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Photosynthesis

Carbon fix for a diatom

Ulf Riebesell

Water — the elixir of life — is often a scarce resource. Many land plants in warm and arid climates conserve water by temporarily closing their 'breathing tubes', the so-called stomata. This strategy has a drawback, however, in that it reduces the flow of CO_2 from the atmosphere into the plant, so lowering its photosynthetic capacity. To solve the dilemma, these plants have devised a mechanism to optimize CO_2 uptake. The key component is a CO_2 storage and transport compound that contains four carbon atoms and gives this process its name — the C_4 pathway. On page 996 of this issue[1], Reinfelder and colleagues show for the first time that a marine microalga, the coastal diatom *Thalassiosira weissflogii*, uses the same C_4 pathway as some of its terrestrial counterparts.

But why would a plant suspended in the ocean use a mechanism otherwise employed to conserve water? The answer is simple: just like a terrestrial plant holding its breath, an alga growing in the sea can suffer from a shortage of CO_2. Although inorganic carbon is abundant in the sea, 90% of it is in the form of bicarbonate ions (HCO_3^-). Less than 1% is present as CO_2, which is the form required by ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco), the enzyme primarily responsible for photosynthetic carbon fixation.

At typical concentrations of CO_2 in sea water, Rubisco operates far below its optimum. Algae usually overcome the problem by increasing the CO_2 concentration at the site of carbon fixation through the active uptake of CO_2 or HCO_3^-, rather than relying on diffusion[2]. Carbonic anhydrase, a zinc-containing enzyme that catalyses the conversion between CO_2 and HCO_3^-, is a central component of this so-called carbon-concentrating mechanism[3]. Reinfelder *et al.*[1] find the strongest expression of C_4 carbon fixation after applying stress to the carbon-concentrating mechanism by reducing CO_2 availability, lowering zinc concentrations (which is thought to reduce carbonic anhydrase activity) or directly inhibiting carbonic anhydrase. The implication is that C_4 fixation operates to feed Rubisco when the carbon-concentrating mechanism cannot.

The Rubisco carbon fixation and C_4 pathway are competitive processes, so it is essential that they are segregated in either space or time. Terrestrial C_4 plants such as sugar cane or maize have chosen the first solution. They fix CO_2 in a four-carbon molecule, malate, in one type of cell, then release it for fixation by Rubisco in another cell type (Fig. 1a, overleaf). Many succulent plants have opted for the temporal solution: their stomata open only at night, when water loss due to transpiration is lowest. CO_2 is bound in malate in the dark and is released for fixation by Rubisco in the day (Fig. 1a). One of the novelties of Reinfelder and colleagues' results is that both processes occur simultaneously in a single-celled organism. According to their data, C_4 carbon fixation may be confined to the cytoplasm, spatially segregated from the Rubisco process, which occurs in the chloroplasts (Fig. 1b).

Like other phytoplankton groups, diatoms can usually satisfy their carbon requirement entirely by way of the 'classical' carbon-concentrating mechanism[2,4]. So the findings of Reinfelder *et al.*[1] raise the intriguing question of why diatoms have

Nanotechnology

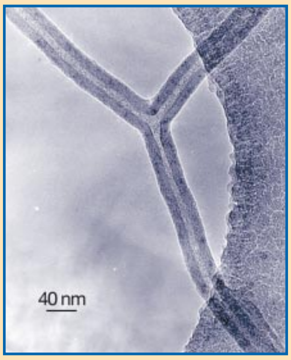
Crossroads in carbon

The smallest electronic device could be based on just one single molecule. Carbon nanotubes — flexible, hollow nanowires with versatile electronic properties — have already proven themselves as miniature diodes and transistors. In a paper in *Applied Physics Letters* (**77**, 2530–2532; 2000), C. Rao and colleagues from the Jawaharlal Nehru Centre for Advanced Scientific Research in India now demonstrate an efficient method for synthesizing a more advanced structure from carbon nanotubes: Y-junctions. Such structures could be used in new types of molecular devices.

