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# Deglacial methane emission signals in the carbon isotopic record of Lake Baikal

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**Abstract**

Changes in the concentrations of atmospheric greenhouse gases constitute an important part of global climate forcing. Here we present the first continental evidence for climatically caused changes in a methane gas hydrate reservoir. The organic carbon stable isotope record from Lake Baikal during the past 130 000 years registers regular emissions of isotopically light carbon by the occurrence of distinct negative shifts of 3–5‰ at every major orbitally forced cold-to-warm climatic transition during the past 130 000 years, including marine oxygen isotope stage boundaries 6/5e, 5d/5c, 5b/5a and 2/1. We conclude that these emissions were associated with decomposition of sedimentary clathrates, widespread in the Baikal basin. Among potential hypotheses to account for these methane episodes, the most probable appears to be hydrate dissociation due to deglacial warming of lake water. We estimate that as much as 12–33 Tg of methane could have been released with each episode. By recording the systematically recurring episodes of massive methane clathrate decomposition closely linked with the northern hemisphere temperatures during major orbital warmings, the new Baikal $\delta^{13}C$ record provides further evidence for the potential involvement of clathrate reservoir in rapid deglacial rises of atmospheric methane levels.


*Keywords:* methane; hydrates; organic carbon; stable isotopes; Lake Baikal; Siberia

## 1. Paleoclimate record of Lake Baikal and the peculiar $\delta^{13}C$ signal

The strata of Lake Baikal bottom sediments preserve a continuous record of paleoenvironmental changes both in the vast watershed of the lake and in the lake itself during the past several million years [1]. Because of the apparent close link with insolation forcing, biogenic silica accumulation in Lake Baikal [2], as well as diatom abundance and species composition [3], provide important benchmark records for Pleistocene climate change in continental interior Asia [4]. In addition to preserving proxies of regional climate change, Baikal sedimentary records also bear a peculiar total organic carbon (TOC) $\delta^{13}C$ signature in Lake Baikal sediments. For instance, significant isotope depletions in primary produced organic

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matter occurred at the last glacial–interglacial transition [5]. Based on the $\delta^{13}C$ record from Baikal Drilling Project core BDP-93-2, we concluded that the peculiar isotope signal in Lake Baikal was associated with changes in the composition of the lake's dissolved inorganic carbon (DIC) pool, and apparently reflected higher availability of depleted carbon to Baikal primary producers [5].

In this work we present a new detailed $\delta^{13}C$ record of the Last Glacial Maximum to Holocene transition and discuss the implications of the new Baikal $\delta^{13}C$ record extended over the last climatic cycle. Our new findings help better explain the nature of the remarkable climate-driven $\delta^{13}C$ shifts in Lake Baikal and the nature of the large $^{14}C$ reservoir effect observed during the last deglaciation [6]. Most importantly, our new data are relevant to the discussion of the sources and release mechanisms of greenhouse gases to the atmosphere during cold-to-warm climatic transitions, because the data provide the first continental evidence for periodic dissociation of sedimentary gas hydrates closely associated with the northern hemisphere temperature changes.

## 2. Materials and methods

For our study we used sediments retrieved by the international Baikal Drilling Project (Fig. 1): cores BDP-93-2 [5] and Ver-92/2 GC-24 containing detailed records of the last glacial–interglacial transition, and the upper 560 cm portion of core BDP-96-2 covering the last climatic cycle (Fig. 2). Based on detailed correlation and age models [2,7], we compare new carbon isotope results with profiles of biogenic silica content (BioSi) and diatom abundance, used as proxies for warm interglacial climate in the region [8,9]. Core BDP-96-2 was sampled at 1 cm (250 year) intervals. This same sampling interval yielded 50–60 year resolution for cores BDP-93-2 and GC-24. The $\delta^{13}C$ of TOC in samples decalcified with 1 M $H_3PO_4$ was measured with an Optima mass spectrometer interfaced with an in-line Fisons NC 1500 Elemental Analyzer for simultaneous TOC and total nitrogen (TN) measurements [5].

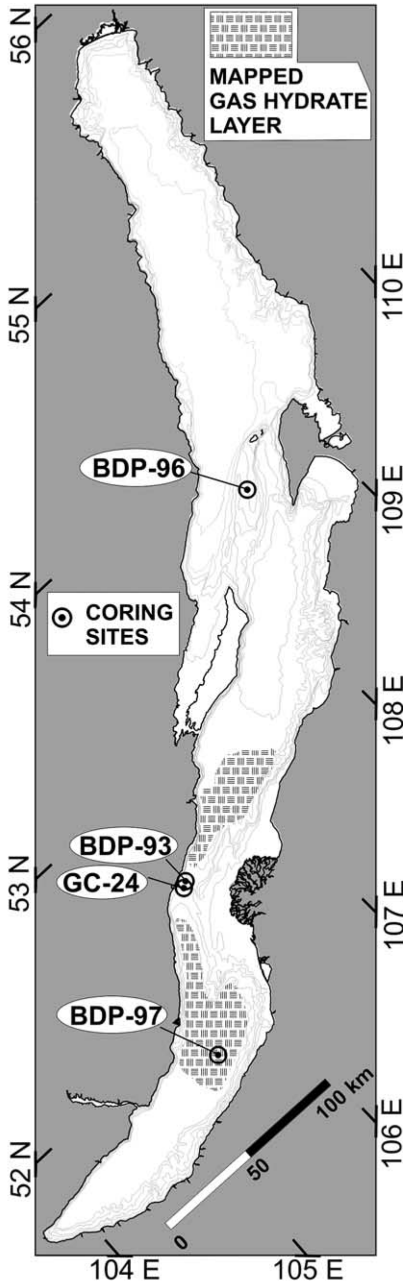


Fig. 1. Location of Lake Baikal sediment cores and mapped distribution of gas hydrate layer (hatching) according to Kuzmin et al. [20].

