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The reef coral two compartment proton flux model: A new approach relating tissue-level physiological processes to gross corallum morphology

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ABSTRACT

A comparison of the equations for photosynthesis and calcification in reef corals suggests that the two processes compete for available inorganic carbon; yet reef corals exhibit simultaneous high rates of photosynthesis and calcification during daylight hours. Also, the extreme metabolic activity observed in corals at high irradiance requires a large net efflux of protons at sites of rapid calcification and respiration. Corals have resolved these problems through development of morphologies that separate the zone of rapid calcification (ZC) from the zone of rapid photosynthesis (ZP), with the fixed-carbon energy supply from the ZP being rapidly translocated to the ZC. Translocation of photosynthate from the ZP serves as a means of transporting protons to the ZC, where they are readily dissipated into the water column. Observations on the spatial relationship of the ZC and ZP, analysis of net proton flux, incorporation of photosynthate translocation coupled with an understanding of the importance of boundary layers (BL) leads to a unified hypothesis that describes the processes involved in coral metabolism. The proposed model is based on the observation that reef corals have evolved a wide range of morphologies, but all of them place the ZC between the ZP and the external seawater. This spatial arrangement places the BL in contact with the ZC in order to facilitate efflux of protons out of the corallum. Placement of the ZC between the ZP and the BL maximizes recycling of the metabolic products O_2 and HCO_3^-. Furthermore, this arrangement maximizes the photosynthetic efficiency of zooxanthellae by producing a canopy structure with the skeletal material in the ZC serving to absorb ultraviolet radiation (UVR) while scattering photosynthetically active radiation (PAR) in a manner that maximizes absorption by the zooxanthellae. The ZP is isolated from the water column by the ZC and the BL. Therefore ZP must exchange metabolic materials with the ZC and with the water column through the ZC and its overlying BL. The resulting configuration is highly efficient and responsive to irradiance direction, irradiance intensity, water motion and coral polyp morphology. The skeletons of corals are thereby passively modified in response to physical factors such as light and water motion regime. The model presents a unified theory of coral metabolism and provides explanations for many paradoxes of coral biology, including plasticity of the diverse growth forms and an explanation for coral skeletal growth response to ocean acidification.

Contents

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1. Introduction

A recent paper (Jokiel, 2011) describes the "proton flux hypothesis" which states that the decreasing calcification rate observed in corals under increasing conditions of ocean acidification can be attributed to higher [H^+] in the seawater. Increasing [H^+] in the water column will decrease the strength of the diffusion gradient which in turn will slow the efflux of H^+ through the boundary layer and slow the rate of calcification. The initial presentation of the hypothesis regarded the corallum as a "black box" and only considered the inputs and outputs through the boundary layer (BL). The purpose of the present paper is to expand these observations in relation to processes within the "black box" and to synthesize existing data into a corallum-based model. Previous studies have focused on the physiology of coral cells and tissues, without consideration of the immense complexity and diversity of corallum morphologies. The proposed unified model is intended to address the processes of photosynthesis, calcification, and translocation of photosynthate in relation to morphology, irradiance field, hydrodynamic environment and BL conditions of the intact corallum.

Reef corals are coelenterates formed by a surface body wall and a basal body wall that enclose a space called the coelenteron. Terminology used here follows that of Galloway et al. (2007). The surface body wall in contact with sea water consists of two tissue layers — an outer epidermis and an inner gastrodermis separated by a jelly-like substance called mesoglea (Fig. 1). Likewise, the basal body wall consists of the calicodermis and a gastrodermis separated by mesoglia. The coelenteron connects the polyps of a colony and opens to the external sea water through their mouths. The surface body wall epidermis contains nematocysts. The symbiotic zooxanthellae are located mainly within the cells of the gastrodermis in the surface body wall.

The zooxanthellae are photosynthetic and capable of providing all of the energy needed by the coral symbiosis (Muscatine et al., 1984). The basal wall consists of two cell layers: the cell layer adjacent to the skeleton is called the calicodermis. A layer of gastrodermis lies between the calicodermis and the coelenteron and separated from the calicodermis by mesoglea.

The discovery that calcification in reef corals is enhanced by light (Kawaguti and Sakumoto, 1948) led to development of models that attempted to explain the mechanisms involved. Over the past 50 years a number of observations, hypotheses and reef coral calcification models have been presented (reviewed by Allemand et al., 2011; Cohen and Holcomb, 2009; Gattuso et al., 1999). Goreau (1959) proposed that calcification is accelerated in light due to removal of CO_2 from calcification sites by photosynthetic zooxanthellae. This model requires placement of the zooxanthellae at or near the calcification sites, but they actually are located far from the site of calcification.

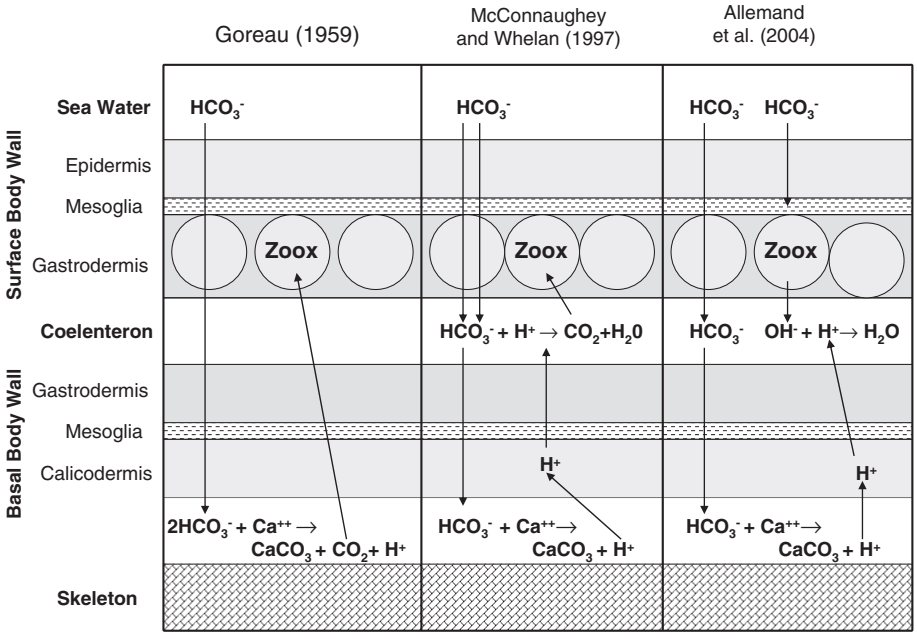

Fig. 1. Simplified diagram summarizing the conceptual relationships between various components of reef coral metabolism according to three prominent hypotheses describing photosynthesis and light-enhanced calcification (simplified from Allemand et al., 2004). Zoox = zooxanthellae.

Further, the proposed chemical reactions have not been supported by experiential data. The "trans-calcification" model (McConnaughey and Whelan, 1997) proposed that calcification in corals enhances photosynthesis by providing a source of protons that convert seawater HCO_3^- to CO_2 and H_2O, thereby supplying some of the CO_2 used in photosynthesis (Fig. 1). Allemand et al. (1998) suggested that OH^- produced by photosynthesis facilitate calcification by buffering the H^+ produced during calcification (Fig. 1). Several studies involved observations on a broader spatial scale. Pearse and Muscatine (1971) showed that carbon is fixed by zooxanthellae on the sides of a coral branch and then transported to the rapidly calcifying branch tip. Coral calcification rate is highest in branch tips where zooxanthellae are not present (Goreau, 1963; Goreau and Goreau, 1959; Pearse and Muscatine, 1971).

