

Anomalous carbon isotope fractionation between atmospheric CO₂ and dissolved inorganic carbon induced by intense photosynthesis

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Abstract—A stable isotope mass-balance of dissolved inorganic carbon during a blue-green algae bloom in a softwater lake demonstrates that at low partial pressure of carbon dioxide there must be a large net negative carbon isotope fractionation between atmospheric CO₂ and the CO₂ absorbed by lake water at pH = 9.5. The net fractionation of CO₂(g) with respect to HCO₃[−] was about −13‰ compared with about +8‰ for water at equilibrium with atmospheric CO₂ at pH ≈ 7. Chemical enhancement of CO₂ invasion at high pH by the reaction CO₂ + OH[−] → HCO₃[−] at large apparent film thicknesses may result in carbon isotope fractionation approaching that for a hydroxide solution. This phenomenon, coupled with a decrease in the photosynthetic fractionation, forced the surface water of a softwater lake to achieve increasingly negative δ¹³C values during an algal bloom, which is in the opposite sense to the trend that results from photosynthesis under less extreme conditions. This and other similar systems must operate under non-equilibrium (kinetic) conditions, causing a large kinetic fractionation during CO₂ invasion at pH > 8 and relatively large film thicknesses (*i.e.*, low wind stress).

INTRODUCTION

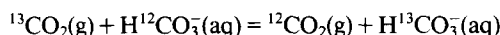
INTENSE BLUE-GREEN algae blooms in freshwater lakes are commonly accompanied by very low partial pressures of carbon dioxide (P_{CO_2}) and consequent high pH (>9) (SCHINDLER and FEE, 1973; SCHINDLER *et al.*, 1973; EMERSON, 1975a; TALLING, 1976). Fractionation of carbon isotopes between blue-green algae and dissolved carbon dioxide (CO₂(aq)) at low P_{CO_2} has been shown to be as low as 0‰ (DEUSER *et al.*, 1968; CALDER and PARKER, 1973). The fractionation is about −13‰ for conditions where algae are not CO₂ limited (CRAIG, 1953; DEGENS *et al.*, 1968). This paper focuses on anomalous trends in the measured carbon isotope composition of dissolved inorganic carbon (DIC) during a blue-green algal bloom in a freshwater lake and the implications of these observed phenomena to other natural systems.

Carbon isotope fractionation is now well characterized for air-seawater exchange (WANNINKHOF, 1985; INOUE and SUGIMURA, 1985). The equilibrium and kinetic fractionation factors derived from the experiments of these workers are strictly applicable in situations where diffusion is the dominant mode of CO₂ transfer. In many freshwater systems where pH's are greater than 9 during summer algal blooms, the reaction between CO₂ and OH[−] at the air-water interface, and the isotope fractionation associated with that reaction, may also be important. An understanding of carbon isotope fractionation during gas exchange is important for applications to carbon cycle studies and paleoenvironment interpretation of ¹³C records of carbonates and organic carbon.

CARBON ISOTOPE FRACTIONATION

Equilibrium fractionation

The isotopic equilibrium reaction involving transfer of CO₂ across the air-water interface and dissociation of dissolved CO₂ to HCO₃[−] may be written as a composite of two processes (*i.e.*, gas exchange and dissociation of carbonic acid):



where

$$K = \frac{[^{12}\text{CO}_2(\text{g})][\text{H}^{13}\text{CO}_3(\text{aq})]}{[^{13}\text{CO}_2(\text{g})][\text{H}^{12}\text{CO}_3(\text{aq})]} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{HCO}_3^-}}{(^{13}\text{C}/^{12}\text{C})_{\text{CO}_2(\text{g})}} = \alpha.$$

The equilibrium constant K is thus equal to the isotope fractionation factor α . Enrichments and depletions are generally given as fractionations: $\epsilon = (\alpha - 1) \cdot 1000\text{‰}$ with values of ϵ for the above reaction of 9.3‰ (0°C) to 6.9‰ (30°C) as determined experimentally by MOOK *et al.*, (1974). They considered that most of the fractionation takes place in the hydration step and not during the transfer of CO₂ across the air-water interface. Hence CO₂(aq) is about 9‰ lighter than HCO₃[−](aq) in natural water at 20°C, while CO₂(g) is 1‰ heavier than CO₂(aq) (see Table 1).

