

A volcanic CO₂ pulse triggered the Cretaceous Oceanic Anoxic Event 1a and a biocalcification crisis

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ABSTRACT

The Aptian Oceanic Anoxic Event 1a (OAE1a, ca.120 Ma ago) is one of the most prominent of a series of geologically brief intervals in the Cretaceous characterized by the deposition of organic carbon-rich sediments. OAEs reflect major perturbations in the global carbon cycle evidenced by sedimentary carbon isotope records. However, the triggering mechanisms for OAEs remain controversial. Here we present a bulk-rock and molecular (marine and terrestrial biomarkers) C isotope record at unprecedented time resolution, from the Cison section of northern Italy, that shows that OAE1a conditions were reached over a period of several thousands of years through a stepwise perturbation of the carbon cycle. The documented sequence of events is most compatible with a trigger associated with increased CO₂ emissions, possibly leading to a doubling of *p*CO₂, which in turn caused larger C isotope fractionation in marine and terrestrial organisms and a major biotic crisis in the calcareous nannoplankton. Our data also show that a release of isotopically light carbon from partial methane hydrate dissociation probably played a minor role in the OAE1a carbon cycle perturbation.

INTRODUCTION

Oceanic Anoxic Event 1a (OAE1a, early Aptian, ca. 120 Ma ago) is defined as a period within which organic carbon-rich marine sediments were accumulated episodically on a global scale. OAE1a lasted ~1 Ma (Li et al., 2008) and coincided with the beginning of one of the largest positive carbon isotope ($\delta^{13}\text{C}$) excursions in the Cretaceous (Weissert and Erba, 2004; Fig. 1). The positive $\delta^{13}\text{C}$ excursion reflects changes in the marine carbon partitioning likely resulting from an increased burial rate of marine and terrestrial organic matter, caused by enhanced primary productivity and/or oxygen deficiency in the oceans (Menegatti et al., 1998, Weissert and Erba, 2004). A remarkable negative $\delta^{13}\text{C}$ spike of as much as 3‰ in marine carbonates and of 4‰–5‰ in the organic carbon (OC) preceded the positive excursion, and defines the beginning of OAE1a (Schlanger and Jenkyns, 1976; Menegatti et al., 1998). This $\delta^{13}\text{C}$ anomaly has been documented as being abrupt (Li et al., 2008) and is believed to reflect a major carbon cycle perturbation, caused by a massive release of ¹³C-depleted carbon into the ocean-atmosphere reservoir. Based on the amount and the isotopic composition of carbon required to produce the observed C isotope anomaly in sedimentary records, the coeval intense submarine volcanic activity in the Pacific Ocean, related to the Ontong Java large igneous province (LIP) and releasing mantle CO₂ at $\delta^{13}\text{C} \sim -5\text{‰}$, was first postulated as the cause of the OAE1a negative C isotope excursion (Menegatti et al., 1998). However, the amount of CO₂ needed for the amplitude of the negative C isotope shift and the rapidity of such a release (6–19 ka, van Breugel et al., 2007; ~40 ka, Li et al., 2008) challenged this hypothesis (Jahren et al., 2005). Subsequently, a methane release with a $\delta^{13}\text{C} \sim -60\text{‰}$ resulting from gas hydrate dissociation was proposed as a more likely explanation for this $\delta^{13}\text{C}$ negative excursion (Beerling et al., 2002; Jahren et al., 2005). Because oceanic and atmospheric carbon pools exchange at shorter time scales than the resolution of C isotope records available so far, and because bulk $\delta^{13}\text{C}$ combines effects