Calcification occurs in the space between the calicodermis and the skeleton through a presumed proton transfer process that increases the pH of the fluid to a point where $CaCO_3$ will crystallize out as aragonite (Allemand et al., 2004; Cohen and Holcomb, 2009; Cohen and McConnaughey, 2003). Calcification in the space between the calicodermis and the skeleton is believed to be controlled by a "proton pump" (Allemand et al., 2004; Cohen and McConnaughey, 2003; Furla et al., 2000a). Such a pump has been demonstrated in sea anemones (Furla et al., 2000b) and is probably present in corals as well. Cohen and Holcomb (2009) suggested that under conditions of increasing OA the corals must expend more energy to remove H^+ from the calcifying space in order to raise the pH of the contained seawater and convert the plentiful HCO_3^- to CO_3^{2-}. At high pH the CO_3^{2-} in the calcifying fluid combines with Ca^{2+} to form the $CaCO_3$ crystals of the skeleton. Up to 30% of the coral's energy budget may be devoted to calcification (Allemand et al., 2011).

In localized areas of the corallum undergoing rapid calcification, the gastrodermal layers are absent (Brown et al., 1983; Gladfelter, 1982, 1983; Tambutté et al., 2007). The result is a two-cell layer of very thin tissue that lacks zooxanthellae. Tambutté et al. (2007) conducted a detailed histological study of reef corals and concluded that tissues which calcify at the highest rates, or which initiate calcification, do not possess zooxanthellae. The contemporary four cell layer model of calcification (Allemand et al., 2004; Furla et al, 2000a) is shown in Fig. 2 compared to a modified version representing the two cell layers found in areas of rapid calcification. Previous models of calcification fall short in that they require placement of zooxanthellae near the site of calcification (Fig. 1) when in fact the rapidly calcifying locations lack the gastrodermis that contains the zooxanthellae (Fig. 2).

2. Background information

2.1. The role of carbonic anhydrase (CA) in coral metabolism

The CO_2, HCO_3^- and H^+ involved in coral metabolism are interrelated by the reversible reaction:

$$HCO_3^- + H^+ \leftrightarrow CO_2 + H_2O \quad (1)$$

The reaction described in Eq. (1) is accelerated by CA which facilitates carbon dioxide transport (Enns, 1967). The reaction rate of CA is among of the fastest of all enzymes, with a rate that typically is limited by the diffusion rate of its substrates. Coral tissues and zooxanthellae contain large amounts of CA (Graham and Smillie, 1976; Weis et al., 1989). CA undoubtedly plays a major role in controlling transport of CO_2 throughout the coral colony. Al-Horani et al. (2003a) identified three CA localities in corals. The first is CA bound to the membranes of the epidermal cells of the surface body wall, the second is CA bound to the membranes of the gastrodermal cells facing the coelenteron and the third is intracellular. Moya et al. (2008) found this enzyme to be localized in the calicodermis, which controls the precipitation of skeletal material. Wherever the conversion between CO_2 and HCO_3^- is very fast in comparison to the rate of diffusion a difference in HCO_3^-

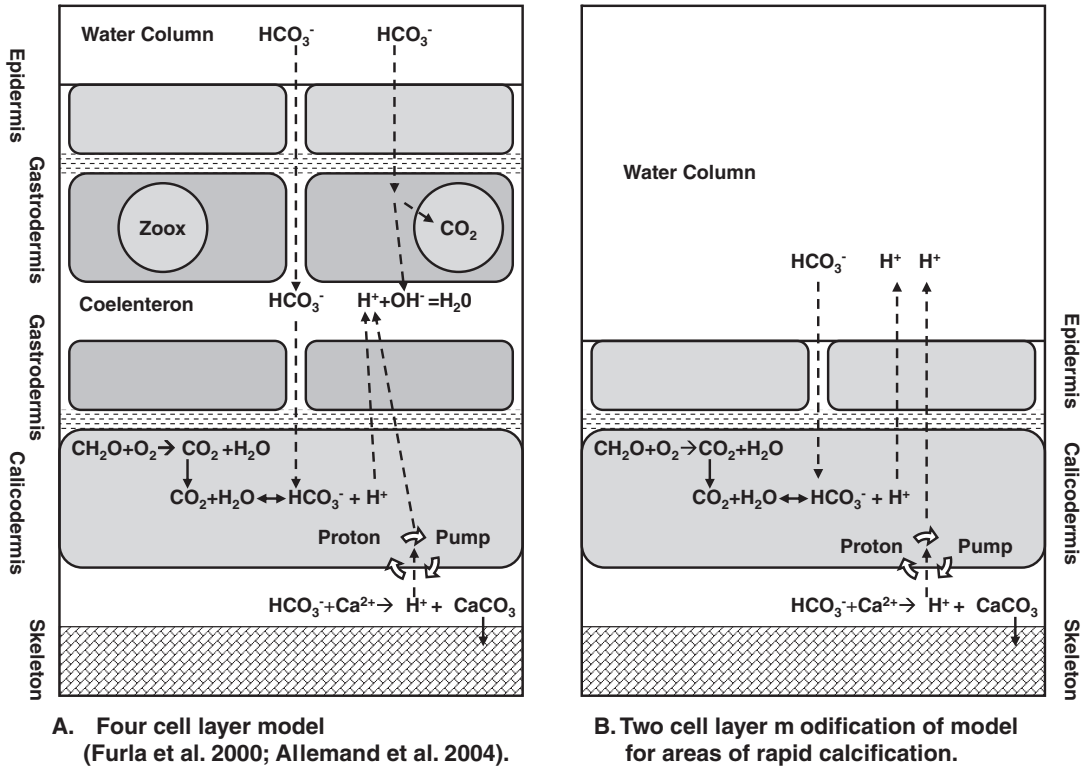

Fig. 2. A. Classic four cell layer model of calcification (Allemand et al. 2004; Furla et al., 2000a). B. Model modified to fit two cell layer structure of rapidly calcifying areas of the corallum as described by Brown et al. (1983), Gladfelter (1982, 1983), Tambutté et al. (2007).

concentration corresponding to the CO_2 tension difference will be established (Enns, 1967). In this case, HCO_3^- diffusion will supplement CO_2 that is being removed by photosynthesis.

2.2. Relationships between coral photosynthesis and calcification

The relationship of photosynthesis to calcification is complex in a coral, but can be reduced to several basic equations. To the extent that CO_2 is the substrate, photosynthesis can be represented as:

$$CO_2 + H_2O \leftrightarrow CH_2O + O_2 \quad (2)$$

Symbiodinium possess RUBISCO type II (Rowan et al., 1996) which has high oxygen affinity and uses CO_2 exclusively as a substrate. CO_2 occurs in very low concentration in sea water and in coral tissues. The CO_2 requirement is met by intracellular conversion of the abundant HCO_3^- through the action of CA as described in Eq. (1) within the plant cells. At the typical pH of seawater, most of the total inorganic carbon (C_T) is in the form of HCO_3^- (Horne, 1969). Bertucci et al. (2010) identified a H^+-ATPase "proton pump" in symbiotic zooxanthellae that appears to be involved in the acidification of the perisymbiotic space, which would promote conversion of the abundant HCO_3^- to CO_2. Where HCO_3^- is the primary source of inorganic carbon used in photosynthesis, as is the case of corals (Furla et al., 2000a; Weis et al., 1989), we can combine Eq. (1) and Eq. (2) into the balanced simplified equation:

$$HCO_3^- + H^+ \leftrightarrow CH_2O + O_2 \quad (3)$$

However, it is important to keep in mind that rapid interconversion between HCO^- and CO_2 is occurring and that balanced Eq. (3) combines the processes shown in Eq. (2) and Eq. (1). Respiration can be represented as the reverse reaction of Eq. (3). Consequently, areas where rapid respiration is occurring will be producing large amounts of H^+ as well as HCO_3^-.