## 3. The last climatic cycle in the Baikal paleoclimate record

The sedimentary BioSi signal of Lake Baikal

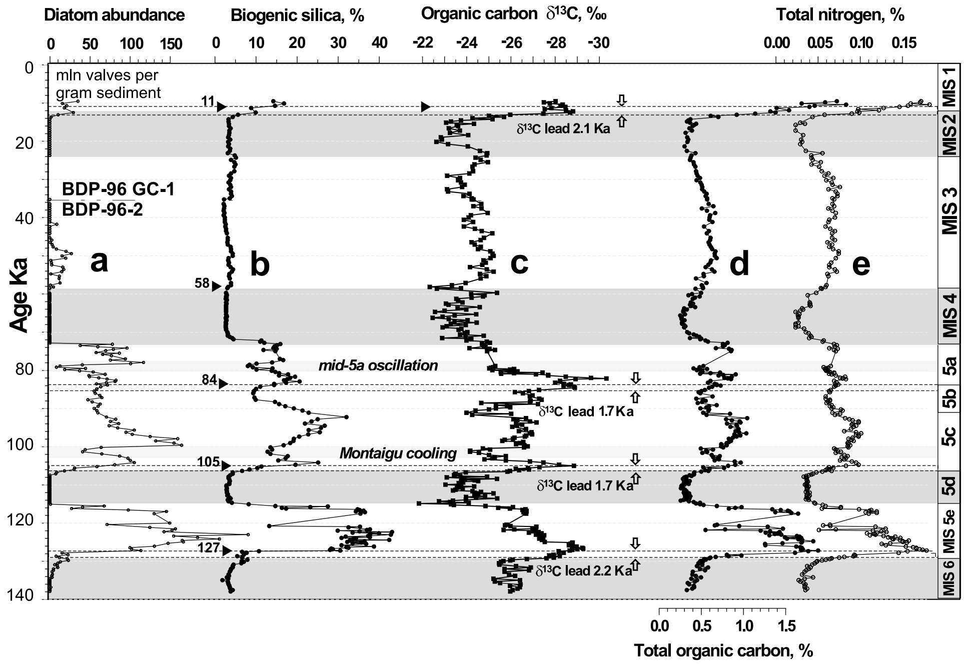


Fig. 2. To construct the age model, the BDP-96 GC-1/BDP-96-2 composite BioSi record is orbitally tuned to maximum June 65°N insolation peaks; the tie points are indicated by labeled arrows [2]. Dark shading indicates regional glacial episodes; lighter shading marks the intervals of short sub-Milankovitch regional climatic oscillations. Organic carbon (d) and nitrogen (e) follow the BioSi (b) and diatom abundance (a) pattern of climatically driven Baikal productivity variations. The $\delta^{13}C$ profile (note the reversed axis) is distinctly different from TOC and TN records suggesting that $\delta^{13}C$ fluctuations were not brought about by changes in planktonic sources of carbon or by terrigenous organic matter input [5].

reflects relative changes in the lake's heat balance, driven by insolation forcing, the water column structure and the associated hydrophysical changes, which strongly affect diatom production [2]. As a result of this link to orbital forcing, the BDP-96-2 record contains distinct intervals equivalent to marine oxygen isotope stages and substages (MIS). For instance, warm intervals MIS 5e, 5c and 5a are marked by maxima in diatom, BioSi and TOC accumulation (Fig. 2a,b). The regional glacial intervals of MIS 2, 4, 6 and 5d contain diatom-barren silty clay with abundant ice- and iceberg-rafted detritus [10]. Further recognition of sub-Milankovitch, millennial-scale climatic oscillations is also possible. For instance, the Younger Dryas cold reversal is recorded in Baikal as an abrupt shift in paleoproductivity proxies [5]. The Montaigu cooling event [11] is recorded around 103 000 years ago in Baikal by a similar proxy response [7] (Fig. 2). These correlations demonstrate that: (1) it is valid to discuss Baikal proxy responses in the context of high-resolution global paleoclimate archives and (2) it is possible to recognize stratigraphic boundaries equivalent to those in detailed marine and ice core paleoclimate records. In this present work emphasis is placed on the climatic transitions MIS 6/5e, 5d/5e, 5b/5a, and 2/1.

## 4. Negative carbon isotope excursions in the Baikal BDP-96-2 drill core record

As shown in Fig. 2c, all the above cold-to-warm climatic transitions in the Baikal BDP-96-2 sedimentary record are associated with pronounced negative carbon isotopic shifts of ca. −3 to −5‰ (Fig. 2). The $\delta^{13}C$ profile, however, is distinctly different from the profiles of productivity proxies. Unlike BioSi, TOC or TN indices, which tend to maintain a rather consistent level throughout interglacial/interstadial intervals (e.g.

MIS 5e, 5c, 5a), the $\delta^{13}C$ signal peaks at the very beginning of the warm interval and then declines by the middle of each of these warm substages (Fig. 2). This pattern is reproduced at every major orbitally forced transition of the last climatic cycle (Fig. 2).