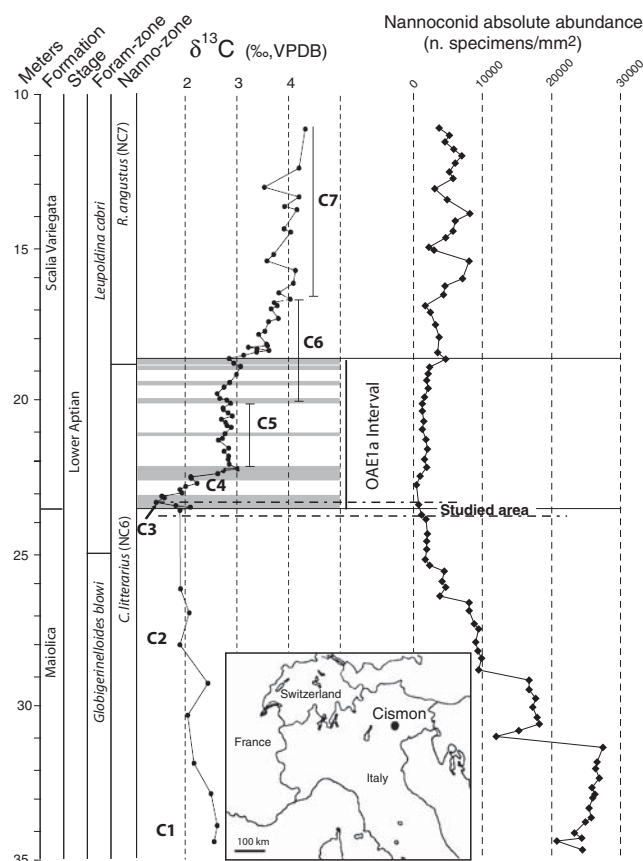


Figure 1. Aptian C isotope stratigraphy from Cison (modified from Menegatti et al., 1998). Nannoconid absolute abundance from Erba and Tremolada (2004). VPDB—Vienna Peedee belemnite.

of a whole ecosystem, higher-resolution C isotope studies on markers of specific organisms are essential for an improved understanding of the causal mechanisms that led to OAE1a. In this study we focus our interest on the negative C isotope anomaly at the base of OAE1a recorded in the Cison core (northern Italy; Fig. 1). We use carbonate C isotope data as a proxy for the oceanic inorganic dissolved carbon pool, and we present a new $\delta^{13}\text{C}$ record of OC and marine and terrestrial biomarkers.

GEOLOGICAL SETTING AND METHODS

The pelagic sediments of the Cison succession were deposited at a water depth of 1000–1500 m in the Belluno Basin at a paleolatitude of ~20°N (Erba et al., 1999). The organic matter preserved in these sediments is of marine origin with a substantial terrestrial contribution (van Breugel et al., 2007). The Cison core was sampled across the negative $\delta^{13}\text{C}$ shift over an interval of 32 cm at the base of OAE1a. Based on average sedimentation rates calculated for OAE1a with astrochronological

methods (Li et al., 2008), the sampled interval corresponds to ~70 ka. Specific biomarker $\delta^{13}\text{C}$ records, nanofossil data, and estimates of C isotope fractionations (ϵ_p) provide information on the variability of the global carbon cycle, on changes in marine and terrestrial carbon sinks, and on trends in atmospheric $p\text{CO}_2$. Details of analytical methods used are described in the GSA Data Repository.¹

RESULTS AND DISCUSSION

In pelagic sediments, short-chain n-alkanes ($n\text{-C}_{17}$ and $n\text{-C}_{19}$) are usually considered to be mainly synthesized by marine algae, whereas long-chain n-alkanes ($n\text{-C}_{27}$, $n\text{-C}_{29}$, and higher) are mostly derived from land plants (Eglinton and Hamilton, 1967). N-alkanes $> n\text{-C}_{30}$ ($n\text{-C}_{31}$, $n\text{-C}_{33}$, $n\text{-C}_{35}$, and $n\text{-C}_{37}$) can also be produced by the diagenetic reduction of alkenones (Volkman et al., 1980). The first occurrence of the main alkenone producers, the coccolithophore haptophyte species *Emiliana huxleyi* and *Gephyrocapsa oceanica*, has been dated as 0.28 Ma and 1.8 Ma ago, respectively. Nevertheless, C_{37} , C_{38} , and C_{39} alkenones have been detected in early Aptian sediments (Dumitrescu and Brassell, 2005), suggesting that haptophyte species were present at that time. In the studied samples, the C_{37} n-alkane shows a low abundance and no longer-chain n-alkanes were detected. However, C_{35} and C_{36} alkenones were recently discovered in cultures of haptophytes and in natural environments in the Ligurian and Black Seas (Prah et al., 2006). Moreover, C_{31} and C_{32} n-alkanes were also identified as degradation products of alkyl compounds synthesized by haptophytes (Volkman et al., 1992; Schaeffer et al., 1995). Therefore, n-alkanes $> \text{C}_{30}$ may partly derive from haptophytes in Cismon samples. This is further suggested by the nanofossil record. In particular, *Watznaueria barnesiae*, considered the Cretaceous equivalent of *E. huxleyi*, is very common and *Biscutum*, *Discorhabdus*, and *Zeughrabdotos* coccoliths are also common in the studied interval (Fig. 2). Their morphological resemblance to the *Emiliana-Gephyrocapsa* family suggests that these taxa might have been Cretaceous alkenone producers. Haptophyte alkenones $\delta^{13}\text{C}$ is used for paleo- $p\text{CO}_2$ reconstruction (Pagani, 2002). The $\delta^{13}\text{C}$ of their reduced derivatives, n-alkanes $> \text{C}_{30}$, could therefore provide a relevant tool for $p\text{CO}_2$ estimates in the Cretaceous.