Measurements of the isotopic composition of CO₂ absorbed by a hydroxide solution (BAERTSCHI, 1952; CRAIG, 1953) showed a depletion of 15‰ relative to CO₂ gas. Reaction of CO₂ with OH[−] is the dominant mode of CO₂ transfer across the air-water interface at high pH though SIEGENTHALER and MUNNICH (1981) considered this process to be unimportant for air-sea-water exchange where diffusion dominates.

Photosynthesis

Photosynthetic algae preferentially incorporate ¹²C into their cells by about 13‰ relative to CO₂(aq) when

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Table 1. Carbon isotope fractionation in natural waters. The value of ϵ is defined as $\epsilon = (\alpha - 1) \cdot 1000$ where α is the fractionation factor for the given reaction or process.

$$\epsilon \text{ (‰)} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{CO}_2(\text{g})}}{(^{13}\text{C}/^{12}\text{C})_{\text{CO}_2(\text{aq})}} - 1$$

$\text{CO}_2(\text{aq}) \rightarrow \text{CO}_2(\text{g})$	ϵ (‰)	ref
$\text{CO}_2(\text{aq}) \rightarrow \text{HCO}_3^-$	+1.1	1
$\text{CO}_2(\text{aq}) + \text{OH}^- \rightarrow \text{HCO}_3^-$	+9 to +12 (25 to 0 °C)	2
$\text{CO}_2(\text{aq}) \rightarrow \text{C}_{\text{org}}$ (photosynthesis)	+15	3
$\text{CO}_2(\text{aq}) \rightarrow \text{C}_{\text{org}}$ (respiration)	0 to -13	4
	$P_{\text{CO}_2} < 10^{-5} \text{ atm to } P_{\text{CO}_2} > 10^{-3.5} \text{ atm}$	5

1. $^1\text{CO}_2(\text{aq}) \rightarrow \text{CO}_2(\text{g}) = -0.373 \cdot 10^3/T + 0.19 \text{ ‰}$ (MOOK *et al.*, 1974)
2. $^2\text{CO}_2(\text{aq}) \rightarrow \text{HCO}_3^- = -9.866 \cdot 10^3/T + 24.12 \text{ ‰}$ (MOOK *et al.*, 1974)
3. BAERTSCH (1952); CRAIG, (1953)
4. CRAIG (1953); DEUSER *et al.*, (1968); DEGENS *et al.*, (1968)
5. WILLIAMS and GORDON (1970)

surface water $P_{\text{CO}_2} \geq$ atmospheric P_{CO_2} . Measurements by RAU (1978) and this work (Tables 2 and 3) show ^{13}C depletion of up to 20‰ for particulate organic carbon when $P_{\text{CO}_2} \gg P_{\text{CO}_2}(\text{atm})$. If CO_2 concentrations in surface water are reduced well below ambient levels, carbon isotope fractionation by blue-green algae has been found to be reduced to 2‰ or smaller relative to $\text{CO}_2(\text{aq})$ (DEUSER *et al.*, 1968; CALDER and PARKER, 1973). The effect of net photosynthesis is an enrichment of the remaining source CO_2 in ^{13}C as a result of conversion of “light” CO_2 to C_{org} .

LAKE DESCRIPTION AND METHODS

Mohonk Lake (41°46'N–74°09'W; surface area, $6.8 \times 10^4 \text{ m}^2$; volume $6.6 \times 10^5 \text{ m}^3$; mean depth 9.7 m; maximum depth 18.6 m) is located about 160 km north of New York City at an elevation of 380 meters in the Shawangunk Mountains. Although the lake receives acidic precipitation (pH ~ 4.2) the water maintains a pH of 6–7 and total alkalinity $\approx 130 \text{ }\mu\text{eq/l}$ throughout most of the year due mainly to acid neutralization reactions with carbonate and silicate minerals within the drainage basin. During the 1984 ice-free season, stratification of the water column began in mid April with the thermocline at 8 meters. The epilimnion thickness decreased to 1–2 m around mid July and increased to 6–8 m by the end of October. Water residence time was about 4.5 years in 1984 with very little inflow after mid-July. The dominant algal species during the time of high productivity (July–August) was cyanophyceae (blue-greens) when Secchi visibility decreased to less than 1.5 meters. The concomitant low P_{CO_2} partial pressures ($<15 \text{ }\mu\text{atm}$) in surface water resulted in pH values greater than 9.5.

Table 2. Carbonate chemistry for Mohonk Lake surface water for some selected days during 1984. Temperature, DIC and P_{CO_2} were measured. Other data are calculated from these data and equilibrium constants given in STUMM and MORGAN (1981).