The calcification process can be represented as:

$$HCO_3^- + Ca^{++} \rightarrow CaCO_3 + H^+ \quad (4)$$

Eq. (4) shows that the areas of a coral undergoing rapid calcification will precipitate the product $CaCO_3$, but must dissipate H^+ away from calcification sites. Eq. (3) and Eq. (4) indicate that both processes would compete for available HCO_3^- if they occurred in the same space. Further, areas of rapid photosynthesis will require a large net influx of H^+ while areas of high calcification and respiration will require a net efflux of H^+. Thus, photosynthesis and calcification will potentially compete with each other for inorganic carbon if they are not spatially separated, while they have opposite and thus complimentary requirements for H^+ flux.

2.3. Spatial relationships

The common Hawaiian coral *Pocillopora meandrina* (Fig. 3) is a typical branched coral species that represents a basic morphology that is most suitable in the visualization of several important spatial patterns as follows:

2.3.1. Spatial patterns of zooxanthellae distribution

The zooxanthellae-rich tissues of a typical branched coral colony are located in the deeper portions of the corallum, with very few of the photosynthetic zooxanthellae in the tissues of the branch tips. Numerous reports note the general lack of zooxanthellae in rapidly calcifying areas of a corallum (Al-Horani et al., 2005; Brown et al., 1983; Crossland and Barnes, 1974; Fang et al., 2004; Jaubert, 1977; Kajiwara et al., 1997; Lamberts, 1974; Marshall and Wright, 1998; Pearse and Muscatine, 1971; Santos et al., 2009; Tambutté et al., 2007). The zooxanthellae are abundant in the tissues on the sides of the branches of *P. meandrina*, but are largely absent on the growing tips (Fig. 3A). The deeper portions of the colony that contain high densities of zooxanthellae comprise an area that will be termed the zone of rapid photosynthesis (ZP).

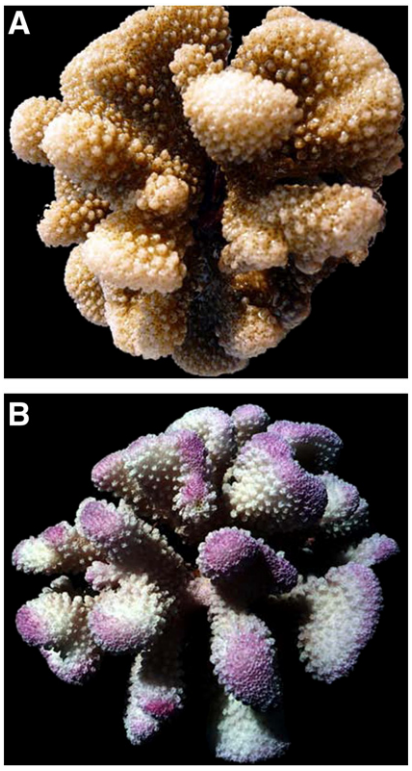

Fig. 3. A living colony of the reef coral *Pocillopora meandrina* (A.) compared to colony that was grown for 24 h in a 20 ppm alizarin dissolved in seawater solution and cleaned of tissue (B.). Note that the branch tips (ZC) that have few zooxanthellae stained heavily with the red dye, but not the deeper skeleton (ZP).

2.3.2. Spatial patterns of skeletal growth

Areas of rapid calcification take up alizarin red stain (Lamberts, 1974). A colony of *P. meandrina* that was grown for 24 h in 20 ppm alizarin red in sea water and then cleaned of tissue is shown in Fig. 3B. Note that the rapidly calcifying tips incorporated the stain into the skeleton, but not in the deeper portions of the colony that had dense concentrations of zooxanthellae. The outer part of the colony that calcifies rapidly will be termed the zone of rapid calcification (ZC).

2.3.3. Spatial hydrodynamic regimes

The structure of the coral skeleton itself creates friction with moving water and reduces flow through the branched colony (Fig. 4). The branch tips that form the ZC are exposed to high water motion (Fig. 4, black arrows) while the polyps within the colony (ZP) experience a very different environment with low water exchange (Fig. 4, white arrows). The layer of slower flowing seawater adjacent to the coral tissue influences flux of material between the coral and the water column by both advective and diffusive processes and is called the boundary layer (BL). Shashar et al. (1996) evaluated three types of hydrodynamic boundary layers over a coral reef. The diffusion boundary layer (DBL) is related to diffusion-limited processes such as respiration, photosynthesis and calcification at the tissue–water interface and has a spatial scale of a few mm. The momentum boundary layer (MBL) is closely related to the skeletal morphology of a single colony which controls water movement in the proximity of the colony and operates on a scale of cm. The MBL is generally thicker than the

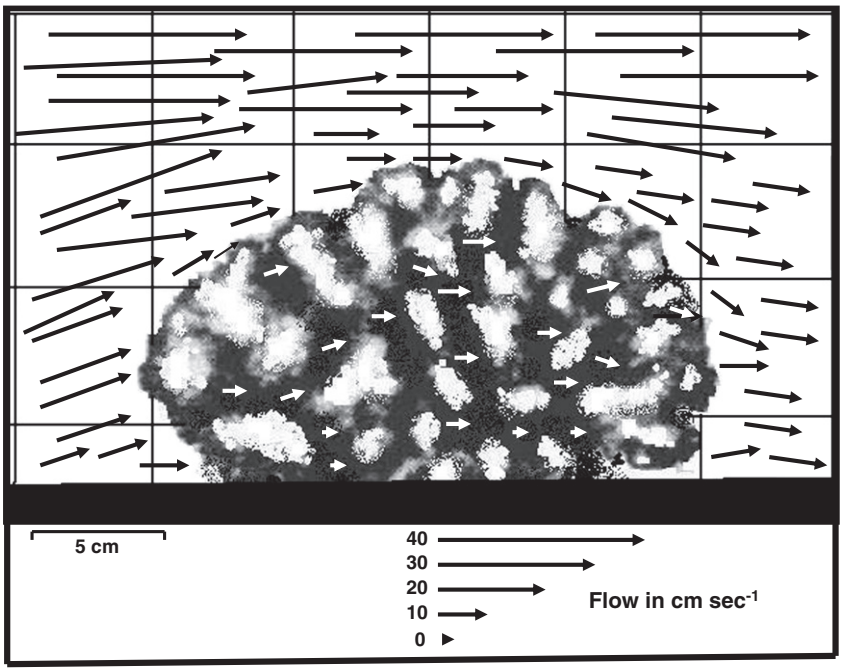

Fig. 4. Water flow around and through a typical branched colony (*Pocillopora meandrina*) in a flume (summarized from data contained in Chamberlain and Graus, 1975). White arrows represent flow between the branches of the colony.

DBL by an order of magnitude. The benthic boundary layer (BBL) controls the interactions of the reef with open seawater and reflects the impact of the overall coral community structure of the reef on material exchange. The BBL is generally on the order of 1 m thick and related to roughness height. However, at the tissue–water interface the DBL is of greatest importance. For most corallum morphologies material exchange between the coral and the water column is controlled by the DBL as modified by the MBL. In some cases, such as massive thickets of the branching reef coral *Acropora*, the BBL may also be important.

As we shall see, the proposed basic model can be applied over multiple levels of organization from tissues (DBL) to colonies (MBL) to massive coral structures (BBL). For purposes of simplicity the term "boundary layer" (BL) will be used for the initial discussion and will include the DBL, MBL and BBL insofar as they influence material exchange between a living reef coral and seawater. For the generalized case (Fig. 5) the relationship between the BL, ZC and ZP in *P. meandrina* is represented in a simplified diagram of three hemispheres. Note the placement of the ZC between the ZP and the BL.

