bryozoan Limestone points to long-term eutrophic conditions [Mutti and Bernoulli, 2003; Reuter et al., 2013], the distinct long-eccentricity forcing until ~13.5 Ma, indicates a strong orbital control on the phosphate formation. This directly links the accumulation of phosphate on the Maiella platform to variations in primary productivity during the Monterey event (Figures 2 and 3, and 9). By extent, the variations in phosphorous accumulation can also be linked to occurring patterns in the global carbon cycle, which are well reflected by the global carbon isotope record [Vincent and Berger, 1985; Jacobs et al., 1996; Abels et al., 2005; Mourik et al., 2011; Holbourn et al., 2015]. The subsequent breakdown in the 405 kyr eccentricity signal after ~13.5 Ma points toward a reorganization of ecological conditions controlling primary productivity at the end of the Monterey event, which directly relates to changes in net phosphate accumulation (Figure 2). Thus the marked shift in the preservation of the 405 kyr cyclicity and a general increasing trend in the GR signal (and thus phosphate accumulation) may point to drastically different primary productivity patterns during the early stages of the middle Miocene climate transition and thus a major reorganization of the marine phosphorus and carbon
cycles. This proposed reorganization in current patterns coincide with the closure of the Tethyan seaway and Antarctic ice sheet expansion during the MMCT [J. C. Zachos et al., 2001a; J. Zachos et al. 2001a; Harzhauser et al., 2007, 2009], and is thus an expression of major paleogeographical and climatological changes during this time.

Our results indicate that the well-known link between the carbon and phosphorous cycle [Föllmi, 1996; Filippelli, 1997; van der Zee et al., 2002; Filippelli, 2011] can now be extended to orbitally driven variations in net phosphorous burial in shallow marine settings. Changes in this forcing appear to be caused by significant global changes, such as the closure of the Tethyan seaway and the Antarctic ice sheet expansion during the MMCT, masking the orbitally paced pattern, which dominated during the Monterey event [Holbourn et al., 2015].

Our results provide insights into the pacing and formation requirements of the widespread middle Miocene shallow marine phosphorite deposits [Compton et al., 1993; Föllmi, 1996; Jacobs et al., 1996; John et al., 2002; Föllmi et al., 2008], and link them to the eccentricity forcing, global productivity, and climate cycles during the Monterey event for the first time. The orbital pacing of phosphogenesis shows that phosphorous accumulation is coupled to known pacing of primary productivity and organic carbon burial, which are proposed as the underlying causes of the Monterey event and the CM-events [see Holbourn et al., 2007; Diester-Haass et al., 2013; Holbourn et al., 2015].

Our model is thus in accordance with the hypothesis that variations in ocean circulation are the cause of the 405 kyr eccentricity-forcing observed in the $\delta^{13}C$ record during the Monterey event [Holbourn et al.,
6. Conclusions

The present study uses LA-ICP-MS data of carbonate grainstone as well as authigenic phosphate to characterize microbiologically mediated phosphogenesis in the middle Miocene Bryozoan Limestone of the Decontra section in the Maiella mountain range (Central Italy). Our results show that: (1) primary microbiologically controlled phosphogenesis persisted throughout the Bryozoan Limestone in accordance with previous studies [Muti and Bernardi, 2003; Reuter et al., 2013]. (2) LA-ICP-MS analyses confirm that phosphate is the primary carrier of uranium within the sediment. (3) The current-dominated, high-energy deposit system of the Bryozoan Limestone removed all other gamma-ray sources from the sediment, leaving phosphates as the primary source of gamma-radiation within the Bryozoan Limestone. This allows the GR data to be used as a high-resolution proxy for the relative phosphate content of the sediment. (4) The strong 405 kyr orbital control on the GR record found in previous studies [Auer et al., 2015] can now be linked to the phosphate content of the section. This link provides new insights into primary productivity and organic carbon burial cycles during the Monterey event. We show that increased calcium fluor apatite burial occurred in shallow marine carbonates during the carbon isotope maxima, which links Miocene phosphogenesis to eccentricity forcing. Phosphogenesis during the middle Miocene in the Mediterranean was thus controlled by the 405 kyr eccentricity and its influence on large-scale paleoproductivity patterns. (5) Significant changes occurred in the phosphate accumulation patterns at the end of the Monterey event, which can be related to changes in ocean circulation patterns caused by the closure of the Tethyan seaway and the onset in Antarctic ice sheet buildup. (6) Shale normalized rare earth element analysis of the investigated phosphates using the Ce anomaly and La/Sm ratio in combination with the Ce/Ce* versus Pr/Pr* and La/Sm versus La/Yb ratio plot proved useful in the reconstruction of their formation conditions, supporting their microbiologically mediated origin in a eutrophic and well-oxygenated setting.

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