Date	Temp °C	DIC $\mu\text{mol/l}$	P_{CO_2} μatm	$\text{CO}_2(\text{aq})$ $\mu\text{mol/l}$	HCO_3^- $\mu\text{mol/l}$	CO_3^{2-} $\mu\text{mol/l}$	pH
May 3	11.1	155	665	35.0	120.0	<0.1	6.92
June 5	18.9	131	173	9.5	121.5	<0.1	7.49
June 22	22.2	135	398	14.8	120.2	<0.1	7.29
July 16	25.6	106	10	0.5	92.5	13.5	9.50
Sept 25	21.1	141	370	14.4	126.6	<0.1	7.33

Surface water was sampled approximately every two weeks from ice-off (April 9) to autumn overturn (November 24) and analyzed for DIC, Σ Alkalinity, P_{CO_2} , $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{POC}}$. pH was calculated from DIC and P_{CO_2} data using the method of HERCZEG and HESSLEIN (1984).

DIC was determined by acidification of 50 mls of water and gas stripping the evolved CO_2 which was quantified on a coulometer after the method of JOHNSON *et al.* (1985). P_{CO_2} was measured by equilibrating about 2.4 liters of water with about 500 ml of air and analysis of an aliquot of the air for CO_2 after conversion to CH_4 on a Perkin-Elmer gas chromatograph equipped with a flame ionization detector. $\delta^{13}\text{C}$ of DIC was measured by acidification and gas stripping of a 100 ml aliquot of water and analysis of the liberated CO_2 on a Micromass 903 mass spectrometer. POC samples were combusted at 800°C in quartz tubes and analyzed as above for $\delta^{13}\text{C}$. Analytical uncertainty for replicates were 1‰ for DIC and P_{CO_2} and 0.2‰ for the $\delta^{13}\text{C}$ analyses.

RESULTS AND DISCUSSION

Figure 1 shows the results of $\delta^{13}\text{C}_{\text{DIC}}$, P_{CO_2} , pH (calculated) and DIC for the Mohonk Lake surface water samples taken in 1984 while Table 2 presents some carbonate speciation calculations from the measured data and Table 3 gives their isotopic composition. The data presented in Fig. 1 show that there was a loss of CO_2 from the lake to the atmosphere from spring over-

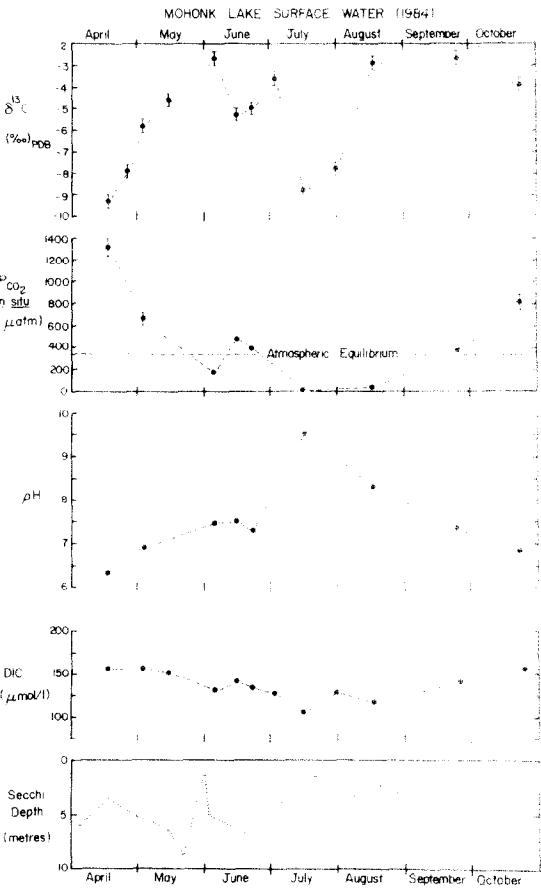


FIG. 1. $\delta^{13}\text{C}_{\text{DIC}}$, P_{CO_2} , pH (calculated), DIC and Secchi depth for Mohonk Lake surface water during the ice-free season of 1984.

Table 3. Carbon-13 composition of DIC and POC species in Mohonk Lake surface water. $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{POC}}$ were measured and all other species calculated from these data and carbonate speciation calculations given in Table 2.