In addition, the relative changes in the $\delta^{13}C$ signal appear more rapid as compared to other proxy responses. Because of such rapid carbon isotope shifts, $\delta^{13}C$ signal seems to have a consistent lead relative to the diatom/BioSi signal, when the midpoints of the most rapid transitions in BioSi and $\delta^{13}C$ are compared. Because BioSi serves as the main climatic index in the Baikal record [8,9,2], we consider the phase relationship between $\delta^{13}C$ and BioSi content to be the most important. When age scale is concerned, the magnitude of the apparent $\delta^{13}C$ lead reaches as much as ca. 1.7–2.2 kyr, according to sedimentation rate estimates based on linear interpolation of orbitally tuned tie points (Fig. 2). The apparent lead of the negative $\delta^{13}C$ shifts relative to Baikal's paleoproductivity response is reproduced at every major orbitally forced warming of the last climatic cycle: at MIS 6/5e, 5d/5c, 5b/5a and 2/1 (Fig. 2).

We interpret this repetitive $\delta^{13}C$ pattern as reflecting changes in the isotopic composition of the Baikal DIC pool utilized by phytoplankton in the trophogenic layer, because autochthonous production is the main source of organic matter in Baikal sediments [12,5].

## 5. Potential sources of Lake Baikal negative carbon isotope excursions

There are a number of ways in which carbon isotope depletions in primary produced organic matter may occur. For instance, $\delta^{13}C$ shifts could possibly result from the addition of depleted respiratory carbon from deep stagnant waters to the trophogenic layer through changes in mixing processes within a water body. Alternatively, $\delta^{13}C$ depletions in planktonic organic matter may result from lowering productivity and thereby increasing the $CO_2$ availability to primary producers. Finally, several scenarios are possible involving addition of $CO_2$ from sources other than the water column itself.

The observed Lake Baikal $\delta^{13}C$ excursions apparently do not involve the first two of the above mechanisms. For instance, all paleoproductivity proxies (TOC, TN, BioSi, diatom abundance) indicate that productivity and biogenic flux to bottom sediments greatly increased during major cold-to-warm climatic transitions of the last climatic cycle at times when the $\delta^{13}C$ excursions occurred in Lake Baikal (Fig. 2). Thus, negative $\delta^{13}C$ shifts could not result from lowering productivity. Instead, they occurred in spite of productivity increases, which would be expected to drive $\delta^{13}C$ of primary produced organic matter towards more positive values.

Potential changes in Baikal's mixing processes are also unlikely to have caused the observed excursions. Under present conditions there are no deep-water anoxic or hypoxic zones in Lake Baikal to accumulate depleted respiratory carbon that could potentially recharge the DIC pool in the photic zone. Presently, lake waters are oxygenated throughout the entire water column year round, and the vertical structure of the water column is defined by the profile of temperature of maximum density ($T_{md}$) for fresh water. Lake Baikal mixes down to ca. 300 m via free temperature/density-driven convection in spring, limited by the $T_{md}$ profile, and down to the greatest depths in autumn when a significant role is played by wind-driven convection in addition to free convection [13,14]. Thermal bars also play an important role in deep-water renewal in Lake Baikal [15]. During glacials the existence of an internal reservoir of respiratory carbon within a water column is even less probable for two reasons. On one hand, the TOC profile of the past 130 kyr makes it evident that carbon flux to deep waters and lake bottom was several times lower than during interglacials (Fig. 2d). On the other hand, as reconstructed by Shimaraev et al. [16], surface waters in pelagic Baikal may not have even reached the $T_{md}$ of 3.96°C during glacial summers. Under such conditions ventilation in Baikal during glacials was even more vigorous than today, because of stronger free convection reaching below 500 m water depth [16]. It is therefore impossible to imagine a scenario in which significant amounts of depleted respiratory DIC could have accumulated in deep waters, which then somehow remained stagnant during glacials when ventilation was more intense than today.

In shallow eutrophic lakes negative $\delta^{13}C$ excursions may occur as a result of increased eutrophication, which leads to the expansion of anaerobic water mass. When an oxic/anoxic interface shifts closer to the surface in a shallow lake, microbially mediated depleted $CO_2$ may be added to the trophogenic zone and utilized by phytoplankton [17]. This mechanism is an unlikely choice for Baikal at present or in the past, given several factors. The lake is not eutrophic even with today's interglacial nutrient loading; it does not have an anoxic zone, besides being several hundred meters deep and well-mixed throughout. During glacial periods, nutrient loading was apparently much lower (judging by TOC and TN in sediments) and ventilation stronger [16], making it highly improbable that eutrophication was operable at glacial–interglacial transitions in Baikal.

Having discounted the productivity or mixing mechanisms as explanations for the remarkable $\delta^{13}C$ changes in the Baikal sedimentary TOC record, we conclude that the plausible mechanism for explaining the $\delta^{13}C$ shifts involves some other external or internal source. Such sources must apparently be capable of providing additional $CO_2$ and/or isotopically depleted (negative) carbon for Lake Baikal plankton not just once but at every major orbital cold-to-warm transitions of the past 130 kyr (Fig. 2). Previously, we assumed the source to be external, and by analogy with the organic $\delta^{13}C$ record from Lake Biwa, Japan [18] we suggested that the negative $\delta^{13}C$ shift in Lake Baikal during the last deglaciation reflected higher $CO_2$ availability, associated with the deglacial rise of atmospheric $pCO_2$ [5]. However, the new Baikal $\delta^{13}C$ record presented here (Fig. 2) is strikingly dissimilar to the ice core atmospheric $pCO_2$ profiles [19], thereby largely undermining a possible atmospheric $pCO_2$-based explanation.

