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Ellen Thomas
Wesleyan University, ethomas@wesleyan.edu

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Balancing the deglacial global carbon budget: the hydrate factor

Mark A. Maslin[a,*], Ellen Thomas[b,c]

[a] Environmental Change Research Centre, Department of Geography, University College, London, 26, Bedford Way, London, WC1H 0AP, UK
[b] Department of Geology and Geophysics, Yale University, New Haven, CT 06520-8102, USA
[c] Department of Earth and Environmental Sciences, Wesleyan University, Middletown, CT 06459-0139, USA

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Abstract

The discovery that methane from dissociation of gas-hydrates could be an important factor in the global carbon cycle resolves the major discrepancy in estimates of the increase of terrestrial biomass from the Last Glacial period to the present. Carbon isotope budgeting using the marine carbon isotopic record results in an estimate centered around 500 GtC, whereas palaeovegetation reconstruction (with biosphere models) gives averages around 1000 GtC. The discrepancy may be resolved by considering release of isotopically light methane through destabilization of gas hydrates. This provides a unique means of estimating the contribution of gas hydrates to the deglacial rise in atmospheric methane. A release of ~120 GtC methane, makes a biospheric carbon transfer of ~1000 GtC compatible with the marine carbon isotope data. This, however, represents less than 30% of the enhanced atmospheric methane production between 18 and 8 ka observed in ice cores, supporting the theory that glacial–interglacial variations in atmospheric methane were driven primarily by changes in the extent of tropical and temperate wetlands and not by methane release from clathrates. By balancing the deglacial carbon budget we demonstrate that global carbon models will have to incorporate glacial–interglacial vegetation shifts of at least 1000 GtC, which many currently find difficult.
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1. Introduction

An important control on the glacial–interglacial carbon cycle is the variation in size of the terrestrial biomass. This biomass increased in volume during deglaciation, providing a major sink for carbon dioxide working against the observed change in atmospheric pCO_2 levels: polar ice core data show a net increase of at least 80 ppmv in atmospheric pCO_2 (Barnola et al., 1987) and 300 ppbv in pCH_4 since the Last Glacial Maximum (LGM) (e.g., Chappellaz et al., 1993; Brook et al., 1996, 2000). Increased storage of carbon in terrestrial biomass at a time of increasing atmospheric pCO_2 and pCH_4 levels during and after deglaciation poses a problem: where does all the carbon originate?

Estimates of the increase in carbon stored in the terrestrial biomass at deglaciation vary between 30 and 1900 GtC (Table 1). One reason for this large range is the fact that estimates are based on different methods. The two most commonly used methods are: (1) carbon isotope budgeting, using the marine carbon isotopic record (e.g., Shackleton, 1977; Bird et al., 1994; Crowley, 1995; Maslin et al., 1995) to give average values around 500 GtC, (2) paleovegetation and carbon storage reconstruction, in some cases combined with biosphere models (e.g., Adams et al., 1990; van Campo et al., 1993; Maslin et al., 1995; Adams and Faure, 1998; Peng et al., 1998; Beerling, 1999; Otto et al., 2002; Kaplan et al., 2002), giving average values around 1100 GtC.

Carbon isotope budgeting assumes that the increase of global oceanic carbon $\delta^{13}C$ values of about 0.4‰ (Table 1) in total dissolved inorganic carbon during the last deglaciation was driven by the uptake of light carbon by the expanding terrestrial biosphere (Fig. 1). Two assumptions may introduce large errors in this simple calculation (Shackleton, 1977). First, one needs to estimate the average $\delta^{13}C$ value for the whole terrestrial biosphere during the LGM and after deglaciation. These two values almost certainly differed, because ratios of C3 to C4 plants (which differ widely in carbon isotopic value) changed as a result of changing humidity, temperature and atmospheric pCO_2 (Ehleringer et al., 1997) during deglaciation. Varying the

*Corresponding author. Tel.: +44-171-380-7556; fax: +44-171-80-7565.
E-mail address: mmaslin@geog.ucl.ac.uk (M.A. Maslin).

