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Evidence for large methane releases to the atmosphere from deep-sea gas-hydrate dissociation during the last glacial episode

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Past atmospheric methane-concentration oscillations recorded in polar ice cores vary together with rapid global climatic changes during the last glacial episode. In the "clathrate gun hypothesis," massive releases of deep-sea methane from marine gas-hydrate dissociation led to these well known, global, abrupt warmings in the past. If evidence for such releases in the water column exists, however, the mechanism and eventual transfer to the atmosphere has not yet been documented clearly. Here we describe a high-resolution marine-sediment record of stable carbon isotopic changes from the Papua Gulf, off Papua New Guinea, which exhibits two extremely depleted excursions (down to -9‰) at $\approx 39,000$ and $\approx 55,000$ years. Morphological, isotopic, and trace metal evidence dismisses authigenic calcite as the main source of depleted carbon. Massive methane release associated with deep-sea gas-hydrate dissociation is the most likely cause for such large depletions of $\delta^{13}\text{C}$. The absence of a $\delta^{13}\text{C}$ gradient in the water column during these events implies that the methane rose through the entire water column, reaching the sea-air interface and thus the atmosphere. Foraminiferal $\delta^{18}\text{O}$ composition suggests that the rise of the methane in the water column created an upwelling flow. These inferred emission events suggest that during the last glacial episode, this process was likely widespread, including tropical regions. Thus, the release of methane from the ocean floor into the atmosphere cannot be dismissed as a strong positive feedback in climate dynamics processes.

During the last glacial episode, rapid climatic changes recorded in ice-core records are closely associated with variations in concentration of atmospheric methane, a powerful greenhouse gas, showing a maximum amplitude of ≈ 200 parts per billion by volume (1). Until recently, the main source of atmospheric methane during the last glacial episode was attributed to low-latitude continental wetlands emissions (2, 3), whereas the potential role of deep-sea and lake-gas hydrates was largely ignored. The accepted hypothesis of a strong link between climate and methane emissions from wetlands was called into question recently by an exhaustive review of the timing and extension in the geological record of these wetlands (4), as well as by numerical simulations of the global carbon cycle (5). Finally, two independent geochemical proxies, the isotopic composition of foraminifera (6) and the molecular composition of the organic matter (7), shed light on the potential role of large methane releases from gas-hydrate dissociation as an important source in the oceanic global carbon cycle. These two records from the Santa Barbara Basin have shown that these inferred methane releases occurred during the last glacial episode in response to a warming of the intermediate waters and thus presumably of the deep-sea sediments. These deep-sea methane emissions occurred synchronously with rapid climate warmings associated with atmospheric methane increases and led Kennett *et al.* (6) to propose the "clathrate gun hypothesis," which postulates that deep-sea methane hydrates played a significant

role in late quaternary climate changes (4). Thus far, evidence for such methane releases in the glacial world is limited to a few regions (8, 9), and the mechanism by which the methane passed through the water column, and eventually to the atmosphere, has not yet been demonstrated. Here we document evidence that two massive methane releases from clathrate dissociation, of amplitude two to three times larger than those inferred in the Santa Barbara Basin, occurred during the last glacial episode in the western Pacific.

Materials and Methods

We studied the IMAGES MD97-2134 piston core located in the Papua Gulf (depth of 760 m, lat $9^{\circ}54'S$, long $144^{\circ}39'E$), ≈ 150 km off the Fly River delta (Fig. 1). High terrigenous inputs from Papua New Guinea lead to high sedimentation rates of ≈ 25 cm \cdot (thousand years) $^{-1}$ (ka) during the last glacial episode (Fig. 2). The core contains dark argillaceous muds with abundant coccoliths, foraminifera, and pteropods. Isotope measurements were conducted at Laboratoire des Sciences du Climat et de l'Environnement (Centre National de la Recherche Scientifique–Commissariat à l'Energie Atomique, Gif-sur-Yvette, France) by using a Kiel device coupled to a Finnigan MAT 251 mass spectrometer. The external precision was 0.05‰ for $\delta^{18}\text{O}$ and 0.03‰ for $\delta^{13}\text{C}$ analysis as determined by repeated measurements of a standard carbonate material, NBS19. Approximately 10–15 foraminifera shells were used for each isotopic measurement. Mg/Ca measurements were conducted by using a Rutgers Varian inductively coupled plasma optical emission spectrometer following the analytical protocol detailed by Rosenthal *et al.* (10). The chronostratigraphy was established by using 13 accelerator mass spectrometer ^{14}C ages on the planktonic foraminifer *Globigerinoides ruber*. To account for past changes in ^{14}C production, these ages were converted to calendar ages assuming 400 years of reservoir age and applying the INTCAL98 calibration curve for ages up to 24 ka (11) and a polynomial calibration based on coupled $^{14}\text{C}/^{230}\text{Th}$ ages in corals for ages >24 ka (12). The Laschamp excursion (1,050 cm) is well marked in the magnetic record (C. L. Blanchet, N. Thouveny, and T.d.G.-T., unpublished results) and provides a chronological datum in marine isotope stage (MIS) 3 at 40 ka (13). The similarity of MD97-2134 paleointensity record with paleomagnetic reference stacks indicates that no hiatus interrupts the sediment record during the last 60 ky. The MIS 4/3 boundary in the oxygen isotope record at 1,600 cm was also tuned to the SPECMAP reference curve (14). The uncertainty of this age model is $\approx 2\text{--}3$ ky.