2.3.4. Primary and secondary calcification spatial patterns

Branches are characterized by rapid growth at the tip (extension) followed by secondary calcification (accretion) on the sides of the branches (Gladfelter, 1982, 1983). Density changes in the skeletons of massive corals result from differing rates of extension vs. accretion under different conditions of temperature, irradiance and water motion that occur on a seasonal cycle to produce skeletal banding patterns (Barnes and Lough, 1993). Fig. 6 shows a longitudinal and a transverse section of a branch of the coral *P. meandrina*. The longitudinal section (Fig. 6A) shows low density skeletal material formed at the growing tip in the area of primary calcification (ZC) with dense secondary thickening of the branch occurring deeper in the branched colony (ZP). The transverse section (Fig. 6B) from near the base of the branch shows the original low density material laid down as primary skeleton (labeled P) and dense secondary calcified material (labeled S) that was deposited on the branch sides in the ZP. Primary–secondary calcification is

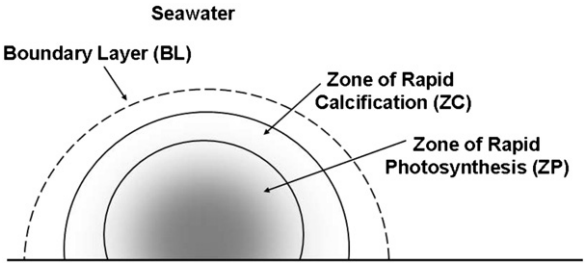

Fig. 5. Cross section of generalized hemispherical reef coral showing the relationship between zone of rapid photosynthesis (ZP), zone of rapid calcification (ZC) and the boundary layer (BL).

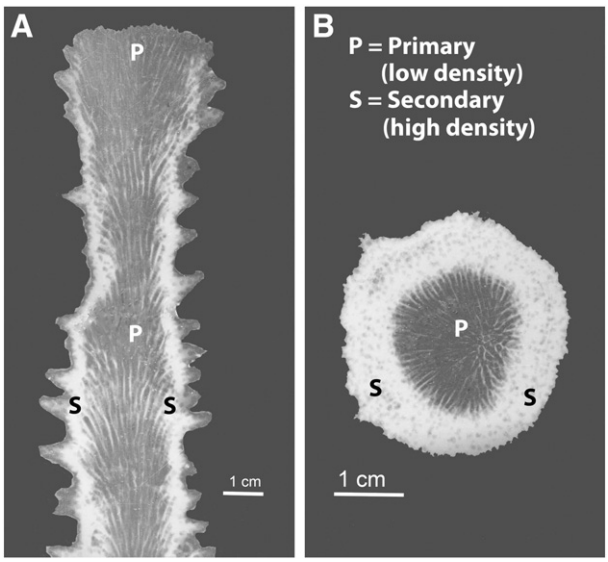

Fig. 6. X-radiograph of a branch of the reef coral *Pocillopora meandrina*. Longitudinal section (A) and transverse section (B) show low density material deposited as primary calcification (P) and high density material deposited as secondary calcification (S).

an important component of coral metabolism that must be included in a universal model.

2.4. Mechanisms controlling material flux

Flux of material between the ZC, ZP and the external water column is controlled by both active and passive processes. The transport of Ca^{++}, CO_2, HCO_3^-, O_2, and H^+ through the BL is limited by the physical processes of diffusion and advection (e.g., Kaandorp et al., 2005, 2011; Shashar et al., 1993, 1996). Kühl et al. (1995) measured strong pH gradients as well as O_2 gradients across the BL of corals. Hurd et al. (2011) showed that various temperate calcifiers show pH gradients within the diffusion boundary layers which appear to act as buffers to mainstream pH. For example, pH at the surface of the coralline algae was ~0.5 units higher in the light and ~0.35 units lower under darkness than in an ambient mainstream seawater. Tambutté et al. (1996) showed that transport of Ca^{++} across the epidermis and gastrodermis is passive, whereas transport across the calicodermis is active. Ca^{++} can diffuse from seawater to the coelenteron (Al-Horani et al., 2003b), but metabolic energy is needed for transport of Ca^{++} across the calicodermis into the enclosed space that forms the skeleton. Ca^{++} is transported over considerable distances within a colony with the direction of transport toward areas of maximum growth and calcification (Taylor, 1977). Likewise, photosynthate (CH_2O) is transported from areas of production toward areas of rapid calcification (Pearse and Muscatine, 1971; Taylor, 1977).

Translocation of metabolic material within the corallum has been demonstrated experimentally (Fine et al., 2002; Pearse and Muscatine, 1971; Rinkevich and Loya, 1983; Taylor, 1977). One mechanism for such transport was described by Gladfelter (1983). Polyps of the coral *Acropora cervicornis* are connected into a complex gastrovascular system, which is lined with flagellated cells that can move the gastrovascular fluid at velocities of more than 2 cm min^{-1}. This type of circulation system serves to exchange fluids between the ZP and the ZC.

Proton flux away from the calcification site must occur for calcification to take place (Allemand et al., 1998; Jokiel, 2011; McConnaughey and Whelan, 1997; Smith and Key, 1975). There is an agreement that protons are stripped from bicarbonate and combined with calcium ion to form carbonate at the site of calcification (Fig. 1). Moya et al. (2008) and Furla et al. (2000a) proposed movement of protons away from the calcification site through two cell layers (calicodermis and gastrodermis) into the coelenteron where they are titrated by OH^- produced by photosynthesis in the overlying gastrodermis. However, Brown et al. (1983), Tambutté et al. (2007) and Gladfelter (1982, 1983) have shown that rapidly calcifying areas of the coral (i.e. ZC) such as branch tips, septal margins, etc. have only two cell layers (calicodermis and epidermis separated by mesoglia) between the calcification site and the water column. These tissues are very thin and are missing the gastrodermis and the contained zooxanthellae. In this case the proton flux must be through the epidermal layers directly into the water column through the BL. OH^- derived from photosynthesis cannot be involved directly because the zooxanthellae are absent (Fig. 2B). The internal pH of coral animal cells is <6.0 (Venn et al., 2009), so there presumably is a strong diffusion gradient between the coral epidermis and the water column (pH approximately 8.1) and consequent rapid flux of H^+ out of the epidermis and into the water column. Regardless of the mechanism of H^+ transport and exchange within the corallum, proton flux out of the ZC into the water column can ultimately be limited by diffusive and advective processes in the BL (Jokiel, 2011).

Corals show diel oxygen fluctuations that range from supersaturation (373% air saturation) in the light to oxygen depletion at darkness (Shashar et al., 1993), suggesting that diffusion is the dominant process controlling O_2 flux throughout the corallum supplemented by transport through the gastrovascular system. During the day high oxygen tension due to photosynthesis will stimulate respiration (Mass et al., 2010). In fact, hyperoxia is required for rapid calcification in corals (Colombo-Pallotta et al., 2010). Respiration at night produces low oxygen tension in the tissues and limits rate of respiration and thus limits rate of calcification.

2.5. Balancing proton flux

A proton centered metabolic model is attractive because $[H^+]$ influences all biochemical reactions in the ZC and ZP. Production, uptake and movement of H^+ within the corallum influence localized pH within cells and tissues that control biochemical processes. Tracking the flow of protons between the calcification site and the water column is a valuable approach to understanding coral metabolism.