Terrigenous organic matter is another potential external source of carbon. In Baikal, terrigenous organic matter, after being transported, altered while settling through several hundred meters of an oxygenated water column, and finally deposited on lake bottom at the rate as slow as 4 cm/kyr, cannot produce the observed carbon isotope values more negative than −28.5 to −30‰. In addition, the close relationship observed between TOC and TN proxy responses (Fig. 2) further weakens any potential explanation involving the input of terrigenous organic matter from Baikal's catchment basin. Because terrestrial organic matter has low nitrogen content, TOC peaks not matched by TN peaks would be expected in such a scenario. These realizations eliminate external $CO_2$ sources to explain the observed negative $\delta^{13}C$ excursions in Baikal.

The exhaustive search for potential mechanisms of the negative $\delta^{13}C$ shifts in Baikal thus narrows our choice of an elusive reservoir for the 'additional' carbon to the lake's internal sources. An important condition is that such an internal source must be able to repeatedly provide isotopically depleted (negative) carbon in order to rapidly change the isotope composition of the DIC pool utilized by Baikal primary producers by several per mil, as observed in the new $\delta^{13}C$ profile for the last 130 kyr (Fig. 2). Since the potential internal source is unlikely to be the water column (as discussed above), our choice is further restricted to some sedimentary source.

Baikal sediments, however, readily offer such a potential source in the form of widespread gas hydrates. The gas hydrates in Lake Baikal: (1) contain highly depleted carbon [20]; (2) are ubiquitously present in the deep southern (1400 m) and central (1600 m) basins of Lake Baikal [21]; and (3) are highly susceptible to destabilization as indicated by detailed seismic surveys [22]. Clathrate presence had been predicted from thermodynamic calculations and measurements of geothermal gradients [23], and traced by a bottom-simulating reflector, which enhances acoustic reflection amplitudes and cross-cuts stratigraphic sequences [20,21,24]. The thickness of the gas hydrate layer varies from 34 m to 450 m, being on average 260 m. Freshwater clathrates sampled for the first time at the BDP-97 drill site at 121 m and 161 m core depth had a chemical composition of $CH_4 \cdot 5H_2O$ and isotope ratios of $-63 \pm 4$‰ [20].

We hypothesize that this large reservoir of sedimentary methane in Baikal could have been partially dissociated during major orbital warmings. In this case, the addition of methane-derived depleted carbon to the lake's pool of DIC via methanotrophy and/or oxidation could create significant $^{13}C$ depletions, which then propagated in the pool of photosynthetically fixed carbon. We therefore conclude that the observed Baikal $\delta^{13}C$ excursions most probably reflect gas hydrate destabilization events, much like the $\delta^{13}C$ signal in Santa Barbara Basin [25]. In this marine record the association of negative $\delta^{13}C$ excursions with the clathrate dissociation was proven using the study of biomarkers indicative of methanotrophy [26]. To certainly prove our interpretation of the Baikal $\delta^{13}C$ excursions, such a biomarker study would also be highly desirable (being planned in the future). There are, nevertheless, indirect ways to test if the gas hydrate explanation is plausible in the case of the Baikal $\delta^{13}C$ record. We review this evidence in Section 6.

## 6. Is the gas hydrate explanation of $\delta^{13}C$ shifts supported by available proxy responses?

Having suggested that hydrate destabilization is the most likely explanation for the Baikal $\delta^{13}C$ signal, how would we expect this signal to behave in relation to climate forcing and to be exhibited in sediments in relation to other available proxies for paleolimnological change? Firstly, one would expect Baikal gas hydrates to destabilize in at least a semi-predictable fashion in response to changes in temperature/pressure conditions. Secondly, one could expect a certain lack of relationship (perhaps decoupling) between $\delta^{13}C$ changes caused by gas hydrate destabilization and the pro-