Our high-resolution carbonate and OC $\delta^{13}\text{C}$ records can be split into five distinct intervals, shown in Figure 3 (A and B). The first 8 cm of the $\delta^{13}\text{C}$ record is marked by a decrease in both the inorganic and organic C isotope curves, from 2.5‰ to 2.3‰ in the carbonates, and from -26.7‰ to -27.9‰ in the OC. This weak trend to lower values is defined as interval I and may be construed as evidence for volcanic CO_2 emission from the coeval Ontong Java LIP. An estimated amount of ~3200 Gt of carbon at -5‰ would produce the recorded decrease in the $\delta^{13}\text{C}_{\text{carbonate}}$ (Higgins and Schrag, 2006).

In interval II, $\delta^{13}\text{C}$ values of OC show a 0.5‰ positive excursion over ~9 ka, which is not recorded in $\delta^{13}\text{C}_{\text{carbonate}}$ values, showing further weak decrease to ~-2.1‰. Since the positive $\delta^{13}\text{C}$ shift is also present in biomarkers of various groups of terrestrial and marine organisms (Fig. 3C), we suggest that it reflects a global change in the marine and terrestrial carbon pools. A similar short-lived positive $\delta^{13}\text{C}$ excursion preceding the negative C isotope decrease has also been documented for the Paleocene–Eocene Thermal Maximum 55.8 Ma ago (Sluijs et al., 2007), but until now, not in the early Aptian, probably because of a lack of resolution or hiatuses in studied sections. A temperature increase of seawater (Ando et al., 2008) could cause an increase in marine algal $\delta^{13}\text{C}$ because of the decreased fractionation between HCO_3^- and CO_2 (Hayes, 1993). A decrease is recorded in marine ϵ_p profiles over interval II (Fig. 4A). For

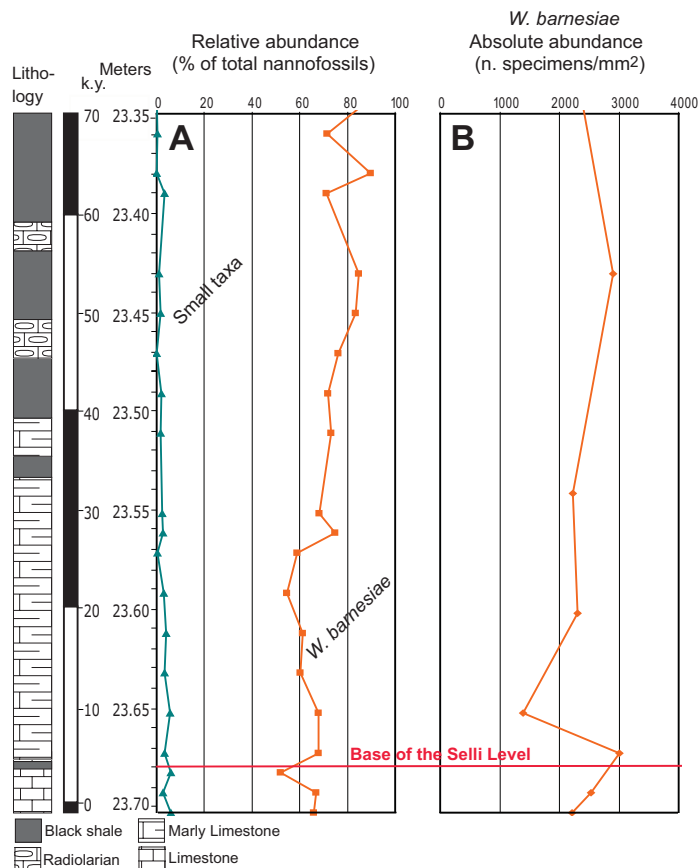


Figure 2. A: Relative abundance of small taxa (*Biscutum costans*, *Discorhabdus rotatorius*, and *Zeughrabdotos erectus*) and of *Watznaueria barnesiae*. B: Absolute abundance of *Watznaueria barnesiae*.

terrestrial plants, ϵ_p is influenced by factors such as humidity, soil moisture, irradiance, and soil temperature (Evans et al., 1986; Jahren et al., 2008). Such environmental changes may have been caused by the continuous emission of volcanic CO_2 . In this respect, the 0.2‰ decrease recorded in the carbonates over interval II suggests an additional release of ~3200 Gt of mantle carbon.