Total alkalinity (A_T) is a key concept to the understanding proton flux and is defined as the capacity of a solution to neutralize hydrogen ions. Coral calcification (Eq. (4)) lowers (A_T) within the corallum "black box". However, there is no change in (A_T) associated with organic carbon production (Smith and Key, 1975), so photosynthesis and respiration (Eq. (3)) can cause dramatic changes in pH within an enclosed area without changing the capacity of the fluid to neutralize H^+. In contrast, calcification rapidly diminishes the ability of the tissues to neutralize protons. A corallum must dissipate approximately 1 mol of protons into the water column for every mole of $CaCO_3$ precipitated as coral skeleton (Eq. (4)). Balance between the corallum and the water column must be achieved either by movement of H^+ through the BL into the water column or by movement of additional ionic inorganic carbon (mostly HCO_3^-) from the water column through the BL and into the corallum. The latter is undesirable because HCO_3^- is the major source of inorganic carbon for both photosynthesis and calcification and is in short supply. One additional mole of HCO_3^- would be needed to neutralize the excess H^+ for every mole of $CaCO_3$ precipitated in addition to the 1 mol of HCO_3^- needed as reactant plus the additional HCO_3^- needed for photosynthesis that ultimately supplies energy for calcification. Therefore a mechanism for rapid net efflux of H^+ from the corallum that does not consume HCO_3^- would be the most efficient means of maintaining a high rate of calcification while still maintaining a high rate of photosynthesis.

3. Synthesis of existing metabolic data into a model

There is a gradient in the density of zooxanthellae from the branch tip to the lower part of the corallum with a consequent gradient in the rates of calcification, respiration and photosynthesis (Goreau, 1959; Pearse and Muscatine, 1971). However, for a first approximation it is useful to simplify coral metabolism into a two compartment (ZP and ZC) model. Focusing on proton flux within the two compartments and between the compartments and the water column provides a unifying dynamic principle that greatly simplifies understanding of coral metabolism. Hence it was given the name "two compartment proton flux model".

3.1. Primary calcification, photosynthesis and translocation of photosynthate

The three dimensional hemispherical layers of the BL, ZC and ZP shown in Fig. 5 are reduced to a two dimensional diagram in Fig. 7. As noted in Section 2.1 the inter-conversion between HCO_3^- and CO_2 (Eq. (1)) occurs at an extremely rapid rate during periods of high metabolism due to abundant CA. Therefore the model can be simplified using reversible Eq. (3) to represent photosynthesis and respiration. The proper spatial relationship places Eq. (3) (photosynthesis) in the ZP in the inner hemisphere. Eq. (4) (secondary calcification) also is shown in the ZP. Eq. (4) (primary calcification) along with Eq. (3) (respiration) is shown in the ZC. The major patterns of flux of H^+, HCO_3^-, O_2 and CH_2O were added as arrows. In Eq. (4) the HCO_3^- and Ca^{2+} are reactants. The arrow in Eq. (4) represents the calcification reaction that occurs within the corallum and may involve a number of

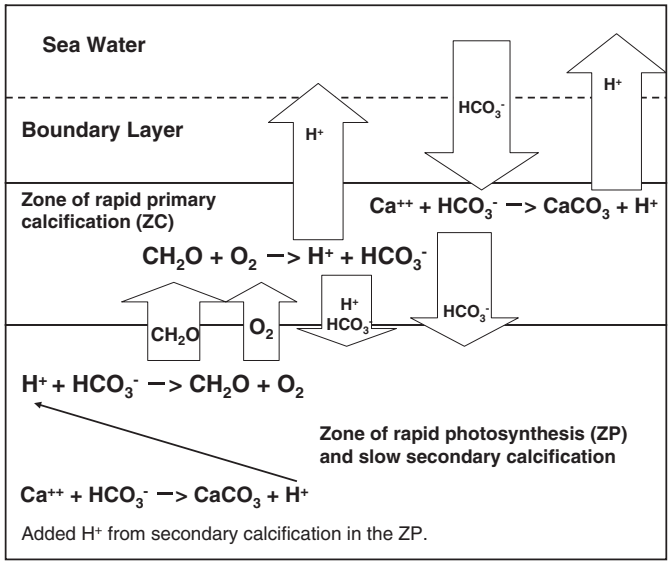

Fig. 7. Simplified model showing the spatial arrangement of the most important chemical reactions and flux of materials with an emphasis on protons. Note that only two equations (Eq. (3) and Eq. (4)) are needed to describe the model.

steps (e.g. Allemand et al., 1998; McConnaughey and Whelan, 1997). The products to the right of the reaction arrow are $CaCO_3$ and H^+. The $CaCO_3$ precipitates out of solution while the H^+ is a waste product that must be removed from the corallum if calcification is to continue. Fig. 7 shows a large efflux out of the ZC and through the BL into the water column. Eq. (4) shows that in order for a coral to continue rapid calcification, there must be continuous supply of the reactants HCO_3^- and Ca^{2+} to the corallum and a continuous net efflux of H^+ into the surrounding seawater (Moya et al., 2008).

Placement of the rapidly calcifying areas in the ZC adjacent to the BL facilitates dissipation of H^+ from areas of primary calcification. The protons being produced by secondary calcification are used in the production of photosynthate which is then translocated to the ZC. Respiration of the photosynthate produces ATP energy and releases the H^+ into the ZC cells adjacent to the BL. These protons supplement those being produced by primary calcification and further lower cellular pH to enhance proton efflux from the growing tips. Thus, translocation of photosynthate serves as a means of transporting waste protons as well as energy from the ZP to the ZC (Fig. 8).

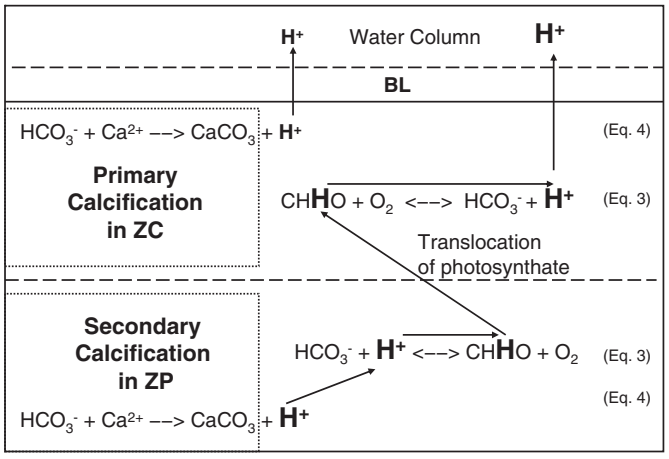

Fig. 8. Model shows protons generated by secondary calcification (H^+ in bold type) are transported from the ZP to the ZC where they join protons generated by primary calcification. These protons can either be dissipated with through the BL or be supplied to the ZP to support photosynthesis (Fig. 7) as needed to balance proton flux.

Important outcomes of this configuration are as follows:

3.1.1 The high oxygen flux required for respiration in the ZC is readily supplied as a by-product from photosynthetic production in the underlying ZP. Colombo-Pallotta et al. (2010) found that high calcification rate in corals depends on hyperoxic conditions. High oxygen concentration facilitates increased mitochondrial respiration in the ZC which, in turn, generates the large amount of ATP needed to support the rapid deposition of $CaCO_3$ in the ZC. During daylight hours much of the oxygen produced in the ZP is consumed by the high rate of respiration in the overlying ZC. Al-Horani et al. (2003a) found that gross photosynthesis was approximately seven times higher than net photosynthesis, indicating that respiration consumes most of the O_2 produced by the zooxanthellae. The respiration rate in light was approximately 12 times higher than in the dark. The coupling of gross photosynthesis and light respiration produces intense cycling of internal carbon and O_2. Thus hyperoxia is a key feature of reef coral metabolism that is managed very well by the coral under normal conditions though a variety of mechanisms. However, high oxygen tension can lead to oxidative stress and bleaching in corals exposed to abnormally high temperature and/or extremely high solar irradiance (Lesser, 2011).

