COMMENT

The effect of anthropogenic CO_2 on the carbon isotope composition of marine phytoplankton

To discriminate ''top down'' (i.e., fishing pressure) from ''bottom up'' (i.e., nutrient supply) control of recently documented declines of top consumers in the Bering Sea, Schell (2000) utilizes an ingenious proxy record to quantify the variability in regional primary production for the period 1947–1997. The study exploits the changes in the stable isotope composition of carbon ($\delta^{13}C$) of long baleen plates obtained from bowhead whales (*Balaena mysticetus*). These plates have annular structures that record the time-varying $\delta^{13}C$ signature of their zooplankton prey. This signature, in turn, is largely determined by phytoplankton isotopic fractionation of inorganic carbon during photosynthesis (Falkowski and Raven 1997).

Over the 31-yr period between 1966 and 1997, Schell (2000) reports a decreasing trend in the $\delta^{13}C$ of the phytoplankton ($\delta^{13}C_p$) of up to ~2.7‰. He attributes this trend to a decrease in the average specific growth rate of phytoplankton in the Bering Sea. Schell's analysis is based on two fundamental assumptions which we discuss below.

1. There is a predictable relationship between the carbon isotopic fractionation in marine phytoplankton and growth rate.
2. ''. . . phytoplankton species composition have remained similar. . . ,'' over the 31-yr time period, ''and . . . the $\delta^{13}C_{aq}$ and seasonal concentrations of dissolved free CO_2 in the euphotic zone have remained relatively constant'' Schell (2000, p. 461).

Based on the foregoing, Schell infers (p. 459) ''a drop in the seasonal carbon fixation of ~30–40%'' from 1966 to 1997 and logically concludes that this ''. . . lowered carrying capacity is a likely contributor to the decline of top consumers. . .'' in the Bering Sea; that is, the system is becoming increasingly limited by primary productivity. Here, we caution that large uncertainties accompanying each of these assumptions may invalidate Schell's conclusion.

Based on both theoretical considerations (Francois et al. 1993; Goericke et al. 1994) and experimental studies (Laws et al. 1995; Bidigare et al. 1997), it has been suggested that when intracellular $[CO_2]_{aq}$ is supplied by diffusion, the cellular growth rate also exerts considerable control on $\delta^{13}C$, insofar as it influences the cellular CO_2 content available for carbon fixation. If intracellular CO_2 is supplied by diffusion, then the magnitude of carbon isotope fractionation during photosynthesis (ε_p) can be expressed as a function of the isotopic fractionation associated with carbon transport and fixation and the CO_2 concentration gradient across the cell

wall (Farquhar et al. 1982). Laws et al. (1995) has suggested that ε_p is linearly dependent on $\mu/[CO_2]_{aq}$ and therefore can be expressed as

$$\varepsilon_p = \varepsilon_f - \frac{b\mu}{[CO_2]_{aq}}, \qquad (1)$$

where ϵ_f is the carbon isotope fractionation associated with photosynthetic fixation, μ is the specific growth rate and b is a species-specific constant. The relationship between the $\delta^{13}C_p$ and ε_p can be expressed as

$$\delta^{13}C_p = \frac{\delta^{13}C_{aq} - \varepsilon_p}{1 + \left(\dfrac{\varepsilon_p}{1000}\right)}, \qquad (2)$$

where $\delta^{13}C_{aq}$ is the stable isotope signature of $[CO_2]_{aq}$.

First, the application of the diffusive transport model to interpret changes in ε_p in terms of μ and/or $[CO_2]_{aq}$, as carried out by Schell (2000), has been questioned by recent single-species laboratory experiments and field studies on mixed populations of marine phytoplankton. Monospecific laboratory studies investigating isotope fractionation in commonly occurring phytoplankters at low $[CO_2]_{aq}$ strongly implicate other mechanisms (e.g., active HCO_3^- transport and/or catalyzed conversion of HCO_3^- to CO_2) for inorganic carbon acquisition in addition to passive CO_2 diffusion (Riebesell et al. 2000). Nondiffusive transport is also strongly supported by various field studies of carbon isotope fractionation in species-dependent biomarkers and natural assemblages of marine phytoplankton (Pancost et al. 1997, 1999; Tortell et al. 1997). These results suggest that a single, simple calibration between ε_p and μ and or $1/[CO_2]_{aq}$ may not exist.

