Mid-Cretaceous marine Os isotope evidence for heterogeneous cause of oceanic anoxic events

Hironao Matsumoto1✉, Rodolfo Coccioni2, Fabrizio Frontalini3, Kotaro Shirai1, Luigi Jovane4, Ricardo Trindade5, Jairo F. Savian6 & Junichiro Kuroda1

During the mid-Cretaceous, the Earth experienced several environmental perturbations, including an extremely warm climate and Oceanic Anoxic Events (OAEs). Submarine volcanic episodes associated with formation of large igneous provinces (LIPs) may have triggered these perturbations. The osmium isotopic ratio (187Os/188Os) is a suitable proxy for tracing hydrothermal activity associated with the LIPs formation, but 187Os/188Os data from the mid-Cretaceous are limited to short time intervals. Here we provide a continuous high-resolution marine 187Os/188Os record covering all mid-Cretaceous OAEs. Several OAEs (OAE1a, Wezel and Fallot events, and OAE2) correspond to unradiogenic 187Os/188Os shifts, suggesting that they were triggered by massive submarine volcanic episodes. However, minor OAEs (OAE1c and OAE1d), which do not show pronounced unradiogenic 187Os/188Os shifts, were likely caused by enhanced monsoonal activity. Because the subaerial LIPs volcanic episodes and Circum-Pacific volcanism correspond to the highest temperature and pCO2 during the mid-Cretaceous, they may have caused the hot mid-Cretaceous climate.

1Atmosphere and Ocean Research Institute, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa 277-8564, Japan. 2University of Urbino, Carlo Bo, 61029 Urbino, Italy. 3DiSPeA, University of Urbino Carlo Bo, Campus Scientifico Enrico Mattei, Località Crocicchia, 61029 Urbino, Italy. 4Instituto Oceanográfico, Universidade de São Paulo, Praça do Oceanográfico, 191, São Paulo, SP 05508-120, Brazil. 5Instituto de Astronomia, Geofísica e Ciências Atmosféricas, Universidade de São Paulo, Rua do Matão, 1226, São Paulo, SP 05508-090, Brazil. 6Departamento de Geologia, Instituto de Geociências, Universidade Federal do Rio Grande do Sul, Avenida Bento Gonçalves, 9500, Porto Alegre, RS 91501-970, Brazil. ✉email: matsumoto@aori.u-toyko.ac.jp
The mid-Cretaceous (late Barremian to Turonian: ~121–90 Ma) is commonly regarded as one of the extremely warm geological intervals of the Phanerozoic Eon. The oxygen isotopic ratio of carbonate ($\delta^{18}$O$_{carb}$) and TEX$_{86}$-Sea Surface Temperature (SST) proxies have revealed that the Cenomanian to Turonian climate was much warmer than that of today1–3. In addition, palaeobotanical4 and palaeontological data from the Late Cretaceous (Turonian to Coniacian)5 suggest that a warm climate prevailed in the Arctic region. The warm climate during the mid-Cretaceous is considered to have been sustained by a high $p$CO$_2$ (e.g., ~1500 ppmv during the Cenomanian6) derived from active outgassing associated with the production of oceanic crust and/or massive volcanic activity7.

This greenhouse world experienced distinctive repeated oceanic anoxic events (OAEs), representing major perturbations in the carbon cycle characterized by deposition of organic-rich sediments in various depositional settings. Many organic-rich lithological intervals have been reported from the mid-Cretaceous Tethyan sedimentary record8,9. The early Aptian OAE1a and late Cenomanian OAE2, the most prominent mid-Cretaceous OAEs, were typified by worldwide deposition of thick organic-rich horizons10 (e.g., ~1–2 m thick at the Umbria–Marche Basin). Additionally, other minor OAEs (e.g., OAE1b, OAE1c, and OAE1d), which have been reported mainly from the Tethys and Atlantic Oceans9,11–13 and a part of the Pacific region14, are regarded as regional to supra-regional marine anoxic events. As mid-Cretaceous OAEs were often accompanied by intensive marine biotic crises15, understanding the factors that triggered the OAEs is important for unraveling the evolution of the Cretaceous marine ecosystem.

Massive volcanic events associated with the formation of large basaltic plateaus called large igneous provinces (LIPs) are the most probable triggering factors of environmental perturbations15. Because the radiometric ages of the basaltic plateaus correspond to the sedimentary ages of major OAEs and the species turnovers of marine calcareous plankton, these events are thought to have been linked15–17. The Os isotopic variations ($^{187}$Os/$^{188}$Os) in the sedimentary record further support a causal linkage between the LIPs volcanism and the onset of marine environmental perturbations. The $^{187}$Os/$^{188}$Os values of seawater represent the balance between radiogenic material from a continental source (~1.0–1.5) and unradiogenic material from hydrothermal activity, weathering of mafic rocks, and extraterrestrial materials (~0.12)18. During the mid-Cretaceous OAEs (e.g., OAE1a and OAE2), the Os isotopic ratios of the sedimentary record show highly unradiogenic values (~0.2), which have been interpreted to indicate massive input of unradiogenic Os associated with LIPs formation19–21. However, the Os isotopic record from the mid-Cretaceous is limited to the latest Barremian to early Albian and Cenomanian–Turonian transitional intervals13,16,19–21, and these records are not sufficiently long to elucidate the evolution of the prolonged hydrothermal activity associated with volcanic episodes during the mid-Cretaceous.