In interval III, $\delta^{13}\text{C}_{\text{OC}}$ data show a major decrease of 1.3‰ over 6–7 ka, coinciding with a black shale deposition, whereas only a minor change is observed in the $\delta^{13}\text{C}_{\text{carbonate}}$ curve, which continues to slowly decrease to ~-1.9‰. This contrasting trend provides clear evidence that the negative shift in $\delta^{13}\text{C}_{\text{OC}}$ does not result from a massive input of light carbon into the ocean-atmosphere reservoir, since this would affect the $\delta^{13}\text{C}$ of both OC and carbonate C. The negative shift is recorded in marine and terrestrial biomarkers, indicating that the bulk $\delta^{13}\text{C}_{\text{OC}}$ shift is not due to a change in the relative contribution of marine versus terrestrial organic matter. Nevertheless, this shows that both atmospheric and oceanic carbon pools were affected.

Remarkably, very long chain n-alkanes show a negative C isotope shift of significantly higher amplitude, ~-6.5‰ for C_{31} and C_{33} n-alkanes, and -9.8‰ for C_{35} n-alkane (Fig. 3D). For $n\text{-C}_{37}$, $\delta^{13}\text{C}$ values are similar to those for $n\text{-C}_{35}$ after the C isotope shift. Unfortunately $n\text{-C}_{37}$ abundance was too low for $\delta^{13}\text{C}$ measurement in intervals I and II. The heavier $\delta^{13}\text{C}$ values of n-alkanes $> \text{C}_{30}$, before this main C isotope decrease, suggest that they did not originate exclusively from terrestrial higher plants and possibly reflect a haptophyte contribution. Because C_{35} and C_{37} n-alkanes are expected to be less influenced by a terrestrial input, they may more readily reveal the haptophyte contribution. The large decrease in the $\delta^{13}\text{C}$ values

¹GSA Data Repository item 2009200, details of bulk and compound-specific $\delta^{13}\text{C}$ and nanofossil analysis, is available online at www.geosociety.org/pubs/ft2009.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

Figure 3. Bulk and molecular $\delta^{13}\text{C}$ curves from Cison core. Relative time scale estimated according to Li et al. (2008). VPDB—Vienna Pee Dee belemnite. A: Carbonate carbon. B: Bulk organic carbon (OC). C: Marine ($n\text{-C}_{17}$ and $n\text{-C}_{19}$) and terrestrial ($n\text{-C}_{27}$ and $n\text{-C}_{29}$) lipid biomarkers. D: Very long-chain n-alkanes ($n\text{-C}_{31}$, $n\text{-C}_{33}$, $n\text{-C}_{35}$, and $n\text{-C}_{37}$). Gray shaded areas represent intervals II (from 23.60 to 23.56 m) and IV (from 23.53 to 23.51 m). Gray hachured areas represent interval where $\delta^{13}\text{C}_{n\text{-alkanes}}$ curve could not be confirmed due to lack of material for n-alkanes $\delta^{13}\text{C}$ analysis.

