Carbon

17

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Contents

Summary

All cyanobacteria are actually or potentially photolithotrophic, with the exception of a recently discovered non-auotrophic free-living diazotroph which is presumably a (photo-) organotroph. Photolithotrophy involves CO_2 assimilation by Form 1A or Form 1B Rubiscos with low affinity for CO_2 and a small discrimination between CO_2 and O_2 and, at present CO_2 levels, invariably involves an inorganic carbon concentrating mechanism (CCM). About half of the cyanobacterial strains tested are facultatively photo-organotrophic, a few of which are also facultative chemo-organotrophs; the rest are obligate photolithotrophs. In the natural environment the best-established cases of photo- or chemo-organotrophy are in symbioses of diazotrophic cyanobacteria with organisms that are already photosynthetic. The quantitative contribution of dissolved organic matter to otherwise photolithotrophically growing cyanobacteria is unclear. Extent cyanobacteria are involved in both biologically mediated calcification (direct role of the organism) and biologically related calcification (indirect role of the organism). The timing of the evolution of cyanobacterial CCM is unclear: the CCM probably evolved in low-CO_2 episodes in the late Neoproterozoic or the Carboniferous, with spread to all cyanobacteria in the already established major clades by horizontal gene transfer. Cyanobacteria may be the last surviving photolithotrophs as the sun emits more energy and (by whatever mechanism) there is a decreased greenhouse gas, including CO_2, content, of the atmosphere.

17.1 Introduction

Cyanobacteria are very important in the global biogeochemical carbon cycle, mainly through their autotrophic inorganic carbon assimilation coupled to oxygenic photosynthesis: essentially all free-living cyanobacteria are thus photolithotrophs, i.e. obtain energy from light and carbon from inorganic carbon (Table 17.1). They are especially important in aquatic

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Table 17.1 Trophic categories of cyanobacteria

Trophic category	Definition	Known distribution
Photolithotrophy	Energy from photons. Carbon from inorganic carbon	All but one known free-living cyanobacterium growing in the light. Illuminated cyanobacteria in symbiosis with non-photosynthetic hosts
Photo-organotrophy	Energy from photons. Carbon from organic carbon	A non-autotrophic free-living diazotrophic cyanobacterium. Illuminated diazotrophic cyanobacteria in symbiosis with photo-lithotrophic hosts. Minor contribution to free-living photolithotrophic cyanobacteria
Chemo-organotrophy	Energy and carbon from organic carbon	Diazotrophic cyanobacteria in light or dark in symbiosis with photolithotrophic hosts

For more detail, see text

ecosystems where they can be the dominant primary producers in some areas. Gadd and Raven (2010) suggest that not more than half of the >50 PgC per year of primary protection in the ocean, mainly in the plankton, is attributable to cyanobacteria, with almost all of the rest from oxygenic photosynthesis by eukaryotic organisms. Only a very small fraction of the primary productivity in the ocean results from chemolithotrophy plus non-oxygenic phototrophic autotrophs, 0.13% (Raven 2009) – 0.17% (Johnson et al. 2009). In inland waters cyanobacteria are very important in freshwaters, dominant in many carbonate lakes, but rare in hypersaline waters relative to eukaryotes.

The mechanism of inorganic carbon acquisition in cyanobacteria involves inorganic carbon concentrating mechanisms (CCMs), and is now known in considerable detail (Badger et al. 2006; Price et al. 2008), and will be discussed as far as it is relevant to the ecology of the organisms. There have been many recent advances in our knowledge and understanding of the spatial and temporal variations in inorganic carbon concentration and speciation in natural water bodies, and these are discussed in the context of the range of inorganic transporters and the regulation of their expression. Little is known of the interaction of the cyanobacterial CCMs with the availability of other resources, even by the standards of the limited knowledge available for eukaryotic algae (Giordano et al. 2005; Raven et al. 2005), and the range of required additional knowledge is indicated.

Cyanobacteria also occur in symbiosis with non-photosynthetic organisms (e.g. fungi, sponges: Chap. 23) where they supply all the inorganic and energy needs of the symbiosis (Table 17.1). In some cases the cyanobionts also fix N_2. Among the points considered are the contribution of these symbioses to global, and local, primary productivity.

While most of the organic matter generated in photosynthesis in cyanobacteria is retained by the cells, there is significant loss of not only respiratory CO_2 but also a range of organic molecules of a variety of sizes, from glycolate to transparent exocellular polysaccharides. Such losses are in part made up for in some cyanobacteria by the uptake of organic matter (Table 17.1). Among the topics discussed in the paper are the extent to which such uptake could permit sapro-organotrophic growth. While there are indications that one free –living cyanobacterium obtains all its organic matter from external organic matter, it is in diazotrophic symbioses with photosynthetic organisms that such growth using organic carbon is best (if still incompletely) understood, both in terms of mechanisms and of contributions to global carbon flow, as discussed in the paper.

A further aspect of the use of carbon in extant is the role of cyanobacteria in producing calcium carbonate deposits. In most cases it seems that the mineral is associated with organic materials produced by the organisms rather than through the direct intervention of the living organisms. The paper considers this calcification by cyanobacteria in both the benthic (e.g. stromatolites) and planktonic environments.

Finally, the evolution of carbon metabolism in cyanobacteria is considered. The evolution of CCMs and of calcification is considered in relation to variations in the inorganic carbon concentration and speciation in natural waters.

17.2 Acquisition and Assimilation of Inorganic Carbon in Photolithotrophy

17.2.1 Inorganic Carbon in the Cyanobacterial Environment

The habitat with the greatest global inorganic carbon assimilation by cyanobacteria is the ocean (Table 17.2). Here the total inorganic carbon concentration is about 2.2 mol m^{-3} and a pH of about 8.2, with the concentration of the three main inorganic carbon species decreasing in the order $HCO_3^- > CO_3^{2-} > CO_2$ (Zeebe and Wolf-Gladrow 2001; see Table 17.3). Photolithotrophy is limited to the upper 100–200 m (Raven et al. 2000), and this is where cyanobacteria and eukaryotic oxygenic organisms can decrease the inorganic carbon concentration relative to the concentration deeper in the ocean, where there is net chemo-organotrophy based on organic substrates generated in the surface ocean. This surface drawdown occurs because primary productivity exceeds invasion by atmospheric CO_2 plus organic carbon recycling by respiration in the surface ocean, in part because some particulate organic carbon sediments out of the euphotic zone. The drawdown of inorganic carbon in the euphotic zone

Table 17.2 Inorganic carbon availability in major habitats occupied by photolithotrophic cyanobacteria (Based on Table 17.1 of Badger et al. (2006), modified using material from Sect. 17.2.1 and Cox et al. (1965), Raven and Samuelsson (1998) and Kühl et al. (2005))

