Osmium Isotopic Evidence for Eccentricity-Paced Increases in Continental Weathering During the Latest Hauterivian, Early Cretaceous

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Abstract The 405-kyr eccentricity cycle is a consistent orbital parameter throughout the Phanerozoic that is associated with long-term variations in global continental weathering. However, a lack of reliable geological evidence has hampered the understanding of the relation between the 405-kyr eccentricity cycle and continental weathering during the Cretaceous. Os isotopic ratios ($^{187}$Os/$^{188}$Os) of the sedimentary record reflect the balance between radiogenic Os derived from continental weathering and Os derived from unradiogenic sources (e.g., hydrothermal activity, weathering of mafic rocks, and extraterrestrial sources). This ratio is therefore considered as a good proxy for the evaluation of short-term changes in continental weathering patterns. To trace orbital-paced continental weathering, this study reconstructs the marine Os isotopic records in upper Hauterivian to lower Barremian (Lower Cretaceous) carbonate rocks in central Italy, where previous studies have reported that variations in clay mineral composition are paced by the 405-kyr cycle. Our new Os isotopic record documents periodic oscillations of $^{187}$Os/$^{188}$Os between 0.7 and 0.9 that correspond to the 405-kyr Earth’s eccentricity cycle. Because the sedimentary interval with radiogenic $^{187}$Os/$^{188}$Os values ($\sim0.9$) corresponds to a time interval characterized by a humid climate in areas surrounding the Tethys, variations in the $^{187}$Os/$^{188}$O values likely reflect cyclic changes in continental weathering caused by eccentricity-paced intensification of monsoonal activity at low latitudes. This variation could have been further amplified by increased input of radiogenic Os from Paleozoic shale and Precambrian crust at higher latitudes that resulted from a latitudinal shift of the intertropical convergence zone.

1. Introduction

Changes in continental weathering and their association with variations in monsoonal activity related to orbital cycles have been widely reported throughout the Phanerozoic (e.g., Clemens et al., 1991; Ikeda et al., 2017; Martinez et al., 2015, 2013; Moiroud et al., 2012; Wehausen & Brumsack, 2002). The intensity of continental weathering during the Quaternary has been commonly linked to monsoonal activity, and the growth and retreat of polar ice sheets that are paced by astronomical cycles (Clemens et al., 1991; Elderfield et al., 2012; Oxburgh et al., 2007; Vance et al., 2009; Wang, 2009). However, during periods when the continents were ice-free, such as during the Mesozoic, monsoonal activity was the predominant influence on global-scale chemical weathering (Ikeda et al., 2017, 2020; Kutzbach & Gallimore, 1989; Wang, 2009). During the Permian and Triassic, for instance, global geochemical cycles were controlled by “mega-monsoons,” the intensity of which was modulated by precession and eccentricity cycles (Ikeda et al., 2017, 2020; Kutzbach & Gallimore, 1989). In contrast, monsoonal intensity was proposed to have weakened during the Cretaceous, as the break-up of the supercontinent Pangea changed the relationship between continents and the ocean (Wang, 2009). However, studies of monsoonal activity during the Cretaceous and its influence on the global geochemical cycle are limited. Recently, 405-kyr eccentricity cycles have been recognized in the Tethyan sedimentary record through changes in gamma ray spectrometry and clay mineral composition (e.g., kaolinite/chlorite ratio) of Valanginian to Barremian (Lower Cretaceous) sedimentary records (Martinez et al., 2013, 2015; Moiroud et al., 2012). Because kaolinite is formed under humid conditions (Martinez et al., 2015), these cycles have been interpreted as eccentricity-paced occurrences of humid conditions in which intensified monsoonal activity enhanced continental weathering (Charbonnier et al., 2016). However, because clay mineral composition was also strongly influenced by the regional, geological, and environmental setting of the Tethyan region, it is unclear whether these changes reflected global variations of monsoonal activity.
The radiogenic isotopic composition of osmium ($^{187}$Os/$^{188}$Os) reflects the balance between radiogenic Os input from continental materials with high $^{187}$Os/$^{188}$Os values (~1–1.5) and unradiogenic Os input with low $^{187}$Os/$^{188}$Os values (~0.1–0.2) from hydrothermal activity, weathering of mafic rocks, and extraterrestrial input (Levasseur et al., 1999). Isotopic variations of Os among these sources represent the differences in $^{187}$Re/$^{188}$Os. Since Re is more incompatible than Os, continental crust tends to have higher $^{187}$Re/$^{188}$Os than mantle due to the differentiation process. Additionally, organic-rich marine sedimentary rocks deposited under the reducing conditions have high $^{187}$Re/$^{188}$Os ratios (Dubin & Peucker-Ehrenbrink, 2015). Due to the β-decay of $^{187}$Re into $^{187}$Os with a half-life of 41.6 Gyr (Smoliar et al., 1996), these rocks tend to have higher $^{187}$Os/$^{188}$Os values than mantle or extraterrestrial material. Consequently, Os supplied from continental crust and the subaerially exposed old organic-rich sedimentary rocks have higher $^{187}$Os/$^{188}$Os values than mantle or extraterrrestrial material. Considering its geologically short residence time in the ocean (10–100 kyr: Levasseur et al., 1998, 1999), which is longer than the representative timescale of oceanic circulation, Os is regarded as a useful tracer of orbital-scale changes for global continental weathering rate (e.g., Oxburgh et al., 2007; Percival et al., 2016; Sekine et al., 2011). To investigate orbital-scale weathering conditions and their relationship to monsoonal activity during Early Cretaceous, we reconstruct an Os isotopic record from the latest Hauterivian to the earliest Barremian, an interval in which natural gamma radiation and clay mineral composition display a distinct cyclicity in the Tethyan sedimentary record (e.g., Martinez et al., 2015; Moiroud et al., 2012).