Abbreviations: ka, thousand years; MIS, marine isotope stage; DIC, dissolved inorganic carbon.

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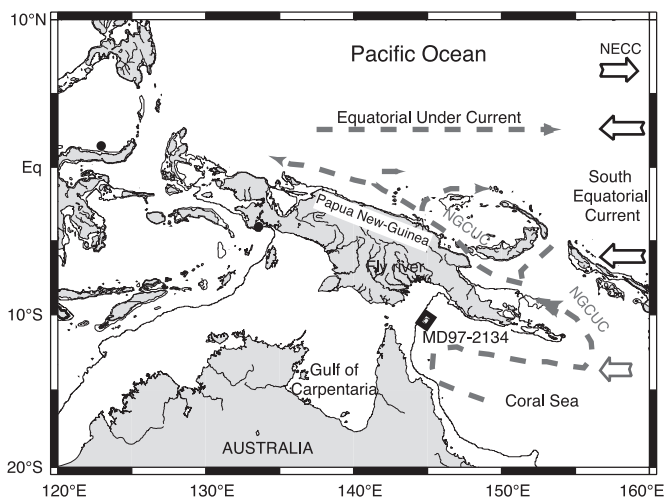


Fig. 1. Map location of the MD97-2134 core in the Papua Gulf. The black circles indicate the position of known bottom-simulating reflectors indicative of deep-sea gas hydrates (36, 37). The shaded rectangle highlights the area taken into account for methane-release estimates.

Results

We document past changes in surface hydrography by using stable isotopes measured in the calcite shells of the planktonic

foraminifera *G. ruber*, a species living primarily in the mixed layer (Fig. 2). The $\delta^{18}\text{O}$ record displays global glacial/interglacial changes associated with the growth and decay of the polar ice sheets. The $\delta^{13}\text{C}$ record of *G. ruber* exhibits glacial-interglacial changes of $\approx 1.2\text{--}1.5\text{‰}$, reflecting changes in the surface productivity. However, two large anomalous negative excursions in this record reach -8.95‰ ($\Delta = -9\text{‰}$ from the background) and -5.62‰ ($\Delta = -5.7\text{‰}$) at 39 and 55 ka, respectively (Fig. 3). Associated with the negative $\delta^{13}\text{C}$ excursions, the $\delta^{18}\text{O}$ of *G. ruber* shows strong positive anomalies reaching -0.45‰ ($\Delta = +1.05\text{‰}$ from the background) and -0.6‰ ($\Delta = +0.7\text{‰}$ from the background) at 39 and 55 ka, respectively. Due to the thickness of the 39-ka excursion (25 cm), bioturbation has no significant dilution effect on its amplitude but may induce a smoothing on the 55-ka event (10 cm thick). To examine whether the entire water column was affected during these events, we analyzed stable isotopes in two other foraminiferal species: *Globorotalia truncatulinoides*, a deep-dweller planktonic species living close to the thermocline, and a benthic species, *Uvigerina* sp. (Fig. 3). The deep-dwelling planktonic species exhibits $\delta^{13}\text{C}$ anomalies at 39 ka reaching -5.8‰ ($\Delta = -5.4\text{‰}$) and at 55 ka reaching -3.12‰ ($\Delta = -2.6\text{‰}$) (Table 1). Likewise, the $\delta^{13}\text{C}$ of benthic foraminifera decreases to -9.4‰ ($\Delta = -8.5\text{‰}$) at 39 ka and to -6.22‰ ($\Delta = -5.2\text{‰}$) at 55 ka. These negative isotopic anomalies were found in replicate analyses of the foraminifera.