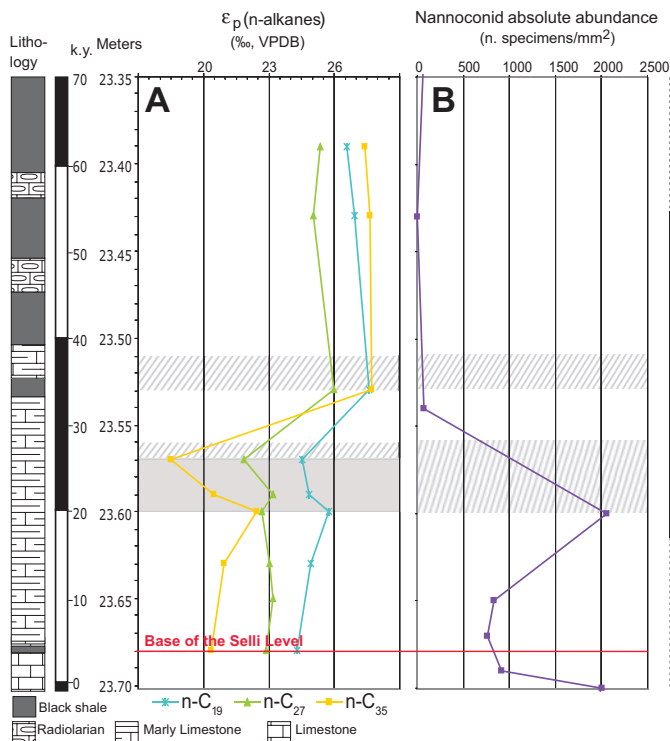
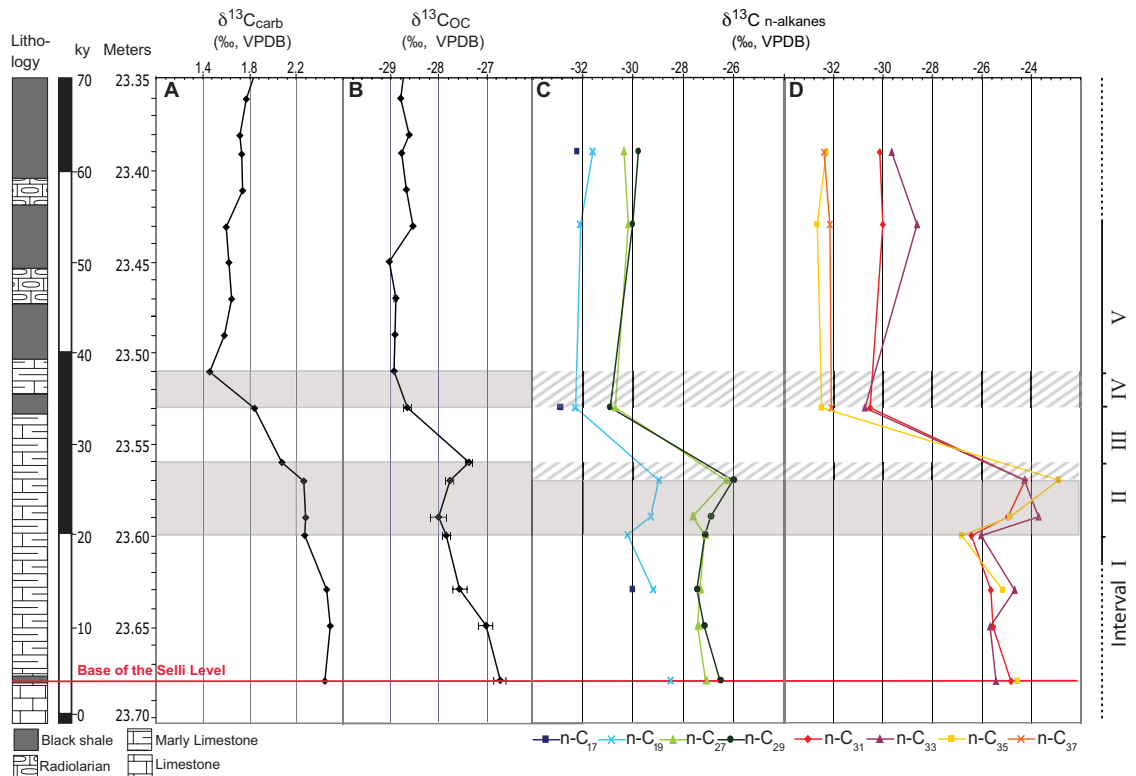


Figure 4. ϵ_p , isotopic fractionation associated with carbon fixation, is estimated according to Hayes et al. (1999): $\epsilon_p = (\delta^{13}\text{C}_{\text{carbonate}} - \delta^{13}\text{C}_{n\text{-alkanes}}) - \Delta_{\text{carbonate}}$ ($\Delta_{\text{carbonate}}$ being the estimated fractionation between aqueous CO_2 and carbonates). A: ϵ_p for $n\text{-C}_{19}$ (marine), $n\text{-C}_{27}$ (terrestrial), and $n\text{-C}_{35}$ (hypothetically haptophytes). B: Absolute abundance of nannoconids. VPDB—Vienna Pee Dee belemnite. Gray shaded areas represent intervals II and IV. Gray hachured areas represent deduced interval on $\delta^{13}\text{C}_{n\text{-alkanes}}$ and nannoconid absolute abundance curves.