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Table 1
Estimates of the expansion of the carbon stored in the terrestrial biosphere since the last glacial maximum using various methods

Source (in date order)	Method	Terrestrial biomass increase (GtC) range (average)
Shackleton (1977)	Ocean $\delta^{13}C$, 0.7‰	1000
Duplessy et al. (1984)	Ocean $\delta^{13}C$, 0.15‰	220
Berger and Vincent (1986)	Ocean $\delta^{13}C$, 0.40‰	570
Curry et al. (1988)	Ocean $\delta^{13}C$, 0.46‰	650
Duplessy et al. (1988)	Ocean $\delta^{13}C$, 0.32‰	450
Adams et al. (1990) Faure et al. (1996)	Palaeoecological data	1350
Prentice and Fung (1990)	Climate model	-30 ± 50
Friedlingstein et al. (1992)	Climate (biosphere) model	300
Broecker and Peng (1993)	Ocean $\delta^{13}C$, 0.35‰	425
Prentice et al. (1993)	Climate (biosphere) model	300–700
van Campo et al. (1993)	Palaeoecological data	430–930 (715)
Bird et al. (1994)	Ocean $\delta^{13}C$	270–720
Friedlingstein et al. (1995)	Climate (biosphere) model	507–717 (612)
Maslin et al. (1995)	Ocean $\delta^{13}C$ 0.40 ± 0.14‰ and palaeoecological data	400–1100 (700)
Crowley (1995)	Terrestrial vegetation data	750–1050
Peng et al. (1995) Peng et al. (1998)	Palaeoecological data, biosphere model	470–1014
Adams and Faure (1998)	Palaeoecological data	900–1900 (1500)
Beerling (1999)	Biosphere model with modelled $\delta^{13}C$ inventory	550–680
Francois et al. (1998)	Biosphere model	134–606
Otto et al. (2002)	DGVM	828–1106
Kaplan et al. (2002)	DGVM	821

DGVM = Dynamic Global Vegetation Model.

average $\delta^{13}C$ of vegetation by 1‰ may make a difference of over 50 GtC in the estimate of increase in terrestrial biomass (Maslin et al., 1995). Second (and in our opinion more importantly), in this calculation there are no sources/sinks of carbon isotopically different from terrestrial organic matter or carbonate (limestone) considered, which can change on a time scale of decades (Kump and Arthur, 1999; Francois, and Godderis, 1998), see Fig. 2. Bovkin et al. (2002), however, demonstrated that it is theoretically possible that changes in the average $\delta^{13}C$ of marine biota during deglaciation account for the $\delta^{13}C$ changes observed in atmospheric carbon dioxide. In contrast, we argue that the most important forgotten source are the large volumes of isotopically light methane gas trapped in solid hydrates (clathrates) in permafrost and continental margin sediments (e.g., MacDonald, 1990; Kvenvolden, 1993, 1998; Henriet and Mienert, 1998; Buffett, 2000).

2. Methane hydrates

Methane hydrates occur wherever there is a combination of low temperatures and/or high pressure and sufficient organic carbon (Henriet and Mienert, 1998; Kvenvolden, 1998; Paull and Dillon, 2001). There may be up to 10,000 GtC carbon stored in methane hydrates (MacDonald, 1990; Kvenvolden, 1993, 1998; Buffett, 2000; Kvenvolden and Lorenson, 2001), i.e., about a third of the amount of carbon in the deep ocean dissolved inorganic carbon, and almost 20 times as much as in the preindustrial atmospheric reservoir. For example there is at least 400 GtC gas hydrates stored in the Arctic permafrost (MacDonald, 1990). Methane in clathrates has extremely depleted $\delta^{13}C$ values (−40‰ to −100‰, average ~ -60‰, MacDonald, 1990; Dickens et al., 1997; Matsumoto et al., 1996; Kvenvolden, 1998; Paull et al., 1991; Buffett, 2000; Dickens, 2001). Below the solid hydrates, large volumes of free methane gas may be trapped (Dickens et al., 1997; Dickens, 2001). A decrease in pressure or an increase in temperature causes destabilization of gas hydrates and possibly catastrophic release of methane gas (MacDonald, 1990; Haq, 1998). During glacial periods, hydrates destabilized locally as a result of sea-level fall concurrent with ice sheet formation (Maslin et al., 1998), but the lower deep water temperatures counteracted this effect (Buffett, 2000). During the slightly warmer interstadials in glacial periods changes in ocean circulation may have caused the local destabilization of gas hydrates in the Gulf of California (Kennett et al., 2000; Kennett and Fackler-Adams, 2000). Kennett et al. (2003) argue that such destabilization as the result of rising intermediate water temperatures could have been more widely distributed, causing the rise in atmospheric methane levels during warm millennial Dansgaard-Oeschger events as well as during the last deglaciation.