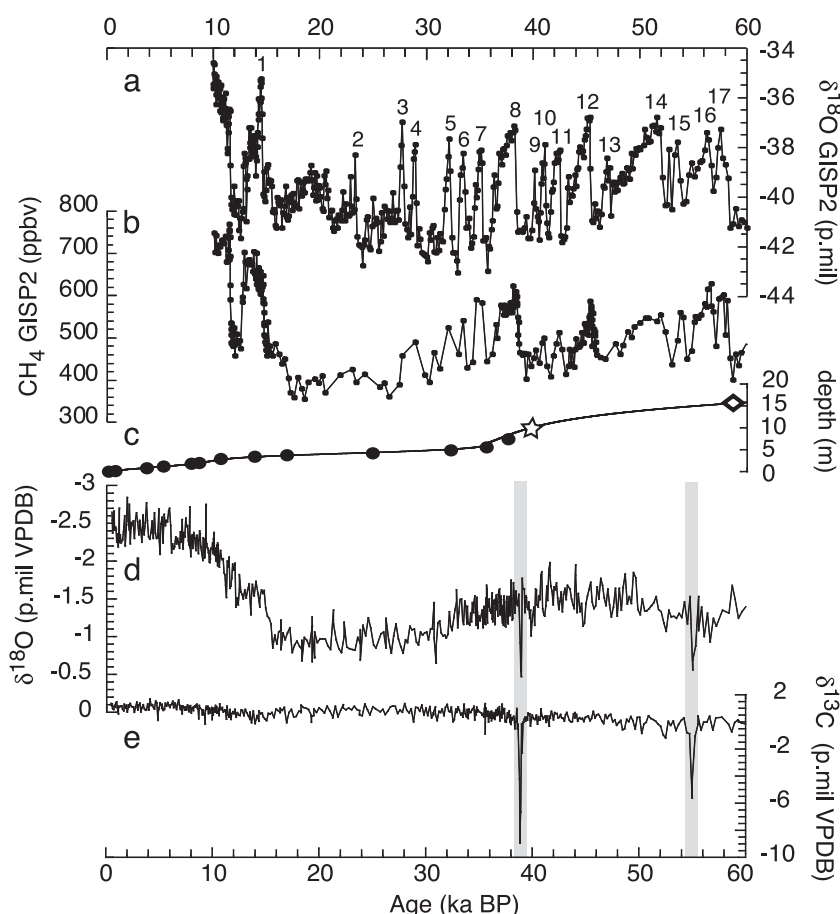
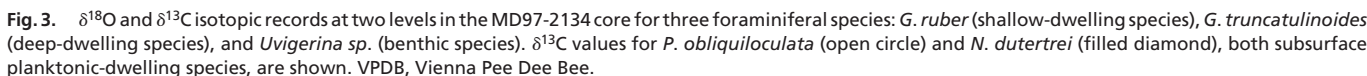


Fig. 2. Comparison of Greenland ice-core record of $\delta^{18}\text{O}$ and atmospheric methane concentration with foraminiferal $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ time series from the MD97-2134 sediment core located in the Papua Gulf. (a) Greenland Ice Sheet Project 2 (GISP2) ice-core record of $\delta^{18}\text{O}$ spanning the last 17 interstadials (38). (b) Atmospheric methane concentration (35). (c) MD97-2134 age-model tie points: circles indicate radiocarbon-calibrated dates, the star refers to the Laschamp paleomagnetic excursion, and the diamond refers to the MIS 4/3 boundary tuned to the SPECMAP stack. Records of $\delta^{18}\text{O}$ (d) and $\delta^{13}\text{C}$ (e) isotopic composition of *G. ruber* in core MD97-2134 are shown also. ppbv, parts per billion by volume; VPDB, Vienna Pee Dee Bee.



