19. Lammert, P. E., Rokhsar, D. S. & Toner, J. Topology and nematic ordering. I. A gauge theory. *Phys. Rev. E* **52,** 1778–1800 (1995).
20. Toner, J., Lammert, P. E. & Rokhsar, D. S. Topology and nematic ordering. II. Observable critical behavior. *Phys. Rev. E* **52,** 1801–1810 (1995).

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# Increased thermohaline stratification as a possible cause for an ocean anoxic event in the Cretaceous period

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**Ocean anoxic events were periods of high carbon burial that led to drawdown of atmospheric carbon dioxide, lowering of bottom-water oxygen concentrations and, in many cases, significant biological extinction[1–5]. Most ocean anoxic events are thought to be caused by high productivity and export of carbon from surface waters which is then preserved in organic-rich sediments, known as black shales. But the factors that triggered some of these events remain uncertain. Here we present stable isotope data from a mid-Cretaceous ocean anoxic event that occurred 112 Myr ago, and that point to increased thermohaline stratification as the probable cause. Ocean anoxic event 1b is associated with an increase in surface-water temperatures and runoff that led to decreased bottom-water formation and elevated carbon burial in the restricted basins of the western Tethys and North Atlantic. This event is in many ways similar to that which led to the more recent Plio-Pleistocene Mediterranean sapropels, but the greater geographical extent and longer duration (~46 kyr) of ocean anoxic event 1b suggest that processes leading to such ocean anoxic events in the North Atlantic and western Tethys were able to act over a much larger region, and sequester far more carbon, than any of the Quaternary sapropels.**

The mid-Cretaceous is associated with ocean anoxic events (OAEs)—periods of elevated carbon burial in marine sediments known primarily from Tethyan basins, the Atlantic and equatorial Pacific. These events have been interpreted as the result of increased surface-water productivity caused by either nutrient leaching of flooded lowlands during transgressions and/or increased continental runoff due to an accelerated hydrological cycle[2,4,6,7]. Recent high-resolution stable isotope studies suggest an intensified vertical mixing and warming of the water column as a cause for the observed productivity increase during early Aptian OAE 1a and late Albian OAE 1d[5,8,9]. For OAE 1d, this intensified mixing is expressed by decreased vertical isotopic gradients and a warming of the entire water-column. High-resolution stable isotope studies on planktic and benthic foraminifers[10] indicate that a bathyal warming and vertical mixing may have caused OAE 2 and its associated extinctions. Or some of the OAEs may reflect decreased vertical mixing and the development of euxinic conditions throughout the water column that permits organic carbon to accumulate on the sea floor[11,12].

Ocean Drilling Program (ODP) Leg 171 B drilled mid-Cretaceous black shales of Albian age in the western subtropical Atlantic, off Florida. ODP Hole 1049C recovered Aptian to Eocene sediments, including a 46-cm-thick succession of laminated black shale, representing early Albian OAE 1b (ref. 13). Total organic carbon (TOC) contents in laminated black shales range from 0.5 to 12.3% (ref. 14). The record of OAE 1b at Site 1049 is unusual for most OAE sediments because the foraminifera are extremely well preserved and can be used to study the geochemical record of the event. Both planktic and benthic species have glassy shells with preserved surface ornamentation and without infilling calcite. In addition, the stable isotope signature of individual species suggests that stable isotopic ratios were not homogenized, which would be expected for diagenetically altered calcite.

Oxygen isotope values for the planktic species *Hedbergella aff. Hedbergella trocoidea* are consistently more negative by 0.7 to 0.1‰ and carbon isotope values heavier by 0.60 to 0.05‰ than for the planktic species *Hedbergella speetonensis tuniensis*, suggesting a deeper habitat for the latter (see Supplementary Information). Benthic species show a constant offset of carbon isotopes with heavier values for *Osangularia schloenbachi* and negative values for *Gyroidinoides nitidus*. This suggests an infaunal habitat for *G. nitidus* and an epifaunal mode of life for *O. schloenbachi*, as infaunal forms tend to yield more negative signals owing to the enrichment of the pore waters with isotopically negative carbon that is derived from oxygenized organic carbon.

We identified four intervals (events I to IV, Fig. 1) that represent significant changes in ocean temperature, salinity and carbon flux during the OAE.

Event I is characterized by stable carbon and oxygen isotope values. Oxygen isotope values are surprisingly positive, suggesting either very cool surface and deep-water temperatures (around 12 °C for surface water and 9 °C for bottom water of an upper bathyal water depth around ~1,000 m) and/or high salinities before the black shale. In addition, oxygen and carbon isotope gradients between the surface and bottom water are very small, indicating a uniform water mass in the upper 1,000 m of the water column during this phase.