Habitat	Common genera	Environmental characteristics	Inorganic carbon supply conditions
Oceanic plankton	*Prochlorococcus* *Synechococcus* *Crocosphaera* *Trichodesmium*	High light oligotrophic to low light higher nutrients. Tropical to (*Synechococcus*) polar	Inorganic carbon about 2 mol m^{-3}, pH 8.0–8.3; lower CO_2 solubility, pK_a values for the first and second dissociations of the inorganic carbon system, than for fresh water
Coastal marine plankton	*Synechococcus* *Oscillatoria* *Phormidium* *Trichodesmium*	Oligotrophic to eutrophic, depending on terrestrial inputs. Turbidity, dissolved material can limit light	As for ocean plankton, but more variable than in open ocean as a function of terrestrial inputs, upwellings and more intensive metabolism
Estuaries	*Anabaena* *Aphanizomenon*	Very variable in salinity, light, temperature and nutrients, leading to blooms on occasion	Inorganic carbon and pH vary with terrestrial inputs
Brackish non-estuarine plankton	*Aphanizomenon* *Anabaena* *Nodularia* *Prochlorothrix*	The Baltic Sea is the main example of a large brackish non-estuarine water body connected to the ocean	Inorganic carbon availability close to that of seawater near the connection to the North Sea. Salinity less than 3 g per kg in the Gulf of Bothnia and the Gulf of Finland, with lower inorganic carbon concentrations
Freshwater Non-bloom plankton	*Cyanobium* *Snethococcus* *Cyanothece* *Aphanocapsa* *Aphanothece* *Chroococcus* *Prochlorothrix*	Waters generally poorly buffered; nutrients from oligotrophic to eutrophic	Inorganic carbon and pH very variable seasonally and on a diel basis. Usually significant inputs of inorganic carbon from terrestrial catchment. HCO_3^- dominant with rapid photosynthesis
Freshwater bloom plankton	*Anabaena* *Aphanizomenon* *Microcystis* *Oscillatoria* *Spirulina*	Gas vacuoles, mixing and stratification can help create bloom conditions, resulting in high O_2 and pH and low inorganic carbon	Factors enumerated for non-bloom phytoplankton apply, but are accentuated under high density bloom conditions
Saline inland water plankton	*Aphanothece* *Euhalothece* *Halothece*	Salinity in excess of 3 g per kg. No cyanobacteria are able to grow in saturated brine	Inorganic carbon speciation in the most saline cyanobacterial habitats is altered more than in sea water relative to freshwater. Decreasing CO_2 solubility with increasing salinity
High-alkalinity Inland water plankton	*Spirulina* *Chroococcus* *Anabaenopsis* (*Oscillatoria* on sediments)	Relatively high to high ionic strength, high carbonate alkalinity	Inorganic carbon concentration can exceed 200 mol m^{-3}. pH up to 10.5
Marine coastal mats	*Microcoleus* *Symploca* *Schizothrix*	High light attenuation coefficient, diffusion limited so anoxia at night, high O_2 and pH and low inorganic carbon in the day; temperatures can be high	Steep opposing gradients of light, temperature, nutrients, inorganic carbon, O_2 and pH mean very variable conditions for regulation of inorganic carbon concentrating mechanisms
Hypersaline mats	*Aphanothece* *Microcoleus* *Halospirulina* *Halomicronema* *Oscillatoria* *Spirulina*	As for marine coastal mats	As for marine coastal mats
Hot spring mats	*Oscillatoria* *Chlorogloeopsis* *Synechococcus*	As for marine coastal mats	As for marine coastal mats
Terrestrial mats	*Crinalium* *Microcoleus* *Chroococcus* *Nostoc*	As for aquatic mats, with the added problem of desiccation	As for aquatic mats, with varying diffusive conductance to inorganic carbon in the gas and liquid phases depending on the degree of hydration of the mat

(continued)

Table 17.2 (continued)

Habitat	Common genera	Environmental characteristics	Inorganic carbon supply conditions
Geosiphon	*Nostoc*	Intracellular in a soil surface glomeromycote fungus	Net photosynthesis by the symbiosis involves transport of external inorganic carbon through the fungus to the *Nostoc*. Also some recycling of fungal CO_2 to the cyanobacteria
Cyanolichens	*Nostoc* *Calothrix* *Scytonema* *Gloeocapsa* *Gloeothece*	Mostly terrestrial, a few aquatic with periodic exposure to air. Cyanobacteria extracellular in fungal thallus, with cyanobacteria exposed to intercellular gas spaces in many cases	Cyanobacteria exposed to intercellular gas spaces rely on gas-phase diffusion of CO_2 to the cyanobacteria; in other cases inorganic carbon must move through the aqueous phase of the fungal thallus. Some recycling of fungal respiratory CO_2 to the cyanobacteria
Marine sponges	*Synechococcus* *Oscillatoria* *Synechocystis*	Cyanobacteria intra- or extra-cellular	Inorganic carbon supply to intracellular cyanobacteria involves movement through sponge tissue. Inorganic carbon supply to all cyanobacteria is aided by mass flow through the sponge driven by light-stimulated flagella activity. Some recycling of respiratory CO_2 from the animal to the cyanobacteria
Marine ascidians	*Prochloron* *Synechocystis* *Acaryochloris*	Cyanobacteria extracellular	Inorganic carbon supply from seawater and from animal respiration
Brackish plankton	*Aphanizomenon* *Anabaena* *Nodularia* *Prochlorothrix*	Major example of a large brackish, non-estuarine water body is the Baltic Sea	Inorganic carbon availability close to that in seawater near the connection to the North Sea; salinity less than 3 g per kg in Gulf of Bothnia and Gulf of Finland, with generally lower inorganic carbon concentration

Table 17.3 Some physicochemical attributes of carbon dioxide and other inorganic carbon species relevant to photolithotrophic cyanobacteria (Based on Table 5.1 of Raven (1984a) and Table 5.2 of Falkowski and Raven (2007))

Parameter	Value in freshwater	Value in seawater (35 g salt per kg)
Concentration of dissolved CO_2 in equilibrium with 40 Pa CO_2 in the gas phase/ mol m^{-3}	25.6 (5°C)	21.5 (5°C)
	18.3 (15°C)	15.4 (15°C)
	13.6 (25°C)	11.7 (25°C)
	10.6 (35°C)	9.3 (35°C)
pK_{a1} of the inorganic carbon system = $-\log([HCO_3^-]/[CO_2 + H_2CO_3])$	6.52 (5°C)	6.05 (5°C)
	6.42 (15°C)	6.05 (15°C)
	6.35 (25°C)	6.00 (25°C)
	6.31 (35°C)	5.97 (35°C)
pK_{a2} of the inorganic system = $-\log([CO_3^{2-}]/[HCO_3^{2-}])$	10.55 (5°C)	9.34 (5°C)
	10.43 (15°C)	9.23 (15°C)
	10.33 (25°C)	9.10 (25°C)
	10.25 (35°C)	8.95 (35°C)
Diffusion coefficient of $CO_2/m^2\ s^{-1}$	0.95×10^{-9} (0°C)	
	1.94×10^{-9} (25°C) (in gas phase, 1.04×10^{-5} (25°C))	
Diffusion coefficient of $HCO_3^-/m^2\ s^{-1}$	0.53×10^{-9} (0°C)	
	1.09×10^{-9} (25°C)	
Diffusion coefficient for $CO_3^{2-}/m^2\ s^{-1}$	0.41×10^{-9} (0°C)	
	0.80×10^{-9} (25°C)	

is greatest when other nutrients are most available, e.g. in areas influenced by riverine input, or by seasonal or permanent ocean upwellings. The inorganic carbon drawdown is much less in oligotrophic areas in the ocean, where there is a low rate of input of non-carbon nutrient elements, and a correspondingly low rate of output of particulate organic carbon by sedimentation.

Lest the impression is given that there is a solely a role for biologically-driven processes (the "Biological Pump") in determining the concentration and speciation of inorganic carbon in the euphotic zone, it is important to mention the "Solubility Pump". This Solubility Pump involves the greater solubility of CO_2 in cooler than in warmer water, so there is a tendency for invasion of CO_2 from the atmosphere into cooler water, and evasion of CO_2 from cooler water into the atmosphere (Raven and Falkowski 1999). This tendency for movement of CO_2 through the atmosphere from the tropical polar ocean to the polar surface ocean is amplified by downwellings of cooler high-latitude surface waters and upwellings into warmer low-latitude waters. Chen and Borges (2009), Doney et al. (2008), and Takahashi et al. (2009) give detailed accounts of the areal distribution of CO_2 concentration in the surface ocean, and the net fluxes of CO_2 between the surface ocean and atmosphere.