Here, we reconstruct a continuous marine Os isotopic record from the middle Albian to the uppermost Cenomanian using a pelagic sedimentary record from the Umbria–Marche Basin (central Italy) and the borehole core from Ocean Drilling Program (ODP) Site 763 (Exmouth Plateau, southeast Indian Ocean) (Fig. 1). Integrating our data with previously published information, we provide a continuous Os isotopic record from the late Barremian to early Turonian, covering all mid-Cretaceous OAEs, and discuss the long-term hydrothermal record of the mid-Cretaceous. As a result, we found that hydrothermal activity associated with the formation of LIPs was enhanced during the mid-Aptian, late Albian, and end-Cenomanian. In addition, temporal intensification of continental weathering was observed during the early Albian, which may be caused by temporal global warming. From the Os isotopic variations, we found that mid-Cretaceous OAEs can be classified into two types according to their triggering factors as: (1) volcanic-induced OAEs (e.g., OAE1a, Wezel Level, Fallot Level, and OAE2) with unradiogenic Os isotopic shifts; and (2) monsoon-induced OAEs (OAE1c and OAE1d) without unradiogenic Os isotopic shifts. Besides, the warmest interval during the mid-Cretaceous corresponded to a phase of enhanced subaerial volcanic episodes with no evidence of long-term enhanced hydrothermal activity. Thus, we conclude that subaerial volcanic episodes and the subsequent outgassing were the main cause of the warm mid-Cretaceous climate.

**Results**

Limestone, marlstone, mudstone, and black shale samples ranging from the middle Albian to the upper Cenomanian were collected from the PLG core (43°32′42.72″N, 12°32′40.92″E) and the Bottaccione section (43°21′56.04″N, 12°34′57.56″E) in the Umbria–Marche Basin (Central Italy). The Umbria–Marche sedimentary record comprises pelagic sedimentary facies of the Tethyan Ocean (Fig. 1) and is characterized by a lack of coarse terrigenous materials. The PLG core is a borehole core drilled near the PLG section12 that covers the uppermost Barremian to the lowest Cenomanian. The Bottaccione section is a pelagic sedimentary sequence located in the same basin that includes, for the Cretaceous, the uppermost Albian to the Maastrichtian9.

Using lithostratigraphy, biostratigraphy, and carbon and osmium isotopic stratigraphy8,9,22, we reconstruct a continuous composite stratigraphic record of the Umbria–Marche Basin during the mid-Cretaceous (Fig. 2). The upper Barremian of the composite record belongs to the Maiolica Formation and consists of white cherty limestone cyclically intercalated with thin (~few centimeters) black shale layers. The ~2 m-thick organic-rich interval, known as the Selli Level23 occurs around the Barremian–Aptian boundary and records the regional sedimentary expression of OAE1a. Above the Selli Level, the Aptian sedimentary record consists of marly limestone with some black shale layers (e.g., the Wezel and Fallot Levels13) belonging to the Marine a Fucomid Formation8. The Fallot and Wezel Levels are only reported from the Tethyan Region. However, their accurate extent has not been constrained so far because of the limited geological research focusing on their equivalent intervals outside the Tethyan region. Several pronounced organic-rich intervals (i.e., Jacob, Kilian, Urbino/Paquier, and Leenhart Levels), collectively called OAE1b, appear around the Aptian–Albian boundary8,12,24. The Albian sediments consist of mudstones intercalated with cyclic thin (~few centimeters) black shale layers8,12,24. A peculiar ~2-m-thick interval in the upper Albian, called the Amadeus Segment24, is located in the middle part of OAE1c that spans almost the entire *Bitticella breggensiis* planktonic foraminiferal Zone8,25. The muddy interval ends in the upper Albian, and the lithology changes to the white and reddish limestones of the Scaglia Bianca Formation8. The last cyclic upper Albian organic-rich layers are known as the Pialli Level26, which represents the regional sedimentary expression of OAE1d9. At the end-Cenomanian, a thick organic-rich interval, known as the Bonarelli Level, is the regional sedimentary expression of OAE29. Osmium and carbon isotopic records from the upper Barremian to lower Albian in the Umbria–Marche Basin have already been reported12,13,16,19,27–29.

Sedimentary rock samples were also collected from ODP Site 763B in the western part of the central Exmouth Plateau (20°35.21′S, 112°12.51′E, northwestern Australian margin, sub-tropical Indian Ocean) at 1368 m below the sea surface30. The sediments were deposited at upper bathyal depth (~200–500 m
Fig. 1 Paleogeographic reconstruction (120 Ma). A: Agulhas Plateau, C: Caribbean Plateau, K: Kerguelen Plateau, H: High Arctic Large Igneous Provinces, He: Hess Rise, O: Ontong Java Nui.