	$\delta^{13}\text{C}_{\text{DIC}}$	$\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$	$\delta^{13}\text{C}_{\text{HCO}_3^-}$	$\delta^{13}\text{C}_{\text{CO}_3^{2-}}$ (‰, PDB)	$\delta^{13}\text{C}_{\text{POC}}$	$\Delta\delta^{13}\text{C}_{(\text{CO}_2(\text{aq})-\text{POC})}$
May 3	-5.8	-14.1	-3.4		-30.8	-15.9
June 5	-2.7	-11.7	-2.0		-31.1	-19.3
June 22	-5.0	-13.3	-4.0		-33.2	-19.7
July 16	-8.8	-18.4	-8.6	-10.1	-18.0	+0.4
Sept 25	-2.7	-11.2	-1.7		-26.4	-14.8

turn to early June (indicated by P_{CO} of surface water $> P_{\text{CO}_2}$ of the atmosphere) with a concomitant increase in $\delta^{13}\text{C}_{\text{DIC}}$ of approximately 6‰. The $\delta^{13}\text{C}$ increased for two reasons. Uptake of isotopically lighter DIC by phytoplankton (see Table 1) enriched the residual DIC with respect to ^{13}C . The $\delta^{13}\text{C}$ of POC in Mohonk Lake was about 16–20‰ more negative than $\text{CO}_2(\text{aq})$ during spring and early summer in 1984 (Table 3). Second, CO_2 evasion to the atmosphere results in preferential loss of ^{13}C , because $\text{CO}_2(\text{aq})$ is 9–12‰ lighter (*i.e.*, less negative) than that of HCO_3^- (MOOK *et al.*, 1974, and see Table 3) and it is this isotopically lighter fraction of DIC that is lost. This is the expected normal trend of increasing enrichment of the heavy isotope, ^{13}C , in the DIC during the photosynthetically active part of the year.

The $\delta^{13}\text{C}_{\text{DIC}}$ results for July 16 and 31 were surprisingly light (−8.8 and −7.8‰, respectively—see Fig. 1) given that they were recorded during an intense blue-green algal bloom (Secchi depth < 1.5 m) when the P_{CO_2} of surface water was less than 5% of atmospheric equilibrium. $\delta^{13}\text{C}$ might be expected to increase during an algal bloom due to removal of isotopically light carbon by the algae (see above) and invasion of CO_2 from the atmosphere (WEILER and NRIAGU, 1978; MCKENZIE, 1982; QUAY *et al.*, 1986). The decrease in $\delta^{13}\text{C}$ could not have been caused by net respiration of particulate organic carbon because the DIC actually decreased during the first two weeks of July. Inflow of isotopically light DIC from the terrestrial drainage basin ($\delta^{13}\text{C} \approx -17$ ‰) was actually less than 10 percent of that required to cause a 5‰ decrease in epilimnion $\delta^{13}\text{C}_{\text{DIC}}$ over the observed two week interval (HERCZEG, 1985). In order to make the surface water DIC isotopically lighter at roughly constant DIC concentration, the isotopic composition of DIC entering the lake must have been lighter than that removed by photosynthesis.

The photosynthetic fractionation between $\text{CO}_2(\text{aq})$ and POC was observed to be about 0.4‰ during the midsummer bloom at Mohonk Lake (*i.e.*, $\Delta\delta^{13}\text{C} = \delta^{13}\text{C}_{\text{POC}} - \delta^{13}\text{C}_{\text{CO}_2(\text{aq})} = -18.0 - -18.4 = +0.4$ ‰—see Table 3). This observation is in agreement with other work that documents a decrease in the photosynthetic fractionation by blue-green algae at low P_{CO_2} (DEUSER *et al.*, 1968; CALDER and PARKER, 1973). Invasion of CO_2 at the high apparent film thickness presumed at the low wind regime prevailing during July was chemically enhanced (EMERSON, 1975a) and the kinetic isotope fractionation during CO_2 invasion

may approach that observed for CO_2 absorption by a hydroxide solution (BAERTSCHI, 1952; CRAIG, 1953; SIEGENTHALER and MUNNICH, 1981). Instead of the equilibrium situation where CO_2 invading a lake is about −9‰ (*i.e.*, 1‰ lighter than atmospheric CO_2), the isotopic composition of invading CO_2 was around −21‰ (*i.e.*, −8‰–13‰) because of a kinetic fractionation of −13‰ relative to atmospheric CO_2 caused by the chemical enhancement. There is no *a priori* reason to accept the hydroxide values as a practical or theoretical limit for the kinetic carbon isotope fractionation induced by chemically enhanced invasion, though it serves as a useful empirical calibration for these purposes. The effect of a large negative isotopic fractionation during chemically enhanced CO_2 invasion coupled with a greatly diminished fractionation for photosynthesis provided a mechanism for decreasing the $\delta^{13}\text{C}_{\text{DIC}}$ of the Mohonk Lake epilimnion during the two weeks of rapid build-up of the algal standing crop (inferred from Secchi disc observations—Fig. 1). Consider a simplified case where CO_2 invasion and net photosynthesis are equal. For each atom of carbon that enters the lake via invasion (−21‰) an atom of carbon leaves the DIC pool *via* net conversion to C_{org} with an average $\delta^{13}\text{C}$ of −18‰ (Fig. 2). The surface water DIC must get progressively lighter at higher rates of invasion and net photosynthesis as there is a net −3‰ fractionation at constant DIC concentration.