3.1.2 High rates of respiration in the ZC produce large amounts of HCO_3^- that is available for calcification. Furla et al. (2000a) determined that the major source of C_T used in calcification is from respiration (70–75% of total $CaCO_3$ deposition), while only 25–30% originates from the external seawater.

3.1.3 The high flux of H^+ being generated in the ZC by calcification and respiration can be partially recycled and utilized in the underlying ZP, but most of the H^+ must be dissipated through the BL as efflux into the surrounding seawater. Placement of the rapidly calcifying areas adjacent to the surrounding sea water facilitates rapid dissipation of the H^+.

3.1.4 Primary calcification (extension) occurs in the ZC and secondary calcification (thickening) occurs in the ZP. Thus the two calcification processes occur in very different physical and chemical environments, so rates of accretion, crystallization pattern and density of skeleton differ.

3.1.5 Positioning of the ZC outside of the ZP results in an optimal photic environment for the zooxanthellae. The aragonite skeleton of the ZC absorbs damaging ultraviolet radiation (Reef et al., 2009), while transmitting and scattering photosynthetically active radiance (PAR) throughout the ZP (Enrıquez et al., 2005). Multiple scattering of the PAR by the skeleton in the ZC greatly increases absorption by the zooxanthellae in the ZP, leading to very high photosynthetic efficiency.

3.1.6 Placement of the ZC between the ZP and the water column allows for the vertical development of a stratified photosynthetic canopy without disruption of the ZC. If the ZP was located between the water column and the ZC, the coral would cease to calcify as the canopy became more highly developed. Jokiel and Morrissey (1986) report that net primary production as well as production efficiency in the coral *Pocillopora damicornis* (Fig. 9D) increases to a very high level with increasing canopy height.

3.2. Secondary calcification and photosynthesis

Once the basic framework is produced by rapid extension of the skeleton in the ZC, accretion continues to occur on the sides of the branches. This secondary calcification process occurs in the ZP and can continue for years. Hughes (1987) concluded that primary calcification allows rapid distal growth of branches which are subsequently strengthened by secondary calcification. The proposed model suggests

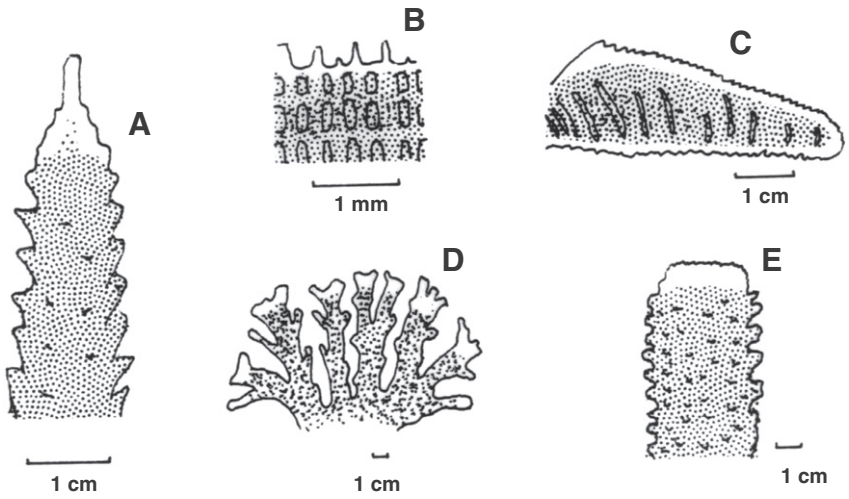

Fig. 9. Spatial relationship between the zone of rapid photosynthesis or ZP (shaded areas with dots representing zooxanthellae) and zone of rapid calcification or ZC (unshaded areas with no zooxanthellae) over a wide range of typical configurations found in reef corals: A. single branch from a colony of the perforate coral (*Acropora* sp.), B. cross section through perforate coral (*Porites*), C. cross section through corallum of solitary mushroom coral *Fungia scutaria*, D. branched imperforate colony (*Pocillopora damiconis*), E. single branch from imperforate branched coral (*Pocillopora meandrina*) showing verrucae on the sides of the branch which increase thickness of the boundary layer.

that secondary calcification has an additional value as a source of protons utilized in the ZP during rapid photosynthesis (Fig. 8).

3.3. Calcification in light and darkness

Photosynthesis ceases in darkness. Oxygen production stops and pH is lowered in the tissues due to respiration. As a result the reactions shown in Fig. 7 will largely be shut down during the night with minimal respiration and calcification. Kühl et al. (1995) report that in the light, photosynthesis resulted in a build-up of O_2 in the photosynthetic tissue of up to 250% air saturation and a tissue pH of up to 8.6, i.e. 0.7 pH units above the pH value of the overlying seawater, due to intense CO_2 fixation. In the dark, O_2 was depleted by the polyp and zooxanthellae respiration, and near anoxic (<2% air saturation) conditions were found in the coral tissue, which now had a low pH of 7.3 to 7.4 and consequently high $[H^+]$. Both O_2 and pH profiles demonstrated the presence of a 200–300 μ thick DBL that separated the coral tissue and the overlying flowing seawater.

4. Application of model at the corallum level of organization

4.1. Corallum morphologies

The generalized relationship shown in Fig. 7 is observed over a wide range of configurations and spatial scales (Fig. 9). Branched morphology creates an outer zone of calcifying branch tips exposed to turbulent water where rapid outward growth of the skeleton occurs and where solar irradiation is very high. Rapid photosynthesis occurs largely in the inner quiescent zone of the corallum. In branched colonies (e.g., Fig. 9A, D, and E) the ZC encompasses the outer tips of the branches. Perforate corals replicate the same spatial configuration but at a scale of mm rather than cm (Fig. 9B). Various combinations can be observed. Branched *Acropora* (Fig. 9A) combines the geometry shown in Fig. 9B and D. Corals with large polyps such as *Fungia scutaria* achieve layering of the ZC above the ZP by sandwiching dense populations of zooxanthellae in tissues between the septal plates (Fig. 9C), allowing rapid calcification to occur on the outer septal edges that project above the ZP.

At the upper end of the spatial scale (DBL) Kajiwara et al. (1997) studied large thickets of the coral *Acropora pulchra* and compared growth of outer white-tipped branches (ZC) to growth of brown-tipped branches (ZP) located deeper in the colony. Zooxanthellae concentration in the white-tipped branches was low compared to the dark-tipped branches. The white-tipped branches showed 3 times the skeletal weight increase and 14 times the linear extension increase of the brown-tipped branches. The authors concluded that white-tipped branches with a lightly-calcified skeleton expand the area covered by the coral colony while brown-tipped branches develop a heavily-calcified skeleton that strengthens the colony. Fang et al. (2004) showed higher concentrations of ATP in the white tip compared to the brown stalk, providing the ready supply of the energy needed for rapid calcification.

At the opposite end of the spatial scale (DBL) Al-Horani et al. (2005) employed microprobes and radioisotope technique to measure distribution of photosynthesis and calcification across polyps of the coral *Galaxea fascicularis*. The highest rates of photosynthesis occurred in the deeper parts of the calyx (ZP) that contained dense concentrations of zooxanthellae. The exert corallite septa that projected into the water column (ZC) incorporated more ^{45}Ca than the deeper portions (ZP) in both light and dark. Marshall and Wright (1998) report that there are essentially no zooxanthellae in the cell tissue covering the exert septa of *G. fascicularis* where calcium incorporation is highest. Therefore a wide range of morphologies from single polyps as well as complex colonial forms fit the general model, often in a fractal patterns (Vicsek, 1989) at different scales.