The studied sequence covers the oldest prominent oceanic anoxic event (OAE) of the Cretaceous (uppermost Hauterivian), the Faraoni Level (Cecca et al., 1994), which is dated at ~127 Ma (Martinez et al., 2015, 2020). The Faraoni Level is widely traceable in the Tethyan and Atlantic region (e.g., Baudin, 2005; Baudin & Riquier, 2014; Cecca et al., 1994; Rodríguez-Tovar & Uchman, 2017). The Faraoni Level is a thin sequence (<1 m) characterized by alternating laminated black shales and micritic white limestones that are easily recognized by a calcareous layer rich in well-preserved ammonites (Cecca et al., 1994). The high organic-carbon content and enrichment in redox-sensitive elements of the black shale layers have been interpreted as the dominance of oxygen-depleted bottom water during the Faraoni OAE (Bodin et al., 2007; Cecca et al., 1994; Charbonnier et al., 2018). Several studies have discussed a relationship between the Faraoni Level and volcanic events associated with the formation of a submarine basaltic plateau (e.g., Baudin, 2005). Because the Os isotopic ratio can be used not only as a proxy of continental weathering but also as a proxy of unradiogenic Os input from hydrothermal activity (Matsumoto et al., 2020; Tejada et al., 2009; Turgeon & Creaser, 2008), our data may offer new and significant insight into the factors triggering the deposition of the Faraoni Level.

2. Geological Setting

The Maiolica Formation, a well-preserved Upper Jurassic to Lower Cretaceous carbonate succession, crops out in the Umbria-Marche region, in central Italy. The Fiume Bosso section, one of the best-studied exposures of Hauterivian strata in the Umbria-Marche Basin, is located on the eastern limb of the Monte Nerone Anticline (Cecca et al., 1994; Coccioni et al., 1998). This section represents a pelagic environment of the central Tethys (Figure 1) (Godet et al., 2006). It primarily consists of yellowish-gray to medium-gray limestone interbedded with dark shale or chert (Coccioni et al., 1998). Here the Faraoni Level is represented by thin beds of black shale and limestone totaling ~25 cm in thickness with the ammonite-rich key bed in the middle (Cecca et al., 1994) (Figure 2). Limestone samples were collected from the upper Hauterivian to lower Barremian interval at the Fiume Bosso section (Coccioni et al., 1998).