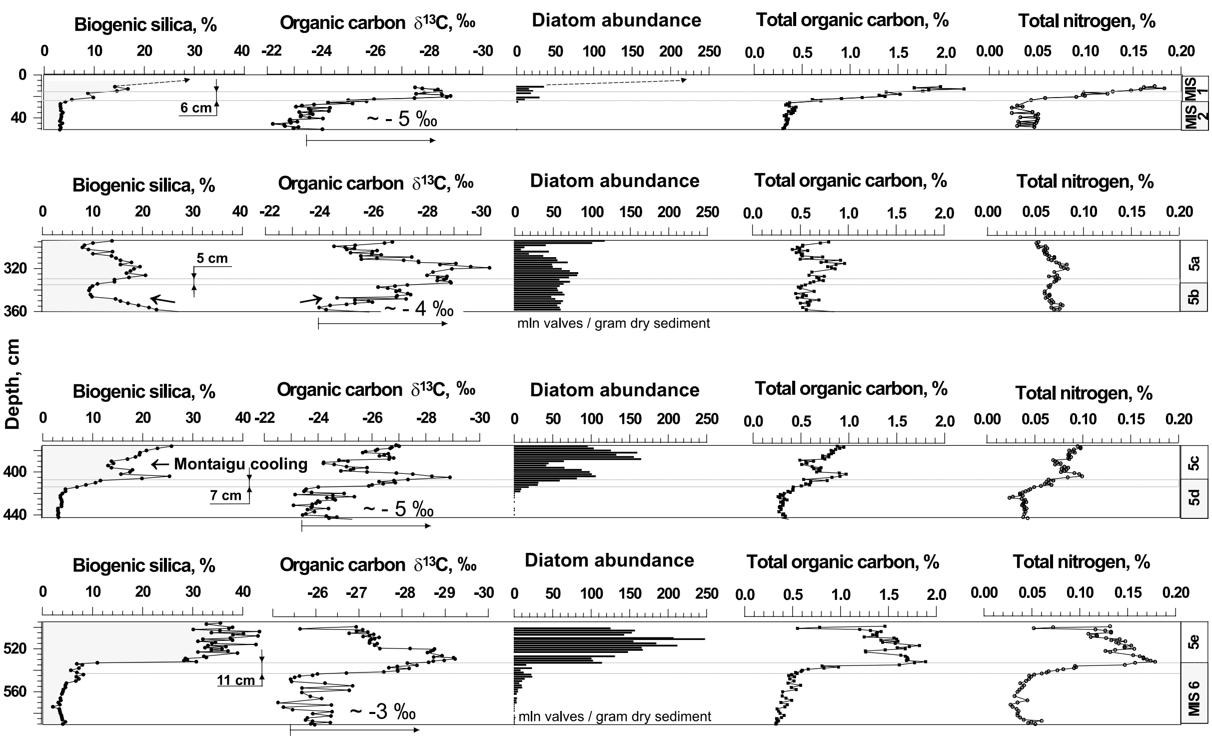


Fig. 3. Lake Baikal proxy responses across the four major orbitally forced warmings of the last climatic cycle, plotted to depth. Given the average sedimentation rate of ca. 4 cm/kyr each BioSi point represents 400–500 years. The phase relationships between $\delta^{13}C$ and BioSi indices are emphasized by dashed lines, which mark the midpoints of the most rapid transitions in these proxy records. Abrupt changes in $\delta^{13}C$ signal produce an apparent lead relative to more gradual BioSi change, also shown to age in Fig. 2.

ductivity proxy responses (e.g. BioSi, TOC, TN). Thirdly, we would expect the $\delta^{13}C$ signals to be in some way independent of species composition changes in Baikal's phytoplankton assemblage. In the case of the Baikal record during the past 130 kyr all these general conditions are met.

As seen in Fig. 2, there were four major $\delta^{13}C$ shifts in Lake Baikal during the last climatic cycle. Each of these shifts corresponds to one of the major regional cold-to-warm climatic transitions, globally recognized as MIS boundaries 6/5e, 5d/5c, 5b/5a and 2/1. These climatic transitions represent the four major orbital warmings in the northern hemisphere during the past 130 kyr. Such major climate changes are certainly expected to result in changes of water temperature and, perhaps, pressure (lake level) in the high-latitude setting of Lake Baikal (Fig. 1), and thereby to affect the extent of the gas hydrate stability zone on the bottom of the Baikal basin.

To better observe the evidence for decoupling between productivity and $\delta^{13}C$ signals, we next plotted the Baikal records of the four major cold-to-warm transitions of the past 130 000 years to depth (Fig. 3). During MIS 5d/5c and especially the 5b/5a transitions, major negative $\delta^{13}C$ excursions on the order of −4‰ to −5‰ occur at the time of relatively minor TOC and TN changes (Fig. 3). During the MIS 5b/5a transition, decoupling of $\delta^{13}C$ from productivity indices is particularly evident: the large-amplitude negative $\delta^{13}C$ peak is recorded at a time of little variation in TOC, TN or BioSi proxy profiles (Fig. 3).

During Terminations I and II (MIS 6/5e and 2/1 boundaries), negative $\delta^{13}C$ shifts in Baikal sedimentary TOC on the order of −3‰ and −5‰ respectively do appear to be somewhat associated with deglacial increases in productivity and biogenic flux to the sediments (as indicated by BioSi, TOC and TN contents) (Fig. 3). Yet, as mentioned above, the apparent lead of the $\delta^{13}C$ signal relative to these paleoproductivity indices does represent a certain degree of decoupling at these major transitions. In fact, when the midpoints of the most rapid transitions in proxy responses are re-plotted to depth (Fig. 3), the $\delta^{13}C$ shift at the MIS 6/5e transition occurs 11 cm below the major increase in BioSi. Similar lead/lag relationships, although less pronounced, may be traced for the rest of the four Baikal $\delta^{13}C$ events (Fig. 3). Given the average sedimentation rate estimated between tie points in tuned Baikal age scale [2], the depth difference at the MIS 6/5e transition in Fig. 3 translates into an approximate age difference of as much as 2.2 kyr between the BioSi and the $\delta^{13}C$ responses. Although rather rough in such a low-resolution record, these lead/lag estimates do illustrate a certain degree of decoupling between productivity and $\delta^{13}C$ responses. In addition, a major decoupling between BioSi and $\delta^{13}C$ responses is clearly observed for MIS 5b–5a interval (Fig. 3).