Second, accepting that diffusive transport models of fractionation are sufficiently precise (but see Bidigare et al. 1997; Rau et al. 1997) and apply to phytoplankton growing in the Bering Sea (where $[CO_2]_{aq}$ is generally >15 μM and growth rates are probably low), an alternative and more parsimonious explanation for the decreasing trend in $\delta^{13}C_p$ is the invasion of ocean surface waters by anthropogenic CO_2. This isotopically light carbon has been released to the atmosphere largely through the burning of fossil fuels (Quay et al. 1992; Francey et al. 1999). The penetration of ocean surface waters by isotopically light carbon has been proposed to explain the discrepancy between measurements of $\delta^{13}C$ on modern particulate organic carbon (POC) and on organic matter from deep-sea surface sediments (Bentaleb
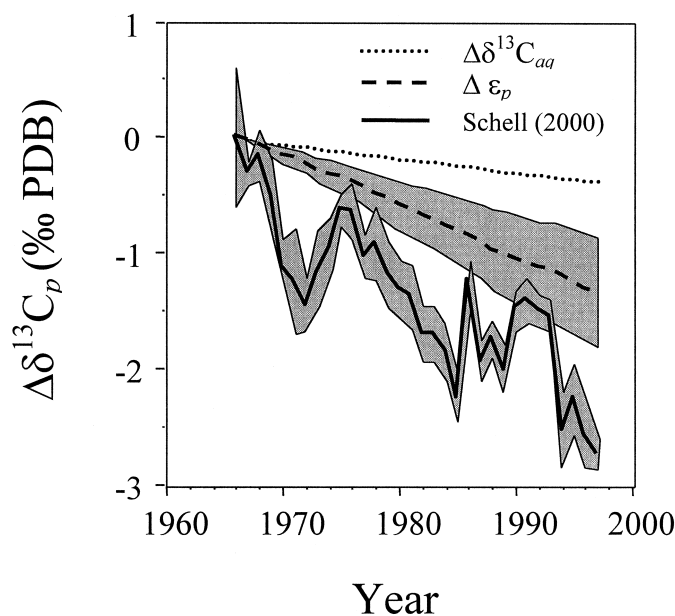
Fig. 1. Estimated changes in the carbon isotopic composition of marine phytoplankton are compared with $\delta^{13}C$ data from long baleen plates of bowhead whales (*Balaena mysticetus*) from the Bering Sea (Schell 2000). The expected change in $\Delta\delta^{13}C_p$ is the sum of the effect of increasing atmospheric pCO_2 on the $\delta^{13}C$ composition of aqueous CO_2 ($\Delta\delta^{13}C_{aq}$; also known as the *Suess effect*), and on the carbon isotopic fractionation by marine phytoplankton ($\Delta\varepsilon_p$). The isotopic fractionation was calculated using the relationship for *Emiliania huxleyi* $\varepsilon_p = 24.6 - (140 \pm 70)\mu/[CO_2]_{aq}$ given by Bidigare et al. (1997). We assumed a growth rate of 0.3–0.4 d^{-1} and $[CO_2]_{aq} = 16$–17 μM (assuming a sea surface temperature (SST) of $5°C$). Based on this relationship, we calculate an ε_p in the range of 16‰ which is consistent with published data for phytoplankton growing under similar conditions in northern latitudes (Goericke and Fry 1994). The shaded area around our predicted change in $\Delta\delta^{13}C_p$ represents the uncertainty in the above relationships (see Popp et al. [1998] for further discussion). The upper bound (smallest $\Delta\delta^{13}C_p$) was obtained using the relationship derived for *Phaeodactylum tricornutum,* a diatom found in warmer, temperate surface waters (Laws et al. 1995). The lower bound (largest $\Delta\delta^{13}C_p$) is more consistent with the data of Popp et al. (1998). The shaded area around Schell's (2000) record reflects uncertainties estimated from standard errors in the whales' data $n = 3$).