3. Methods

3.1. Carbon Isotopic Ratio of Carbonate

Stable carbon and oxygen isotope ratios of carbonate ($\delta^{13}$C and $\delta^{18}$O) of powdered 41 limestone, three cherty limestone, and one chert samples were measured with an isotope ratio mass spectrometer (Delta V plus, Thermo Fisher Scientific, USA), equipped with an automated carbonate reaction device (GasBench II, Thermo Fisher Scientific, USA), at Atmosphere and Ocean Research Institute, The University of Tokyo (Japan). All isotopic values are reported using delta notation with respect to PeeDee Belemnite. External reproducibility was calculated from the repeated analysis of NBS-19 standard. Typical values are better than 0.05‰ and 0.08‰ for $\delta^{18}$O and $\delta^{13}$C, respectively. Detailed analytical methods are described in Shirai et al. (2018).
3.2. Re-Os Analysis

We performed Re-Os analyses on 23 limestone samples and two cherty limestone samples from the study section. Because the black shale in the outcrop is subject to weathering that affects its Re-Os system (Jaffe et al., 2002), we measured the Os isotopic ratio of two limestone samples between the black shale layers in the Faraoni Level (Figure 2c). Considering the short duration of the Faraoni Event (∼100 kyr: Martinez et al., 2015) and the residence time of Os (10–100 kyr: Levasseur et al., 1998, 1999), we assumed that these samples would fairly represent the marine Os isotopic signature during the deposition of the black shale beds.

We extracted Re and Os from the bulk rock samples with an inverse aqua regia digestion method. The rock samples were washed ultrasonically and ground in an agate mill. After spiking with $^{186}$Os- and $^{185}$Re-rich solutions, samples (~1.0 g) were sealed in a Carius tube (Shirey & Walker, 1995) with 4 mL of inverse aqua regia (1 mL of 30 wt% HCl plus 3 mL of 68 wt% HNO₃). Carius tubes were heated at 240°C for 48 hr, then the supernatant and residue were separated by centrifugation. Os was separated from the leachate with 3 mL of carbon tetrachloride (CCl₄) in three successive extractions. The extracted Os was reduced to a non-volatile form by adding 3 mL of 9N HBr into the CCl₄ and purified by micro-distillation (Birck et al., 1997). Re was separated from the leachate using Bio-Rad AG1-X8 anion exchange resin (100–200 mesh). Os abundances and isotopic compositions were determined by negative thermal ionization mass spectrometry (Thermal Electron TRITON) (Kuroda et al., 2010 and references therein) at the Japan Agency for Marine-Earth Science and Technology (JAMSTEC).

Figure 1. (a) Paleogeography and intertropical convergence zone (ITCZ) position in the Early Cretaceous based on Armstrong et al. (2016) and (b) detailed paleoceanographic reconstruction modified from Baudin (2005). Red and blue lines represent the position of ITCZ and the dashed red line represents the minor branch of ITCZ.
and Re abundances were determined by quadrupole inductively coupled plasma mass spectrometry (iCapQ) at JAMSTEC. All data were corrected for procedural blanks, which averaged 0.33 ± 0.25 pg Os with $^{187}\text{Os}/^{188}\text{Os}$ of 0.11 ± 0.04 and 2.6 ± 1.3 pg Re. The initial $^{187}\text{Os}/^{188}\text{Os}$ ($^{187}\text{Os}/^{188}\text{Os}_i$) was calculated as:

$$^{187}\text{Os}/^{188}\text{Os}_i = ^{187}\text{Os}/^{188}\text{Os}_m - \left[ \exp \left\{ /\text{u1D706} \times \text{age (yr)} \right\} - 1 \right] \times ^{187}\text{Re}/^{188}\text{Os}_m,$$

where $/\text{u1D706}$ is the decay constant of $1.666 \times 10^{-11}$ yr$^{-1}$ and the subscript “m” signifies measured values.

To ensure verify that Os isotopic variations resulting from the inverse aqua regia digestion methods reflect hydrogenous fraction, we conducted additional Re-Os measurements using the weak leaching method following Dunlea et al. (2021). In this analysis, 200 mg of limestone samples from the Fiume Bosso section were dissolved in 1 M HCl for 24 hr at room temperature. The leachate, separated from the residue using centrifugation, was spiked and sealed in a Carius Tube with 4 ml of inverse aqua regia (mixture of 68 wt% of HNO$_3$ and 1 ml of 30 wt% HCl). The succeeding separation procedure was the same as the inverse aqua regia digestion method described above. This digestion method does not strongly attack silicate minerals and is, therefore, expected to extract Os more accurately from hydrogenous fractions.

4. Results

4.1. Carbon and Oxygen Isotopic Ratios of Carbonate

Nearly all $\delta^{13}\text{C}_{\text{carb}}$ values in the study section clustered tightly between 1.6‰ and 1.9‰ (Figure 2, Matsumoto et al., 2021a). The poor correlation between $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ values suggests that samples had not experienced strong diagenetic alteration (Figure 3a). One chert sample yielded relatively low $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ values (1.43‰ and −3.93‰, respectively: Figure 3a, Matsumoto et al., 2021a) compared to the limestone samples.
Because chert does not undergo the same diagenetic processes as limestone, we excluded this sample from further consideration.