Fig. 2 $^{187}$O/$^{188}$Os, and $\delta^{13}$C$_{carb}$ records of the Umbria–Marche Basin and ODP Site 763B. a Umbria–Marche Basin: lithology, biostratigraphy, biostratigraphy, and geochemical data are from Coccioni et al.8,12, Coccioni and Premoli Silva9, Coccioni65, Turgeon and Creaser;19 Tejada et al.20, Li et al.27, Savian et al.28, Matsumoto et al.13,16, Percival et al.29, and this study. ODP Site 763B: lithology, biostratigraphy, and geochemical data are from Haq et al.30, Bralower et al.35, and this study. Ma. Maiolica, Sc. Ro. Scaglia Rossa, Ba. Barremian, Tur. Turonian, G. Globigerinelloides, apt aptiensis, L. Leupoldina, fer. ferreolensis, alg. algerianus, H. Hedbergella, troc. trocoidea, M. Microhedbergella, P. Paraticinella, mini. miniglobularis, reni. renilaevis, T. Ticinella, B. Biticinella, Ps. Pseudothalamminella, su. subticinensis, tic. ticcinensis, Pth. Parathalmanninella, appen. appenninica, Th. Thalmaninella, R. Rotalipora, r. reichi, g. globotruncanoides, W. Whiteinella, a. archaeocretacea, H. Helvetoglobotruncana, H. Helvetica, J Jacob, K Kilian, U Urbino, L Leenhardt.
below sea level\(^{30}\) and consisted of calcareous claystone to clayey nannofossil chalk. The Aptian–Albian boundary is estimated to lie between cores 37 and 36, but the exact position is uncertain (Fig. 2b)\(^{31}\). The Cenomanian–Albian boundary falls in the gap between cores 23 and 22 (Fig. 2b). We collected sedimentary rock samples from ODP Site 763B cores 36 to 21, which cover the middle Albian to lowest Turonian.

The \(\delta^{13}C_{\text{carb}}\) record of sedimentary rock samples from the Umbria–Marche Basin (PLG core and Bottaccione section) shows a gradual decline from \(-3\)% in the middle Albian (\(-40\) m: Fig. 2) to \(-2.1\)% in the Pialli Level (\(-90\) m: Fig. 2, Supplementary Tables 1 and 2). The \(\delta^{13}C_{\text{carb}}\) curve shows a slight positive excursions (\(+0.4\)%/°C) within the Pialli Level (\(-90\) m). Above this level, \(\delta^{13}C_{\text{carb}}\) shows a gradual positive shift from \(-2\)%o (\(-110\) m) to \(-3\)%o toward the end of Cenomanian (\(-130\) m) (Fig. 2a). Our data are concordant with those of the previous studies\(^{9,32}\). At ODP Site 763B, \(\delta^{13}C_{\text{carb}}\) shows a gradual negative shift from \(-3\)%o at the Aptian–Albian boundary (\(-520\) meters below the sea level [mbfsl]) to \(-1\)%o around the Albian–Cenomanian boundary (\(-434\) mbfsl) (Fig. 2b). The \(\delta^{13}C_{\text{carb}}\) values of some core samples are highly negative (\(<-2\)%o to \(-0.5\)%o), which might indicate some diagenetic alteration possibly caused by remineralization of organic matter. The \(\delta^{13}C_{\text{carb}}\) values increase during the Cenomanian (from 420 to 410 mbfsl), which are concordant with the Tethyan sedimentary record (Fig. 2b). The \(\delta^{13}C_{\text{carb}}\) data exhibit a large negative shift from \(-2\)%o at 410 mbfsl to \(-3\)%o at the Cenomanian–Turonian boundary (\(-380\) mbfsl) (Fig. 2b). Albian–Cenomanian sedimentary rock samples from ODP Site 762 C (western part of the Exmouth Plateau) also show highly negative \(\delta^{13}C_{\text{carb}}\) values, which are interpreted to indicate diagenetic alteration\(^{33}\). Although the exact mechanism is unclear at present, it is likely that the carbon isotopic records at ODP Sites 763B and 762 C have experienced a similar diagenetic overprint around the Cenomanian–Turonian boundary.

In the Umbria–Marche sedimentary record (PLG core and Bottaccione section), \(187\)Os/\(188\)Os varies from 0.37 to 0.75, except for one sample (BTT450) with an extraordinarily high value (\(<-1.1\)) and a relatively high \(187\)Re/\(188\)Os ratio (\(<-10\)) (Supplementary Tables 3 and 4). Because the Re–Os information of outcrop samples with high Re/Os values can be easily altered by weathering\(^{16}\), we considered this point as an outlier and excluded it from our discussions. The \(187\)Os/\(188\)Os values of ODP Site 763B span from 0.47 to 0.75; this range is concordant with the Tethyan sedimentary record (Figs. 2 and 3).

Discussion

Mid-Cretaceous Os isotopic fluctuations. The composite mid-Cretaceous Os isotopic data reveal that pronounced unradiogenic shifts (i.e., lower values) occurred during the early to mid-Aptian, late Albian, and end-Cenomanian, and radiogenic shifts took place at the Aptian–Albian boundary and during the Cenomanian (Figs. 2 and 3a). As marine Os isotopic ratios (\(187\)Os/\(188\)Os) represent the balance between unradiogenic Os input (mantle and extraterrestrial material) and radiogenic Os input (continental material), these Os isotopic variations reflect changes in the Os fluxes from these sources.