and Fontugne 1996; Fischer et al. 1998; Rosenthal et al. 2000). The penetration of anthropogenic carbon into the upper ocean is well documented (Quay et al. 1992) and results in both an increase in $[CO_2]_{aq}$ and a decrease of $\delta^{13}C_{aq}$ (also known as the *Suess effect*). Although the latter effect is small (typically 0.01–0.02‰ yr^{-1}, Quay et al. 1992; Sonnerup et al. 1999), the effect of increasing $[CO_2]_{aq}$ concentrations on carbon isotopic fractionation in marine phytoplankton may be more significant (Fig. 1).

Calculating the effect of varying $[CO_2]_{aq}$ on $\Delta\varepsilon_p$ is highly dependent on the empirical calibration used and assumes that surface waters of the Bering Sea have been in equilibrium with atmospheric pCO_2. Similar to Schell (2000), our calculation of $\Delta\varepsilon_p$ was based on the relationships of Bidigare et al. (1997) and Laws et al. (1995). It is important to point out that the resulting $\Delta\delta^{13}C_p$ calculated relies on the rela-

tionship used as well as the values of μ, $[CO_2]_{aq}$ adopted, and the species composition of the resident phytoplankton community likely to be found at the study site. In addition, we assume surface waters of the Bering Sea have been in equilibrium with increasing atmospheric pCO_2 during the period considered, whereas Schell (2000) assumes that surface water $[CO_2]_{aq}$ has remained constant. Although there are no direct measurements documenting the effect of anthropogenic CO_2 on Bering Sea surface water, the penetration of chlorofluorocarbons (CFCs) (Warner and Roden 1995) and $\delta^{13}C_{DIC}$ anomalies (Ortiz et al. 2000) into subsurface waters ($\sigma_\theta < 26.8$) of the subarctic northeast Pacific suggest that anthropogenic CO_2 has invaded surface and subsurface waters of the Bering Sea.

For the time period considered by Schell (2000), we calculated an increase in surface water $[CO_2]_{aq}$ of 2.3 μM (assuming a constant mean annual sea surface temperature of $5°C$), with a concomitant $\delta^{13}C_{aq}$ decrease of ~ 0.3‰. The change in carbon isotopic fractionation ε_p due to the anthropogenic increase of $[CO_2]_{aq}$ was estimated using the relationship of Bidigare et al. (1997) and Laws et al. (1995) as in Schell (2000) (*see Fig. 1 legend for details*). We estimate that increased $[CO_2]_{aq}$ concentration resulted in an increase of carbon isotopic fractionation by marine phytoplankton of $\Delta\varepsilon_p = -1.1 \pm 0.5$‰ (Fig. 1). When combined with the decrease in $\delta^{13}C_{aq}$, the total $\Delta\delta^{13}C_p$ in the Bering Sea for the 31-yr period is predicted to have been -1.4 ± 0.5‰.

Although our calculations do not rule out the possibility that phytoplankton growth rates have changed over the 50-yr record presented by Schell (2000), they do suggest that a large fraction ($\sim 50\%$) of the change in isotopic fractionation and the general trend (but not the interannual variability) in his record could be attributed to a change in the atmospheric source carbon. Our conclusions imply that the phenomenon observed by Schell should be global, whereas if Schell's proposed mechanism is valid, the phenomenon should be regional. Clearly time and more isotopic records will help to discriminate between the two hypotheses.

Jay T. Cullen[1]
Yair Rosenthal
Paul G. Falkowski

Institute of Marine and Coastal Sciences
Rutgers University
71 Dudley Road
New Brunswick, New Jersey 08901

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[1] Corresponding author (cullen@imcs.rutgers.edu).

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