### 4.2. Re-Os Analysis

Os and Re abundances, extracted by inverse aqua regia, ranged from 8.0 to 18.9 pg g⁻¹ and 10.0–71.0 pg g⁻¹, respectively (Figure 2, Matsumoto et al., 2021b). The Os isotopic ratios of measured values (¹⁸⁷Os/¹⁸⁸Osₘ) and initial values (¹⁸⁷Os/¹⁸⁸Osᵢ) ranged from 0.70 to 0.97 and from 0.68 to 0.93, respectively (Figure 2, Matsumoto et al., 2021b). ¹⁸⁷Os/¹⁸⁸Osᵢ oscillated cyclically between ∼0.7 and ∼0.9 during the uppermost Hauterivian (Figure 2). The ¹⁸⁷Os/¹⁸⁸Osᵢ values of organic-rich sediments with high ¹⁸⁷Re/¹⁸⁸Os ratios are easily disturbed by leaching of Re and Os following oxidation of sedimentary rocks after exposure on land (Jaffe et al., 2002). However, considering the low ¹⁸⁷Re/¹⁸⁸Os of our limestone samples and the small difference between their measured and age-corrected initial ¹⁸⁷Os/¹⁸⁸Os values (at most 6.6%), weathering could not have caused a significant alteration of the original ¹⁸⁷Os/¹⁸⁸Os values. Besides, Selby and Creaser (2003) proposed that CrO₃–H₂SO₄ is a more appropriate method to extract the hydrogenous fraction of Re-Os information than aqua regia because CrO₃–H₂SO₄ weakly attacked silicate minerals, such as quartz and feldspar. However, the Re-Os information extracted with these two methods is almost identical (Matsumoto et al., 2020; Sekine et al., 2011; Selby & Creaser, 2003). Accordingly, Matsumoto et al. (2020) applied both extraction methods for the Re-Os analysis Cretaceous sedimentary rock samples collected from the Umbria–Marche Basin and the reconstructed ¹⁸⁷Os/¹⁸⁸Os values of both high Os-black shale and low-Os carbonate samples are almost identical. This suggests that Re-Os information extracted using inverse aqua regia digestion methods can mainly reflect the hydrogenous fraction of Re-Os. In addition, the Re-Os variation of the Umbria–Marche sedimentary record is concordant with that outside the Tethyan region, which rules out the possibility of a strong regional effect (Matsumoto et al., 2020). Because ¹⁸⁷Os/¹⁸⁸Osᵢ and Os abundance have no more than a weak Pearson linear correlation (Figure 3b), simple contamination by radiogenic Os from terrigenous material cannot explain the obtained fluctuation of ¹⁸⁷Os/¹⁸⁸Osᵢ.

Os and Re concentrations obtained by the HCl extraction method are much lower than those obtained by the inverse aqua regia digestion method (Figure 2). Although the overall variation patterns seem similar between these methods, measured and initial Os isotopic ratios (¹⁸⁷Os/¹⁸⁸Os) obtained by the HCl extraction method show less radiogenic values than those obtained by the inverse aqua regia digestion method (Figure 2). Besides, Os isotopic variations obtained by the HCl extraction method lack some radiogenic peaks (e.g., 8.41 m) that are observed in the Os data extracted by the inverse aqua regia digestion method.

![Figure 3.](image-url)
5. Discussion

5.1. Comparison of Os Isotopic Variations: The Inverse Aqua Regia Versus Weak-Leaching Methods

One possible reason for the discrepancy in Os isotopic values between the two digestion methods (i.e., inverse aqua regia and 1 M HCl) is the different degree of contamination of the radiogenic Os from silicate minerals. The inverse aqua regia more strongly attacks the clay minerals than 1 M HCl (Dunlea et al., 2021). Therefore, more radiogenic Os isotopic values obtained by the inverse aqua regia digestion method may be attributed to the higher contamination of radiogenic Os from clay minerals. However, considering Os isotopic ratios do not take radiogenic values during the Faraoni Level, where the enrichment of kaolinite is observed (Figure 4) (Moiroud et al., 2012), the contamination of terrestrial radiogenic Os from clay minerals may be substantially insignificant in our samples. Thus, the difference in the degrees of radiogenic Os contamination from clay minerals cannot fully explain the dissimilar Os isotopic trends between these two methods.