The massive increase in atmospheric methane at the end of the Last Glacial period, however (Chappellaz et al., 1993), has generated most speculation: could this increase have been caused by methane release from gas hydrates (e.g., Nisbet, 1990; Haq, 1998; Kennett et al., 2003). If so, was it of enough significance to accelerate the rate and extent of ice sheet melting because of increased greenhouse warming? (MacDonald, 1990; Nisbet, 1990; Paull et al., 1991; Haq, 1998). Deglacial destabilization of gas hydrates could have been triggered in several ways (Nisbet, 1992). Permafrost below ice sheets may have melted by a combination of pressure release and temperature increase when the ice sheets were removed. Permafrost flooded by the sea after the

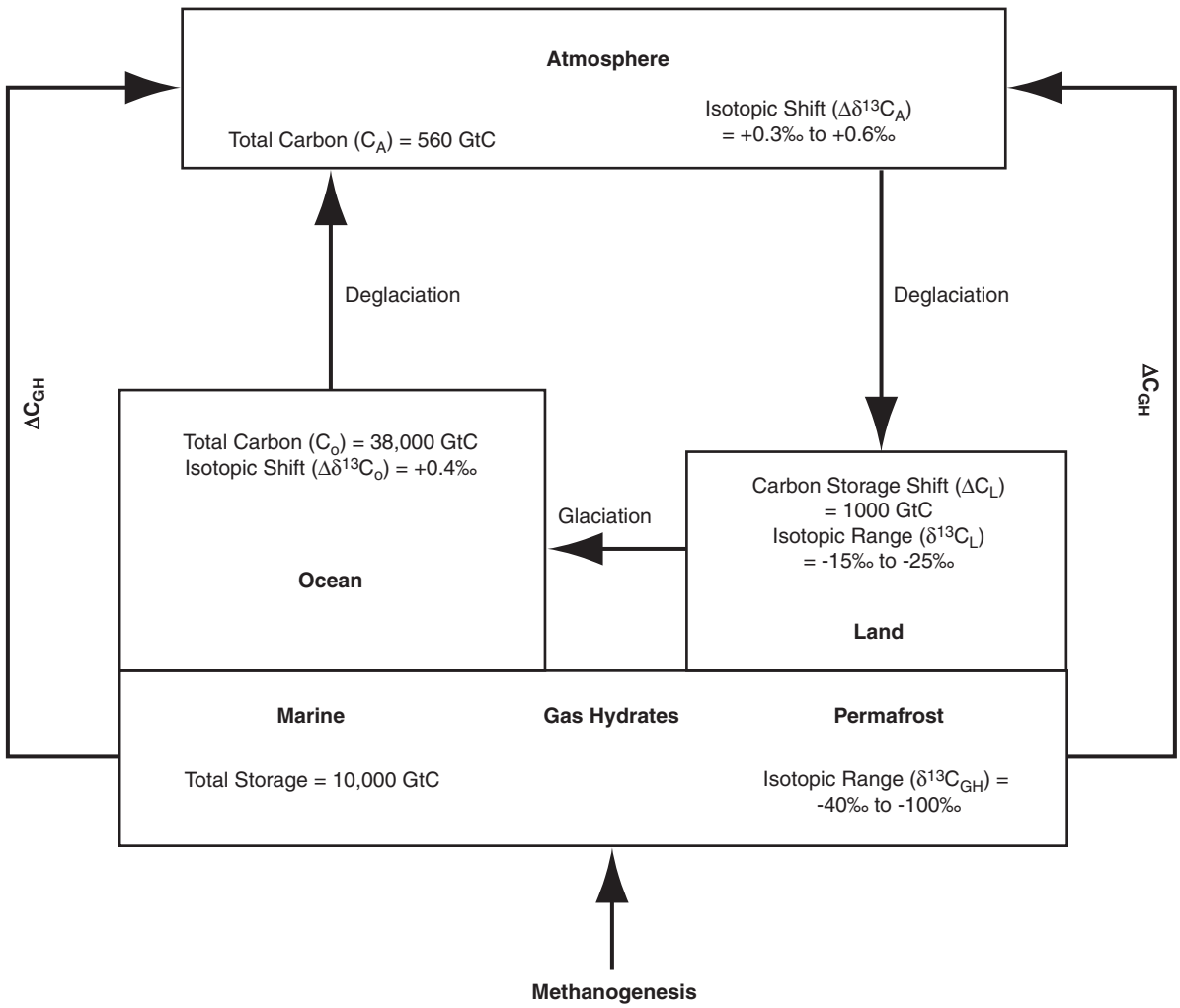

Fig. 1. Adapted carbon isotope budget method for estimating glacial–interglacial shifts in land biomass and the release of gas hydrate carbon.

retreat of ice sheets would have been suddenly covered by water ($-1°C$), in contrast with the temperature of permafrost ($< -20°C$), leading to destabilization, as observed to have occurred between 14 and 9 ka on the Greenland margin (Smith et al., 2001). Permafrost adjacent to ice sheets may have melted when regional temperatures increased. Continental margin gas hydrates could have destabilized when deep ocean temperatures increased during deglaciation (Kennett et al., 2003), or as a result of isostatic or sea-level rise induced seismicity, exacerbated by the increased sediment supply to the continental margins due to ice sheet melting and increased precipitation. Margin failure did occur: huge submarine slides are common in the northeastern Atlantic Basin (Bugge et al., 1988; Laberg et al., 2000) and at least some of them have been dated to the deglaciation or slightly after (Kennett et al., 2003; Maslin et al., submitted). One of these slides alone could have generated up to 5 GtC of methane (Laberg et al., 2000).

3. Calculating the deglacial methane hydrate release

By adapting carbon isotope budgeting to include methane release from hydrates we can calculate the amount of possible methane hydrate released during deglaciation (see Fig. 1 and equation below). We have adapted Shackleton (1977) original method and the calculation is as follows:

$$(C_O \times \Delta\delta^{13}C_O) + (C_A \times \Delta\delta^{13}C_A) + (\Delta C_L \times \delta^{13}C_L) + (\Delta C_{GH} \times \delta^{13}C_{GH}) = 0,$$

where C_O is the total carbon storage of the ocean ($\sim 38,000$ GtC), $\Delta\delta^{13}C_O$ the deglacial ocean carbon isotopic shift (~ 0.4‰, see text below), C_A the carbon storage of the atmosphere at the end of the last deglaciation (~ 560 GtC), $\Delta\delta^{13}C_A$ the deglacial atmospheric carbon isotopic shift (in the range of 0.3–0.6‰, average 0.45‰ used), ΔC_L the shift in carbon storage of the land biomass (vegetation and soils) in GtC, $\delta^{13}C_L$