We examine different hypotheses that might explain the large negative $\delta^{13}\text{C}$ anomalies observed in our record. Foraminifera $\delta^{13}\text{C}$ is a function of the $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC), air–sea exchange rate, and temperature. The latter two factors have only a minor influence on $\delta^{13}\text{C}$ (15). First, we exclude the hypothesis of a change in the biological productivity, because the observed range in the modern and past foraminifera composition $\delta^{13}\text{C}$ spans 0 to -2‰ (16). Four other ^{13}C -depleted sources have been invoked to explain past excursions in the DIC isotopic composition. (i) Volcanic and hydrothermal activities release large amounts of CO_2 with $\delta^{13}\text{C}$ of approximately -5‰ (17). This value, however, is too positive to explain the carbon isotope excursions seen in our record. (ii) There is exceptional freshwater flow from the Fly River with $\delta^{13}\text{C}_{\text{DIC}}$ of approximately -10‰ . Three arguments rule out this hypothesis. First, atmosphere–river CO_2 exchange tends to modify the DIC isotopic composition toward the equilibrium value of $\delta^{13}\text{C}_{\text{DIC}} \approx 1\text{‰}$ (18). The “flow hypothesis” would also imply that the isotopic composition of the 700-m-thick water column reflects only the riverine pool, with no influence from the seawater pool. Moreover, the Fly River flow scenario is not supported by the positive $\approx 0.8\text{‰}$ peak occurring simultaneously in the planktonic $\delta^{18}\text{O}$ records. This shift corresponds to a minimal 2°C cooling and/or an increase in $\delta^{18}\text{O}$ of seawater, whereas a massive increase of riverine input from the Fly River should have caused a negative $\delta^{18}\text{O}$ excursion. (iii) Oxidation of the low $\delta^{13}\text{C}$

We consider unlikely the possibility of significant diagenetic recrystallization in the sediment from pore waters isotopically modified by the *in situ* dissociation of methane gas hydrates, because such events are associated with strong disturbance of the sediments, which are lacking in core MD97-2134. The source of inferred methane releases during these events is thus not at the location of the core but was likely close to the site. This conclusion is supported by the depth of the MD97-2134 core, at which such releases can potentially occur, and because benthic foraminifera $\delta^{13}\text{C}$ records these events. A species-dependent mass-balanced recrystallization of the calcite from pore waters linked to *in situ* gas-hydrate dissociation also cannot account for

Event age, ka B.P.	Depth, cm	Species	$\delta^{18}\text{O}$, ‰ VPDB	$\delta^{13}\text{C}$, ‰ VPDB	Mg/Ca, mmol/mol
39	970	<i>G. ruber</i>	-0.54	-8.95	
	968	<i>Pulleniatina obliquiloculata</i>	0.08	-3.11	3.27
	968	<i>Neogloboquadrina dutertrei</i>	-0.02	-3.52	2.59
	972	<i>G. truncatulinoides</i>	1.59	-5.80	
	970	<i>Uvigerina</i> sp.	3.65	-9.34	
55	1,530	<i>G. ruber</i>	-0.56	-5.62	
	1,530	<i>G. truncatulinoides</i>	1.39	-1.23	
	1,530	<i>Uvigerina</i> sp.	3.70	-6.24	

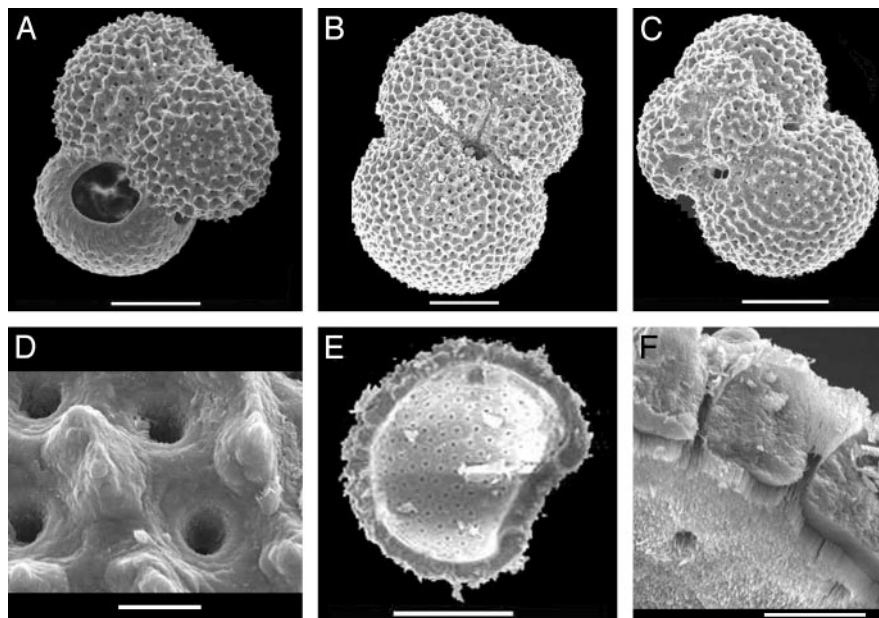


Fig. 4. Scanning electron microscope pictures of well preserved planktonic foraminifera from the ^{13}C minimum level at 968 cm in sediment core MD97-2134. *G. ruber* umbilical (A) and extraumbilical (B and C) views by scanning electron microscopy at 968 cm in core MD97-2134, in the $\delta^{13}\text{C}$ minimum. At higher resolution, the specimen (C) exhibits a typical external porosity (D). Calcite layers and inner porosity are also well preserved (F) of the crushed *G. ruber* (E). (Scale bars: A–C and E, 100 μm ; D and F, 10 μm .)