4.2. Plasticity of corallum growth form in relation to water motion and irradiance

From a topological point of view we can treat the myriad coral growth forms (Fig. 9) as simple hemispheres, with the hemispherical ZC encapsulating the ZP. The ZP is cut off from direct contact with the external seawater column by the ZC. The ZC can be highly porous to external seawater as in the case of loosely branched colony and less porous in tightly branched colonies. In perforate corals (Fig. 9B) and polyps (Fig. 9C) the ZP is isolated from the water column by the ZC. The ZC is isolated from the water column by the BL. Flux of materials at the tissue–water interface will respond in a classic hydrodynamic manner. The inner interface of the ZC exchanges materials with the ZP. The ZP contact with the outer seawater column is through the ZC, so influx and efflux of materials responds to changes in the chemistry of the ZC as well as conditions outside of the corallum.

The model as presented in Fig. 7 represents a cross section at a given point on the hemispherical corallum. Water motion and irradiance are not uniform over the surface. Coral reef environments show strong vertical and horizontal gradients of both water motion and irradiance. A simple diagram showing how variation in water motion and

irradiance can influence colony growth form is shown in Fig. 10 for a massive coral and a branched coral. The colonies of many massive and branching coral species become more flattened and plate-like with increasing depth (e.g. Graus and MacIntire, 1976; Jaubert, 1977; Roos, 1967) in response to submarine radiance distribution (direction and intensity). Growth along an axis diminishes with decreasing irradiance. The Hawaiian coral *Montipora capitata*, for example, is a highly polymorphic species that can display a full range of growth forms from massive to branched to plate-like within a single large colony in response to localized differences in irradiance (Fig. 11A). The colony in the figure lacks zooxanthellae in the growing branch tips (white color) and the outer growing margins of the plates. The mechanism behind this remarkable growth response becomes clear if we examine the results of Jaubert (1977) in studies of the coral *Synaraea convexa* (Fig. 11B) in relation to the proposed model. In shallow water, the zooxanthellae must avoid extreme levels of solar irradiance that would lead to photooxidation of photosynthetic pigments and develop dense concentrations deeper within the branched corallum where irradiance is optimal (Jokiel and Morrissey, 1986). Thus at high light intensity the colonies become hemispherical with branches lacking zooxanthellae at the tips. Irradiance is increasingly attenuated with water depth and the corallum flattens into plates that are oriented perpendicular to the axis of incoming irradiance. Encrusting and plate-like morphologies are simply modifications of the general hemispherical growth form with suppression of calcification along the vertical axis caused by encroachment of the ZP into the ZC (Fig. 10). Jaubert (1977) observed that at high irradiance the reef coral *S. convexa* grows into a branched morphology with tips that are free of zooxanthellae (Fig. 11). In deeper water the irradiance is diminished and the corals become plate-like, with the zooxanthellae occurring within 1.2 mm of the surface of the perforate corallum (Fig. 11B, "Platelike a type"). As light diminishes further with increasing seawater depth, the zooxanthellae became more concentrated into a layer of less than 0.4 mm of the surface of the skeletal framework (Fig. 11B, "Platelike b type"). Thus in low light environments the highest concentrations of zooxanthellae are found near or above the skeleton surface where according to the proposed model they would interfere with calcification by competing for HCO_3^- and disrupting H^+ flux. In such cases, growth along the vertical is impaired relative to horizontal growth. Calcification can only continue in the horizontal plane along the margins and underside edges of the plates where irradiance is too low to support zooxanthellae. Such modification of colony growth into a horizontal plate is advantageous because a flat surface (cosine collector) is the most efficient morphology for collecting such vertical down-welling irradiance. Furthermore, formation of a thin skeletal plate requires a minimal expenditure of energy. The massive skeleton found in turbulent shallow waters is not needed in quiescent deep environments. Santos et al. (2009) described the movement of zooxanthellae through the perforate skeleton of *M. capitata* (Fig. 11A). When flat plates with dense populations of zooxanthellae on the upper surface were overturned, the zooxanthellae migrated or were transported vertically through the perforate skeleton over a period of several days. The zooxanthellae occupied the colorless tissues of the former underside to re-establish the original configuration.

Venn et al. (2011) studied calcification in micro-colonies of the coral *Stylophora pistillata* that were grown on glass microscope slides. The small corals grew outward rapidly along the margins of the thin flat corallum, allowing observation and measurement of the calcification process under the thin spreading tissues. The tissues growing at the edge of the flat disk were lacking zooxanthellae and thus were transparent. The use of pH indicator dyes confirmed high pH conditions in the calcifying space under the calicodermis. The micro-colonies existed as flat two-dimensional plates with polyps in the center (ZP) and a rapidly growing margin (ZC) that lacked zooxanthellae. According to the proposed model the zooxanthellae rich tissue in the center of the disk-shaped corallum will slow the underlying calcification (secondary calcification) with rapid growth on the edges (primary calcification). Therefore we only see rapid growth along the edges of the "pancake" until slow secondary calcification in the center (ZP) can build enough vertical structure to allow the coral to go into the branching mode of this species with the ZC at the tips. Presumably the rapidly growing edges of the corallum lack gastroderm as well as lacking zooxanthellae. This pattern is typical of the early stages of a newly settled planula larva.

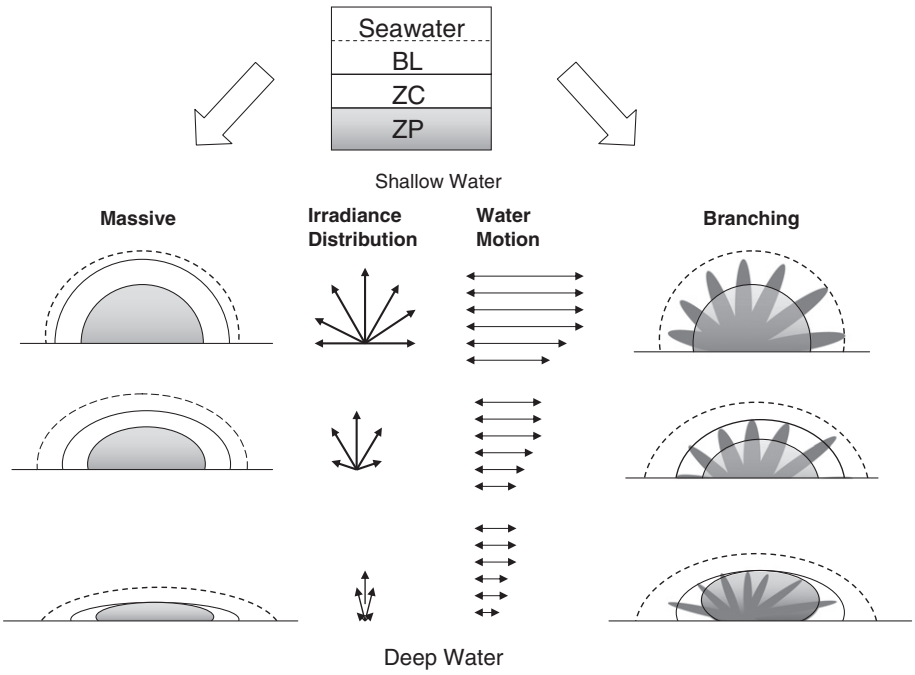

Fig. 10. The relationship between the zone of primary calcification (ZC), zone of primary photosynthesis (ZP) and the boundary layer (BL) showing the relative changes across the corallum in relation to the localized changes in irradiance and water motion that occur with increasing water depth for a massive and a branched coral.

