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initial conditions in the collision complex and predicts reaction rates solely on the basis of energetics (7).

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- We thank A. C. Luntz for helpful discussions. Financial support was provided by the Swiss National Science Foundation (grant no. 124666) and the École Polytechnique Fédérale de Lausanne.

Supporting Online Material

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Materials and Methods

Figs. S1 to S12

References

3 May 2010; accepted 2 July 2010

10.1126/science.1191751

Decrease in the CO₂ Uptake Capacity in an Ice-Free Arctic Ocean Basin

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It has been predicted that the Arctic Ocean will sequester much greater amounts of carbon dioxide (CO₂) from the atmosphere as a result of sea ice melt and increasing primary productivity. However, this prediction was made on the basis of observations from either highly productive ocean margins or ice-covered basins before the recent major ice retreat. We report here a high-resolution survey of sea-surface CO₂ concentration across the Canada Basin, showing a great increase relative to earlier observations. Rapid CO₂ invasion from the atmosphere and low biological CO₂ drawdown are the main causes for the higher CO₂, which also acts as a barrier to further CO₂ invasion. Contrary to the current view, we predict that the Arctic Ocean basin will not become a large atmospheric CO₂ sink under ice-free conditions.

The CO₂ concentration in the atmosphere has increased greatly since the industrial revolution, and ~30% of the CO₂ released has been taken up by the ocean. This process slows the increase of this greenhouse gas in the atmosphere and thus global warming (1), but will likely affect ocean ecosystems via acidification

(2, 3). The Arctic Ocean has great potential for taking up atmospheric CO₂ owing to high biological production in the large ocean margin areas and low temperature (4, 5). A recent synthesis suggested that the Arctic Ocean, though constituting only 3% of the world's ocean surface area and mostly ice-covered, accounts for 5 to 14% of the total ocean CO₂ uptake (6). This value is highly uncertain, however, owing to relatively few observations and rapid climate changes. The Arctic is widely viewed as the area on Earth most sensitive to climate changes (1), with acidification more pronounced than that of any other ocean (2). Sea ice melt in the Arctic Ocean has increased steadily over recent decades, proceeding faster in the past three summers (2007 to 2009) than any model prediction (Fig. 1) (7–9). It has been postulated that an ice-free condition in the Arctic Ocean basins would allow for uptake of a substantial amount of additional CO₂ from the atmosphere (6). How CO₂ concentrations in the Arctic surface water may change in response to sea ice melt is, therefore, an important issue for the scientific community and general public.

In the summer of 2008, we conducted a high-resolution underway survey of partial pressure of CO₂ (*p*CO₂) across the Canada Basin in the western Arctic Ocean where substantial melting of ice had occurred (Fig. 1 and fig. S1). Surface-water temperature was as high as 0° to 5°C in the central Canada Basin (Fig. 2A). Extensive ice melt in this region resulted in salinity values as low as 24 parts per thousand (‰) (Fig. 2B) and ice concentration less than 15% (Fig. 1). Compared to an earlier underway survey in summer 1999, temperatures had increased by 3°C and salinities decreased by ~2‰ (Fig. 2, D and E). During the Arctic Ocean Section (AOS) study in summer 1994, all areas north of 72°N were under ice cover (Fig. 1) with surface seawater temperatures below -1.5°C and salinities above 30‰ (Fig. 2, D and E).

During the summer of 2008, surface-water *p*CO₂ was below the atmospheric level (~375 μatm) in the entire survey area (Fig. 2C). The lowest *p*CO₂ (120 to 250 μatm) occurred in marginal sea areas, in agreement with earlier observations (4, 10–13). In the ice-free region of the Canada Basin to the northeast, however, there was a large area of relatively high *p*CO₂ (320 to 365 μatm) that had not been observed before. It contrasted sharply with *p*CO₂ values of 260 to 300 μatm in the summer of 1999 and the very low *p*CO₂ (<260 μatm) from the summer of 1994 (Fig. 2F). Further north (≥77°N), where melting of ice in 2008 was less extensive, *p*CO₂ dropped quickly to below 280 μatm (Fig. 2C). Surface *p*CO₂ also decreased from the central Canada Basin to areas west of 170°W, where ice cover was relatively heavy, temperature was lower, and salinity was higher.