Smaller contributions to global primary are made by cyanobacteria in inland waters and on land. Freshwaters (salinity not greater than 3 g/kg water) and saline waters (salinity not less than 3) occupy approximately equal areas and volumes of inland waters (see Horne and Goldman 1994; Giordano et al. 2008). Cyanobacteria make significant contributions to primary productivity in all but the most acidic (Steinberg et al. 1998) and most saline (Chap. 15) of these

inland waters which support photolithotrophy, where eukaryotic algae are predominant primary producers. Cyanobacteria are particularly important in waters of high carbonate alkalinity (some over 200 mol-equivalents m^{-3}, which qualifies as saline) and pH (some over 10.5) (Talling 1965; Talling and Talling 1965; Talling et al. 1973; Melack and Kilham 1974; Melack 1979; Jones et al. 1998; Kompantseva et al. 2009), although diatoms are also important (Hecky and Kilham 1973). While cyanobacteria are generally held to not grow at low external pH values, Steinberg et al. (1998) report filamentous cyanobacteria growing in flooded lignite mine sites at pH 2.9, although picocyanobacteria were not found below pH 4.5. HCO_3^- would have been a very small fraction of the total inorganic carbon at these acid pH values, and especially at pH 2.9: CO_2 would have comprised more than 99.9% of the total inorganic carbon

Surface water bodies receive inputs of carbonate alkalinity from weathering on land (Berner and Berner 1996), as well as organic carbon and dissolved CO_2 in groundwater from terrestrial primary productivity. Organic carbon in soil water comes below-ground parts of plants and any above-ground plant parts that become mixed into soil, while the CO_2 comes from respiration of this organic carbon in soil, ground-water and the resulting surface water bodies. These inputs impact on the inorganic status of inland waters to a relatively greater extent than on the ocean, and result in the totality of inland waters acting as a CO_2 source to the atmosphere (Cole et al. 1994; Maberly 1996; Sobek et al. 2005a, b; Duarte et al. 2008). In the case of the Dead Sea (too saline to be a significant cyanobacterial habitat) with minimal allochthonous organic carbon inputs the present fivefold CO_2 supersaturation of surface waters relative to atmospheric equilibrium is apparently due to CO_2 release from aragonite precipitation (Barkan et al. 2001).

On land, using atmospheric CO_2 as the inorganic carbon source, free-living cyanobacteria and cyanolichens in which cyanobacteria are the only photobionts are important in some areas with periodic water availability, including some arid areas with only a short period of photosynthesis possible after early in the photoperiod before dew has evaporated.

17.2.2 Mechanisms of Inorganic Carbon Acquisition and Assimilation by Cyanobacteria

The essential features of carbon acquisition and assimilation in cyanobacteria are that they have C_3 biochemistry, i.e. the initial autotrophic carboxylase is the CO_2-assimilating Rubisco embedded in the Calvin-Benson-Bassham cycle. The Rubiscos in cyanobacteria are invariably Form I, i.e. with 8 large catalytic and 8 small regulatory subunits: usually it is Form IB but a few oligotrophic ocean cyanobacteria have Form IA (Badger et al. 2002; Scott et al. 2007). Regardless of the phylogenetic subgroup to which the Rubiscos belong, they are characterized by a high CO_2-saturated specific carboxylation rates (mol CO_2 mol^{-1} Rubisco s^{-1}) and a relatively low CO_2 affinity, CO_2/O_2 selectivity and capacity to discriminate between $^{13}CO_2$ and $^{12}CO_2$ (Badger 1980; Kaplan et al. 1980; Badger et al. 2002, 2006; Giordano et al. 2005; Tcherkez et al. 2006; Price et al. 2008; Raven 2009).

The kinetic characteristics of the cyanobacterial Rubiscos are such that diffusive entry of CO_2 from an air-equilibrium solution to Rubisco would give no, or negligible, net photosynthesis (Badger 1980; Kaplan et al. 1980; Scott et al. 2007). All cyanobacteria have inorganic carbon concentrating mechanisms (CCMs) which accumulate CO_2 to higher concentrations round Rubisco in vivo than in an air-equilibrium medium. Cyanobacteria take up both CO_2 and HCO_3^- from the medium into the cytosol across the cell membrane. CO_2 enters by diffusion through the lipid bilayer component of the membrane but mainly through protein channels and is converted, with OH^-, into HCO_3^- into HCO_3^- by an energized reaction on the outer surface of the thylakoid. HCO_3^- crosses the cell membrane by active transport. The cyanobacteria with Form IB Rubisco (β-cyanobacteria) have thylakoid-expressed genes that account for high- and low-affinity CO_2-based CCMs, while those with the Form IA Rubisco (α-cyanobacteria) only have the low-affinity CO_2-based CCM (Badger et al. 2006; Price et al. 2008). Similarly, β-cyanobacteria have a high-affinity HCO_3^- transporter and one or more low-affinity HCO_3^- transporters, while α-cyanobacteria only have a low-affinity HCO_3^- transporter (Badger et al. 2006; Price et al. 2008). The result is a higher concentration of HCO_3^- in the cytosol that in the medium. The active Rubisco of cyanobacteria is all in protein-coated bodies termed carboxysomes, as is one or more forms of carbonic anhydrase. The protein coat is permeable to anions, and the anion stoichiometry (with anionic charges rounded to integers) 1 $RuBP^{2-}$ and 1 HCO_3^- enter the carboxysome. There the HCO_3^- is converted by carbonic anhydrase to CO_2, which is, with 1 H_2O and 1 $RuBP^{2-}$, into 2 PGA^-. The 2 PGA^-, with the 1 OH^-, moves to the cytosol, where the 2 PGA^- are used in the remaining reactions of the Calvin-Benson-Bassham cycle to produce 1 $RuBP^{2-}$, used in another Rubisco carboxylase reaction, and the 1C in the reduced, neutral C product denoted 1 (CH_2O). The fraction of the 1 OH^- from the carboxysome that is equivalent to the inorganic C entering the cell as CO_2 is used in another round of energized conversion of CO_2 to HCO_3^- on the thylakoid, while the fraction of the OH^- equivalent to HCO_3^- entry across the plasmalemma is lost to the medium. This sequence accounts for charge and acid-base-balance, and the overall reaction is equivalent to the conversion of one external CO_2 to one (CH_2O).

The stoichiometry of this scheme does not take into account any leakage of CO_2 from the carboxysome, and also

assumes that the accumulation of CO_2 in the carboxysomes is sufficient to cause complete competitive suppression of the oxygenase activity of Rubisco. Neither of these assumptions is correct. How CCMs minimize leakage is still incompletely understood in quantitative terms: clearly there is a significant CO_2 permeability of the cell membrane because this is part of the involvement of external CO_2 in the CCM (Badger et al. 2006; Price et al. 2008). As for oxygenase activity of Rubisco, it is now clear that there is invariably residual oxygenase activity that is not suppressed by the CCM, and that there is an apparently unique means of metabolizing phosphoglycolate to sugar phosphates that is a mixture of the plant photorespiratory carbon oxidation cycle and the bacterial glycerate (tartronic semialdehyde) pathway, and they can also completely convert glycolate to CO_2 via glyoxylate, oxalate and formate (Eisenhut et al. 2006, 2008). A triple mutant lacking all three pathways of glycolate metabolism was lethal for growth at air levels of CO_2 (Eisenhut et al. 2008).

A final point about the cell physiology of cyanobacterial photosynthetic inorganic carbon assimilation is that the both Rubiscos (cyanobacterial Form 1A and cyanobacterial Form 1B) have relatively low discrimination between $^{13}CO_2$ and $^{12}CO_2$ compared to the Form 1B Rubisco in embryophytic plants and the Form 1D Rubisco in eukaryotic algae with their higher CO_2/O_2 selectivity, higher CO_2 affinities and lower CO_2–saturated specific reaction than the cyanobacterial enzymes (Tcherkez et al. 2006; Scott et al. 2007). Taking this into account, the carbon isotope ratio of organic matter in free-living cyanobacteria and the symbioses in which cyanobacteria supply all or almost all the organic carbon can, with other evidence, help to indicate the extent of leakage from the CCM and the extent of limitation by diffusion of inorganic carbon (Raven et al. 2002).

17.2.3 Regulation of the CCM

It is now clear that CCM expression in β-cyanobacteria is a function of the inorganic carbon concentration inside the cells, with a minor role for O_2 concentration, rather than the external concentration of CO_2 which regulates the CCM in the diatoms and green algae that have been tested (Badger and Price 2003; Giordano et al. 2005; Woodger et al. 2005; Badger et al. 2006; Hammer et al. 2006; Raven 2006; Price et al. 2008; Lieman-Hurwtiz et al. 2009). The α-cyanobacteria only have a low affinity CO_2-based CCM, and a low-affinity HCO_3^- based CCM: these are constitutively expressed (Badger and Price 2003; Badger et al. 2006; Price et al. 2008). The occurrence of acclimation of CCMs and of purely constitutive CCMs in, respectively, β- and α-cyanobacteria agrees in broad terms with the habitats in which the organisms are found (Table 17.1 of Badger et al. 2006).