Carbon nanotubes are known for their remarkable property to be either a semiconductor or a metal, depending on their diameter and the winding of the carbon sheet from which the nanowire is made. A sharp bend in a nanotube can actually be thought of as a junction between two nanotubes with different electronic behaviour and so provide a transition from semiconductor to metal over a distance of just a few nanometres. Such sharply bent tubes have already been used as molecular diodes. But scientists are always on the lookout for more complex structures based on carbon nanotubes. A Y-junction can be thought of as a connection between three different carbon nanotubes, which could form, for example, a microscopic metal–semiconductor–metal contact.

In previous attempts to construct complex junctions, two nanotubes have been crossed or Y-shaped templates have been used to laboriously mould a junction from a single nanotube. A simple method to produce carbon nanotubes is pyrolysis of organic molecules. In this process, carbon-containing molecules are decomposed at high temperatures, using appropriate catalysts. Rao and co-workers have finely tuned this method to create their Y-tubes, with a 70% yield. They decompose nickelocene, an organic molecule containing a nickel atom, along with another organic molecule, thiophene, at a temperature of 1,273 K. An electron microscope image of the product (shown here) reveals that the Y-shaped nanotubes are multi-walled and have an outer diameter of about 40 nanometres. The angle between the upper arms is almost 90°.

One of the current objectives in nanotube synthesis is to have control over the electronic properties of the end product. Although the electronic structure of these Y-junctions is not known exactly, initial measurements by Rao and co-



workers show that their Y-junctions can behave like diodes. This work is still preliminary, but it will inspire further studies into making three-point nanotube junctions with specific semiconductor–metal transitions. Such molecular junctions will be useful building blocks in the continuing miniaturization of complex electronic devices.

Liesbeth Venema

two means (the C_4 pathway and the carbon-concentrating mechanism) to the same end. But under what particular circumstances might C_4 carbon fixation cut in? Here's some speculation.

The C_4 pathway is of greatest advantage in plants requiring temporary storage of CO_2. This is obviously the case for plants in which Rubisco carbon fixation occurs partly or entirely when the stomata are closed. In aquatic environments, on the other hand, CO_2 and HCO_3^- availability is comparatively stable over time. Here, it is the photosynthetic fixation of carbon that is highly variable because of the unpredictable amount of light available to phytoplankton. Superimposed on the diurnal solar cycle, phytoplankton experience large fluctuations in light intensity, because they may be swept up and down in the water column by vertical mixing within the ocean surface layer. Temporary storage of CO_2 at times of low irradiance, and its release at times of increased photosynthetic carbon demand during high illumination close to the surface, could be used for intermittent supplementation of carbon from the carbon-concentrating mechanism. Interestingly, diatoms typically dominate the phytoplankton in turbulent waters with relatively deep mixing of the water column[5]. Using two processes, one to ensure a steady flow of CO_2 (the carbon-concentrating mechanism), the other to provide an extra dose during periods of high CO_2 use (C_4), may be part of a strategy that allows diatoms to flourish in a fluctuating environment.

From an evolutionary point of view, diatoms are the most likely phytoplankton group to have developed a C_4 pathway. As Reinfelder *et al.*[1] point out, diatoms underwent their main evolutionary diversification during an era when atmospheric CO_2 concentrations were relatively low. In contrast, most other groups of phytoplankton such as cyanobacteria, green algae and dinoflagellates evolved earlier[6], when there were higher levels of CO_2. Increased selective pressure for more efficient use of CO_2 may also be reflected in the higher CO_2 specificity of diatom Rubisco compared to that of more ancient groups[7]. If C_4 photosynthesis occurs in marine diatoms generally, its evolution predated that in terrestrial C_4 plants by a long time. So unravelling the evolutionary roots of C_4 photosynthesis in algae opens an exciting line of research.

To assess the implications of marine C_4 photosynthesis, we must question the importance of this process in the natural environment. Reinfelder *et al.* grew *T. weissflogii* under zinc concentrations that were far lower than would be experienced by coastal diatoms[8]. This may have placed unusual stress on the carbon-concentrating mechanism, thus inducing C_4 metabolism in their experiments.