In the uppermost Barremian, \(187\)Os/\(188\)Os exhibits relatively radiogenic values (\(+0.6–0.7\)) in the Umbria–Marche Basin (Gorgo a Cerbara section and PLG core) and the Pacific record (Deep Sea Drilling Project [DSDP] Site 463) (Figs. 2 and 3a)\(^{20,21,29}\). On the contrary, \(187\)Os/\(188\)Os shows sharp drops to \(-0.2–0.3\) in the lower to mid-Aptian black shales, namely the Selli, Wezel, and Fallot Levels (Figs. 2 and 3a)\(^{13,20,21,29}\). As the sedimentary ages of these unradiogenic Os isotopic shifts correspond to the radiometric ages of the Ontong Java, Manihiki, and Hikurangi Plateaus, which once formed a single large oceanic plateau called Ontong Java Nui (OJN) (Fig. 3a, e), these unradiogenic Os isotopic shifts were likely triggered by a massive input of mantle-derived unradiogenic Os through hydrothermal activity and warm- and low-temperature submarine weathering at OJN\(^{13,20,21,34}\). This possibility is further supported by \(87\)Sr/\(86\)Sr and sulfur isotopic evidence (Fig. 3b, c). Hydrothermal fluid is characterized by unradiogenic \(87\)Sr/\(86\)Sr and more negative \(\delta^{34}\)S values than those of seawater; thus, the unradiogenic \(87\)Sr/\(86\)Sr values (e.g., Fig. 3b)\(^{35}\) and negative sulfur isotopic (\(\delta^{34}\)S\(_{\text{barite}}\)) excursion (Fig. 3c)\(^{36}\) during the early to mid-Albian further support the hypothesis of enhanced hydrothermal activity and of warm- and low-temperature submarine weathering.

Lecler et al.\(^{37}\) suggested that, in addition to hydrothermal activity, subaerial weathering of OJN basalt could have played a significant role in causing large unradiogenic shifts. However, modeling studies have indicated that weathering of a huge amount (~30–60%) of the Ontong Java Plateau would have been required to explain such large unradiogenic Os isotopic shifts.\(^{20}\) Given that most of the plateau was emplaced under submarine conditions\(^{38}\), we infer that hydrothermal activity was likely the major cause of early to mid-Aptian unradiogenic Os isotopic shifts.

During OAE1b, the \(187\)Os/\(188\)Os values of Tethyan and Pacific sedimentary records show a radiogenic shift from 0.5 to 0.7 (Fig. 2)\(^{16}\). Our \(187\)Os/\(188\)Os data from ODP Site 763B also reveal that radiogenic \(187\)Os/\(188\)Os values prevailed during the early Albian (Figs. 2 and 3a). The radiogenic shift of \(187\)Os/\(188\)Os corresponds to the \(40\)Ar/\(39\)Ar ages of the Kerguelen Plateau basalts (Fig. 3)\(^{39–41}\) and an increase in temperature, as indicated by \(187\)Os/\(188\)Os of belemnites, the TEX\(_{86}\)-SST index, and the demise of glendonite (a pseudomorph after kaite that is a hydrated calcium carbonate formed under low-temperature conditions) in the Arctic region (Fig. 3a, d, e)\(^{42–44}\). Thus, the radiogenic Os isotopic shift during OAE1b has been interpreted as indicating enhanced continental weathering triggered by global warming caused by outgassing from volcanic episodes at the Kerguelen Plateau\(^{16}\). As most of the Kerguelen Plateau was emplaced subaerially at a high latitude in the Indian Ocean, radiogenic Os inputs from hydrothermal activity and weathering of the basaltic rock were insignificant and did not influence the marine Os isotopic record\(^{16}\). In addition, \(87\)Sr/\(86\)Sr values show a radiogenic shift during the early Albian\(^{35}\), which also supports enhanced continental weathering during OAE1b\(^{16}\).

The \(187\)Os/\(188\)Os data exhibit two pronounced unradiogenic shifts during OAE1c (Figs. 2 and 3a). These excursions, which were observed in both the Tethyan Realm (Umbria–Marche Basin) and in the Indian Realm (ODP Site 763B) (Figs. 2 and 3), can be ascribed to a decrease in the radiogenic Os input through continental weathering or an increase in the unradiogenic Os input from the mantle or extraterrestrial material. To explain the unradiogenic shifts solely by the decreased continental weathering, a rapid decrease in temperature is required; however, no data support this possibility. Therefore, the two unradiogenic shifts may represent an increase in the input of unradiogenic Os. One of the possible sources of unradiogenic Os is extraterrestrial materials, but the unradiogenic shifts during OAE1c are much longer and smaller (~1 Myr and \(187\)Os/\(188\)Os ~0.4) than those during massive meteorite impacts (~200 kyr, \(187\)Os/\(188\)Os ~0.1–0.2)\(^{45}\). In addition, subaerial basaltic eruptions at low latitudes have not been reported during OAE1c. Thus, the most probable candidate for the unradiogenic shifts during OAE1c is an increase in hydrothermal activity. Indeed, \(\delta^{34}\)S\(_{\text{barite}}\) data show negative values during OAE1c (Fig. 3c), which implies
hydrothermal sulfur input. However, the $^{87}\text{Sr}/^{86}\text{Sr}$ values do not show a significant unradiogenic shift, possibly because of the long residence time of Sr (~3 Myr) compared to that of Os (20–50 kyr) and the volatile feature of the highly oxidized form of OsO$_4$.