In eukaryotic algae CCMs are regulated not just by the inorganic carbon availability but also by the availability of such other resources as PAR, N, P and Fe (Raven 1984a, b; Giordano et al. 2005; Raven et al. 2005; Xu and Gao 2009; Hu and Zhou 2010), as well as UVB (Giordano et al. 2005; Raven et al. 2008a; Xu and Gao 2009). For cyanobacteria the only other environmental factors that have been tested for effects on CCM expression are PAR and UVB and, among nutrient elements, Fe.

Beardall (1991) showed for *Anabaena* that low PAR irradiance decreases CCM expression relative to the light-saturated conditions usually used for work on CCMs, in a manner similar to that found in eukaryotic algae (Giordano et al. 2005). Raven et al. (2000) suggest that decreased expression of CCMs at low irradiances for growth could be related to the probably increase in energy cost for active transport per net C assimilated at low irradiances where leakage of accumulated inorganic C becomes a larger fraction of the gross inorganic C efflux. This contrasts with the constant ratio of oxygenase to carboxylase activity of Rubisco for given internal (intracarboxysome for cyanobacteria) CO_2 and O_2; while a decreased expression of the CCM at low irradiances would mean a lower internal CO_2:O_2 ratio and hence a higher energy cost for Rubisco oxygenase and glycolate metabolism, there could still be an energy saving relative to leakage from a more highly expressed CCM (Raven et al. 2000). Poza-Carrión et al. (2001) examined the effects of fluctuating irradiance, pH and inorganic C on photosynthesis in *Nostoc* sp., though not in the context of CCM functioning. Campbell and colleagues (MacKenzie et al. 2004, 2005a, b; Burns et al. 2005; MacKenzie and Campbell 2005; Burns et al. 2006) examined the influence of the acclimation state of the CCM and inorganic C availability in *Synechococcus elongates* on the stoichiometry and performance of the thylakoid reactions of photosynthesis. Later work (Brown et al. 2008) on *Trichodesmium* photosynthetic flux capacity and acclimation costs have not been extended from thylakoid reactions and Rubisco to the CCM. Again, the CCM is generally taken as a given here, and the focus is on the effects of the inorganic carbon condition on the thylakoid reactions.

Song and Qiu (2007) examined the effect of UVB on the CCM of *Microcystis aeruginosa*: while UVB altered the contribution of the different components of the CCM, there was very little change in the overall inorganic C affinity for CCM, although there were fewer carboxysome per cell. For eukaryotic algae there are several studies, with results for different species ranging from a lower sensitivity of the CCM than of the downstream reactions of photosynthesis to the reverse (Giordano et al. 2005; Raven et al. 2008a).

Fu et al. (2008) examined the effect of elevated CO_2 on the growth of Fe-replete and Fe-deficient cultures of the unicellular marine diazotroph *Crocosphaera*, and found that

added CO_2 increased the growth rate of Fe-replete but not of Fe-deficient cultures. Further work is needed to examine effects on components of the CCM.

17.2.4 CO_2 and pH Dependence of Photosynthesis and Growth

At least the β-cyanobacteria have the capacity to express CCMs that allow photosynthesis and growth to be saturated by CO_2 at well below the present (temperature-dependent) air-equilibrium concentrations, and even α-cyanobacteria are CO_2 –saturated for growth (cell division) at present air-equilibrium concentrations (Kaplan et al. 1980; Kaplan and Reinhold 1999; Palinska et al. 2002; Badger and Price 2003, 2006; Price et al. 2008; Fu et al. 2007). This does not prevent increased CO_2 from increasing photosynthetic rate and carbon per cell in marine *Prochlorococcus* and *Synechococcus* (Fu et al. 2007), and may also increase the excretion of dissolved organic carbon (Raven et al. 2005). The organisms used in these studies are filaments or unicells grown in suspension, and so have minimal boundary layers (~1–10 μm), especially if the medium in which the inorganic carbon affinity is measured is stirred. However, not all such organisms are in organic-carbon saturated for growth in their natural environment: an example is the unicellular marine diazotroph *Crocosphaera* , at least when growth is not Fe-limited (Fu et al. 2008).

Since larger organisms in water have thicker diffusion boundary layers, we would expect that cyanobacteria that form colonies (Beardall et al. 2009), or form photosynthetic symbioses with larger, non- photosynthetic organisms (Raven 1993, 1999; Usher et al. 2007) would have lower affinities for inorganic carbon expressed in terms of the inorganic carbon concentration in the bulk medium. An example that has been subject to intensive recent investigation is another marine diazotroph that is not inorganic carbon-saturated for growth in air-equilibrium seawater, the filamentous, often colonial (Beardall et al. 2009) planktonic *Trichodesmium* (Hutchins et al. 2007; Levitan et al. 2007; Ramos et al. 2007; Kranz et al. 2009, 2010; Levitan et al. 2010). It is not always possible to decide if the work was done on isolated filaments or on colonies of many filaments, but the outcomes of all of the growth experiments are similar. Work on freshwater planktonic non-diazotrophic cyanobacteria has involved *Microcystis aeruginosa* (Xu and Song 2007) and *Gloeotrichia echinulata* (Vuorio et al. 2009). For three strains of *Microcystis aeruginosa* the half-saturation concentration of inorganic carbon is less than 50 mmol m^{-3} and the maximum rate increases from an external pH of 7.0–9.0 (Xu and Song 2007), so the boundary layer effect does not make the colonies inorganic carbon limited in air-equilibrium solution. The study of Vuorio et al. (2009) used the difference in stable isotope ratio in organic matter in the *Gloeotrichia ecinulata* colonies relative to that of the inorganic carbon in the lake water in which the colonies grew. For both lakes examined the largest fractionation relative to source carbon was in the smaller colonies, consistent with a greater diffusive limitation resulting from of thicker boundary layers round larger colonies. Vuorio et al. (2009) did not report the inorganic carbon affinity of growth or photosynthesis.

In benthic habitats in the sea, inland waters and on land there are cyanobacterial films and microbialites. Significant attention has been paid to colonies of the filamentous, heterocystous cyanobacterium *Nostoc* in freshwaters and on land (Dodds et al. 1995; Gao and Yu 2000; Qiu and Gao 2001, 2002a, b; Gao and Zou 2001; Gao and Ai 2004; Li and Gao 2004; Sand-Jensen 2009; Sand-Jensen et al. 2009). We deal first with the aquatic examples, since this is the ancestral condition. Li and Gao (2004) examined the benthic colonies of *Nostoc sphaeroides* found in paddy fields, and found that the inorganic carbon affinity decreased with increasing colony size.

Raun et al. (2009), Sand-Jensen (2009), and Sand-Jensen et al. (2009) examined inorganic carbon acquisition by approximately spherical 10–50 mm diameter colonies of the aquatic benthic *Nostoc zetterstedtii* from soft-water lakes in Europe. The paper does not directly report the dependence of photosynthesis or growth on external inorganic carbon: there is a large accumulation of inorganic carbon within the colonies that complicates this relationship. Even on a whole colony basis the accumulation of inorganic carbon over the external concentration (≤1 mmol m^{-3}) is up to 150-fold: in the absence of estimates of the fraction of colony volume occupied by cells the intracellular concentration of inorganic carbon cannot be determined but since the filaments are largely confined to the peripheral 2 mm of the colony the intracellular concentration must be at least 1,500-fold the external value, i.e. to ≥1.5 mol $m^{-3,}$ if all the accumulated inorganic carbon is in the cells. Sand-Jensen et al. (2009) comment that accumulation ratio of inorganic carbon for unicellular or filamentous non-colonial cyanobacteria is 500–1,000-fold (Kaplan et al. 1980; Badger and Price 2003). The extracellular oxygen concentration within photosynthesizing colonies (Sand-Jensen et al. 2009) is less than for some bulky photosynthetic tissues (Raven and Larkum 2007) despite the lengthy diffusion path for oxygen efflux, presumably the result of the low photosynthetic rates. The main function of the colony in the carbon economy of the organism seems to be a major restriction on the loss of respiratory inorganic carbon in the dark, analogous to the Crassulacean Acid Metabolism in some vascular plants: the restricted access to the cells of external inorganic carbon (and other nutrients) is offset by recirculation of endogenous inorganic carbon. The observed, high natural abundance ratio of ^{13}C to ^{12}C of organic matter in the *Nostoc* relative to source