Lastly, we examine the potential influence of floral changes on the observed $\delta^{13}C$ responses. It could be argued that changes in the species composition of Baikal plankton, for instance, shifts from diatoms to picoplankton [27], may have affected the $\delta^{13}C$ of TOC deposited on Baikal's bottom. This possibility cannot be directly discounted given the current lack of data to support or disprove it. It is unlikely, however, that floral changes are responsible for the observed Baikal $\delta^{13}C$ record of the past 130 kyr. For instance, the $\delta^{13}C$ shift at the MIS 6/5e transition starts prior to the diatom expansion and steadily carries on further across the climatic transition (Fig. 2), in spite of the rapidly expanding pelagic diatom assemblage as a main source of organic matter. Moreover, by the middle of MIS 5e the $\delta^{13}C$ values become positive despite the fact that the level of diatom production, as reflected by BioSi and TOC fluxes, remained essentially the same (Figs. 2 and 3). The lack of signals correlative with $\delta^{13}C$ excursions in available Baikal biomarker records [28] during the last deglaciation further suggests that floral changes are unlikely to be the principal factor in controlling the $\delta^{13}C$ excursions. Furthermore, the diatom abundance profile over the MIS 5b–5a interval (Fig. 3) shows that the major $\delta^{13}C$ event recorded there was not associated with significant changes in the composition of Baikal's primary producers.

Summarizing the above discussion of indirect evidence, we conclude that the distinct negative $\delta^{13}C$ events in Lake Baikal, which occurred during each of the four major orbitally forced cold-to-warm climatic transitions, were associated with periodic additions of depleted carbon to the DIC pool utilized by Baikal primary producers. These additions generally followed the same climate-driven pattern: they occurred early during the initial warming stage of MIS 5e, 5c, 5a and the last deglaciation, as indicated by rapid −3‰ to −5‰ negative shifts in $\delta^{13}C$ of sedimentary organic matter. By the middle of each of these warm intervals, however, $\delta^{13}C$ drifted by ca. 2‰ towards more positive values (Figs. 2 and 3). Considerations of potential sources of depleted carbon, and the observations of decoupling between $\delta^{13}C$ and productivity proxy signals, lead us to conclude that periodic emissions of depleted carbon in Lake Baikal were associated with periodic dissociation of sedimentary gas hydrates. In the following sections we discuss the likely cause of climatically driven hydrate destabilization events in Baikal and speculate on the possible significance of the hydrate destabilization patterns in Lake Baikal.

## 7. Likely causes of hydrate dissociation in Lake Baikal at orbital warmings

Based on thermodynamics, destabilization of sedimentary methane clathrates may result from decreased pressure (lake or sea level) or increased temperature. During the last glacial–interglacial transition, destabilization of Baikal's gas hydrates from decreased pressure is an unlikely explanation, because lake level terraces of the last glacial are 4–15 m higher, not lower, than the present lake level [29,30]. Thus, Lake Baikal did not experience significant water level decreases during the last deglaciation sufficient to destabilize lake bottom gas hydrates. It is also difficult to invoke a lake level mechanism to explain the dramatic $\delta^{13}C$ shifts during the Younger Dryas [5]. Older Baikal lake level changes of significant magnitude are equally unlikely during the last 130 000 years, as suggested by the lack of terraces [29], by the considerations of hydrologic balance and basin morphology [31], and by the undisturbed accumulation of deep-water pelagic sediments at the BDP drill sites in 250–350 m water depth [1,9].

We now consider temperature change as a potential cause of hydrate destabilization. Surface water temperatures in Baikal today vary seasonally from 0 to 12–13°C, and temperature is most variable in the upper 150–250 m above the mesothermal maximum layer (defined by $T_{md}$ profile) [14,32]. Deep-water temperatures below 250 m remain rather stable at 3.2–3.6°C [32], and stable gas hydrates in Baikal are observed today below 500 m water depth [20]. During glacials, the conditions were quite different. Surface water temperatures are estimated to have been around 2.2°C during glacial episodes in Lake Baikal (June–October cumulative average), which is significantly lower than today's 7.5°C [16]. Because surface water temperatures during glacials may not have been reaching the $T_{md}$ of 3.96°C, free (temperature-driven) convection was reaching below 500 m depth, as opposed to today's limit of 250–300 m water depth [16]. This is of great consequence not only from the viewpoint of more vigorous ventilation, which was discussed above. Importantly, deeper free convection also implies that bottom water temperatures in Lake Baikal within the depth range of 300–500 m could have been significantly colder than today. Lower bottom temperatures in this depth range would in turn allow hydrates to remain stable at lower pressures. Therefore, it is possible that during glacials the upper limit of the hydrate stability zone in Lake Baikal was not at ca. 500 m of water and below, as today, but in a shallower zone. The expansion of the hydrate stability zone into a shallower depth range could thereby create an 'additional' sedimentary gas hydrate reservoir prone to destabilization during deglacial warmings, which were quite significant in Lake Baikal. For instance, during glacial to interglacial transitions, surface waters warmed more than threefold, seasonal ice-cover period became two months shorter, heat accumulation in the lake increased by as much as 26%, and the zone of free temperature-driven convection shrank from over 500 m to the upper 250–300 m [16]. Thus, deglacial warmings of waters in the intermediate depth range were likely of sufficient magnitude to destabilize the uppermost part of the expanded glacial gas hydrate reservoir.

To sum up, the distinct periodicity observed for the Baikal $\delta^{13}C$ deglacial excursions favors orbitally driven changes in lake water temperature over other possible explanations. Methane from warming permafrost in the watershed is unlikely to have caused the dramatic $\delta^{13}C$ shifts in the lake, because modern measurements in the Arctic have shown that methane emitted from thawing permafrost is rapidly lost to the atmosphere and is not carried by runoff beyond the immediate vicinity of the source (G.W. Kling, personal communication). In addition, even today, annual runoff to Baikal does not exceed 0.26% of its volume [23].