In ocean margin areas where *p*CO₂ was very low, dissolved inorganic carbon (DIC) was greatly depleted relative to alkalinity (TA), a quasi-conservative tracer (Fig. 3). Such a DIC decrease indicates net ecosystem production of organic carbon or removal of CO₂ in the surface mixed layer (5). In the ice-free region of the Canada Basin, however, both DIC and TA followed the theoretical mixing line of seawater and ice meltwater, indicating no appreciable net biolog-

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ical removal. In the partially ice-covered basin areas, moderate DIC depletion or CO₂ removal against TA was observed (Fig. 3).

Surface-water pCO₂ in the Arctic Ocean is affected by several processes, including mixing of various source waters (i.e., seawater, river wa-

ter, and meltwater), temperature change, air-sea gas exchange, biological CO₂ fixation, and microbial recycling of organic carbon (Fig. 4) (4–6). Assisted by prolonged daylight, nutrient-rich Pacific source water results in high biological CO₂ assimilation (“B” in Fig. 4) in the western Arctic

marginal seas (5, 14) [net primary production rate (NPP) was measured as $114 \pm 132 \text{ mmol m}^{-2} \text{ day}^{-1}$ during summer 2008, table S1]. This water is diluted by river water and ice meltwater as it flows through the ocean margins and basins. However, the mixing of river-seawater (“R” in Fig. 4) does not change the pCO₂ level substantially at S > 15%. Melting of sea ice (“I” in Fig. 4), by contrast, will greatly reduce pCO₂ because of a very low pCO₂ level in the meltwater (15).

Our observations of high pCO₂ values in the Canada Basin in summer 2008 reveal a dynamic feature of how surface pCO₂ in the Arctic Ocean may respond to ice melt. Warming (“W” in Fig. 4) in the basin would partly explain the pCO₂ increase (5, 10). However, when all pCO₂ values are normalized (or scaled) to the same temperature, the 2008 values are still much higher than those of 1994 and 1999 except in heavily ice-covered areas (fig. S2), indicating the importance of other processes. We offer the following explanation for this behavior. On the basis of the linear DIC-TA relation (Fig. 3) and very low nutrient supplies (14), we assume near-zero net biological CO₂ fixation in the Canada Basin. Moreover, we assume that before the ice melts in early spring,

Fig. 1. Arctic ice concentrations from the Advanced Microwave Scanning Radiometer for Earth-Observing System (AMSR-E) for the first week of September 2008. The blue color contour line indicates the ice edge on 12 August when the survey vessel first reached 75°N. Ice edge is defined as 15% of ice concentration. The gold and red lines represent the ice edge in the first week of September 1994 and 1999, respectively. Data are from http://nsidc.org/data/docs/daac/ae_si12_12km_tb_sea_ice_and_snow.gd.html.