inorganic carbon is consistent with very little leakage from the accumulated inorganic carbon pool (Sand-Jensen et al. 2009). The colonies also have a very large package effect for absorption of photosynthetically active radiation which is essentially independent of colony size (Sand-Jensen et al. 2009; cf. Li and Gao 2004) meaning a small relative return per unit time in a given PAR field on the investment in photosynthetic machinery relative to smaller organisms (see Raven 1984a, b). Furthermore, there is a higher dark respiration per unit photosynthesis than in smaller cyanobacteria and a large allocation of photosynthate to extracellular matrix (Sand-Jensen et al. 2009). The photosynthetic and respiratory rates show that it must take several years for a colony to grow to 50 mm diameter; the correspondingly low mortality rate is consistent with the absence of invertebrate or vertebrate grazers (Sand-Jensen et al. 2009). Clearly the *Nostoc* colonies can compete with eukaryotic macroalgae as well as mosses and vascular plants.

The carbon dioxide dependence of photosynthesis and growth in terrestrial *Nostoc flagelliforme* mats have been investigated by Gao and Yu (2000) and Qiu and Gao (2001, 2002a): both processes are CO_2-limited at present atmospheric levels. The highest rates occur at intermediate water contents: at high water contents the rate is limited by diffusion of CO_2 through the surface water layer, while at lower water contents the rate is limited by desiccation effects on metabolism.

Microbial mats in saline waters dominated by cyanobacteria (*Calothrix crustacea* or *Lyngbya aestuarii*) or containing diatoms as well as a cyanobacterium (*Microcoleus chthonoplastes*) were studied by Rothschild and Mancinelli (1990) as models for stromatolites, using the ^{14}C-inorganic C technique. 2 mol m^{-3} dissolved inorganic carbon gives photosynthetic rates of 0.1–0.2 of the inorganic C-saturated rate for submerged mats, while present-day atmospheric CO_2 concentrations give rates about 0.01 of the CO_2-saturated rate for emersed mats; the CO_2-saturated rates are somewhat lower when measured on emersed mats than when measured on submersed mats, an effect more pronounced at low substrate concentrations. However, the rates here, especially at rate-limiting inorganic carbon concentrations, are under-estimates by 2–5-fold when based (as in Rothschild and Mancinelli 1990) on the bulk phase inorganic ^{14}C specific activity rather than that in the interstitial water in the mat (Revsbeck et al. 1981). Nevertheless, it is likely that cyanobacterial mats and stromatolites are not saturated with inorganic carbon is media with 2 mol m^{-3} inorganic C in equilibrium with the present atmosphere (Raven et al. 2008a).

The intertidal cyanolichen *Lichina pygmaea* is inorganic carbon saturated in both the present atmosphere and in stirred air-equilibrium seawater (Raven et al. 1990). The *Calothrix* cyanobiont is internal to the fungal hyphae and it is possible that the fungal component has a function other than allowing inorganic C diffusion; whatever the mechanism it results in a low discrimination among carbon isotopes (Raven et al. 1990). For terrestrial cyanolichens there are typically intercellular gas spaces on which the cyanobionts abut; these gas spaces are maintained inter alia by hydrophobins (hydrophobic proteins) in the cell walls, operating in a manner analogous to that of the internal cuticle in vascular plant (and many bryophyte) sporophytes (Honegger 1998; Dyer 2002; Raven 2002; see also Raven 1986, 1993, 2003). In these cases the affinity of the cyanolichen for CO_2 is similar to that of the isolated cyanobiont, with a relatively similar extent of carbon isotope discrimination, so that both in hospice and ex hospice a CCM is involved and there is not a major additional diffusion limitation in hospice (Cowan et al. 1992; Palmqvist 1993, 2000; Palmqvist et al. 1994; Maguas et al. 1995; Smith and Griffiths 1998). The terrestrial free-living cyanobacteria lack the hydrophobic surfaces that could permit gas-phase diffusion into mats in the manner found in lichens with gas spaces, thus accounting for the gas exchange and growth characteristics of *Nostoc flagelliforme* found by Gao and Yu (2000) and Qiu and Gao (2001, 2002a) that are indicative of significant diffusive limitation. Free-living cyanobacteria thus resemble cyanolichens lacking intercellular air spaces ion terms of inorganic carbon supply, and are analagous to hornworts, which are bryophytes with no gas spaces in their gametophytes but with, in many species, a CCM (Meyer et al. 2008).

A final example of host interactions with cyanobiont inorganic carbon acquisition is that of marine tropical and warm temperate shallow-water sponges, where among the many archaeal, bacterial and eukarytic microbial associates are three clades of mutualistic photosynthetic cyanobacteria (Taylor et al. 2007; Usher et al. 2007; Lemloh et al. 2009). Raven (1993, 1999, 2003) cites evidence that, unlike non-symbiotic sponges which have similar rates of flagella-induced water flow through the organism in light and dark, sponges with photosynthetic cyanobionts have several-fold greater rates of water flow through the symbiosis in the photophase than the scotophase. This is consistent with the water flow supplying respiratory oxygen and particulate organic matter, and removing carbon dioxide and other excretory products, and egesta, in non-symbiotic sponges, but predominantly supplying inorganic carbon and other nutrient elements in the sponges with sufficient cyanobionts to provide most of the of the organic carbon needed by the symbiosis. Provision of inorganic carbon throughout the sponge is needed in view of the role of silica in dispersing photosynthetically active radiation within the organism (Brummer et al. 2008). The small discrimation between carbon isotopes in cyanosponges is consistent with some diffusion limitation of inorganic C supply and little leakage of inorganic C from pool accumulated in the cyanobiont by the CCM (Raven et al. 2002). However, more data are needed, for example of

the kind provided by Sand-Jensen and Pedersen (1994) for the freshwater *Spongilla lacustris* with *Chlorella* (Trebouxiophyceae: Chlorophyta) symbionts, where saturation of photosynthesis requires a higher concentration of inorganic carbon than occurs in air-equilibrium lake water. Sand-Jensen and Pedersen (1994) commented that none of the freshwater green algal-phagotroph symbioses examined can use HCO_3^-, and that *Spongilla lacustustris* grow faster in rivers than in lakes, suggesting that external water flow is important in supplying metabolic substrates for photosynthesis and phagotrophy and removing waste products.

The measurements of almost instantaneous effects of varied inorganic carbon supply on photosynthetic rate do not allow acclimation. Growth with different inorganic carbon supplies does show acclimation. However, no experiments have been made using long-term growth (of the order of 1,000 generations) of a cyanobacterium at varying inorganic carbon concentrations of the kind performed with *Chlamydomonas reinhardtii* to investigate the possibility of genetic adaptation (Collins and Bell 2004).

Many cyanobacteria are able to grow photolithotrophically at high pH e.g. in carbonate lakes. The maximum pH at which net photosynthesis can occur is defined by the pH compensation value (the highest pH that can be achieved in a pH drift experiment) (Allen and Spence 1981; Maberly 1983; Maberly and Spence 1983), which ideally corresponds to the compensation CO_2 concentration (the steady-state CO_2 concentration achieved by photosynthesis in a limited volume of medium containing inorganic carbon) (Birmingham and Colman 1979). The pH compensation value has been criticized as an indicator of the mechanism of inorganic carbon assimilation, e.g. because the upper limit of attainable pH could be set by pH per se rather than inorganic carbon concentration and speciation (Hansen et al. 2007); however, it can still give very useful information (Maberly et al. 2009).