these excursions. To imprint a -8.5‰ excursion in the benthic foraminifer calcite $\delta^{13}\text{C}$ and of -9‰ in the surface-dwelling planktonic foraminifera requires that a similar amount ($\approx 12\text{--}15\text{‰}$) of the calcite in both taxa come from the $\delta^{13}\text{C}$ hydrate pool of approximately -65‰ . This percentage cannot be reconciled with the oxygen isotopic data that imply a differential species-dependant recrystallization of 60% and 25%, respectively, for these two taxa. For this calculation, we assume that the $\delta^{18}\text{O}$ of the pore waters was of $\approx 1.4\text{‰}$, accounting for (i) the $\approx 1\text{‰}$ enrichment due to the glacial polar ice sheet that trapped depleted ^{18}O (22) and (ii) an $\approx 0.4\text{‰}$ increase linked to the gas-hydrate fractionation process (23).

The original ultrastructures of foraminiferal tests are well preserved across the negative carbon isotopic excursions, as revealed by visual observation and scanning electron microscope observations in the $\delta^{13}\text{C}$ minimum at 968 cm (Fig. 4). At this level, inner and outer sectors of pores are well connected, exhibiting similar patterns to modern forms (24) and to another core level (945 cm) with normal $\delta^{13}\text{C}$ values. The possible presence of diagenetic calcite that might not be visible in scanning electron microscope investigation has been evaluated further by determining Mg/Ca on two deep-dwelling foraminifera species: *Neoglobobulimina dutertrei* and *Pulleniatina obliquiloculata*. Mg/Ca in foraminiferal tests has been shown to be a sensitive marker of diagenetic alteration, with values up to 150–250 mmol/mol depending on the amount of authigenic calcite (25, 26). The paucity of *G. ruber* across the negative carbon excursion prevented trace metal analysis on this species. The $\delta^{13}\text{C}$ composition of *N. dutertrei* and *P. obliquiloculata* are consistently depleted with values of -3.5‰ and -3.1‰ , respectively, at 968 cm. At this level, preliminary analyses in inductively coupled plasma optical emission spectrometry of Mg/Ca indicate a value of 2.57 mmol/mol for *N. dutertrei* and 3.18 mmol/mol for *P. obliquiloculata*. These values are in the same range as the background values measured at 1,015 cm, with 2.69 mmol/mol for *N. dutertrei* and ≈ 2.34 mmol/mol in *P. obliquiloculata*, although slightly higher for the latter. This approach confirms that the existence of a ^{13}C -depleted and

Mg/Ca-enriched crust is minimal in the interval studied. The lower carbon and higher oxygen isotopic values in the various foraminiferal taxa cannot be accounted for by authigenic recrystallization. These isotopic anomalies must reflect changes in seawater chemistry in agreement with the combined isotopic and molecular evidence previously shown for the Santa Barbara Basin (7).

The stability of gas hydrates varies with temperature and pressure (27). During MIS 3, sea level was lower by ≈ 80 m (28), reducing the hydrostatic pressure and enhancing the probability of hydrate dissociations (29). However, abrupt changes in sea level did not exceed $\approx 15\text{-m}$ amplitude and are unlikely, therefore, to have triggered methane releases (28). The largest excursion at 39 ka is marked by two successive steps. First, a slight $\delta^{18}\text{O}$ decrease in benthic foraminifera, which might indicate a warming ($\approx 1^\circ\text{C}$) of deep-sea waters preceding the inferred hydrate dissociation event. Although earthquakes or tsunamis might also have triggered dissociation of hydrates, this slight increase in temperature is in agreement with recent experimental studies emphasizing the critical role of temperature in the dissociation of hydrates (e.g., ref. 30). Second, this trend is interrupted by a significant 0.4‰ increase of the oxygen isotopic signal, in phase with the carbon isotopic anomaly (Fig. 3). That latter increase in $\delta^{18}\text{O}$ is similar to the interstitial water anomaly observed during gas-hydrate dissociation on Blake Ridge (23) and in agreement with the shallow infaunal habitat of *Uvigerina* sp. The largest $\delta^{18}\text{O}$ increase in the surface waters ($\Delta \delta^{18}\text{O} \approx +1\text{‰}$ in *G. ruber*) is by far too large to be attributed to the same process. This enrichment could be interpreted as a local cooling in upper surface waters ($\approx 3\text{--}4^\circ\text{C}$), resulting from the mixing of the water column through upwelling of cold deep waters induced by the thermal dissociation of gas hydrates. The chronological succession is less clear for the 55-ka excursion. The lower sedimentation rate during this interval and thus a stronger effect of the bioturbation is likely to have removed small-scale details.