The estimated ages of the Hikurangi Plateau$^{46}$, Kerguelen Plateau$^{39,40}$, Hess Rise$^{47}$, and Agulhas Plateau$^{48}$ cover the sedimentary ages of OAE1c (Fig. 3). Thus, the hydrothermal activity associated with the formation of these oceanic plateaus may have triggered the unradiogenic Os isotopic shifts. However, the age constraints on the Hikurangi Plateau, Hess Rise, and Agulhas Plateau are too poor to conclude when the hydrothermal activity occurred, and further studies are required to determine the exact source of these unradiogenic Os shifts.

After OAE1c, the $^{187}\text{Os}/^{188}\text{Os}$ values gradually shift to be more radiogenic ~0.7 (Fig. 3a), which may reflect the weakening of hydrothermal activity. This possibility is supported by the sulfur isotope ratio and strontium isotopic evidence: $\delta^{34}\text{S}_{\text{barite}}$ shows a positive excursion during the late Albian (Fig. 3c) that can be interpreted as a decrease in the hydrothermal sulfur input with low $\delta^{34}\text{S}_{\text{barite}}$. The positive excursion of $\delta^{34}\text{S}_{\text{barite}}$ can be also explained by an increase in sulfur reduction during the early Cenomanian. However, considering the organic-rich sediments are more pronounced during Albian than Cenomanian at the Umbria–Marche Basin, sulfate reduction should also have been more significant during the Albian than Cenomanian. Therefore, we consider that the decrease in the volcanic sulfur is a more important factor for explaining the positive $\delta^{34}\text{S}_{\text{barite}}$ excursion than the sulfate reduction. The positive excursion of $\delta^{34}\text{S}_{\text{barite}}$ during the Cenomanian postdates the cessation of the Os isotopic fluctuations (Fig. 3a, c). Since the residence time of sulfur in the ocean is longer than Os, the onset of the changes of $\delta^{34}\text{S}_{\text{barite}}$ could have been more gradual and possibly postdated the radiogenic Os isotopic shift. In addition, $^{87}\text{Sr}/^{86}\text{Sr}$ show radiogenic values (Fig. 3b) that also support the weakening of the input of hydrothermal unradiogenic Sr$^{35}$. The $^{187}\text{Os}/^{188}\text{Os}$ values do not show any significant fluctuation during OAE1d, which likely suggests the absence of intensive submarine volcanism.

The $\delta^{18}\text{O}_{\text{carb}}$ values of benthic and planktonic foraminifera suggest a temperature increase during the Cenomanian, with the warmest conditions recorded from the Cenomanian to Turonian$^{1,2}$. The enhanced chemical weathering caused by the warm climate may have accelerated and intensified inputs in radiogenic continental Os, which may also have contributed to the radiogenic $^{187}\text{Os}/^{188}\text{Os}$ shifts after OAE1c (Fig. 3).
Stable radiogenic $^{187}$Os/$^{188}$Os values during the Cenomanian (~0.7) were followed by a sudden drop just below the OAE2 interval (Fig. 3)9,30. As the sedimentary ages of the unradiogenic shifts correspond to the $^{40}$Ar/$^{39}$Ar ages of the Caribbean Plateau43, the unradiogenic shifts can be explained by an increase in the unradiogenic Os input associated with emplacement of the submarine basal plate. This possibility is further supported by the unradiogenic shift of $^{87}$Sr/$^{86}$Sr after OAE235. Although the weathering of the basal plate may have contributed to the unradiogenic Os isotopic shifts, geological evidence of how much of the plateau was exposed subaerially is still lacking, precluding further discussion of this possibility. $^{34}$S$_{CAS}$ data around OAE2 are scarce, but $^{34}$S of pyrite and carbonate-associated sulfates (CAS) around OAE225 has been intensively investigated instead. $^{34}$S$_{CAS}$ and $^{34}$S$_{pyrite}$ showed a positive excursion (2–4%) across the OAE2, suggesting an enhanced sulfate reduction22. Considering the global oceanic anoxia and short duration of unradiogenic Os isotopic shift during OAE2 (~600 kyr), the effect of the sulfate reduction could have overwhelmed the effect of volcanic sulfur input.