The CO_2 compensation concentration in aqueous medium for the free-living freshwater cyanobacteria examined is low, as expected for organism expressing a CCM (Birmingham and Colman 1979), as well as for the intertidal cyanobacterial lichen *Lichina* (Raven et al. 1990) and a number of terrestrial cyanolichens measured in air (Maguas et al. 1995). The pH compensation value is 9.74 for *Lichina* in seawater at 5°C (Raven et al. 1990), and higher for freshwater cyanobacteria, i.e. 10.44–11.67 for 19 strains of the planktonic colonial *Microcystis aeruginosa* at 24°C (Bañares-España et al. 2006) and 10.97–11.07 for the benthic colonial *Nostoc zetterstedtii* at 15°C (Sand-Jensen et al. 2009). For the terrestrial *Nostoc flagelliforme* submerged at 20°C in water with 3.3 mol inorganic C m^{-3} to mimic rainfall on the alkaline soil on which it grows the pH compensation value was 10.8 (Gao and Zou 2001). The high values for pH compensation in freshwater media than in seawater is presumably a function of the lower pK_{a1} and pK_{a2} of the inorganic carbon system in seawater, so that the equilibrium CO_2 concentration is lower in seawater than in freshwater for a given pH in the range mentioned above for a given initial inorganic carbon concentration and alkalinity (Table 17.3; Falkowski and Raven 2007).

An extreme case of freshwater cyanobacterial exposure to CO_2 in the laboratory was reported by Thomas et al. (2005), who showed that growth could continue in 100 kPa (about one atmosphere) CO_2. The equilibrium concentration in solution at 25°C is 34 CO_2 mol m^{-3} (see Table 17.3). By contrast, the CO_2 concentration in a soda lake with 200 mol equiv m^{-3} carbonate alkalinity and pH 10.5 is only 0.8 mmol m^{-3} at 25°C, assuming sea-water salinity (Sect. 17.2.1; Table 17.3).

17.3 Acquisition and Assimilation of Organic Carbon for (Photo)Organotrophy

17.3.1 Organic Carbon in the Cyanobacterial Environment

Aquatic environments have a wide range of dissolved organic carbon compounds from terrestrial inputs, loss of organic carbon from growing primary producers, autocatalytic (including apoptotic) cell death, the influence of viral and other pathogens on organisms, and decomposition of dead particulate organic matter; many of these compounds are intractable to both biological and physicochemical processes and hence are very long-lived (Hellebust 1974; Arnon and Benner 1994; Berner and Berner 1996; Fuhrman 1999; Hansell et al. 2004; Berman-Frank et al. 2007). The extent to which the saprophytic potential of those cyanobacteria which have transporters and assimilatory enzymes for a range of simple organic compounds are expressed is not clear, with even less information on more complex organic molecules (17.3.2). Diazotrophic cyanobacteria symbiotic in photosynthetic organisms have a limited photosynthetic capacity and use one or more organic compounds from the photosynthetic host (17.3.3).

17.3.2 Organic Carbon Acquisition and Assimilation in Free-Living Cyanobacteria

The two forms of organotrophy are photo-organotrophy (energy from light; carbon from organic carbon) and chemo-organotrophy (both energy and carbon from organic carbon): see Table 17.1. The only known case in which there has to be dissolved organic carbon assimilation by a free-living cyanobacterium is the recently discovered globally distributed but as yet uncultivated marine diazotrophic organism that lacks photosystem II, and hence oxygenic photosynthesis, and autotrophic carbon metabolism (Zehr et al. 2008).

Since this organism has photosystem I, and hence can presumably generate a proton gradient and generate ATP by cyclic photophosphorylation, it can function as do the Archaea and Bacteria with bacterio-/halo-/proteo-rhodopsin and the anoxygenic aerobic bacteria containing a photosystem I-like bacteriochlorophyll-based photosynthetic apparatus, and also lack autotrophic inorganic carbon assimilation (Raven 2009). All of these organisms can in principle produce more biomass from a given quantity of a given dissolved organic substrate than can organisms lacking energy-conserving photochemistry. In the light photochemistry can generate ion gradients used in solute transport and flagellar motility, and ATP usable in a wide range of endergonic biochemical and biophysical processes, all of which would otherwise involve respiratory energy transduction using organic substrates (Raven 2009). In the diazotrophic cyanobacterium lacking photosystem II, the photochemistry could also (as in heterocysts) generate a stronger reductant for use in diazotrophy than is produced in respiratory metabolism.

For other free living cyanobacteria, with the capacity for photolithotrophy, a distinction is drawn between those that are obligate photolithotrophs and those that can grow chemo-organotrophically (Droop 1974; Zhang et al. 1998; Zubkov 2009). Obligate photolithotrophy is a subset of obligate autotrophy, including obligate chemolithotrophy and, according to some authors, methanotrophy (Kelly 1971; Rittenberg 1972; Wood et al. 2004; Zhang et al. 1998). It is clear that obligate autotrophy does not necessarily mean that organic compounds cannot be taken up and incorporated during growth in the light on inorganic compounds, although there may not be an increase in growth rate as a result of the assimilation of organic compounds, even when photosynthetic energy supply limits the growth rate. For compounds with only C, H and O this is illustrated by the uptake of glucose by *Prochlorococcus* (Gomez-Baena et al. 2008) and fructose uptake by *Anabaena* (Ungerer et al. 2008). There is also the incidental entry of organic carbon in the capacity to use organic nitrogen as N-source (e.g. Mary et al. 2008; Zubkov 2009; see Martiny et al. 2009). An exception to organic carbon entry in the use of organic nitrogen is the use of an extracellular amino-acid oxidase with uptake of the resulting ammonium, but not the N-free (for an amino-acid with only one N per molecule) 2-oxo-acid, a mechanism found in several species of marine and freshwater cyanobacteria, including *Synechococus* (Bockholt et al. 1996; Wawrick et al. 2009), *Trichodesmium* (Mulholland et al. 1998) and *Synechocystis* (Schreik et al. 2007). For the use of external organic P compounds, much evidence supports the enzymic hydrolysis of phosphate esters outside the cells with subsequent uptake of the inorganic phosphate but not necessarily of the organic moiety (Whitton et al. 2005). However, Whitton et al. (2005) also suggest that uptake of the intact phosphate esters by cyanobacteria is also possible. Phosphonates, with C-P bonds, can be used by some cyanobacteria; they are taken up intact, so organic C also enters the cells (Dyhrman and Haley 2006; Dyhrman et al. 2006; Illykchyan et al. 2009). The restricted availability of phosphonates, the restricted distribution of phosphonate use among cyanobacteria, and the low C:P ratio in phosphonates relative to the Redfield Ratio atomic C:P of 106:1, mean that the global supply of organic C to cyanobacteria from phosphonates is limited, while the occurrence of phosphate ester uptake by cyanobacteria needs further investigation.

Zhang et al. (1998) point out that only about half of the cyanobacterial strains tested are capable of photoorganotrophic or, more rarely, chemoorganotrophic growth, almost invariable with a sugar (strain-specific) as the only acceptable substrate. Chemoorganotrophy is found in, for example, strains of *Nostoc, Plectonema* and *Synechocystis* (of which strain PCC6714 was the first cyanobacterium for which the complete genome sequence was available). Zhang et al. (1998) found a correlation between the occurrence of photo- or organotrophic growth on glucose in strains of these three genera and the occurrence of active influx of glucose and the presence of the *glcP* gene coding for a proton-glucose symporter. Transfer of the *glcP* into an obligately photolithotrophic strain of *Synechocystis* did not result in the capacity for photo- or chemo-oranotrophic growth, at least over more than a short period, even when added as a replicative plasmid (Zhang et al. 1998).

For strains of the heterocystous diaotroph *Anabaena*, Ungerer et al. (2008) examined two *Anabaena* strains, one with the capacity to grow photo- or chemo-organotrophically on fructose as well as photolithotrophically, the other not. Insertion of an ABC-type (i.e. directly ATP-using) fructose active transporter gene on a replicative plasmid into the strain incapable of photo- or chemo-organotrophic growth permits chemo-organotrophic growth, but only in the present of a regulatory gene, and does not permit photo-organotrophic growth of this strain. It is clear that the causes of the various trophic modes of cyanobacteria with respect to carbon and energy sources are not simple. It is also difficult to evaluate quantitatively the ecological and evolutionary significance of the capacity for photo- or chemo-organotrophic growth on a very restricted range of organic compounds in many natural environments, an exception being cyanobacterial diazotrophs, i.e. species of *Nostoc* and, it was thought, *Anabaena*, growing in symbiosis with photosynthetic hosts (Usher et al. 2007). Ungerer et al. (2008) suggest that free-living strains of *Anabaena* that can use fructose for photo- or chemo-organotrophic growth could be derived from symbionts; however, as Ungerer et al. (2008) point out, although it was thought that the diazotrophic symbionts of *Azolla* was *Anabaena azollae*, it is now believed that the true symbiont has not yet been cultured, and there are no known symbiotic

strains of *Anabaena.* Later work by Ran et al. (2010) shows that the *Azolla* symbiont (‘*Nostoc azollae*’) has significantly fewer genes in a smaller genome than in relatives capable of independent existence, and so is not capable of independent growth.