Another possibility is the partial dissolution of unradiogenic Os sources (e.g., extraterrestrial materials). Dunlea et al. (2021) revealed that Os isotopic ratio extracted from the pelagic clay samples using extremely weakly acidified conditions (0.05–0.1 M HCl) shows more unradiogenic values than the coeval marine Os isotopic ratios. This difference was interpreted as the dissolution of different Os complexities and Os bearing phases (extraterrestrial materials) or the local unradiogenic Os sources. Thus, the higher partial dissolution from the unradiogenic Os sources in our samples may be able to explain less unradiogenic Os isotopic values resulting from the weak-leaching methods.

The last possibility is the uncertainties in blank corrections. Because of the limited amount of samples (~200 mg) and very low Os concentration of the leachable fraction (4–7 pg g⁻¹), the blank corrections are very critical in the Os isotopic measurement applied by the weak-leaching method. For example, Os isotopic ratios (¹⁸⁷Os/¹⁸⁸Os)
before blank corrections ranges between 0.37 and 0.53 while Os isotopic ratio after blank corrections ranges 0.61 and 0.83. Thus, the unknown variations of Os blanks in our measurements may have largely altered Os isotopic values obtained by the HCl digestion method toward less radiogenic values. Since very small errors of estimated Os blank (~0.1–0.2 pg) can explain the differences in Os isotopic values between these two digestion methods, we consider that the last factor has the most critical effect. To extract more reliable Re-Os information using this weakly leaching method, it is required to dissolve a larger amount of samples than the present one and reduce the Os procedural blanks.

Since large Os isotopic variations (especially, rapid Os isotopic shift to radiogenic values after the Faraoni Level) could be observed regardless of the digestion methods and overall trends are similar, we consider that Os isotopic variation patterns obtained by the inverse aqua regia digestion method could reflect marine Os isotopic variations. Besides, to apply the weak-leaching method to our samples, further improvement of Os blank and reanalysis under more suitable digestion conditions are essential. Therefore, we mainly use the Os isotopic data acquired by the inverse aqua regia digestion method in the following discussions.

5.2. Orbital-Scale Os Isotopic Fluctuations in the Uppermost Hauterivian

The $^{187}$Os/$^{188}$Os values of the uppermost Hauterivian part of our study section vary periodically between ∼0.7 and ∼0.9 (Figure 2). These oscillations are weaker above the stratigraphic height of 12.5 m in the section (Figure 2). Recent studies relying on astronomical tuning have shown that the ages of the base of the CM4 geomagnetic polarity chron, the Faraoni Level, and the Hauterivian–Barremian boundary are ∼127.1, 126.7, and 126.0 Ma, respectively (Figure 1: Martínez et al., 2015). In addition, the base of the CM5 geomagnetic polarity chron, which is located at the base of the study section, is at 127.7 Ma (Martínez et al., 2015). Assuming a constant sedimentation rate between these tie points, each cycle of Os isotopic fluctuations corresponds to ∼400 kyr (Figure 2), which is consistent with the eccentricity cycle of 405 kyr. Martínez et al. (2015, 2020) have identified 14 of these 405-kyr cycles (H1 to H13 and H/B) within the Hauterivian section at La Charge-Pommerol in the Vocontian Basin (southeast France) and the Río Argos in the Subbetic Domain (southeast Spain). Five of these cycles (H10, H11, H12, H13, and H/B) are between the base of the CM5 chron and the Hauterivian–Barremian boundary (Figure 2). Therefore, we suggest that $^{187}$Os/$^{188}$Os fluctuations correspond to the 405-kyr eccentricity cycle. Moreover, Martínez et al. (2015) reported that the eccentricity cycle detected in the magnetic susceptibility record and kaolinite/chlorite contents decreased abruptly in intensity after H12 at the Río Argos section. The similar decreasing trend appears in the Os isotopic record in our study section (Figures 2 and 4b).