The above scenario may be tested by comparing two independent estimates of the net CO_2 invasion rate in Mohonk Lake over the time interval July 4 to July 16, 1984. The first estimate is based on a DI^{12}C - DI^{13}C mass-balance calculation and the other by a stagnant

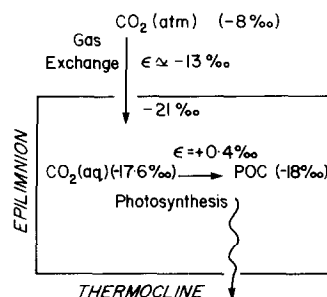


FIG. 2. Schematic diagram of simplified model depicting fluxes of ^{13}C during intense photosynthesis in Mohonk Lake. The fractionation associated with CO_2 invasion is given as −13‰ and the mean photosynthetic fractionation is +0.4‰.

boundary-layer model. For the mass-balance, two equations can be set up for ¹²C and ¹³C which can be solved simultaneously to obtain two unknowns: the net CO₂ invasion rate and the net rate of photosynthesis where all the other parameters are measured or calculated independently. Given that the upper mixed layer (epilimnion) volume did not change significantly over the time period of interest, the DI¹²C balance can be expressed as:

$$\frac{\Delta[\text{DIC}]_E}{\Delta t} \cdot V_E = \Sigma \text{DIC}_I - \text{DIC}_O + \text{Inv} - P + S + D_H \quad (1)$$

and the DI¹³C balance as:

$$\frac{\Delta([\text{DIC}]_E \cdot R_E)}{\Delta t} \cdot V_E = \Sigma \text{DIC}_I \cdot R_I - \text{DIC}_O \cdot R_O + \text{Inv} \cdot R_{\text{Inv}} - P \cdot R_{\text{POC}} + S \cdot R_S + D_H \cdot R_H \quad (2)$$

where

- Δ[DIC]_E = change in DIC concentration of the epilimnion
- V_E = volume of the epilimnion
- ΣDIC_I and DIC_O = flux of DIC via inflow and outflow respectively
- Inv = net invasion rate in moles C d⁻¹
- P = net photosynthesis in moles C d⁻¹
- S = porewater flux of DIC from epilimnion sediments
- D_H = eddy diffusion of DIC from below the epilimnion

and

$$R_x = \frac{(^{13}\text{C}/^{12}\text{C})_x}{(^{13}\text{C}/^{12}\text{C})_{\text{PDB}}} = \frac{\delta^{13}\text{C}}{1000} + 1.$$

The values of the measured input parameters are given in Table 4; then substituting these into Eqns. (1) and (2) and solving simultaneously gives a net CO₂ invasion rate of 27 ± 7 mmol m⁻² d⁻¹ and a rate of net photosynthesis of 30 ± 9 mmol m⁻² d⁻¹.

The stagnant-boundary layer model of LEWIS and WHITMAN (1924) envisions gas exchange as diffusion across an imaginary film at the air-water interface. Incorporating an additional term for chemical enhancement due to reaction of CO₂ with OH

(EMERSON, 1975b) the rate of CO₂ invasion may be given by:

$$\text{Inv} = \frac{D \cdot \beta}{z} \cdot (P_{\text{CO}_2(\text{atm})} \cdot K_H + [\text{CO}_2(\text{aq})]_i) \quad (3)$$

where

- Inv = net CO₂ flux across the air-water interface
- D = diffusivity of CO₂ in pure water at 25°C (LERMAN, 1979)
= 1.9 × 10⁻⁵ cm² sec⁻¹
- β = chemical enhancement factor (EMERSON, 1975a; SMITH, 1985)
= 5 ± 1
- z = stagnant film thickness = 350 ± 100 μm
- P_{CO₂(atm)} = CO₂ partial pressure in air above the lake
= 360 ± 30 μatm
- K_H = solubility of CO₂ in water at 25°C (HARNED and DAVIS, 1943)
= 3.4 × 10⁻² M/atm
- [CO₂(aq)]_F = concentration of dissolved CO₂ in surface water = 0.5 ± 0.3 μmol/l.