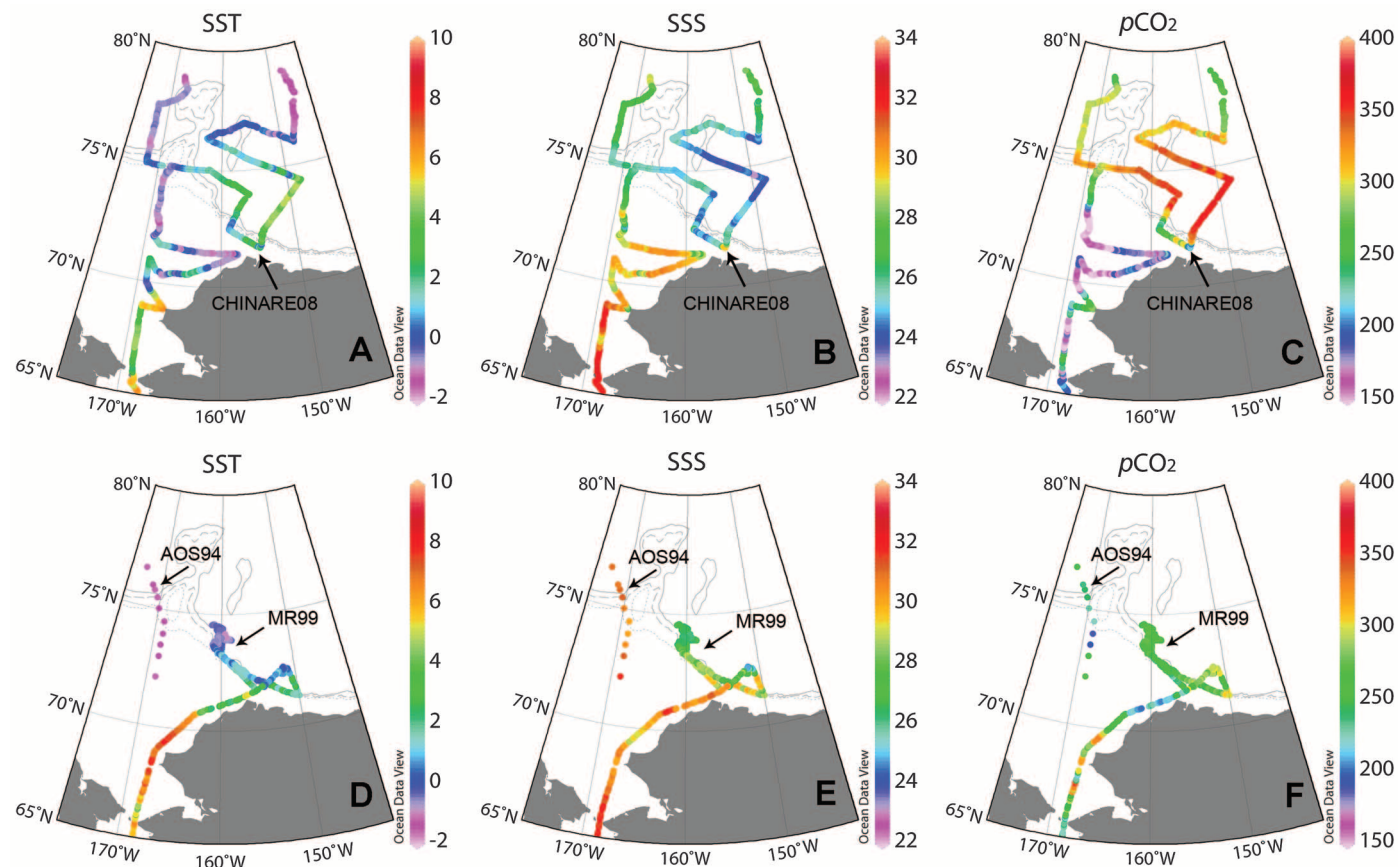
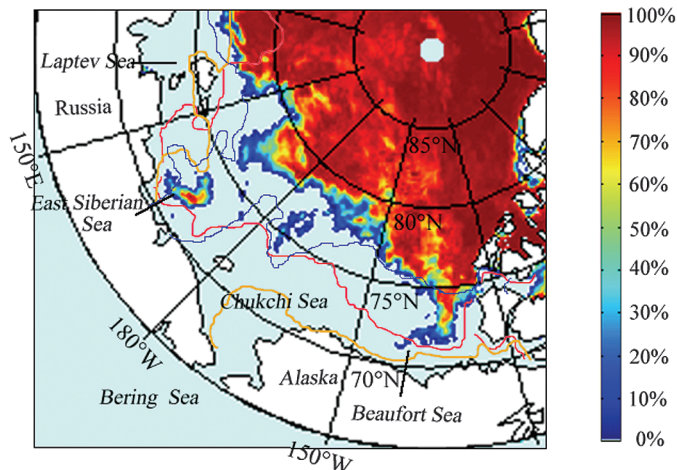