The amplitude of the benthic carbon isotopic excursions associated with warm intervals during MIS 3 observed in the Santa Barbara Basin is lower than the amplitude of the anom-

alies recorded in core MD97-2134 (maxima of $\approx 4.5\%$ and $\approx 9\%$, respectively) (6). Moreover, the $\delta^{18}\text{O}$ increases in the planktonic records were not observed in the Santa Barbara Basin during the largest events at 37.5 and 44 ka. This difference is likely to reflect a stronger physical mixing in the water column in the Gulf of Papua, indicative of a much larger flux of methane, in agreement with the $\delta^{13}\text{C}$ excursion.

An additional question is whether the methane was oxidized close to the sea floor or whether it was oxidized throughout the water column, implying that some of the methane was outgassed into the atmosphere. Considering the order of magnitude of diffusion coefficients arising from turbulent mixing in the open ocean as well as typical upwelling velocities, it seems highly unlikely that the $\delta^{13}\text{C}_{\text{DIC}}$ in the water column would have been homogenized after methane oxidation at the sea floor.

In advection-diffusion problems, the ratio of transport to diffusion is usually given by the adimensional Peclet number $Pe = V \times L/D$, where V is a characteristic velocity, L is a characteristic length, and D is the diffusion coefficient. For $Pe \gg 1$, the advection is dominant, whereas diffusion is dominant for $Pe \ll 1$. When diffusion (or turbulent mixing described with an effective diffusion coefficient) occurs orthogonally to the main transport direction, the geometrical aspect ratio of the system must also be taken into account, which can be done by defining a transverse Peclet number $PeT = V \times H/D$, where V is the velocity of the water layer, H is its thickness, and D is the diffusion coefficient. Then, the ratio of horizontal advection to vertical diffusion is $(H/L)PeT$, where L is the horizontal length scale.

In the Papua Gulf, V ranges from 0.01 to 1 m/s, H from 100 to 700 m, and D from 3.10^{-5} to 3.10^{-4} m²/s (31); thus, PeT may range 3.10^3 to 2.10^7 . The horizontal length scale necessary for homogenization is thus large, because L must exceed 100 km for a $(H/L)PeT$ of 1, even assuming a very low average current speed of 1 cm/s. The implication is that the water column can only be homogenized several hundred kilometers downstream of the light DIC source, assuming this source only affects the lower part of the water column. This approach does not take into account the effect of horizontal dispersion (which may be increased by oscillating tidal flows) and exchange with the atmosphere. However, these processes do not favor vertical homogenization. Therefore, homogenization of $\delta^{13}\text{C}_{\text{DIC}}$ is unlikely to result from only diffusive mixing unless light $\delta^{13}\text{C}$ sources were distributed over a wide area covering most of the Gulf of Papua.

Vertical upwelling due to the Ekman transport is an alternative possibility, but again, a wide source area is required as well as upwelling rates in the upper range of typical values associated with extraordinary wind stress. Oxidation of methane at all levels in the water column associated with upwelling flow induced by methane rise seems to be the most likely explanation to reconcile $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data. This hypothesis is supported by the description of a modern upwelling flow induced by methane seeps on the western American margin (32). In this modern analog, the methane bubbling induces vertical velocities up to 1 m/s, which modify the local properties of the seawater column. Moreover, the methane is oxidized during the vertical transfer and is eventually outgassed into the atmosphere. Likewise, but at a larger scale, the isotopic records in core MD97-2134 indicate that methane passed throughout the water column and reached the sea-air interface.