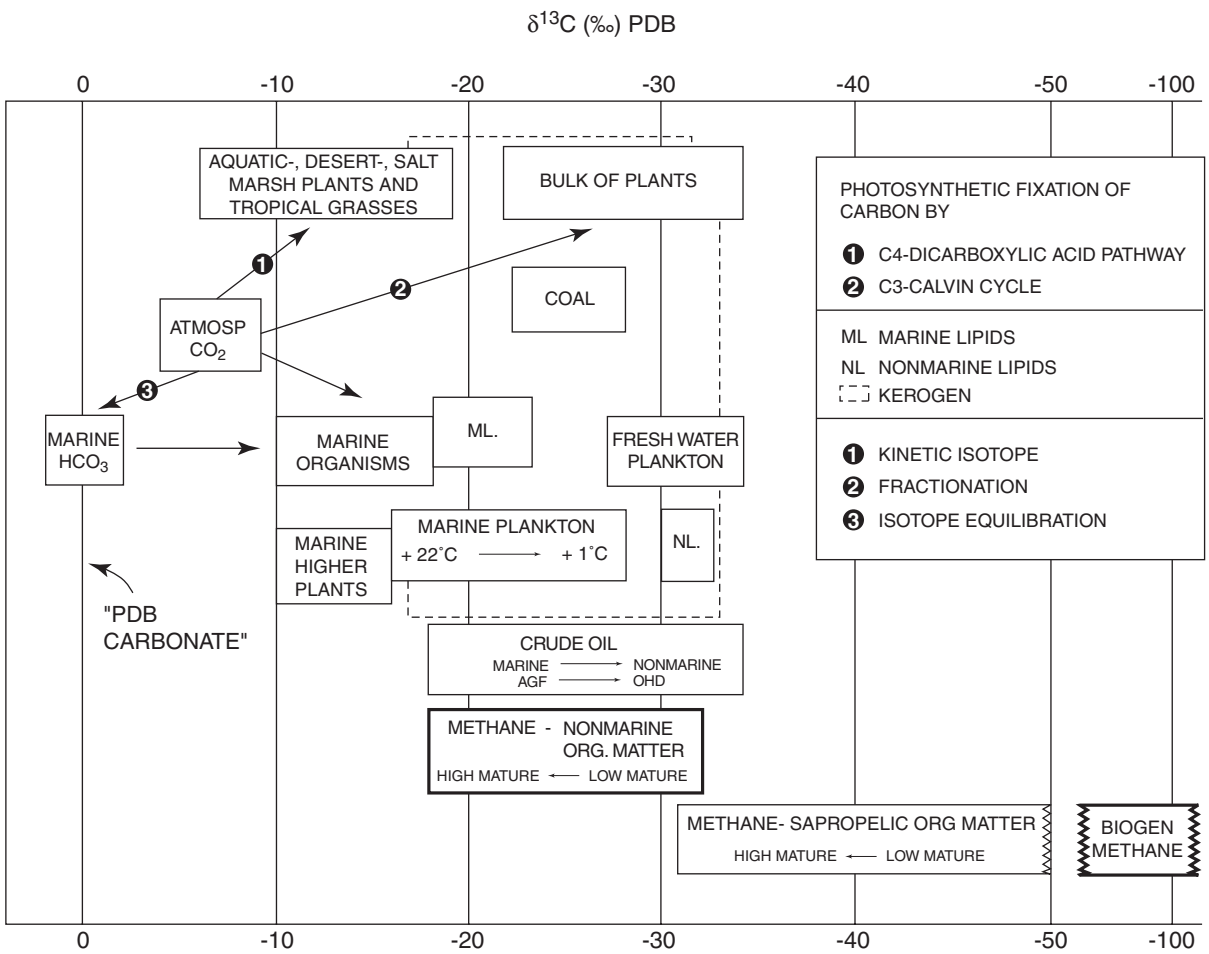

Fig. 2. Compilation of the different carbon isotopic ratios of organic and inorganic carbon reservoirs.

the average carbon isotopic composition of land biomass expansion, (−15 to −25‰, see text below), ΔC_{GH} the gas hydrate release during the last deglaciation in GtC and $\delta^{13}C_{GH}$ the average carbon isotopic composition of gas hydrates released (−40‰ to −100‰).

3.1. *The average shift in the global oceanic carbon* $\delta^{13}C$ *values* ($\Delta\delta^{13}C_O$)

The average of the best estimates is about 0.4‰ ± 0.05‰ (Berger and Vincent, 1986; Curry et al., 1988; Duplessy et al., 1988; Broecker and Peng, 1993, see Table 1). A *caveat* is that these estimates do not include changes in the carbon isotopic composition of dissolved inorganic carbon in the top 1 km of the ocean water column (Marchitto and Toggweiler, pers comm., 2002). The effects of changing this assumption can be seen in Fig. 3.

3.2. *The expansion of the terrestrial biomass* (ΔC_L)

From our review of palaeovegetation data we estimate that the maximum shift in terrestrial biomass