Event II marks a large 1.6‰ negative oxygen isotopic shift in planktic foraminifers below the base of the black shale. This decrease is paralleled by a 0.9‰ increase of planktic $\delta^{13}C$ values, followed by a decrease of the same magnitude at the base of the black shale. Benthic values in this interval remain relatively constant for the carbon isotopes, but oxygen isotopic values of benthic foraminifers show a slight decrease in the lowermost part of the black shale that occurs later than the negative shift of planktic foraminifers. The steep decrease in oxygen isotope values below the black shale is difficult to explain with a rise of sea surface temperatures only, as it would reflect a geologically rapid and significant rise of approximately 10 °C. However, this decrease could be explained by a combination of salinity decrease and temperature increase of surface waters. The small increase in the vertical carbon gradient may point to an increase of surface-water productivity before the black shale, leading to increased carbon export and greater carbon isotope gradients between surface and bottom water. This interpretation is supported by the synchronous presence of benthic foraminifers that indicate high organic carbon fluxes to the sea floor[15,16]. The decrease of carbon isotope values at the base of the black shale is difficult to explain, but might be connected to the presence of negative organic carbon in the black shale. However, constant sedimentation rates and the lack of compositional changes

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of organic matter between marls and black shales suggest that productivity was not a primary factor controlling the positive carbon excursion[14]. An alternative cause for the positive carbon shift is degassing of carbon dioxide from surface water, coupled with a decreased supply of isotopically negative carbon from deep water during the observed warming of surface waters (M. A. Arthur, personal communication).

Event III marks a brief increase of planktic oxygen isotope values while benthic oxygen isotopes and carbon isotope values for both benthic and planktic foraminifers remain stable. This rise of $\delta^{18}O$ values may reflect a short drop in temperature and/or a rise in surface-water salinity and is paralleled by a repopulation of benthic foraminifers indicating a synchronous reoxygenation at the sea floor[15,16].

Event IV marks the long-term evolution towards pre-event values of planktic oxygen isotope values in the upper part and above the black shale. We note that the re-establishment of low oxygen isotope gradients from the surface to deep water does not coincide with the top of the black shale, but occurs about 1.4 m above it. This discrepancy might be explained by "burn down" of organic matter following reoxygenation of the sea floor, as was observed in modern Mediterranean sapropels[17]. However, reoccurrence of benthic foraminifers just above the black shale suggests termination of bottom-water dysoxia at the top of the preserved black shale.