Similar but smaller amplitude oscillations (∼0.15) of Os isotopic composition paced by glacial and interglacial cycles have been reported in several Quaternary sedimentary records (e.g., Lund & Asimow, 2011; Oxburgh et al., 2007). These have been mainly explained by changes in hydrothermal intensity due to variations in magma production at mid-ocean ridges caused by sea-level changes (e.g., Lund & Asimow, 2011), changes in surface temperature and precipitation during glacial and interglacial cycles (Oxburgh et al., 2007), and increased radiogenic Os flux from high-latitude rocks exposed by retreating ice sheets (Oxburgh et al., 2007). In all three hypotheses, Os isotopic variation is associated with the waning and waxing of polar ice sheets and ensuing environmental perturbations. However, no evidence has been produced for large ice sheets during the Hauterivian. In addition, although Haq (2014) has reported several high-amplitude sea-level changes during the Early Cretaceous, their timing does not match with those of our Os isotopic fluctuations. We therefore rule out ice sheets as a triggering factor.

5.3. Os Isotopic Fluctuations Triggered by Eccentricity-Paced Changes in Continental Weathering

We propose that cyclic changes in continental weathering intensity regulated by monsoon dynamics paced by Milankovitch cycles may be the cause of the cyclic variations in our Os isotopic record. During the Quaternary, the precession-paced North African summer monsoon and Mediterranean storm track caused cyclic intensifications of precipitation and runoff of continental material around the Mediterranean. Their intensity at perihelion was controlled by the 100-kyr eccentricity cycle (Toucanne et al., 2015). Orbital-paced changes in monsoonal activity have been also proposed to explain the Triassic–Jurassic climate state, when the extremely large thermal contrast between Pangea and the super-ocean Panthalassa created a strong “mega-monsoon” (Ikeda et al., 2017; Kutzbach & Gallimore, 1989). The intensity of the mega-monsoon and the latitudinal shift of intertropical convergence
zones (ITCZ) were both strongly influenced by the precession cycle (Ikeda et al., 2017). The eccentricity cycle does not change the total insolation, but it contributes to changes in continental weathering by enhancing the seasonality changes of the precession cycle (Ikeda et al., 2017). Thus, temperature and precipitation at summertime perihelion were intensified during times of high eccentricity, which in turn enhanced continental weathering. During high eccentricity, this effect was amplified by the contrast between the wet and dry seasons, which accelerates physical and chemical weathering at low latitudes compared to weathering rates during times of low eccentricity (De Vleeschouwer et al., 2020). Assuming that similar climatic changes occurred at low latitudes during the Early Cretaceous, eccentricity-paced intensification of monsoonal activity and precipitation could have periodically enhanced continental weathering and led to an increase in marine $^{187}$Os/$^{188}$Os values (Figure 4).

Following the simple box model of Tejada et al. (2009) (Text S1 in Supporting Information S1), the radiogenic peaks of $^{187}$Os/$^{188}$Os$_i$ ($\sim$0.9) would require at most twice as much continental derived radiogenic Os as unradio-