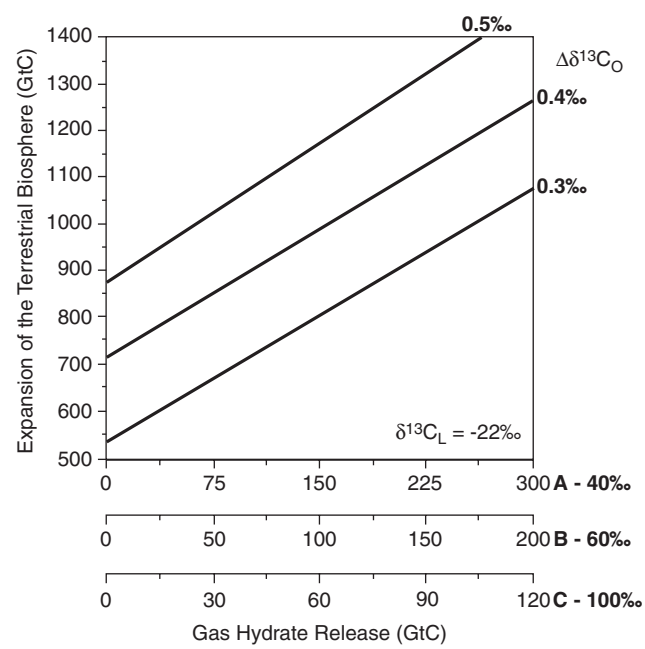

Fig. 3. Carbon isotope budget method results assuming a range of values for the average ocean carbon isotope shift (see Table 1) while maintaining the average $\delta^{13}C$ of terrestrial biosphere expansion constant at −22‰.