## 8. Methane emissions in Lake Baikal and climate change

Several features attract immediate attention to the Baikal $\delta^{13}C$ record: (1) the repetitive character of the negative isotopic signal, concurrent with every strong precessional insolation maximum of the last climatic cycle; (2) the apparent lead of the rapid $\delta^{13}C$ shift relative to paleoproductivity proxy signals; and (3) the consistent pattern of initial isotope depletion followed by a subsequent enrichment, which occurred by the middle of all orbital interstadial/interglacial periods including MIS 5e, 5c, 5a (Figs. 2 and 3) and the Holocene (Fig. 4). The regularity, timing and the pattern of the Baikal $\delta^{13}C$ changes during the last climatic cycle, as well as the spectacular $\delta^{13}C$ shifts during sub-Milankovitch cold events, such as the Younger Dryas (Fig. 4) and the Montaigu event (Figs. 2 and 3), argue for a close linkage of Baikal methane emissions with northern hemisphere temperature changes.

Important evidence further associating the Baikal $\delta^{13}C$ signal with climatic forcing comes from the close correlation with the GISP2 temperature-driven oxygen isotope record [33] during the Younger Dryas. Deglacial changes in the Baikal $\delta^{13}C$ closely followed northern hemisphere temperatures (Fig. 4). The pronounced $\delta^{13}C$ shifts in the new continuous record GC-24 clearly demarcate both the beginning and the end of the

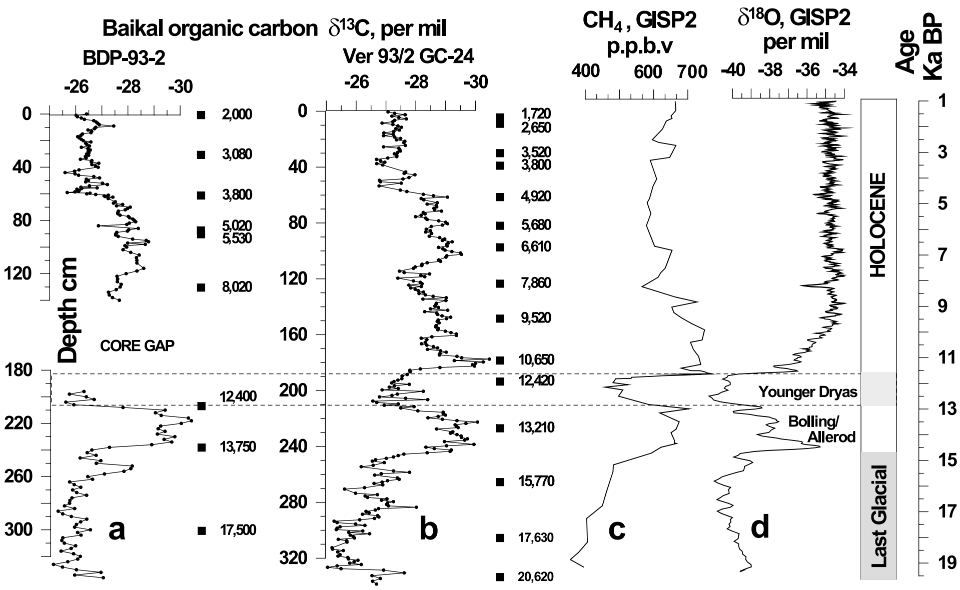


Fig. 4. Correlation of the Baikal $\delta^{13}C$ records (a,b) with the GISP2 atmospheric methane record (c) [35] and with the GISP2 $\delta^{18}O$ paleotemperature proxy (d) [33]. TOC AMS radiocarbon dates for core BDP-93-2 [37] and for core GC-24 indicate a significant (up to 2 kyr) reservoir effect during deglaciation. Note the pronounced negative $\delta^{13}C$ shifts in the Baikal record (axis reversed) during Bølling/Allerød and during the Younger Dryas–Holocene transition, parallel to increases in atmospheric methane. Decline in global methane emissions during the Younger Dryas is associated with dramatic carbon isotope enrichment in the Baikal $\delta^{13}C$ record.

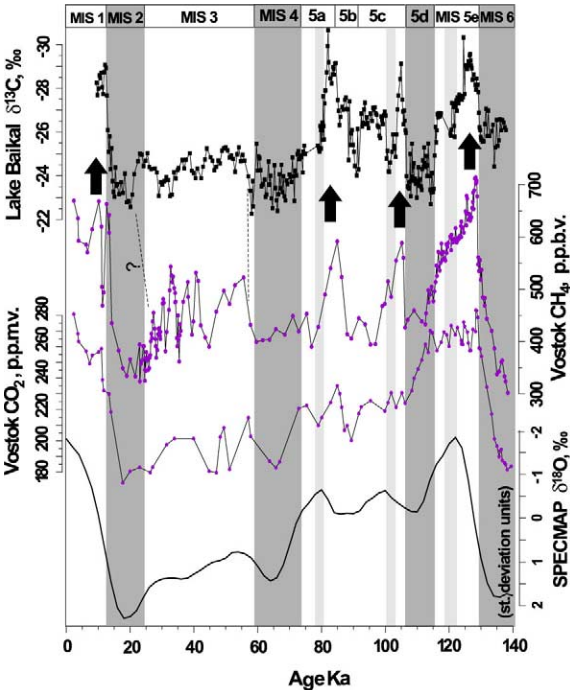


Fig. 5. Correlation of the Baikal $\delta^{13}C$ with the Vostok ice core records of atmospheric greenhouse gases [34] and with SPECMAP template [38] using original age models. Note the good agreement between the duration of Baikal $\delta^{13}C$ events and Vostok methane events. During both MIS 5c and MIS 5a the methane levels and Baikal $\delta^{13}C$ depletion indicate that methane emissions declined by the middle parts of these warm intervals.

cold interval correlative with the Younger Dryas reversal (Fig. 4). Similar to the incomplete record of BDP-93-2 [5], the new complete GC-24 sedimentary record indicates a significant reservoir effect on the order of 2 kyr for Baikal radiocarbon dates around the last deglaciation, because unadjusted AMS age estimates roughly correspond to calendar ages in GISP2 ice core (Fig. 4). This significant reservoir effect [6], consistent in different cores (Fig. 4), is another clear indication of the addition of old depleted carbon to the DIC pool of Lake Baikal during the last deglaciation.