Linkages between massive volcanic events and the mid-Cretaceous oceanic anoxic events. Previous studies have revealed that the onsets of the major Cretaceous OAEs (OAE1a, Wezel, Fallot, and OAE2) in the Tethyan region correspond to unradiogenic Os isotopic shifts13,16,19–23, which is compatible with synchronicity between massive submarine volcanism and OAEs. During these OAEs, unradiogenic Os shifts are often accompanied by the negative carbon isotopic excursions19–21,29, implying the volcanic events supply mantle-derived CO$_2$ with negative carbon isotopic values. Besides, a 2–16 times increase in the input of mantle-derived Os is required to explain these unradiogenic Os isotopic shifts. Considering that Os could have been supplied in highly volatile oxidized form (OsO$_4$), enormous amounts of other volatile trace metal elements could have been also injected into the ocean-atmosphere system during the most prominent unradiogenic Os isotopic shifts in these OAEs (OAE1a, Wezel and Fallot events, and OAE2). This possibility supports the linkage between bio-limiting trace metal input and the high productivity53. The proposed triggering mechanism of the OAEs is as follows77: massive volcanic events released large quantities of greenhouse gases into the atmosphere that caused an increase in the temperature; as a result, enhanced continental weathering supplied the nutrients to the ocean that led to enhanced primary productivity and ultimately to ocean eutrophication57. In addition, the volcanic activity could have provided iron and other bio-limiting trace metals to the ocean, which might have further stimulated the primary productivity17,53. In addition, the warming of deep-, intermediate-, and surface- water could have disrupted the thermocline, which triggered sustained upwelling and maintained the high primary productivity17. The decomposition of a large amount of organic matter at the seafloor consumed oxygen and expanded the oxygen minimum zones.

Our Os isotopic data revealed that multiple volcanic signals also correspond to the base and top of OAE1c (Figs. 2 and 3a); however, the unradiogenic shift does not cover the most prominent organic-rich interval of the OAE1c, called the Amadeus Segments (Figs. 2 and 3a). In addition, $^{187}$Os/$^{188}$Os values do not show any significant fluctuation during OAE1d, which suggests the absence of intensive submarine volcanic activity. Therefore, we consider that the onsets of OAE1c and OAE1d were unrelated to massive submarine volcanism, unlike other major mid-Cretaceous OAEs. A mercury anomaly has been reported just below the OAE1d horizon at the Youxia section, the eastern Tethys, which has been interpreted as the submarine volcanic eruption at the Kerguelen Plateau54. However, considering the lack of Os isotopic variations around OAE1d, this mercury enrichment is probably more related to local perturbations with limited influence on global climate. Major Cretaceous OAEs (OAE1a, Wezel, Fallot, and OAE2) are represented by thick (~6 cm to 2 m) organic-rich intervals, whereas the sedimentary expression of OAE1c and OAE1d in the Umbria–Marche Basin consist of cyclic alternations of thin black shales5. Similar cyclic intercalations of thin black shale layers in a carbonate sequence have been observed in the Valanginian–Barremian, Albian, and upper Cenomanian in the Umbria–Marche Basin (Fig. 3)8,22. During the Quaternary, astronomically modulated monsoonal activity cyclically enhanced the hydrology of the Mediterranean Sea at low latitude, which supplied freshwater and nutrients to the peri-continental ocean55. The resulting input of terrigenous organic matter, stratification, and slightly enhanced productivity led to oxygen-depleted bottom-water conditions and the deposition of organic-rich sediments dominated by terrigenous sources56. Thus, the lack of the unradiogenic Os isotopic shift and the cyclic deposition of thin black shale layers during OAE1c and OAE1d may suggest a regional-scale weak marine anoxia caused by monsoonal activity modulated by astronomical cycles as proposed by previous studies59 rather than an episodic large volcanic event54. The increase in primary productivity was not significant in the Tethyan region during OAE1c56. However, a small positive carbon isotopic excursion during OAE1d suggests a slight increase in the primary production (Fig. 2). In addition, organic-rich sediments are reported from the Calera Limestone in California, which was deposited in the Pacific Ocean, and thus the oxygen-depleted condition could have prevailed in the East Pacific as well14. Thus, the latter process can also cause a supra-regional increase in productivity to some extent.

The organic geochemical properties of mid-Cretaceous black shale horizons are also consistent with differences in the origins of mid-Cretaceous OAEs. Erbacher et al.57 proposed to classify mid-Cretaceous OAEs into two types on the basis of organic geochemistry and radiolarian occurrences: (1) productivity (P-) OAEs (e.g., OAE1a, OAE1d, and OAE2); and (2) detrital (D-) OAEs (e.g., OAE1c). Organic matter deposited in the Umbria–Marche Basin during OAE1a and OAE2 is close to Type II kerogen, which is derived from marine organisms57, whereas the organic matter of the OAE1c and OAE1d black shales is classified as Type III kerogen, which has a continental origin57. However, OAE1d and part of OAE2 are classified as P-OAE, although their organic matter was identified as Type III kerogen of continental origin57. To solve this contradiction, the classification of OAE types should be modified. Thus, on the basis of the organic geochemistry and Os isotopic data, we here propose to classify the mid-Cretaceous OAEs into: (1) volcanic-induced OAEs triggered by episodic burial of organic-rich sediments derived from marine organisms; and (2) monsoon-induced OAEs that are mainly caused by water-mass stratification triggered by freshwater input caused by the cyclic intensification of monsoonal activity. The organic matter of monsoon-induced OAEs is mainly composed of terrestrial materials and an increase in productivity is less significant56.