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**Figure 5.** (a) Reconstructed $^{187}$Os/$^{188}$Os values (black circles) and the calculated values (red lines) using a simple box model, and (b) changes in the continental radiogenic Os input. Magnetostratigraphy and biostratigraphy is based on Coccioni et al. (1998). Ages of $^{187}$Os/$^{188}$Os are corrected using the 405-kyr eccentricity cycles suggested by Martinez et al. (2015).
genic peaks of $^{187}$Os/$^{188}$Os$_{\text{carb}}$ (~0.7) (Figure 5). The size of this difference in continental weathering is concordant with model calculation results on eccentricity-paced continental weathering during the Miocene Climatic Optimum (Ma et al., 2011). Here, our box model calculation is a very simplified case and does not take into account changes in the Os isotope ratio of riverine Os and the contamination of terrigenous materials. Thus, the actual magnitude of variations of the riverine Os flux could have been smaller than that of our estimation. Within the Hauterivian and Barremian stages, the kaolinite/chlorite ratio in the Río Argos section varies according to the 405-kyr eccentricity cycle, and its variation decreases above the Faraoni Level (Figure 4) (Martinez et al., 2015; Moiroud et al., 2012). As a proxy for humid conditions, the record of kaolinite content can be interpreted in terms of summer precipitation according to the 405-kyr eccentricity cycle (Martinez et al., 2015). Considering that the radiogenic peak of $^{187}$Os/$^{188}$Os$_{\text{carb}}$ corresponds to the peak of the kaolinite-rich interval (Figure 4), we infer that intensified monsoonal activity paced by eccentricity promoted an increase in temperature and precipitation at low latitudes during the summer perihelion and enhanced the seasonal wet/dry contrast. Consequently, chemical weathering accelerated at low latitudes and marine $^{187}$Os/$^{188}$Os shifted toward radiogenic values as input of continental radiogenic Os increased (Figure 4). Considering that the cyclic enrichment of kaolinite roughly corresponds to the radiogenic Os isotopic peaks, the changes in the clay mineral composition in the sediment rocks may have triggered the cyclic radiogenic Os isotopic peaks. However, pronounced enrichment of kaolinite is reported not only from the radiogenic Os isotopic peaks (~12, 8.5, and 4 m) but also from the Faraoni Level with relatively unradiogenic Os isotopic values ~0.7 (Figure 4). Thus, changes in the clay mineral composition in the sediments (e.g., kaolinite content) are unlikely the cause of cyclic Os isotopic shifts to the radiogenic values. Cenozoic 405-kyr eccentricity cycles were commonly accompanied by fluctuations of $\delta^{13}$C$_{\text{carb}}$ in benthic and planktonic foraminiferal tests that were related to variations in primary productivity (e.g., Wang et al., 2010). However, $\delta^{13}$C$_{\text{carb}}$ in bulk rock samples from the Fiume Bosso section did not show a pronounced variation paced by eccentricity (Figure 2). Although Sprovieri et al. (2006) conducted an astronomical tuning using $\delta^{13}$C$_{\text{carb}}$ of bulk rock samples of Maiolica Formation, they largely underestimated the number of 405-kyr eccentricity cycles in Hauterivian compared to the latest work (Martinez et al., 2015, 2020). Because the limestone samples of Maiolica Formation were mixtures of planktonic and benthic foraminifers and calcareous nanofossils, changes in their proportions may have obscured subtle orbital-scale carbon isotope fluctuations. Indeed, the $\delta^{13}$C$_{\text{carb}}$ values of benthic foraminifera and bulk rock samples take different values and their detailed variations often do not coincide with each other (e.g., Huber et al., 2011).

Changes in weathering patterns or the source of radiogenic Os caused by ITCZ migration can also influence the marine Os isotopic record. Indeed, it is known that weathering of organic-rich sedimentary rocks with high $^{187}$Os/$^{188}$Os (~2.2; Dubin & Peucker-Ehrenbrink, 2015) has a potential to alter the oceanic Os isotopic ratio rapidly. Besides, in Canada, for example, Precambrian shield rocks and Paleozoic organic-rich sediments have extremely radiogenic $^{187}$Os/$^{188}$Os values (Huh et al., 2004). Indeed, Precambrian continental rocks and orogenic belts in western and southern Africa (Begg et al., 2009) may have highly radiogenic $^{187}$Os/$^{188}$Os values. Therefore, during the eccentricity-paced ITCZ migration toward higher latitudes (Ikeda et al., 2020), the increased Os input from more radiogenic sources could have contributed to the increase in marine $^{187}$Os/$^{188}$Os values. Although this factor must be important for the changes in the marine Os isotopic record, it is difficult to precisely estimate the influence from precipitation patterns, the resulting changes in local weathering rates, and their contribution to marine $^{187}$Os/$^{188}$Os values.

High $^{187}$Os/$^{188}$Os values roughly correspond to gray-colored intervals in the study section (Figure 2a), which have pronounced enrichments in Re and Os (Figure 2). Our box-model calculation suggests the cyclic increase in the input of continental Os into the ocean, which could have caused the enrichment of Re and Os to explain the Os isotopic fluctuations. However, increases in the Os concentration by a factor of 2 and Re concentration by a factor of 8 are too large compared to the changes in the marine Os and Re concentration caused solely by the increase in the continental weathering. It is also known that Re and Os concentrations and total organic carbon content are positively correlated (e.g., Matsumoto et al., 2020; Selby & Creaser, 2003). As organic matter is well preserved under reducing conditions, Re and Os enrichments can be interpreted as the presence of reducing bottom water. In the Quaternary Mediterranean Sea, orbital-paced increases in monsoonal activity cyclically enhanced continental runoff and riverine freshwater supply, which resulted in high primary productivity and marine stratification (Toucanne et al., 2015). The resulting high input of organic carbon to the seafloor and reducing bottom water conditions triggered the periodic deposition of organic-rich sediments paced by the precession and eccentricity cycles (e.g., Hilgen, 1991; Sierro et al., 2000; Toucanne et al., 2015). Therefore, similar riverine fresh water and nutrient
input in the Tethys Ocean may have caused the weakly reducing condition in the Tethyan region. However, the depositional setting of Umbria–Marche Basin was considered more pelagic and the degree of reducing condition could be weaker than the Quaternary Mediterranean. Under the assumption that the gray interval (Figure 2a) of the Fiume Bosso section corresponds to a humid interval with strong continental weathering (Figure 4), we conclude that eccentricity-paced monsoonal activity accelerated the input of freshwater and continental materials including nutrients into the Tethys, leading to reducing bottom water conditions.