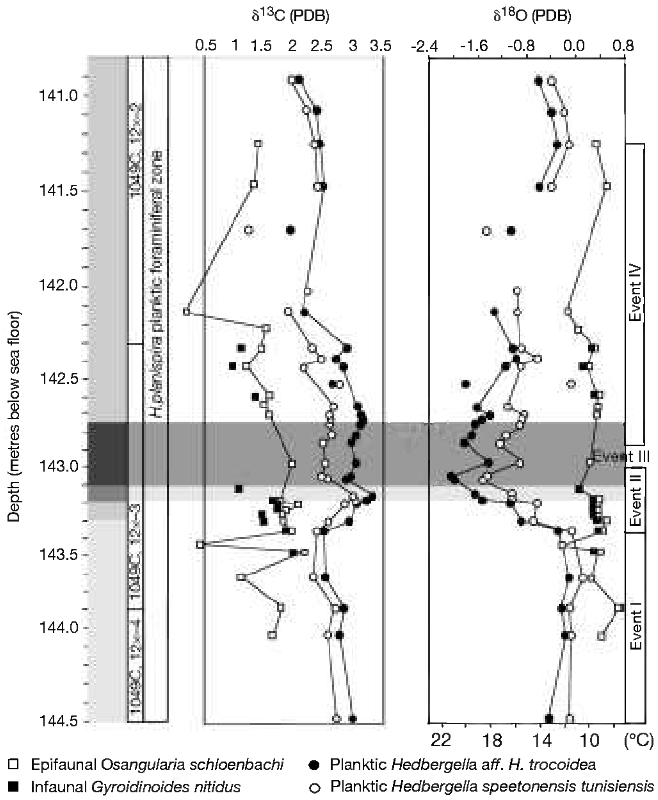


**Figure 1** Lithology, and oxygen and carbon isotopes of planktic and benthic foraminifers plotted against depth of ODP Hole 1049C, western subtropical Atlantic. The benthic foraminiferal isotope record is shown in open (epifaunal *Osangularia schloenbachi*) and filled squares (infaunal *Gyroidinoides nitidus*), amd the planktic foraminiferal isotope record is shown in open (*Hedbergella speetonensis tuniensis*) and filled circles (*Hedbergella aff. H. trocoidea*). The shaded bar indicates the laminated black shale interval representing OAE 1b (dark: distinctly laminated; light: not laminated). Palaeotemperatures were calculated using the equation of Erez and Luz[27] and the standard mean ocean water (SMOW)/PDB conversion of −0.27 (ref. 28), assuming −1.2‰$_{SMOW}$ for a non-glacial world[29]. Four events (I to IV) are identified in the OAE 1b stable isotope record. Nomenclature: '1049 C, 12×−4' indicates ODP Hole 1049 C, Core 12×, Section 4.

Our observations suggest that a well mixed, well ventilated, low-nutrient water column with relatively high salinities and cool temperatures increased moderately in temperature at the same time as surface-water salinity decreased, causing pronounced thermohaline stratification of the water column. This is documented by a large increase in the oxygen isotope gradients from the surface to deep water observed in our record and suggests that black shale deposition was triggered by a reduction in ventilation of subthermocline water. The termination of OAE 1b was caused by a gradual reduction of vertical temperature and salinity gradients. The increased vertical oxygen isotopic gradient cannot represent an evolutionary change in depth habitats of the analysed planktic organisms, as, first, a synchronous depth-habitat modification of two different species is very unlikely and, second, the observed change is reversed above the dark shales.

Tuned cycle stratigraphy yielded[18] calculated sedimentation rates of approximately 1.0 cm $kyr^{-1}$ for the early Albian interval of ODP Site 1049. According to these data the drop of $\delta^{18}O$ values during event II lasted approximately 32 kyr, the rise of $\delta^{18}O$ values (event IV) persisted for 175 kyr, and the duration of black shale deposition was about 46 kyr. The total duration of the OAE 1b interval (from base of event II to the top of event IV) is estimated to be approximately 210 kyr.

It has been suggested that OAE 1b was caused by an increase in surface-water productivity similar to other OAEs[15,19]. In contrast to other OAEs, which have mostly been explained by an intensified vertical mixing of intermediate and surface waters, our data show that productivity seems to play a minor role as a factor controlling OAE 1b.

The importance of variation in precipitation and/or continental runoff as a mechanism for changing deep water convection has been demonstrated in a series of ocean model experiments[20]. Such hydrologic changes have been attributed as the cause for formation of sapropels in the Mediterranean during the Quaternary. We consider this model of sapropel formation to be the best analogue to black shale formation during OAE Ib.

In the modern and Quaternary Mediterranean, vertical temperature gradients are very low, as can be observed during our event I. During sapropel formation, a steep decrease of $\delta^{18}O$ values observed in planktic foraminifera has been related to a drop of surface-water salinity and minor increases in surface-water temperatures[21]. The increased surface stratification is believed to be caused by increased continental runoff during warm periods, resulting in a positive freshwater balance and a switch from an anti-estuarine to estuarine circulation in the Mediterranean[21,22]. Such an estuarine circulation system is controlled by the presence of sills in the gateways between the western and eastern Mediterranean Sea and the Atlantic Ocean.

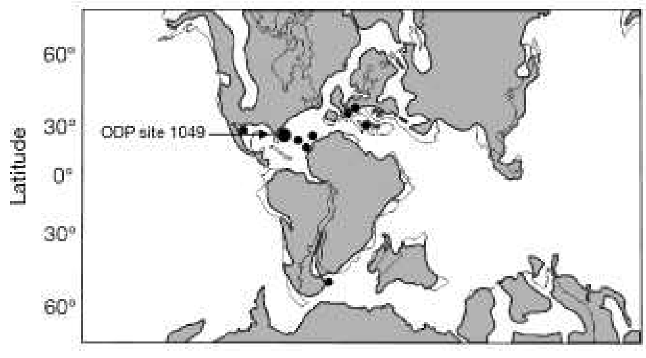


**Figure 2** Palaeogeographic reconstruction for the late Aptian (120 Myr ago) with the positions of the biostratigraphically well dated, known OAE 1b occurrences. Modified after refs 19 and 30. We note that OAE 1b sections are only known from Tethyan basins, North and South Atlantic.

Recent investigations documented reoxygenation horizons from several Mediterranean sapropels, similar to the one we described, which are considered to be the result of short (approximately 500 years) phases of vertical mixing. Palaeotemperature records document a phase of cool surface-water temperatures during these interruptions, again similar to what our data suggest for the reoxygenation during event III of OAE Ib (ref. 25).