Fig. 2. Distribution of sea surface temperature (SST) in °C (A), salinity (SSS) in ‰ (B), and pCO₂ in µatm or 10⁻⁶ atm (C) during summer 2008 as well as temperature (D), salinity (E), and pCO₂ (F) in summer 1999 and 1994. CHINARE08, China National Arctic Research Expedition 2008. MR99 underway survey data were obtained in summer 1999. AOS94, Arctic Ocean Section 1994. During CHINARE08, the survey vessel arrived at 66°N

on 1 August, 75°N, 168°W on 6 August, 75°N, 155°W on 12 August, and 85°N on 28 August, and it returned to 75°N, 172°W on 6 September. The atmospheric pCO₂ was 375 and 360 µatm, respectively, in the summer of 2008 and 1999. Ocean Data View (<http://odv.awi.de>) was used for the plots. From the shore to the central basin, the three lines (dotted, dashed, and solid) indicate 250-, 500-, and 1000-m water depth, respectively.

$p\text{CO}_2$ in the basin was similar to the value under ice-covered conditions measured during the summer of 1994 at 225 μatm (Fig. 2F). Then, the mixing of seawater with low- CO_2 meltwater would reduce $p\text{CO}_2$ by 50 to 60 μatm (Fig. 4). An increase in temperature of 4° to 6°C in summer 2008 would increase $p\text{CO}_2$ by about 50 μatm (i.e., $\sim 4.2\%/^\circ\text{C}$) (5, 10). Thus, CO_2 increase due to

warming would roughly cancel out CO_2 reduction due to mixing with meltwater in the ice-free region.

The main factor increasing the surface-water $p\text{CO}_2$ is CO_2 uptake from the atmosphere. For a 1.5- to 2-month ice-free period (by the end of August), CO_2 replenishment from the atmosphere would raise the surface-seawater $p\text{CO}_2$ to about

340 μatm at a temperature of 4°C in this area (Fig. 4), which is similar to our observations [see text in supporting online material (SOM) for the model simulation]. This conclusion would be strengthened if $p\text{CO}_2$ in the early spring was higher than we have assumed as a result of accumulation from the previous summer. The same is true if the mixed layer depth is shallower or the wind speed is stronger than we used for simulations. Similarly, for a 1-month ice-free period, CO_2 uptake would increase the surface $p\text{CO}_2$ to 280 μatm in the summer of 1999 (Fig. 4).

This atmospheric CO_2 control mechanism operates because of a shallow mixed-layer depth of less than 20 m in the Canada Basin during summertime (fig. S3). This shallow depth and strong stratification allow a relatively quick re-equilibration with the atmosphere. The rapid increase in surface $p\text{CO}_2$, then, slows further CO_2 uptake by decreasing air-sea $p\text{CO}_2$ gradient ($\Delta p\text{CO}_2$), the driving force for the gas exchange. $\Delta p\text{CO}_2$ was as high as 60 to 80 μatm in the southern Canada Basin in September 1999. It dropped sharply to only 10 to 55 μatm in August 2008. When this reduction in driving force is included, the CO_2 invasion for a 100-day ice-free period is 0.64 mol m^{-2} (or 6.4 $\text{mmol m}^{-2} \text{day}^{-1}$) in 2008 (see SOM text). This flux is 85% less than the previous estimate of 46 $\text{mmol m}^{-2} \text{day}^{-1}$ based on an open-water condition measured during summer 2002 to 2004 at the southern margin of the Canada Basin (5). If we apply this asymptotic reduction of driving force to the newly ice-free basin area of $0.6 \times 10^{12} \text{m}^2$, we estimate an extra CO_2 invasion flux of only $4.6 \times 10^{12} \text{g C year}^{-1}$, compared to a much higher estimate of $33 \times 10^{12} \text{g C year}^{-1}$ under constant $\Delta p\text{CO}_2$ (6).