In a first step, we estimate the minimum amount of oxidized methane in the water column by using a C-isotope mass-balance

equation, assuming that a single event created these anomalies. We arbitrarily assume that the releases affected an oceanic volume of 1,000 km³ (Fig. 1), which is not unrealistic given the surface of the Papua Gulf and its location in the open Pacific. The minimal volume of methane degassed and oxidized in the water column during the main event at ≈ 39 ka is estimated at $\approx 5.5 \times 10^9$ m³.^{||} It corresponds to ≈ 4 Tg (teragrams) of methane, which is approximately two to three times higher than estimates made for the Santa Barbara Basin (6). The lack of a water-column vertical gradient in the $\delta^{13}\text{C}$ record and the long stratigraphic extension of these anomalies indicate that these inferred emissions were sustained for a period longer than a few generations of foraminifera. Regardless of the uncertainties in the duration, assuming a minimal 10-year methane-venting scenario with a residence time of ≈ 2 months implies a total release of methane of at least ≈ 200 Tg, with an annual flux of ≈ 20 Tg. This corresponds to $\approx 3.5\%$ of the modern annual source of methane to the atmosphere (34) but reaches $\approx 10\%$ of the glacial emission rate. If we speculate that an equivalent quantity of methane oxidized in the water column is outgassed into the atmosphere, the direct radiative effect of the 39-ka excursion reaches at least $\approx 0.3 \text{ W}\cdot\text{m}^{-2}$ (34). In comparison, the preindustrial radiative forcing of the well mixed greenhouses gases (CO_2 , CH_4 , N_2O , and halocarbons) is $\approx 2.5 \text{ W}\cdot\text{m}^{-2}$. In the glacial episode, this methane release could have contributed significantly to increase the global radiative forcing due to the methane and thus warmed the atmosphere. Although ice-core records suggest large increases in atmospheric concentration in phase with the 39- and 55-ka B.P. methane releases (35), present chronological uncertainties in both ice-core and marine sediment records are still too large to determine accurately whether the Papua Gulf methane releases are synchronous with increases in methane atmospheric concentration.

Thus, although the area of the Fly River shelf is small, it produced a significant deep-sea methane hydrate source for the global methane cycle. The paucity of other high-sedimentation-rate records from other low-latitude shelves could explain the lack of other evidence of methane gas-hydrate destabilization during the last glacial episode. If such events were widespread and more common during MIS 3, this source could explain a large part of the methane fluctuation recorded in ice cores as hypothesized in the clathrate gun hypothesis (4). In conclusion, our record demonstrates that significant volumes of methane can be transported through the entire water column in association with a physical mixing of the water column and be released into the atmosphere.

^{||}For this estimation, we assume that the isotopic anomaly in the $\delta^{13}\text{C}_{\text{G. ruber}}$ of -8.31% results from a linear mixing between the methane pool (-65%) (21) and the seawater pool (corresponding to the background value of 0.31%) in a single event release. The DIC concentration in the western Pacific is $0.0022 \text{ mol}\cdot\text{liter}^{-1}$ (33).

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1. Chappellaz, J., Blunier, T., Raynaud, D., Barnola, J.-M., Schwander, J., & Stauffer, B. (1993) *Nature* **366**, 443–445.
2. Chappellaz, J., Blunier, T., Kints, S., Dallenbach, A., Barnola, J.-M., Raynaud, D., & Stauffer, B. (1997) *J. Geophys. Res.* **102**, 15987–15998.
3. Dallenbach, A., Blunier, T., Flückiger, J., Stauffer, B., Chappellaz, J., & Raynaud, D. (2000) *Geophys. Res. Lett.* **27**, 1005–1008.

4. Kennett, J. P., Cannariato, K. G., Hendy, I. L., & Behl, R. J. (2002) *Methane Hydrates in Quaternary Climate Changes: The Clathrate Gun Hypothesis* (Am. Geophys. Union, Washington, DC).
5. Kaplan, J. O. (2002) *Geophys. Res. Lett.*, 10.1029/2001GL013366.
6. Kennett, J. P., Cannariato, K. G., Hendy, I. L., & Behl, R. J. (2000) *Science* **288**, 128–133.