of n-alkanes $>\text{C}_{30}$ in interval III could be attributed to a change in the relative contribution from the precursor organisms. However, coccolith distribution through intervals I–V (Fig. 2) indicates that haptophytes were relatively constant in abundance, diversity, and assemblage composition. Thus, the main shift in $\delta^{13}\text{C}_{\text{COC}}$ at the base of the OAE1a was more likely caused by a significant ϵ_p increase in marine and terrestrial organisms.

In interval III, ϵ_p displays an abrupt increase of 3‰ and 4.2‰ for marine $n\text{-C}_{19}$ and terrestrial $n\text{-C}_{27}$, respectively (Fig. 4A). However, both markers are not very specific, whereas the C_{35} n-alkane, with a 9.4‰ increase, may predominantly record the contribution of haptophyte algae. For one specific algae species, ϵ_p depends mainly on temperature, nutrient availability, and $p\text{CO}_2$ (Pagani, 2002). A warming episode of as much as 8 °C is associated with the onset of OAE1a (Ando et al., 2008), but this alone could not explain the amplitude of the observed ϵ_p increase (Hayes et al., 1999). Furthermore, marine and terrestrial ϵ_p values follow the same pattern in interval III, suggesting that nutrient availability was not the controlling factor for this ϵ_p shift. Thus, we conclude that the most probable explanation for the observed increase in ϵ_p is a major increase in $p\text{CO}_2$. Calcareous nannofossil data support this interpretation. Indeed, the heavily calcifying nannoconids show a crash in calcification in interval III (Fig. 4B), likely induced by acidification of the surface ocean by excess CO_2 (Weissert and Erba, 2004). The source of this CO_2 cannot be strongly depleted in ^{13}C , as only a minor shift is recorded in the bulk carbonate. On a short time scale of 6–7 ka, the observed changes are compatible only with a CO_2 emission from the contemporaneous Ontong Java LIP. An estimated release of ~3200 Gt of mantle carbon would result in a 0.2‰ decrease in the carbonates recorded in interval III and in high $p\text{CO}_2$. A first order estimation of paleo- $p\text{CO}_2$ based on $\epsilon_p(n\text{-C}_{35})$ (Freeman and Hayes, 1992) suggests a doubling of $p\text{CO}_2$ related to this event. The intervals I and II indicate that volcanism was already intense in the preceding 30 ka. Recent osmium isotope studies further support the hypothesis of enhanced volcanic activity at the onset of OAEs (Suzuki et al., 2007; Turgeon and Creaser, 2008).

After the large decrease in the $\delta^{13}\text{C}_{\text{OC}}$, a simultaneous negative shift of 0.4‰ is observed in the carbonates and OC over a period of ~5 ka corresponding to interval IV. This interval shows the most negative values of the OAE1a C isotope spike. Although, because of lack of material, this interval could not be analyzed for compound-specific $\delta^{13}\text{C}$, we suggest that this negative shift reflects an additional release of ^{13}C -depleted carbon into the ocean-atmosphere reservoir. For a methane source with $\delta^{13}\text{C}$ of -60‰, ~270 Gt of carbon are sufficient to cause this shift. Hence the partial dissociation of methane hydrates, even considering that in the Cretaceous methane hydrates were probably present in lower amounts than in the modern ocean (Milkov, 2004), can explain this $\delta^{13}\text{C}_{\text{carbonate}}$ shift. A warming, related to preceding high $p\text{CO}_2$ conditions, could have triggered methane hydrate destabilization. A release of this amount of carbon would not significantly affect the atmospheric C reservoir because it is ~12 times smaller than the release of volcanic CO_2 in interval III. Thus, no further increase in ϵ_p is expected in interval IV, which is consistent with the constant ϵ_p values recorded in this interval. Alternatively, the high ϵ_p of 25.4‰–27.4‰ at the end of interval III may be close to the maximum possible fractionation, which is considered to be between 25‰ and 28‰, depending on the species (Pagani, 2002). Therefore, it is also possible that no further increase in ϵ_p can be observed after interval III.

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