Light-limited biological primary production rate will increase when sea ice is thinning and melting and with increased open-water area and longer ice-free period (7, 14, 16). Indeed, we observed increased biological CO_2 removal in the partially ice-covered basin areas (Figs. 2 and 3). Once the region was ice-free, however, the linear mixing behavior of DIC relative to TA in 2008 indicates a negligible net ecosystem production rate in the central basin areas (Fig. 3). Measured NPP rates ($1.9 \pm 1.0 \text{mmol m}^{-2} \text{day}^{-1}$, table S1) in the ice-free region in summer 2008 indicate no increase or even possibly a decrease in biological production compared to the ice-covered conditions in summer 1994 ($2.5 \pm 1.1 \text{mmol m}^{-2} \text{day}^{-1}$) (17). Our conclusion is consistent with the observation of no increase in satellite-derived chlorophyll concentrations between 2003 and 2008 in the basin area (18). Low net biological CO_2 fixation in the Canada Basin is likely due to a poor supply of nitrate to the surface mixed layer as a result of strong stratification from greatly increased meltwater input (fig. S3) (7, 16, 19). Nutrient availability to surface water would limit not only water column productivity (14, 16) but also ice-algal productivity (20). High stratification and limited nutrient supply to the surface water may have already caused a shift in ecosystem toward

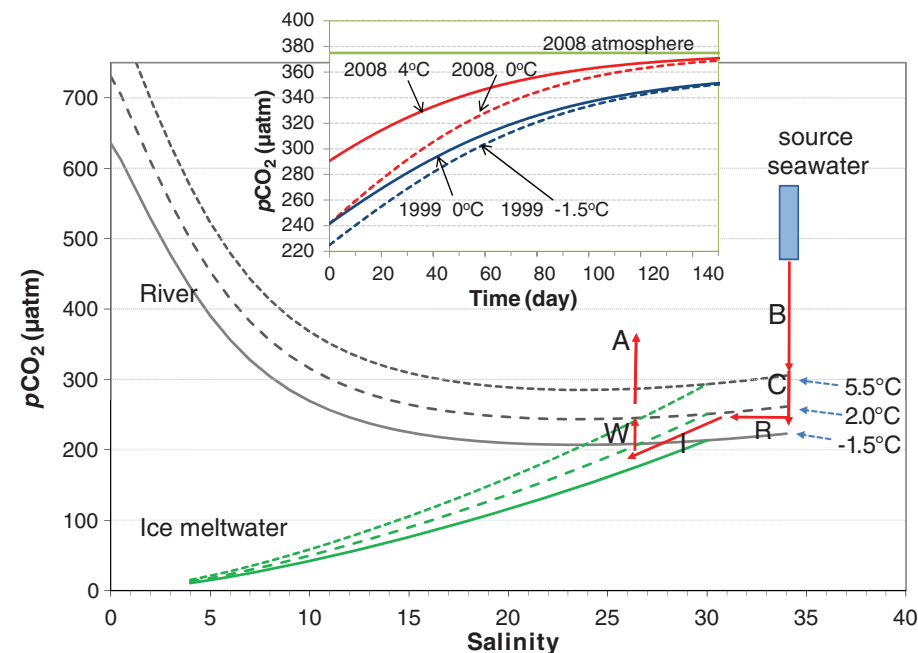
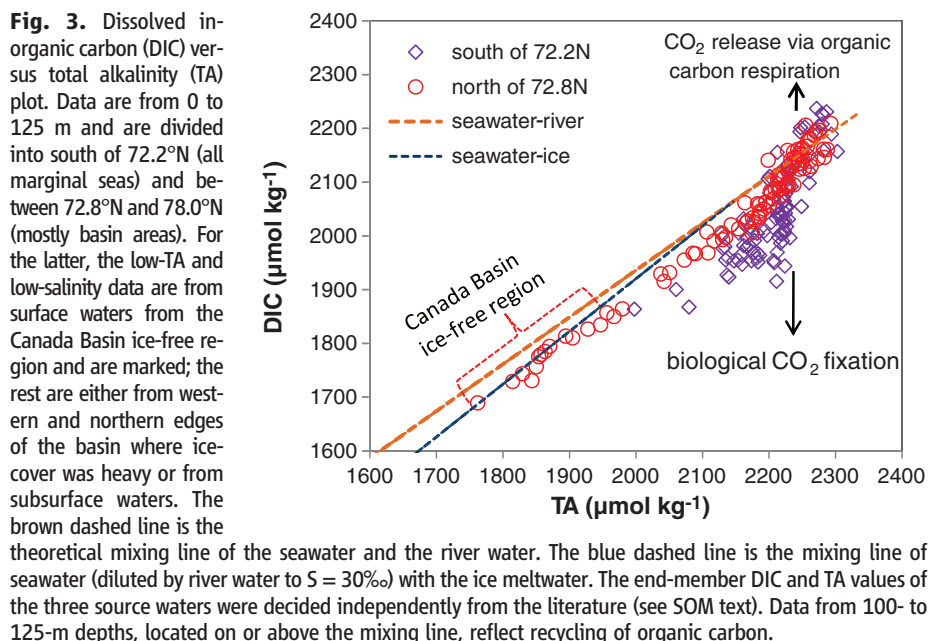