The cyclicity of $^{187}\text{Os}/^{188}\text{Os}$, and reducing bottom water conditions weakens and disappears above the Faraoni Level, as do the cyclic variations in the kaolinite/chlorite ratio (Figure 4). We interpret these trends as the weakening of monsoonal activity and subsequent decrease in precipitation.

5.4. Implication for the Faraoni Level

The eruptions of large igneous provinces (e.g., the Ontong Java, Kerguelen, and Caribbean Plateaus) have been considered as the triggers of major Cretaceous OAEs (e.g., Matsumoto et al., 2020; Percival et al., 2021; Tejada et al., 2009; Turgeon & Creaser, 2008). Signs of these OAEs include sharp negative shifts in $\delta^{13}\text{C}_{\text{carb}}$ attributed to massive inputs of $^{12}\text{C}$-rich carbon due to intensive volcanic degassing (e.g., Price, 2003). In the Faraoni Level, $\delta^{13}\text{C}_{\text{carb}}$ does not display negative excursions (Figure 3). Indeed, during the early Aptian OAEs (OAE1a, Wezel, and Fallot) and the late Cenomanian OAE2, sharp excursions of $^{187}\text{Os}/^{188}\text{Os}$ toward unradiogenic values have been interpreted as the input of unradiogenic Os through massive hydrothermal activity on submarine basaltic plateaus (Matsumoto et al., 2021; Tejada et al., 2009; Turgeon & Creaser, 2008). However, our Os isotopic record shows no $^{187}\text{Os}/^{188}\text{Os}$ excursion across the Faraoni Level, suggesting the absence of volcanic activity (Figure 2). The lack of evidence of volcanic events during the Faraoni Level is also supported by the mercury anomaly (Charbonnier et al., 2018). These pieces of evidence imply that the Faraoni Level represents an episodic event unrelated to massive volcanic episodes (Figure 2).

6. Conclusion

Marine Os isotopic ratios ($^{187}\text{Os}/^{188}\text{Os}$) in the uppermost Hauterivian sedimentary record at the Fiume Bosso section show cyclic fluctuations that are paced by the 405-kyr orbital eccentricity cycle. During intervals of high eccentricity, the increase in precipitation at low latitudes caused by intensified monsoonal activity accelerated continental weathering. The poleward shift of the ITCZ during those times could also have accelerated Os input from more radiogenic sources, contributing to increased $^{185}\text{Os}/^{188}\text{Os}$ values. During intervals of low eccentricity, decreased summer precipitation caused a weakening of continental weathering. We conclude that oscillations in marine Os isotope ratios can be interpreted as cyclic enhancements of continental weathering and changes in Os sources caused by intensified monsoonal activity. Because the Faraoni Level does not contain an unradiogenic Os isotopic shift, it instead represents an episodic event unrelated to massive volcanic episodes.

Data Availability Statement

Raw data are archived in PANGAEA data repository (carbon isotopic ratio: https://doi.pangaea.de/10.1594/PANGAEA.934454, Re-Os data obtained by the inverse aqua regia digestion method: https://doi.pangaea.de/10.1594/PANGAEA.934455, Re-Os data obtained by the weak-leaching method: https://doi.org/10.1594/PANGAEA.938379).

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Acknowledgments

The authors are indebted to Dr. K. Suzuki, Dr. T. Nozaki, and Y. Otsuki for their support of the Re-Os analysis. The authors thank K. Tanaka and N. Izumoto for their assistance in the carbon isotopic measurements. Sincere gratitude is expressed to Dr. Mathieu Martinez, Dr. Bernhard Peucker-Ehrenbrink, and an anonymous reviewer for the constructive comments. This study was partly supported by a Grant-in-aid for Research Fellow (No. 19J20708) from the Japan Society for the Promotion of Science.
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Erratum

In the originally published article, Figure 4 listed the age of the base of the studied section as 131.0 Ma. The correct age is 127.7 Ma as written in Figure 2. The figure has been updated, and this version may be considered the authoritative version of record.