7. Hinrichs, K.-U., Hemlo, L. R. & Sylva, S. P. (2003) *Science* **299**, 1214–1217.
8. Keigwin, L. D. (2002) *J. Oceanogr.* **58**, 421–432.
9. Smith, L. M., Sachs, J. P., Jennings, A. E., Anderson, D. M. & deVernal, A. (2001) *Geophys. Res. Lett.* **28**, 2217–2220.
10. Rosenthal, Y., Field, F. & Sherrell, R. M. (1999) *Anal. Chem.* **71**, 3248–3253.
11. Stuiver, M., Reimer, P. J., Bard, E., Beck, J. W., Burr, G. S., Hughen, K. A., Kromer, B., McCormac, F. G., van den Plicht, J. & Spurk, M. (1998) *Radiocarbon* **40**, 1041–1083.
12. Bard, E. (1998) *Geochim. Cosmochim. Acta* **62**, 2025–2038.
13. Gillot, P. Y., Labeyrie, J., Laj, C., Guérin, G., Poupeau, G. & Delibrias, G. (1979) *Earth Planet. Sci. Lett.* **42**, 444–450.
14. Imbrie, J., Hays, J. D., Martinson, D. G., McIntyre, A., Mix, A. C., Morley, J. J., Pisias, N. G., Prell, W. L. & Shackleton, N. J. (1984) in *Milankovitch and Climate*, ed. Berger, A. L. (D. Reidel, Dordrecht, The Netherlands), Vol. 1, pp. 269–305.
15. Lynch-Stieglitz, J., Stocker, T. F., Broecker, W. S. & Fairbanks, R. G. (1995) *Global Biogeochem. Cycles* **9**, 653–665.
16. Berger, W. H. & Vincent, E. (1986) *Geol. Rundsch.* **75**, 249–269.
17. Wignall, P. B. (2001) *Earth Sci. Rev.* **53**, 1–33.
18. Yang, C., Telmer, K. & Veizer, J. (1996) *Geochim. Cosmochim. Acta* **60**, 851–866.
19. Schoell, M. (1988) *Chem. Geol.* **71**, 1–10.
20. Stott, L. D., Bunn, T., Prokopenko, M., Mahn, C., Gieskes, J. & Bernhard, J. M. (2002) *Geochem. Geophys. Geosyst.* **3**, 1–16.
21. Kvenvolden, K. A. (1995) *Org. Geochem.* **23**, 997–1008.
22. Schrag, D. P. & DePaolo, D. J. (1993) *Paleoceanography* **8**, 1–6.
23. Matsumoto, R. & Borowski, W. S. (2000) in *Proceedings of the Ocean Drilling Program*, eds. Paull, C. K., Matsumoto, R., Wallace, P. J. & Dillon, W. P. (Ocean Drilling Program, College Station, TX), Vol. 164, pp. 59–66.
24. Cifelli, R. (1982) *Smithson. Contrib. Paleobiol.* **45**, 1–45.
25. Torres, M. E., Mix, A. C., Kinports, K., Haley, B., Klinkhammer, G. P., McManus, J. & de Angelis, M. A. (2003) *Paleoceanography* **18**, 10.129/2002PA000824.
26. Greinert, J. (1999) in *GEOMAR* (Christian-Albrechts University, Kiel, Germany), pp. 217.
27. Kvenvolden, K. A. (1988) *Global Biogeochem. Cycles* **2**, 221–229.
28. Yokoyama, Y., Esat, T. M. & Lambeck, K. (2001) *Earth Planet. Sci. Lett.* **193**, 579–587.
29. Nisbet, E. G. (1992) *J. Geophys. Res.* **97**, 12859–12867.
30. Buffett, B. A. (2000) *Annu. Rev. Earth Planet. Sci.* **28**, 477–507.
31. Munk, W. & Wunsch, C. (1998) *Deep-Sea Res. Part I* **45**, 1977–2010.
32. Leifer, I., Clark, J. F. & Chen, R. B. (2000) *Geophys. Res. Lett.* **27**, 3711–3714.
33. Zhang, J. & Quay, P. D. (1997) *Deep-Sea Res. Part II* **44**, 2163–2190.
34. Houghton, J. T., Ding, Y., Griggs, D. J., Noguer, M., van der Linden, P. J. & Xiaosu, D. (2001) *Climate Change, 2001: The Scientific Basis—Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change (IPCC)* (Cambridge Univ. Press, Cambridge, U.K.).
35. Blunier, T. & Brook, E. J. (2001) *Science* **291**, 109–112.
36. Hardjono, Asikin, T. S., Purnomo, J. & Rau, J. L. e. (1998) *Thirty-Third Annual Session of the Coordinating Committee for Coastal and Offshore Geoscience Programmes in East and Southeast Asia* **33**, Part II, 56–83.
37. Neben, S., Hinz, K. & Beiersdorf, H. (1998) in *Gas Hydrates—Relevance to World Margin Stability and Climatic Change*, eds. Henriot, J.-P. & Mienert, J. (The Geological Society, London), Vol. 137, pp. 255–265.
38. Dansgaard, W., Johnsen, S. J., Clausen, H. B., Dahl-Jensen, D., Gundestrup, N. S., Hammer, C. U., Hvidberg, C. S., Steffensen, J. P., Sveinbjörnsdóttir, A. E., Jouzel, J., et al. (1993) *Nature* **364**, 218–220.