If C_4 photosynthesis does account for a significant portion of marine carbon fixation, it will affect various aspects of marine ecology and biogeochemistry. For example, the presence of the C_4 pathway is likely to influence algal sensitivity to changes in CO_2 concentrations. As in terrestrial ecosystems, C_4 photosynthesis may therefore be a factor that is shaping species distribution and succession if it occurs in only some members of the phytoplankton. It could operate both on geological timescales and in response to the present rise in atmospheric CO_2 concentrations.

Furthermore, C_4 photosynthesis lowers the 'discrimination' against the heavy isotope ^{13}C during photosynthetic carbon fixation, so the organic matter produced through the C_4 pathway is comparatively less depleted in ^{13}C. If this pathway turns out to be quantitatively significant in the production of marine organic matter, it will necessitate a re-interpretation of carbon isotope ratios in both phytoplankton and ocean sediments. The latter are used as proxy data in various applications. Examples are in studying food-web structure and the marine carbon cycle, and in attempting to reconstruct CO_2 levels or phytoplankton growth rates in the past.

So much may (or may not) stem from the results of Reinfelder *et al.* At the very least, however, the existence of C_4 photosynthesis in diatoms demonstrates their tremendous flexibility in responding to environmental variability. ■

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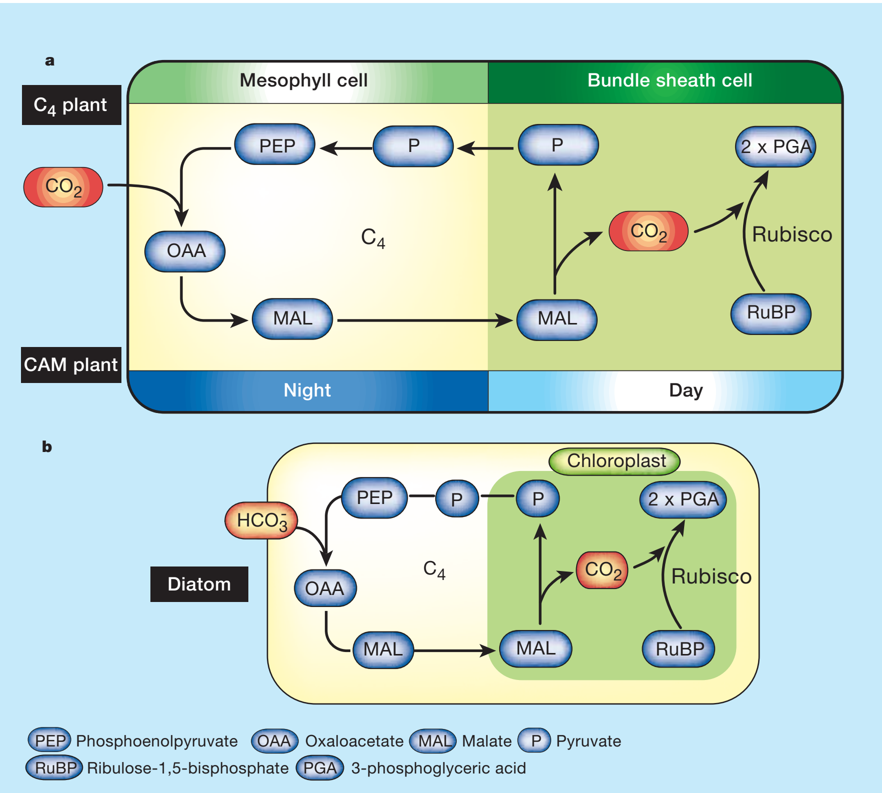

Figure 1 **Fixation of CO_2 in the C_4 pathway.** a, **In land plants the competitive processes of C_4 (left) and Rubisco (right) carbon fixation are segregated. Segregation can be spatial, as in sugar cane and maize; or it can be temporal, as in the reaction cycle, known as crassulacean acid metabolism (CAM), that occurs in many succulent plants.** b, **Equivalent events in the single-celled diatom *Thalassiosira weissflogii*, as proposed by Reinfelder *et al.*[1]. Here the two processes can happen simultaneously because one occurs in the cytoplasm and the other in chloroplasts. After further reactions, the product of the biochemical cycles shown here, PGA, can be used to produce fatty acids, amino acids or sugars.**

Daedalus

David Jones

David Jones, author of the Daedalus column, is indisposed.