Fig. 4. Model simulations of factors influencing surface-water $p\text{CO}_2$ in the Arctic Ocean. The red arrows represent processes denoted by B (biology), C (cooling), R (river input), I (ice melt), W (warming), and A (atmospheric CO_2 invasion). The three black curves represent $p\text{CO}_2$ variation during the mixing between seawater and river water at these temperatures, whereas the three green curves represent mixing between seawater and meltwater at these temperatures. The source water, Bering Sea slope water at 200 m upwelled to the sea surface, has a $p\text{CO}_2$ of 420 to 572 μatm , which is reduced to 223 to 306 μatm by a biological CO_2 fixation of 95 $\mu\text{mol kg}^{-1}$. This water is diluted by river water to $S = 30\text{‰}$, and then by ice meltwater. The time course of CO_2 invasion into the surface water is simulated in the inserted graph (see SOM for details).

smallest algae in the Canada Basin, potentially favoring carbon retention and CO₂ release (19). However, it is difficult to predict the net role of increased stratification versus sustained wind mixing in these newly ice free regions. Wind-driven upwelling and mixing of nutrient and CO₂ rich subsurface water is expected or already has been shown to have a major impact on carbon dynamics and ecosystem in the Arctic (21) or Antarctic (22) marginal areas. Such an impact is likely small in the central Canada Basin where increased stratification is a dominant feature (fig. S3).

In addition, warmer temperatures likely would enhance microbial respiration of organic carbon, potentially reducing net community production (23). Moreover, increased warming also would promote permafrost thawing and coastal erosion in the Arctic continents, increasing riverine inputs of organic carbon (24, 25) that is subsequently metabolized to CO₂, thus further contributing to the elevated pCO₂. Finally, in future years, when sea surface temperature further increases after all ice is melted during summertime, as is predicted to occur within 30 years (9), the Arctic Ocean basin CO₂ uptake capacity would reduce further because of the warming effect on surface-water pCO₂.

The observed summer 2008 pCO₂ distribution suggests that, as ice continues to melt in the near future, the air-sea CO₂ flux will be enhanced in the Arctic Ocean owing to the increased area of open water and longer period of ice-free time. The increase in surface-water pCO₂ due to this CO₂ uptake would accelerate the negative impact of ocean acidification on pelagic and benthic ecosystems. However, the CO₂ uptake would quickly weaken

because surface-water pCO₂ will equilibrate with the atmosphere within a short time owing to a shallow mixed-layer depth, strong surface-water stratification, surface warming, and low biological CO₂ fixation.