Among the mid-Cretaceous OAEs, OAE1b is a problematic example. In the Umbria–Marche Basin OAE1b is composed of several major organic-rich horizons (Jacob, Kilian, Urbino, and Leenhardt Levels) intercalated with numerous thin black shale horizons52. Although the short unradiogenic Os isotopic shifts have been reported around the Kilian Level, other black shale horizons lack unradiogenic Os isotopic shifts16. Besides, the upper part of the OAE1b is characterized by the temporal radiogenic Os isotopic excursions, which constitute a different feature from other mid-Cretaceous OAEs. Since OAE1b...
continued for several million years and contains different types of organic-rich sediments, we considered that OAE1b may be a mixture of volcanic- and monsoon-induced OAEs.

**Cause of the temperature variations during the mid-Cretaceous.** The mid-Cretaceous has often been regarded as a warm geological interval caused by high $pCO_2$, which was sustained by enhanced hydrothermal activity associated with oceanic crustal production. Considering the extremely high temperature and $pCO_2$ during major OAEs (OAE1a and OAE1b), this model seems correct over a short time scale. However, the model cannot explain the long-term temperature variations of the mid-Cretaceous. The $187Os/188Os$, $87Sr/86Sr$, and $\delta^{13}C$ records suggest an intensification of hydrothermal activity during the Aptian, corresponding to the relatively cool interval during the mid-Cretaceous (Fig. 3). Furthermore, the highest temperature during the mid-Cretaceous was recorded during the Cenomanian–Turonian. However, no long-term hydrothermal activity associated with LIPs formation has been reported during the Cenomanian (Fig. 3).

This contradiction may be explained by the location and style of the volcanic activity. When a basaltic plateau was emplaced under submarine conditions, outgassing from submarine volcanism and the expansion of the volcanic to shallower waters could have been suppressed by high hydrostatic pressure, and, thus, they may not have contributed to the long-term increase in the $pCO_2$. Indeed, most of OJN was emplaced under submarine conditions during the Aptian and may not have caused a long-term increase in $pCO_2$. The temperature started to increase at the Aptian–Albian boundary and reached a maximum at the Cenomanian, which corresponded to the subaerial eruption of the Kerguelen Plateau (Fig. 3). As most of the Kerguelen Plateau was emplaced under subaerial conditions, a large amount of $CO_2$ could have been directly released into the atmosphere, and could have contributed to the increase in $pCO_2$ and temperature. During the Cenomanian, subaerial volcanic eruptions occurred at Kerguelen and the High Arctic Large Igneous Province, which could have caused the increase in temperature during the Cenomanian–Turonian interval. In addition, subaerial volcanic activity in the circum-Pacific region was active during the mid-Cretaceous. For example, the volcanic events associated with the formation of Japanese granitoids were most active during the Cretaceous. For example, the volcanic events associated with the formation of LIPs were suppressed by high hydrostatic pressure, and, thus, CO$_2$ and temperature.

**Methods**

**Re-Os analysis.** We followed the analytical methods described by Matsumoto et al. Cleaned sedimentary rocks were powdered in an agate mill. After spiking with $^{186}$Os- and $^{188}$Re-rich solutions, Re and Os of the carbonate rocks were extracted by the inverse aqua regia (mixture of 30 wt% HCl 1 ml and 68% HNO$_3$ 3 ml) under 240 °C for 48 h. After Os was purified by CCl$_4$ extraction, HBr extraction, and micro-distillation, Os abundances and isotopic compositions were determined by negative thermal ionization–mass spectrometry (TRITON, Thermo Fisher Scientific, USA) at the Japan Agency for Marine-Earth Science and Technology (JAMSTEC, Japan). The abundances of Re were determined by a quadrupole inductively coupled plasma-mass spectrometer (ICP Qc, Thermo Fisher Scientific, USA) at JAMSTEC. Initial $185Os/188Os$ values ($187Os/188Os$) were calculated from the measured $185Os/188Os$ and $187Re/188Os$ values, the estimated ages (Supplementary Tables 1–3), and the $187Re$ decay constant ($1.666 \times 10^{-11}$ yr$^{-1}$). The average procedural blanks of Os and $185Os/188Os$ were 0.8 ± 0.5 pg and 0.13 ± 0.04, respectively. The average Re-procedural blank was 14 ± 11 pg.

**Stable carbon isotopic ratio of carbonate.** The stable carbon isotope ratio of carbonate ($\delta^{13}C_{carb}$) was 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 the Atmospheric and Ocean Research Institute, University of Tokyo (Japan). Isotopic values are reported in delta notation with respect to PeeDee Belemnite (PDB), based on an NBS-19 value of +1.95% for $\delta^{13}C$. External reproducibility was estimated from repeated analysis of the NBS-19 standard ($n = 20$) within an analytical batch; the typical values were better than 0.05% and 0.08% for $\delta^{13}C$ and $\delta^{18}O$, respectively (1 SD) (Supplementary Tables 2 and 3).

**Data availability**

The authors declare that the Os and carbon isotopic data generated in this study are provided in the Supplementary Information.