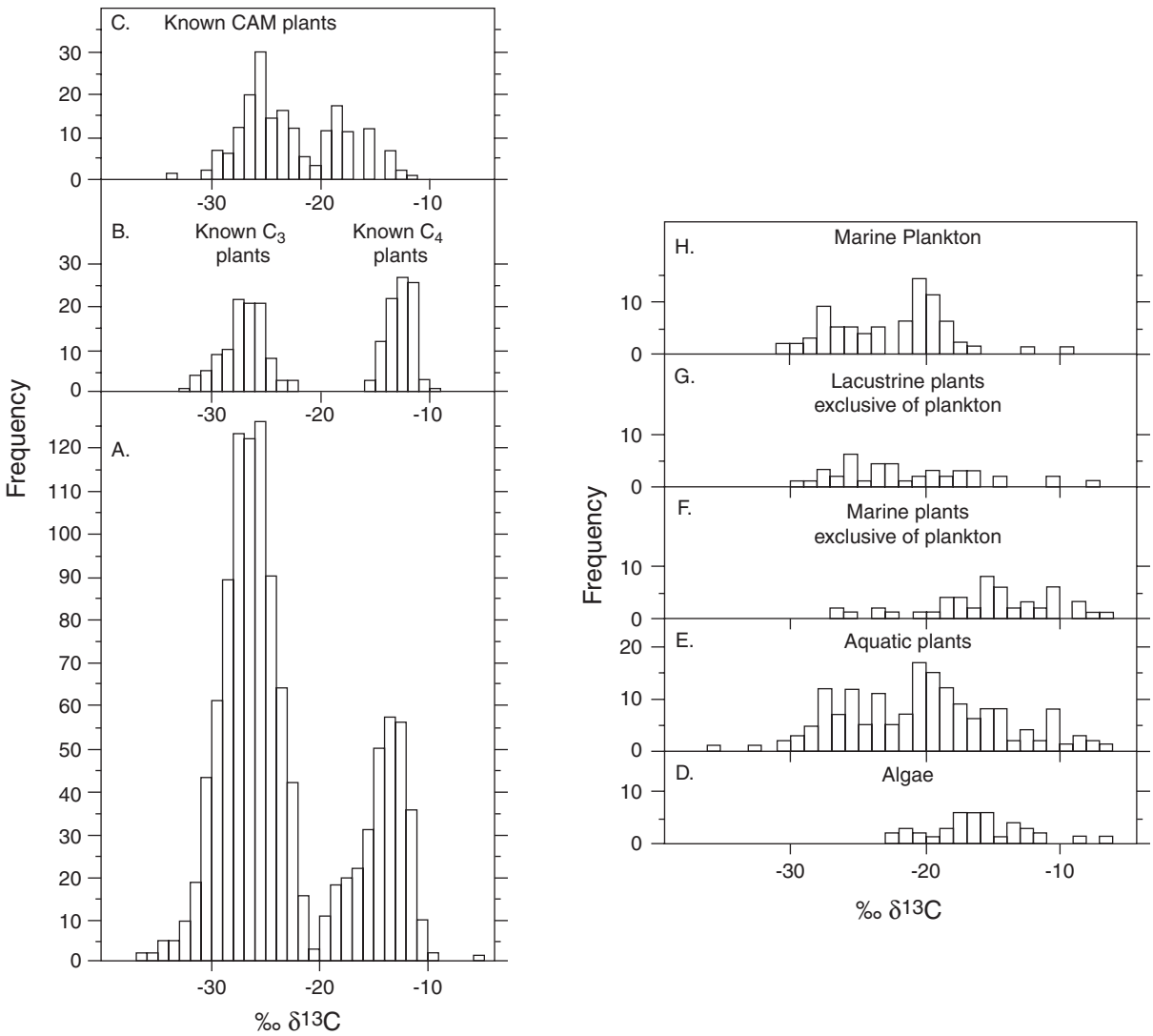

Fig. 4. Compilation of the occurrence carbon isotopic ratios of land and marine plants.

expansion between 18 and 8 ka is ~1000 GtC, in agreement with the conservative estimate using the palaeovegetation mapping approach (Adams et al., 1990; Maslin et al., 1995) and with recent dynamic global vegetation models (DGVMs) which suggest a shift of between 820 and 1100 GtC (Otto et al., 2002; Kaplan et al., 2002). We suggest that the upper range of the DGVMs results should be considered, as neither model takes into account the peat accumulation during the late Holocene, which could contribute up to several hundreds of GtC (e.g., Gajewski et al., 2001).

3.3. *The average isotope value of the deglacial vegetation expansion* ($\delta^{13}C_L$)

To estimate the average $\delta^{13}C$ of this terrestrial biomass, we assume that the vegetation expansion since the last glacial period was probably dominated by C3 plants ($\delta^{13}C$ range −22‰ to −30‰, average −27‰) (Ehleringer et al., 1997), see Fig. 4. C4 plants ($\delta^{13}C$ range = −9‰ to −15‰, average −13‰) generally out-compete C3 plants at low humidity and low pCO_2 conditions such as during the LGM, because they have an internal 'carbon pump' system, and