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- We thank R. Wanninkhof, P. Yager, and N. Bates for discussions; J. Zhao for the salinity and temperature data; and H. Li and S. Gao for sample collection. Funding for the CHINARE CO₂ survey and subsequent synthesis was provided by the Ministry of Science and Technology of China (2009DFA22920), the Natural Science Foundation of China (40531007), and the U.S. National Oceanic and Atmospheric Administration (NA05OAR4311161 and NA09OAR4310078) and NSF (ARC-0909330). The measurements for primary production of phytoplankton were funded by a Korean Arctic Research project (PM09020). We also thank the Chinese Arctic and Antarctic Administration and the Polar Research Institute of China for their support. We are grateful to the captain and crew of icebreaker *Xuelong*.

Supporting Online Material

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9 March 2010; accepted 28 June 2010
Published online 22 July 2010;
10.1126/science.1189338
Include this information when citing this paper.

Microbial Biosynthesis of Alkanes

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Alkanes, the major constituents of gasoline, diesel, and jet fuel, are naturally produced by diverse species; however, the genetics and biochemistry behind this biology have remained elusive. Here we describe the discovery of an alkane biosynthesis pathway from cyanobacteria. The pathway consists of an acyl–acyl carrier protein reductase and an aldehyde decarbonylase, which together convert intermediates of fatty acid metabolism to alkanes and alkenes. The aldehyde decarbonylase is related to the broadly functional nonheme diiron enzymes. Heterologous expression of the alkane operon in *Escherichia coli* leads to the production and secretion of C13 to C17 mixtures of alkanes and alkenes. These genes and enzymes can now be leveraged for the simple and direct conversion of renewable raw materials to fungible hydrocarbon fuels.

Efforts to transition from fossil fuels to renewable alternatives have focused on the conversion of renewable biomass to “drop-in” compatible fuels and chemicals (1–3). Routes to renewable hydrocarbons are emerging, but to date, these require expensive chemical hydrogenation. Alkanes, observed throughout nature, are produced directly from fatty acid metabolites—for

example, as plant cuticular waxes (4), as insect pheromones (5), and with unknown functions in numerous organisms (6–9). Biochemical studies of alkane biosynthesis have focused on eukaryotic systems, with most evidence supporting a decarbonylation of fatty aldehydes as the primary mechanism (10, 11). Although *cer1* from *Arabidopsis thaliana* has been proposed as a candidate gene encoding this activity (12), no studies conclusively associate any gene with these biochemical activities.

Alkanes have been reported in a diversity of microorganisms, but some results remain con-

troversial (13, 14). From our assessment, the most consistent reports are from the cyanobacteria (9, 15, 16) and natural habitats dominated by cyanobacteria (17). Heptadecane is the most abundant alkane reported in these photoautotrophic bacteria, an observation consistent with the “*n* – 1” rule for alkanes, resulting from decarbonylation of typically even-numbered fatty aldehydes. Because cyanobacteria are phylogenetically homogeneous, with more than 50 sequenced genomes publicly available, our search began with comparative biochemistry and genomics. Eleven cyanobacterial strains of known sequence were photoautotrophically grown, and their culture extracts were evaluated for hydrocarbon production (Table 1). Ten of these strains produced alkanes, mainly heptadecane and penta-decane, along with alkenes, presumably derived from unsaturated fatty aldehydes. However, one strain, *Synechococcus* sp. PCC7002, did not produce alkanes. On the assumption that an alkane biosynthesis pathway was not present in *Synechococcus* sp. PCC7002, we undertook a subtractive genome analysis. The 10 genomes of the alkane-producing cyanobacteria were intersected, and the PCC7002 genome was subtracted by using a 40% sequence identity cut-off to select orthologs. Seventeen genes common to the 10 producing strains remained, and 10 of these already had assigned

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