Film thickness was estimated from values of z calculated for other lakes of similar size and wind regime (EMERSON, 1975b; BROECKER *et al.*, 1980; WANNINKHOF *et al.*, 1985) and the enhancement factor was calculated from pH and z (EMERSON, 1975a; SMITH, 1985). Solving for Inv gives a net CO₂ invasion rate = 28 ± 8 mmol m⁻² d⁻¹.

Given the uncertainty involved in many of the input parameters for each of the above models, the values of CO₂ invasion calculated from the stagnant boundary-layer model (28 ± 8 mmol m⁻² d⁻¹) is in good agreement with the mass balance calculations (27 ± 7 mmol m⁻² d⁻¹). Therefore, the suggested model for carbon isotope fractionation at low P_{CO₂} seems to be reasonable.

The importance of the reaction of CO₂ with OH⁻ to carbon isotope fractionation in other aquatic systems depends on the pH and thickness of the stagnant boundary film (z). The rate of CO₂ exchange can be envisioned as competition between diffusion of CO₂ through a boundary film and reaction of CO₂ with OH⁻ (EMERSON, 1975a). Diffusion will be the dominant process at lower pH's and high wind stress, while chemical enhancement is important at higher pH and low wind stress (SMITH, 1985). Fractionation by the reaction pathway is unimportant in seawater because at pH = 8.3 and z ≈ 50 μm this amounts to less than -0.2‰ (SIEGENTHALER and MUNNICH, 1981). The importance of the fractionation which accompanies chemical enhancement may be seen from Table 5 which displays some calculated values for the fractionation between CO₂(atm) and invaded CO₂ as a function of pH and film thickness using the method given in HERCZEG (1985). Even at pH as low as 8, significant chemically enhanced fractionation may occur at a film thickness of 250 μm or greater. Similarly, at pH > 9

Table 4. Measured input parameters for the DI¹²C-DI¹³C mass balance (equations 1 and 2 in the text) for the Mohonk Lake epilimnion. The values quoted for fluxes, concentrations and isotopic ratios are taken from HERCZEG (1985)

ΣDIC _I = 50±20 moles C d ⁻¹	δ ¹³ C _I = -17±2 ‰
DIC _O = 4±2 moles C d ⁻¹	δ ¹³ C _E = -6.2±0.5 ‰
[DIC] _E = 177 μmol l ⁻¹	ΔR _F = 5.2 × 10 ⁻³
Δ[DIC] _E = -22±5 μmol l ⁻¹	δ ¹³ C _{Inv} = 21 ‰
V _E = (10±2) × 10 ⁷ l	δ ¹³ C _{POC} = -18±1 ‰
S = 18±5 moles C d ⁻¹	δ ¹³ C _S = -10 ‰
D _H = 4±2 moles C d ⁻¹	δ ¹³ C _H = -3 ‰

Table 5. Calculated kinetic fractionation (expressed as per mil) for the reaction $\text{CO}_2(\text{aq}) + \text{OH}^- = \text{HCO}_3^-$ as a function of film thickness (z) and pH.

$z(\mu)$	50	100	250	400
pH				
10	-7.0	-11.6	-14.3	-14.7
9	-1.2	-3.8	-10.2	-12.7
8	-0.1	-0.5	-2.6	-5.3
7	-0.01	-0.1	-0.3	-0.8

and moderate to high wind stress this phenomenon must be accounted for.

CONCLUSIONS

The data and calculations presented in this paper show that high rates of photosynthesis not only cause chemically enhanced invasion but also the predominant role of invading CO_2 highly depleted in ^{13}C . This effect must be accounted for when interpreting $\delta^{13}\text{D}_{\text{DIC}}$ trends in surface waters and may be recorded as ^{13}C depleted CaCO_3 in some freshwater lakes. Thus, down core negative excursions of $\delta^{13}\text{C}$ of authigenic CaCO_3 preserved in lacustrine sediments may not be indicative of a decrease in lake productivity and/or increase in terrestrial carbon supply to the lake DIC pool. Great care should be exercised in any paleolimnological reconstruction of past climates based on stable carbon isotope records in lake sediments.

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