their primary carbon fixing enzyme (PEP-carboxylase) does not react with oxygen, hence increased photorespiration under low carbon dioxide condition does not inhibit photosynthesis (e.g., Ehleringer et al., 1997). In addition, areas currently dominated by C3 plant such as temperate boreal forest and other higher latitude habitats were barren of vegetation during the LGM due to ice sheets. From paleovegetation maps we estimate that C3-dominated vegetation types expanded approximately four times more than C4-dominated types (Maslin et al., 1995; Adams et al., 1990; Adams and Faure, 1998) during the last deglaciation, producing an average $\delta^{13}C$ value of the terrestrial biomass expansion of about −22‰, consistent with Beerling

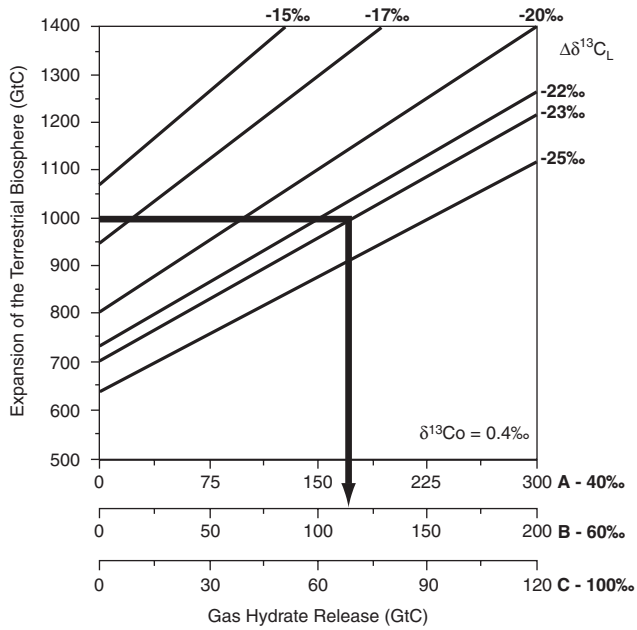

Fig. 5. Carbon isotope budget method results assuming a range of values for the average carbon isotope value of the expanding terrestrial biosphere, while maintaining the average carbon shift in the ocean as +0.4‰. Using the best estimates of both the expansion of the terrestrial biosphere using the paleovegetation method (1000 GtC) and the average $\delta^{13}C$ of that terrestrial biosphere expansion (−22‰) have been added as constraint on the amount of gas hydrate released.