17.3.3 Organic Carbon Acquisition and Assimilation in Diazotrophic Cyanobacterial Symbioses with Photosynthetic Hosts

Diazotrophic cyanobacterial symbioses with photosynthetic hosts occur under the soil in cycads and *Gunnera*, so they clearly cannot photosynthesise (Tredici et al. 1988; Rai et al. 2000; Black et al. 2002; Black and Osborne 2004): Table 17.1. Even when they are illuminated to varying extents (cyanobacteria in cephalodia in lichens with photosynthate from green algal photobionts, marine diatoms with *Richelia*, freshwater diatoms with small nitrogen-fixing bodies derived from cyanobacteria, liverworts, hornworts and *Azolla* with *Nostoc*) they have a limited, or no capacity for photosynthesis (Steinberg and Meeks 1989; Rai et al. 2000, 2002; Kneip et al. 2007, 2008; Adams and Duggan 2008; Wouters et al. 2009; Ran et al. 2010): Table 17.1. In the cases examined, organic carbon from the photosynthetic host is supplied to the cyanobiont as sugars such as, in embryophytes, glucose, fructose or sucrose (Rai et al. 2000, 2002). There may be similarities to the form in which organic carbon is transferred from vegetative cells to heterocysts within a heterocystous cyanobacterium (Cumino et al. 2007).

17.4 Conversion of Dissolved Inorganic Carbon into Calcium Carbonate Minerals

The cyanobacteria lack of an endomembrane system of the kind found in eukaryotes, permitting both endocytosis and exocytosis of solutions and particles (Gadd and Raven 2010; Raven and Knoll 2010). This lack means that cyanobacteria are unable to exocytose any $CaCO_3$ produced in intracellular vesicles: intracellular calcification with subsequent externalization occurs in certain eukaryotes, e.g. coccolithophores and many foraminiferans (Gadd and Raven 2010; Raven and Knoll 2010). Such $CaCO_3$ deposition as cyanobacteria are involved in is precipitated outside the cells as biominerals and organominerals, with no evidence suggesting intracellular calcification (Raven and Giordano 2009; see Lee et al. 2004; Riding 2006, 2008). The distinction between biominerals and organominerals (Perry et al. 2007) is that biominerals are produced directly by organisms by precipitation using soluble substrates in biologically mediated calcification, while organominerals are affected by organic compounds in biologically related calcification, e.g. mineral particles trapped by stromatolites. “Affected by organic compounds” opens the way to “biomimetic” structures, e.g. that stromatolite structures may occur some distance from the organism producing the organic polymer occurs (Grotzinger and Rothman 1996; Grotzinger and Knoll 1999; Mcloughlin et al. 2008). This topic is revisited when considering the evolution of how cyanobacteria interact with inorganic carbon.

The present surface ocean is almost all supersaturated with respect to all of the major crystalline forms of $CaCO_3$, i.e. aragonite, calcite and high-magnesium calcite, although this supersaturation will decrease, and become undersaturation, with increasing anthropogenic CO_2 production (Doney et al. 2009). Some inland waters are also supersaturated with $CaCO_3$ (Arp et al. 1999; Dittrich and Obst 2004; Dittrich et al. 2004). Overall, photosynthesis and net primary productivity in aquatic habitats removes CO_2 from the water, regardless of the inorganic C species entering when intracellular acid–base balance has been the taken into account. This alters the inorganic C speciation around the cells, such that CO_2 and HCO_3^- decrease, as does H^+, while CO_3^{2-} and OH^- increase, so that the saturation status of the mineral phases of $CaCO_3$ is also increased. However, this is still insufficient to cause production of the mineral phase: this needs both nucleation sites and the absence or near-absence of inhibitors, e.g. phosphates, of crystal growth: Arp et al. (1999), Dittrich and Obst (2004), Dittrich et al. (2004). Kosamu and Obst (2009), and Obst et al. (2009) suggest that the surface of picocyanobacteria can act as a template that causes nucleation, accounting for “whiting” ($CaCO_3$ particles in the water body: Riding 2006; see Chap. 16), although in other case (alkaline salt lakes) extracellular polymeric substances, mainly produced by the cyanobacteria but not necessarily still associated with them, are involved (Arp et al. 1999). A similar sequence of events presumably occurs in the production of stromatolites in shallow subtropical seawater (Shark Bay, Western Australia: Konishi et al. 2001), thrombolites in a lake with seasonally variable salinity (Lake Clifton, Western Australia) and very large (40 m tall) microbialites in Lake Van (the largest soda lake in the world) in Anatolia, Turkey (Kempe et al. 1991; Benzerana et al. 2006). However, it must be borne in mind that at least present-day calcitic microbialites in inland waters relate to non-cyanobacterial algae.

17.5 Cyanobacterial Interactions with Inorganic Carbon in the Past

Cyanobacteria have existed for at least 2.4 billion years (Rasmussen et al. 2008; cf. Brocks and Pearson 2005; Mulkadjinian et al. 2006; Tomitani et al. 2006; Falkowski

and Raven 2007; Raven et al. 2008a, b; Shi and Falkowski 2008: see Chap. 2). Over that time there have been low CO_2 episodes in the Precambrian, as judged from icehouse episodes some 2.3–2.2, 0.75 and 0.6 billion years ago as well as in the Phanerozoic (see Giordano et al. 2005; Kopp et al. 2005), as well, from non-icehouse evidence, as an episode with rather less low CO_2 some 1.3–1.4 billion years ago. In the Carboniferous about 300 million years ago there is evidence not just of glaciations and, though a number of proxies, low carbon dioxide as well. In the late Neogene, including the Pleistocene glaciations, there is evidence of cold and glacial episodes and, in parallel, proxies for low CO_2 and, for the last 800,000 years, direct evidence of atmospheric CO_2 from ice cores. Raven (1997) and Badger et al. (2002) suggested that the cyanobacterial CCM evolved in the Carboniferous. By this time the major clades of cyanobacteria were established (Tomitani et al. 2006; Shi and Falkowski 2008), so the distribution of CCMs must have involved horizontal gene transfer (HGT). This also accounts for the occurrence of Form IA Rubisco in the α-cyanobacteria (Scott et al. 2007), though the occurrence of α-carboxysomes evolved in the α-cyanobacteria is presumably the result of evolution within the clade, with occurrence of α-carboxysomes in anoxygenic phototrophs apparently a result of HGT (Badger et al. 2002). Interestingly, CCM-specific genes are not specifically mentioned in the analysis by Shi and Falkowski (2008) of the stable core and the variable shell of genes in genome evolution of cyanobacteria.

However, there is also the possibility of evolution of CCMs in earlier low-CO_2 episodes (Giordano et al. 2005; Riding 2006; Raven et al. 2008a). Riding (2006) makes a case for the origin of CCMs in parallel with the onset of sheath calcification of cyanobacteria in time period 0.7–0.57 billion years ago. CCMs, by increasing the possibility of inorganic carbon drawdown with a decreased CO_2 compensation concentration and increased pH compensation value, can cause, or increase a pre-existing, local carbonate saturation and hence favour precipitation, provided there is a nucleation catalyst and an insufficient concentration of crystal growth inhibitor to prevent crystal growth. As with the earlier suggestion of a Carboniferous origin of CCMs, the major clades of cyanobacteria had been established by the late Neoproterozoic (Tomitani et al. 2006) so horizontal gene transfer is again required to account for the universal distribution of CCMs among photolithotrophic cells of cyanobacteria. In view of suggestions as to the occurrence of Snowball Earth (or Slushball Earth) episodes during these low-CO_2 episodes, it is helpful that there are now known fossils of micro-organisms, albeit with limited taxonomic resolution, from strata of this age confirming the continuity of a diversity of organisms through this time (Corsetti et al. 2003), a continuity that imposes restrictions on the spatial extent of a Snowball Earth.