In addition to appearing responsive to northern hemisphere temperature change, Baikal $\delta^{13}C$ records show remarkable correspondence with ice core records of atmospheric methane levels (Figs. 4 and 5). For instance, both the timing and duration of the major $\delta^{13}C$ peaks at MIS 6/5e, 5d/5c, 5b/5a boundaries appear to agree with those in the Vostok record [34] (Fig. 4). During the last glacial–interglacial transition, Baikal $\delta^{13}C$ also appears to closely follow the GISP2 atmospheric methane profile [35] (Fig. 3). The decline of the Baikal $\delta^{13}C$ response by the middle parts of both MIS 5c and 5a (Fig. 4) may be suggesting that by the middle of warm intervals potentially unstable components of the hydrate reservoir in Baikal were released. This pattern also appears to parallel changes in atmospheric methane levels (Fig. 5). The apparent visual correlation between the Baikal $\delta^{13}C$ and Vostok methane records (Fig. 5) suggests that there might be a causal link between the rates of buildup of depleted methane-derived carbon in Baikal's carbon pool and the buildup of methane in the atmosphere. The likely link between these processes is the pattern of northern hemisphere temperature changes of the past 130 000 years.

To estimate the minimum amount of methane released from sediments to account for the observed $\delta^{13}C$ negative excursions in Santa Barbara Basin, Kennett et al. [25] used the relationship $\delta^{13}C_{CH4}\cdot[C_{CH4}]+\delta^{13}C_{DICbefore}\cdot[C_{DICbefore}] = \delta^{13}C_{DICafter}\cdot[C_{DICafter}]$, assuming the instantaneous exchange of carbon between $CH_4$ and DIC. Using this same equation to estimate the amount of methane released in Lake Baikal, we arrive at an estimated 26–33 Tg of methane to produce a negative shift of −4 to −5‰, using $[C_{DICbefore}] = [C_{DICafter}] = 50$ mg/l calculated from the alkalinity of 1.1 meq/l, Baikal methane $\delta^{13}C$ of −63‰ and the 23 050 $km^3$ lake volume [32]. Alternatively, if it is presumed that only DIC of the upper 400 m layer was affected by methane, the estimated value is about 12–15 Tg. In any case, the amount of released $CH_4$ is underestimated, because no account is taken of methane escaping directly to the atmosphere. The residence time for depleted carbon in Baikal is perhaps on the order of decades, as suggested by the $\delta^{13}C$ record: the release of isotopically light carbon in Baikal dropped rapidly during sub-Milankovitch cooling episodes, such as the Montaigu event (Figs. 2 and 3) and Younger Dryas (Fig. 4).

It is important to mention that currently the observations of millennial-scale changes in Baikal methane release rates, as interpreted from $\delta^{13}C$ signals in sedimentary organic matter, are confined to the two most pronounced events, the Montaigu event and the Younger Dryas. Apparently, unlike in the high-resolution record of methane releases in Santa Barbara Basin [25], the sedimentation rate of 4 cm/kyr in the Baikal BDP-96-2 record is too low to register possible methane releases associated with flickering Dansgaard–Oeschger climatic oscillations, even if such events have occurred in Lake Baikal.

## 9. Conclusions

For the first time in a continental basin, we demonstrate that the Baikal carbon isotope record registers regular, climate-driven additions of isotopically depleted carbon to the pool of photosynthetically fixed carbon. We associate the isotope changes with methane emissions from sedimentary clathrates during deglacial warmings of the past climatic cycle. Each of these emissions resulted in oxidation of as much as 12–33 Tg of methane in lake waters. This estimate for a single continental basin is a substantial number by itself, but the most important finding is imbedded in the timing and pattern of methane releases. Baikal data, in agreement with the Santa Barbara $\delta^{13}C$ record [25], have implications for understanding deglacial climate change because they confirm that globally, the dissociation of sedimentary clathrates during the late Quaternary could have been a systematic feature of each glacial–interglacial transition.

It can be argued that the mechanism of periodic methane release from sedimentary hydrates [36] presumed to operate in Santa Barbara Basin, possibly also in Baikal, is a local phenomenon. However, one could instead argue that the *preservation* of geochemical signals related to methane releases is a local phenomenon. In open continental margin settings (likely the main deglacial source of methane), the methane-derived $\delta^{13}C$ signals perhaps are never recorded because of vigorous water mass exchange. Only in basins with reduced circulation or in basins with limited water mass exchange is it possible to prevent dilution of methane-driven $\delta^{13}C$ depletions in DIC and allow their propagation into various pools of carbon to be recorded in sediments. Therefore, in terms of their methane hydrate dynamics, related to the basinal character of Santa Barbara Basin and Baikal, these environments may provide invaluable model systems to study the role of methane hydrates in response to or in modulation of climate change.

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