Mediterranean sapropels are the result of monsoonal fluctuation during the Quaternary resulting in a cyclic presence of numerous sapropels. In contrast to Site 1049, where the described black shale horizon is the only carbonaceous layer, late Aptian to early Albian sections in the western Tethyan basins show numerous black shales that have been described as being cyclic[24,25]. A comparable situation can be observed in the Quaternary Mediterranean, where only the best developed sapropels in the restricted eastern basin are present in the more open western basin[26].

We believe that the mechanisms leading to OAE 1b reflect conditions similar to those leading to Quaternary Mediterranean sapropels. However, the geographical extent of OAE 1b was much larger and, according to the age model available at present, the duration of OAE 1b was much longer, suggesting the North Atlantic/western Tethyan Ocean remained in a "super-sapropel stage" for approximately four times longer than the longest of the Plio-Pleistocene Mediterranean sapropels. The great extent of OAE 1b (Fig. 2) suggests that processes that restricted ventilation of the North Atlantic and Tethys were able to act over a much larger region than ever occurred during the Plio-Pleistocene interval of sapropel formation. We suggest that the partial tectonic isolation of the various basins in the Tethys and Atlantic, a low sea level and the initiation of warm global climates may be important factors in setting up oceanic stagnation during OAE 1b. □

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1. Arthur, M. A., Brumsack, H.-H., Jenkyns, H. C. & Schlanger, S. O. in *Cretaceous Resources, Events and Rhythms* (eds Ginsburg, R. N. & Beaudoin, B.) 75–119 (Kluwer, Dordrecht, 1990).
2. Erbacher, J., Thurow, J. & Littke, R. Evolution patterns of radiolaria and organic matter variations—a new approach to identify sea-level changes in mid-Cretaceous pelagic environments. *Geology* 24, 499–502 (1996).
3. Kuypers, M. M. M., Pancost, R. D. & Sinninghe Damsté, J. S. A large and abrupt fall in atmospheric $CO_2$ concentrations during Cretaceous times. *Nature* **399**, 342–345 (1999).
4. Jenkyns, H. C. Mesozoic anoxic events and paleoclimate. *Zbl. Geol. Paläont. Teil 1.* **7–9**, 943–949 (1997).
5. Hochuli, P. A. *et al.* Episodes of high productivity and cooling in the early Aptian Alpine Tethys. *Geology* **27**, 657–666 (1999).
6. Thurow, J., Brumsack, H.-J., Rullkötter, J. & Meyers, P. The Cenomanian/Turonian Boundary Event in the Indian Ocean—a key to understand the global picture. *Geophys. Monogr.* **70**, 253–273 (1992).
7. Weissert, H., Lini, A., Föllmi, K. B. & Kuhn, O. Correlation of Early Cretaceous carbon isotope stratigraphy and platform drowning events: a possible link? *Palaeogeogr. Palaeoclim. Palaeecol.* **137**, 189–203 (1998).
8. Wilson, P. A., Norris, R. D. & Erbacher, J. Tropical sea surface temperature records and black shale deposition in the mid-Cretaceous western Atlantic (Blake Nose and Demerara Rise). *Eos* **80**, F488 (1999).
9. Menegatti, A. P. *et al.* High-resolution $\delta^{13}C$ stratigraphy through the early Aptian "Livello Selli" of the Alpine Tethys. *Paleoceanography* **13**, 530–545 (1998).
10. Huber, B. T., Leckie, R. M., Norris, R. D., Bralower, T. J. & CoBabe, E. Foraminiferal assemblages and stable isotopic change across the Cenomanian-Turonian Boundary in the subtropical North Atlantic. *J. Foram. Res.* **29**, 392–417 (1999).
11. Sinninghe Damsté, J. S. & Köster, J. A euxinic southern North Atlantic Ocean during the Cenomanian/Turonian oceanic anoxic event. *Earth Planet. Sci. Lett.* **158**, 165–173 (1998).
12. Fischer, A. G. & Arthur, M. A. Secular variations in the pelagic realm. *SEPM Spec. Publ.* **25**, 19–50 (1977).
13. Norris, R. D. *et al.* Blake Nose paleoceanographic transect, Western North Atlantic. *Proc. ODP Init. Rep. B* **171**, 1–749 (1998).
14. Barker, C. E., Pawlewicz, M. & Cobabe, E. A. in *Western North Atlantic Palaeogene and Cretaceous Palaeoceanography* (eds Kroon, D., Norris, R. D. & Klaus, A.) (Geological Society, London, in the press).