Received: 21 July 2021; Accepted: 8 December 2021;
Published online: 11 January 2022

**References**

1. Huber, B. T., MacLeod, K. G., Watkins, D. K. & Coffin, M. F. The rise and fall of the Cretaceous Hot greenhouse climate. Glob. Planet. Change 167, 1–23 (2018).
2. Friedrich, O., Norris, R. D. & Erbacher, J. Evolution of middle to Late Cretaceous oceans—a 55 my record of Earth’s temperature and carbon cycle. Geology 40, 107–110 (2012).
3. O’Brien, C. L. et al. Cretaceous sea-surface temperature evolution: constraints from TEX86 and planktonic foraminiferal oxygen isotopes. Earth Sci. Rev. 172, 224–247 (2017).
4. Herman, A. B., Spicer, R. A. & Spicer, T. E. Environmental constraints on terrestrial vertebrate behaviour and reproduction in the high Arctic of the Late Cretaceous. Palaeogeogr. Palaeoclim. Palaeoecol. 441, 317–338 (2016).
5. Vanderkam, D., Tarduno, J. A. & Brinkman, D. B. A fossil champsosaur population from the high Arctic: implications for Late Cretaceous palaeotemperatures. Palaeogeogr. Palaeoclim. Palaeoecol. 248, 49–59 (2007).
6. Hong, S. K. & Lee, Y. I. Revised Upper Albian-Maastrichtian paleotemperatures. Earth Planet. Sci. Lett. 327, 23–28 (2012).
7. Larson, R. L. Geological consequences of superplumes. Geology 19, 963–996 (1991).
8. Coccioni, R. et al. Umbria-Marche Basin, Central Italy: a reference section for the Aptian-Albian interval at low latitudes. Sci. Drill. 13, 42–46 (2012).
9. Coccioni, R. & Premoli Silva, I. Revised Upper Albian-Maastrichtian planktonic foraminiferal biostratigraphy and magnetostratigraphy of the classical Tethyan Gubbio section (Italy). Newsl. Stratigr. 48, 47–90 (2015).
10. Schlanger, S. O. & Jenkyns, H. C. Cretaceous oceanic anoxic events: causes and consequences. Geol. en. Mijnb. 55, 179–184 (1976).
11. Huber, B. T., MacLeod, K. G., Gröcke, D. R. & Kucera, M. Paleotemperature and paleosalinity inferences and chemotrastrigraphy across the Aptian/Albian.
paleoceanographic event: the Goban Spur stable isotope record. *Palaeogeogr. Palaeocl.* **201**, 51–66 (2003).

69. Moriya, K., Wilson, P. A., Friedrich, O., Erbacher, J. & Kawahata, H. Testing for ice sheets during the mid-Cretaceous greenhouse using glassy foraminiferal calcite from the mid-Cenomanian tropics on Demerara Rise. *Geology* **35**, 615–618 (2007).

70. Petrizzo, M. R., Huber, B. T., Wilson, P. A. & MacLeod, K. G. Late Albian paleoceanography of the western subtropical North Atlantic. *Paleoceanography* **23**, PA1213 (2008).

71. Gale, A. S. et al. In *Geologic Time Scale 2020* (1023–1086). (Elsevier, 2020).

72. Mahoney, J. J., Storey, M., Duncan, R. A., Spencer, K. J. & Pringle, M. In *The Mesozoic Pacific: Geology, Tectonics, and Volcanism* (eds. Pringle, M. S., Sager, W. W., Sliter, W., and Stein, S.), vol. **77**, 233–261 (Geophysical Monograph, AGU, 1993).

73. Tejada, M. L. G., Mahoney, J. I., Neal, C. R., Duncan, R. A. & Petterson, M. G. Basement geochemistry and geochronology of Central Malaita, Solomon Islands, with implications for the origin and evolution of the Ontong Java Plateau. *J. Pet.* **43**, 449–484 (2002).

74. Ingle, S. et al. Depleted mantle wedge and sediment fingerprint in unusual basalts from the Manihiki Plateau, central Pacific Ocean. *Geology* **35**, 595–598 (2007).

75. Timm, C. et al. Age and geochemistry of the oceanic Manihiki Plateau, SW Pacific: dence for a plume origin. *Earth Planet. Sci. Lett.* **304**, 135–146 (2011).

Acknowledgements

We thank Dr. K. Suzuki, Dr. T. Nozaki, and Y. Otsuki for their support in Re-Os analysis. We express sincere gratitude to K. Tanaka and N. Izumoto for their support in δ13Ccarb analysis. We warmly thank Dr. K. Matsuzaki for the constructive advice on the manuscript. This study was financially supported by Grant-in-aid for JSPS Research Fellow (19H0708) and JSPS KAKENHI (21H01203). R.C. and R.T. acknowledge the FUSP (Fundação de Apoio à Universidade de São Paulo)-Petrobras BARREMAG and 2405 projects for the financial support of the PLG core drilling.

Author contributions

H.M. conceived and designed this work and wrote the original manuscript. H.M., R.C., F.F., L.J., R.T. and J.F.S. collected samples. H.M. and J.K. conducted Re-Os analysis. H.N. and K.S. conducted the carbon isotopic analysis. All authors discussed and interpreted the results and contributed to the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-021-27817-0.

Correspondence and requests for materials should be addressed to Hironao Matsumoto.

Peer review information *Nature Communications* thanks Jochen Erbache and the other anonymous reviewers for their contribution to the peer review of this work. Peer reviewer reports are available.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2022