(1999). For completeness we show calculations for various values of average $\delta^{13}C$ (−15 to −25‰, Fig. 2).

3.4. The average isotopic value of the gas hydrate methane released ($\delta^{13}C_{GH}$)

We use a range of isotopic composition of gas hydrates between −40‰ or −100‰ (MacDonald, 1990; Matsumoto et al., 1996; Dickens et al., 1997; Kvenvolden, 1998; Buffett, 2000) as suggested by the literature, and −60‰ as the best guess (Dickens, 2001).

Using these constraints the estimate of carbon transfer into terrestrial biomass from the marine isotope record can be made compatible with that from palaeovegetation estimates by a gas hydrate release in the range of 70–180 GtC (Fig. 5). This represents only 1–2‰ of the present gas hydrate reservoir (MacDonald, 1990; Kvenvolden, 1998) and less than half of the present reservoir in the Arctic permafrost (MacDonald, 1990). If the gas hydrate $\delta^{13}C$ composition was close to the average observed value of −60‰, and the average biosphere $\delta^{13}C$ value close to −22‰, a release of 120 GtC would be sufficient.

4. Conclusion

Our best estimate of 120 GtC (1.2‰ of the present gas hydrate reservoir), constitutes less than 30% of the additional methane that accumulated in the atmosphere between 18 and 8 ka (Severinghaus and Brook, 1999; Brook et al., 1999, 2000); i.e., the extra methane required to increase the atmospheric methane concentration above the glacial background composition of 400 ppbV (assuming a constant 11 year residence time for methane in the atmosphere after which it oxidises, Chappellaz et al., 1993). If we consider the total methane production between 18 and 8 ka then 120 GtC only represents 10% of all the methane produced. The only way it is possible for carbon budget model to release enough gas hydrate to account for all the additional methane released during deglaciation is if we take the most extreme estimates for each variable e.g., $\delta^{13}C_L = -25‰$, $\Delta C_L = 1300$ GtC, $\Delta\delta^{13}C_O = 0.3‰$, and $\delta^{13}C_{GH} = -40‰$. We thus disagree with Kennett et al. (2003), who argue that clathrate methane is the source of the atmosphere rise in pCH_4, with the exclusion of the wetland-source. As these authors do not take into account the oceanic carbon isotopic record, which is in disagreement with their argument.

The possible sources of the other 70% of the enhanced atmospheric methane added during deglaciation must reside in tropical wetlands and temperate wetlands-peatlands (Brook et al., 1996, 1999, 2000; Kalin and Jirikowic, 1996; Thorpe et al., 1996, 1998; Raynaud et al., 1998). Our reinterpretation of the carbon budgeting method thus supports the hypothesis that tropical wetland expansion was the main cause of the increase in atmospheric methane levels at deglaciation (Brook et al., 1996, 1999, 2000; Kalin and Jirikowic, 1996; Raynaud et al., 1998; Thorpe et al., 1998; Maslin and Burns, 2000), in contrast to Kennett et al. (2003). We argue, however, in agreement with Kennett et al. (2003) that gas hydrate methane release could have contributed significantly to the Pre-boreal methane peak seen in the ice core records (Brook et al., 1996). The mean inter-polar gradients differed between the Bølling-Allerod and Preboreal, with Northern Hemisphere sources dominating the Preboreal (Chapellaz et al., 1997; Brook et al., 2000). Gas hydrate methane from Arctic permafrost and northern ocean continental margins would indeed constitute such a Northern Hemisphere methane source (Bugge et al., 1988; Evans et al., 1996; Laberg et al., 2000; Kuijpers et al., 2001; Smith et al., 2001). The contribution of approximately 120 GtC of gas hydrate methane during the deglacial period may explain the drop in the atmospheric methane record seen at 8 ka. By that time the rate of climate change and sea level rise had slowed down, so that destabilization of gas hydrate ended. The atmospheric methane levels thus could fall again to interglacial levels, maintained by emissions from temperate and tropical wetlands (Kennett et al., 2003). The subsequent rise in methane in the late Holocene has been subscribed to either precessional-driven increased wetness in

Amazonia (Maslin and Burns, 2000; Mayle et al., 2000) or human influences (Ruddiman and Thomson, 2001).

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