15. Erbacher, J., Hemleben, C., Huber, B. & Markey, M. Correlating environmental changes during early Albian oceanic anoxic event 1b using benthic foraminiferal paleoecology. *Mar. Micropal.* **38**, 7–28 (1999).
16. Holbourn, A., Kuhnt, W. & Erbacher, J. Benthic foraminifers from lower Albian black shales (Site 1049, ODP Leg 171): evidence for a non "uniformitarian" record. *J. Foram. Res.* (in the press).
17. Mercone, D. *et al.* Duration of S1, the most recent sapropel in the eastern Mediterranean Sea, as indicated by accelerator mass spectrometry radiocarbon and geochemical evidence. *Paleoceanography* **15**, 336–347 (2000).
18. Ogg, J. G., Röhl, U. & Geib, T. Astronomical tuning of Aptian-Albian boundary interval: oceanic anoxic event 1b through lower Albian magnetic suchron M″-2″r. *Eos* **80**, F491–F492 (1999).
19. Bralower, T. J. *et al.* Dysoxic/Anoxic episodes in the Aptian-Albian (Early Cretaceous). *Geophys. Monogr.* **77**, 5–37 (1993).
20. Bice, K. L., Barron, E. J. & Peterson, W. H. Continental runoff and early Cenozoic bottom-water sources. *Geology* **25**, 951–954 (1997).
21. Emeis, K.-C. *et al.* Stable isotope and alkenone temperature records of sapropels from Sites 964 and 967: constraining the physical environment of sapropel formation in the eastern Mediterranean Sea. *Proc. ODP Sci. Res.* **160**, 309–331 (1998).
22. Rohling, E. J. Review and new aspects concerning the formation of eastern Mediterranean sapropels. *Mar. Geol.* **122**, 1–28 (1994).
23. Myers, G. P. & Rohling, E. J. Modeling a 200-yr interruption of the Holocene sapropel S1. *Quat. Res.* **53**, 98–104 (2000).
24. Wortmann, U. G., Hesse, R. & Zacher, W. Major-element analysis of cyclic black shales: Paleoceanographic implications for the Early Cretaceous deep western Tethys. *Paleoceanography* **14**, 525–541 (1999).
25. De Boer, P. L. Aspects of middle cretaceous pelagic sedimentation in Southern Europe. *Geol. Ultraiectina* **31**, 1–112 (1983).
26. Meyers, P. A. & Doose, H. Sources, preservation and thermal maturity of organic matter in Pliocene-Pleistocene organic-carbon-rich sediments of the western Mediterranean Sea. *Proc. ODP Sci. Res.* **161**, 383–390 (1999).
27. Erez, J. & Luz, B. Experimental paleotemperature equation for planktonic foraminifera. *Geochim. Cosmochim. Acta* **47**, 1025–1031 (1983).
28. Hut, G. Consultants group meeting on stable isotope reference samples for geochemical and hydrological investigations. 1–42 (Report to Director General of the Institute of Atomic Energy Agency, Vienna, 1987).
29. Shackleton, N. J. & Kennett, J. P. Paleotemperature history of the Cenozoic and the initiation of Antarctic glaciation: oxygen and carbon isotope analyses in DSDP Sites 277, 279 and 281. *DSDP Init. Rep.* **29**, 743–755 (1975).
30. Barron, E. J., Harrison, C. G., Sloan, J. L. & Hay, W. W. Paleogeography, 80 million years ago to present. *Eclog. Geol. Helv.* **74**, 443–470 (1981).


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# 300-Myr-old magmatic $CO_2$ in natural gas reservoirs of the west Texas Permian basin

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**Except in regions of recent crustal extension[1], the dominant origin of carbon dioxide in fluids in sedimentary basins has been assumed to be from crustal organic matter[2] or mineral reactions[3,4]. Here we show, by contrast, that Rayleigh fractionation caused by partial degassing of a magma body can explain the $CO_2/^3He$ ratios and $\delta^{13}C(CO_2)$ values observed in $CO_2$-rich natural gases in the west Texas Val Verde basin and also the mantle $^3He/^{22}Ne$ ratios observed in other basin systems[5]. Regional changes in $CO_2/^3He$ and $CO_2/CH_4$ ratios can be explained if the $CO_2$ input pre-dates methane generation in the basin, which occurred about 280 Myr ago[6]. Uplift to the north of the Val Verde basin between 310 and 280 Myr ago[6] appears to be the only tectonic event with appropriate timing and location to be the source of the magmatic $CO_2$. Our identification of magmatic $CO_2$ in a foreland basin indicates that the origin of $CO_2$ in other mid-continent basin systems should be re-evaluated. Also, the inferred closed-system preservation of natural gas in a trapping structure**