Regardless of when the cyanobacterial CCM evolved, there is the problem of how the CCM was maintained over the lengthy (>100 million year) periods between low-CO_2 episodes (Raven et al. 2008a). Habitats such as stromatolites provide a potential low-CO_2 habitat in these high-CO_2 intervals (Raven et al. 2008a), and the invocation of HGT to explain the universal occurrence among cyanobacteria of a trait that evolved well after the origin of cyanobacteria potentially accounts for the spread of CCMs to all cyanobacteria in subsequent global low-CO_2 episodes and the present universal occurrence of CCMs in photolithotrophic cells of cyanobacteria. Raven et al. (2011) suggest that interactions of CCMs with other environmental factors which vary with water temperature could help to retain CCMs in high-CO_2 episodes. Turning from "when" to "whence", the relatively late evolution of CCMs in cyanobacteria is consistent with the re-use of proteins with functions other than in CCMs in producing the structures and catalysts used in the CCM (Raven et al. 2008a, b).

For the evolution of calcification by cyanobacteria, calcium carbonate deposits are always extracellular, and it has already been pointed out that the absence of an endomembrane system of the kind found in eukaryotes that allows externalization of particles formed in intracellular vesicles means that precipitation cannot have been originally. This limits the extent to which the organism can modify the calcification environment in a manner favouring calcification in habitats that are undersaturated with respect to any solid phase of calcium carbonate (Gadd and Raven 2010; Raven and Knoll 2010). Riding (2006) considers the origin of sheath calcification, a spatially specific kind of biologically mediated calcification in cyanobacteria in the Neoproterozoic in the context of the inorganic carbon environment and UV-B and the origin of the CCM. Stromatolites significantly predate widespread sheath calcification, though it must be borne in mind that the calcium carbonate in stromatolites (used broadly to include other microbialites) could originate from organisms other than cyanobacteria, or could even be abiogenic (Riding 2008; Raven and Giordano 2009; Gadd and Raven 2010). Phanerozoic stromatolites and their relationship to cyanobacteria are considered by Kah and Riding (2007), Riding (2008, 2009), and Oliveri et al. (2010): see also Breecker et al. (2010).

17.6 Cyanobacteria and Inorganic Carbon in the Future

Earlier in this article work on the effects of increased CO_2 to the levels predicted by the end of the present century, showing that some cyanobacteria (e.g. the marine picoplanktonic *Prochlorococcus, Synechococcus*) show no increase in growth rate (rate of cell division) in high CO_2 but an increase in

organic C per cell, while others (e.g. the marine diazotrophs *Crocosphaera* and *Trichodesmium*) show an increase in the rate of cell division with increased CO_2. As was also indicated earlier, these studies relate to the acclimation of extant genomes, not to the possibilities of genetic adaptation (cf. Collins and Bell 2004). This makes it difficult to predict what will happen to the properties, and regulation, of the cyanobacterial CCM during the 2100s, especially since there are a variety of methods for experimentally simulating the effects of increased CO_2 on aquatic photolithotrophy each with varying degrees of realism and technical difficulty (Rost et al. 2008; Gattuso and Lavigne 2009; Hurd et al. 2009; Schulz et al. 2009; Shi et al. 2009). The situation is made more difficult for cyanobacteria in their natural environment because there are several other environmental changes, e.g. increased temperature (addressed in relation to CO_2 increase in the study by Fu et al. 2007), altered availability of other nutrients (addressed in relation to Fe and its interactions with CO_2) and altered mixed layer depth and hence mean PAR: (see Finkel et al. 2010; Raven et al. 2011). There is also a relative lack of studies of the interaction of increased CO_2 with other environmental changes (discussed above), e.g. changes in nutrient supply (except Fe: Fu et al. 2007): other studies deal with effects of PAR (Beardall 1991) and UV-B (Song and Qiu 2007) on functioning of the CCM rather than effects of enhanced CO_2 for interacting with changed electromagnetic radiation. Here we know very little about acclimatory interactions between CO_2 increase and changes in other environmental factors, and nothing about genetic adaptation.

In the far distant future the increasing radiation output from the sun will eventually boil off the oceans, destroying the (photosynthetic) biosphere, then all life, well before the sun turns supernova. A decreased atmospheric content of greenhouse gases could delay the heat death of the (surface) biosphere. Lovelock and Whitfield (1982) considered the effects of such a reduction on the quantity of the major (in an oxygenated atmosphere) greenhouse gas CO_2 on the potential for photosynthesis in the context of C_3 terrestrial plants with their relatively high CO_2 compensation concentration and low in vivo affinity for CO_2. Caldeira and Kasting (1992) extend this to terrestrial C_4 plants with their lower CO_2 compensation concentration and their higher in vivo affinity for CO_2 and suggest that this mechanism could extend the life-span of the (photosynthetic) biosphere by a few 100 million years. Extending this to CCMs other than those of C_4 land plants, Raven et al. (2008b) speak of such prolongation of the life of the (photosynthetically driven) biosphere as "salvation through CCMs", noting that this is independent of how the CO_2 content of the biosphere is decreased: a Gaian feedback is not an essential part of the suggestion, although clearly some mechanism is needed. Further discussion on the end of the biosphere is to be found in Sherrat and Wilkinson (2009).

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Note added in Proof

The paper of Roberts et al. (2012) on the isolation and characterisation of carboxysomes from the α-cyanobacterium *Prochlorococcus* is relevant to Section 17.2.2. Roberts et al. (2012) isolated pure carboxysomes from *Prochlorococcus* MRD4, and found a novel shell protein CsoS1D which is shared with other α-cyanobacteria. The function of CsoS1D is suggested to relate to metabolite transfer across the carboxysome shell (Roberts et al. 2012); how this relates to the ecology of these marine cyanobacteria requires further investigation.

Work on the tricarboxylic acid cycle in cyanobacteria (Zhang and Bryant 2011) is relevant to the nature of obligate photolithotrophy in cyanobacteria (Section 17.3.2). An attractive hypothesis to explain the obligate photolithotrophy in many cyanobacteria is that, because they lack 2-oxoglutarate dehydrogenase, they have an incomplete tricarboxylic acid cycle and so have problems with the energetics of chemo-organotrophic and, perhaps, photo-organotrophic growth (Zhang and Bryant 2011). However, Zhang and Bryant (2011) found that the β-cyanobacteria, but not α-cyanobacteria, which they examined possess two enzymes (2-oxoglutarate decarboxylase and succinic semialdehyde dehydrogenase) which can substitute for 2-oxoglutarate dehydrogenase. The results of Zhang and Roberts (2011) have important implications for the functional basis of obligate photolithotrophy in cyanobacteria. The view that obligate photolithotrophy in cyanobacteria is a result of an incomplete tricarboxylic acid cycle due to the absence of 2-oxoglutarate dehydrogenase has been shown to only apply to *Prochlorococcus* and marine *Synechococcus* (Zhang and Bryant 2011). For all of other cyanobacteria two novel enzymes, 2-oxoglutarate decarboxylase and succinic semialdehyde dehydrogenase, catalyse the tricarboxylic acid cycle reactions, which are usually catalysed by 2-oxoglutarate dehydrogenase and succinyl-CoA synthetase (Zhang and Bryant 2011). These important results mean that the functional basis for obligate photolithotrophy in cyanobacteria other than *Prochlorococcus* and marine *Synechococcus* must be sought elsewhere than in an incomplete tricarboxylic acid cycle.

Raven et al. (2012) consider the evolution of inorganic carbon acquisition in cyanobacteria (and algae) in relation to the origins of the components of the metabolic pathways involved and the variations in atmospheric composition over the last 2.4 billion years (Section 17.5), emphasising the recent evidence for the freshwater origin of cyanobacteria (Sánchez-Baracaldo et al. 2005, Blank and Sánchez-Baracaldo 2010).

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