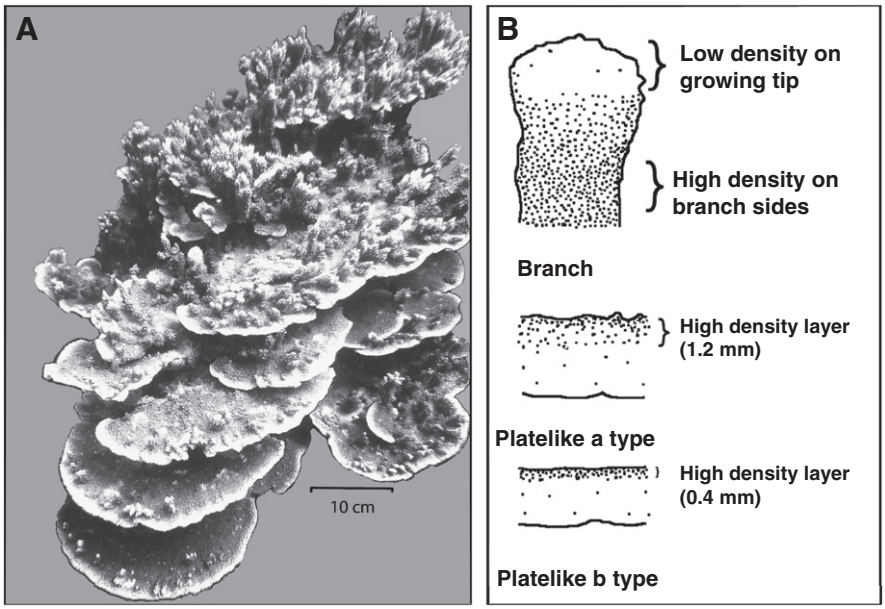

Fig. 11. A. Single large colony of the reef coral *Montipora capitata* shows branching morphology in shallow water grading into plate-like growth form in deeper water. B. Illustrations after Jaubert (1977) for the perforate coral *Synaraea convexa* showing the change in growth form and distribution of zooxanthellae that occur with increasing depth and decreasing irradiance. (Zooxanthellae represented as dots.)

4.3. Other responses of the corallum to hydrodynamic regime

Areas between the polyps of certain species contain small spines or projections. Areas of the skeleton covered by the thin colorless tissue are more responsive to changes in water motion than adjacent areas (Jokiel, 1978). Increased water flow reduces the BL over these projections, increasing local skeletal growth and giving rise to the accessory projections (e.g., hoods, papillae, spines) that characterize many species of reef corals (e.g., Fig. 9A and E). In turbulent water these projections grow outward and increase frictional drag and protect the polyp. In calm, low light environments they remain oppressed. In addition to ability to modify their skeletons in response to hydrodynamic conditions, corals show remarkable biochemical plasticity that can augment the delivery of carbon to the site of assimilation. Lesser et al. (1994) showed a significant increase in photosynthesis, respiration and antioxidant enzymes under conditions of increased water motion.

4.4. Irradiance vs. hydrodynamics as forcing functions in computer simulations

Graus and MacIntire (1976) employed a computer simulation based on underwater radiance distribution at different depths and various skeletal growth parameters using the reef coral *Montastrea annularis* as a model. The resulting computer images are very similar to the actual radiographic images of coral skeletons taken from different light environments, suggesting that direction and intensity of irradiance control skeletal morphogenesis. On the other hand, Kaandorp et al. (2005) performed computer simulation experiments of growth in the coral *Madracis mirabilis*. Their model is entirely driven by a diffusion-limited BL process and can generate coral growth patterns and morphologies that are virtually indistinguishable from three dimensional images of the actual colonies. There is an apparent contradiction between the two models. Graus and MacIntire (1976) showed that irradiance controls colony growth form while Kaandorp et al. (2005) state that coral growth form is controlled by water motion and diffusion limitation. The two compartment proton flux model relies on an interaction of both factors and suggests that existing computer based simulations need to integrate ambient irradiance response with hydrodynamic regime response (Fig. 10). Irradiance and water motion are correlated on coral reefs. Both factors decrease with increasing depth. Computer models based on only one of the two factors will still produce relevant output that is partially correct. Hydrodynamic factors impacting the BL will dominate in situations where irradiance is very high and saturates photosynthesis. Deep environments are characterized by low irradiance and low water motion that limits photosynthesis and calcification. The Kaandorp et al. (2005, 2011) model successfully produces three dimensional images of complex coral growth forms based on advection–diffusion limited absorption of C_T in a hydrodynamic field, but will fail to simulate the transitions into the flattened form observed at lower irradiance. Incorporation of the two compartment proton flux model with irradiance associated changes in the position of the ZP relative to the ZC will resolve this issue.

C_T in the ocean will increase with increasing OA. Therefore, the model of Kaandorp et al. (2005, 2011) falls short in that it is based on diffusion-limited C_T supply on the reactant side of Eq. (4). This model will result in a prediction of increased coral growth under conditions of increasing OA when actually the opposite will be happening (Jokiel, 2011). The model could be improved by including the effect of diffusion-limited efflux of $[H^+]$ on the product side of the equation in addition to the effect of C_T on the supply side.

4.5. Evolutionary considerations

Early in the evolution of reef corals their energy was obtained primarily through heterotrophic feeding. New possibilities arose once a symbiosis between zooxanthellae and the coral animal was established. Photosynthesis by the zooxanthellae provided the energy needed by the host coral in order to form the fast growing skeletons that give corals a competitive advantage over other sessile organisms. Natural selection favored the ever increasing rates of photosynthesis in shallow tropical seas where plankton is scarce, but where solar radiation is abundant. The evolution of skeletal architectures that place the ZC between the ZP and the surrounding seawater solved the problem of ridding excess protons while providing many other advantages. The success of two important scleractinian coral families (Acroporidae, Poritidae) can be attributed to the innovation of the perforate skeleton, which allows extremely efficient layering of the ZC over the ZP with retention of H^+ from secondary calcification in the ZP. Placement of the zooxanthellae within the porous skeleton reduces the importance of the polyps as photosynthetic sites. This in turn allows reduction in polyp size and

further diminishes barriers between calcification sites and the environment. Dense concentrations of zooxanthellae can develop at any depth within the perforate skeleton.

5. Conclusions

A synthesis of existing information on coral reef metabolism into a spatially correct corallum model reconciles many paradoxes surrounding reef coral biology and leads to important hypotheses. Spatial separation of the areas of rapid photosynthesis from the areas of rapid calcification reduces competition for HCO_3^- between photosynthesis (Eq. (3)) and calcification (Eq. (4)) and simultaneously enhances rapid recycling of materials between the two processes. The model emphasizes the importance of the spatial arrangement of ZP, ZC and BL in regard to proton flux between the compartments, and with the external seawater. Potentially toxic O_2 from photosynthesis in the ZP becomes an asset when consumed by rapid respiration in the ZC to provide the energy for high rates of calcification. In turn, the HCO_3^- produced by respiration in the ZC supports the high rate of photosynthesis in the underlying ZP. Placement of the ZC outside of the ZP facilitates rapid efflux of H^+ into the water column during periods of rapid calcification. Translocation of photosynthate serves a dual role of transporting the waste product H^+ from secondary calcification as well as photosynthetic energy from the ZP to the ZC where the excess protons can be readily dissipated into the water column. The proposed two compartment proton flux model is consistent with results of diverse reef coral experiments and observations ranging from biochemical to ecological. Furthermore, the proposed scheme provides a means of synthesizing past results to explain many puzzling aspects of coral growth form and function. This model is consistent with the conclusion (Jokiel, 2011) that reduced coral skeletal growth rate under conditions of increasing global OA is caused by diffusion limitation of net H^+ transport through the boundary due to increasing of $[H^+]$ in the water column.

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References

Al-Horani, F.A., Al-Moghrabi, S.M., De Beer, D., 2003a. Microsensor study of photosynthesis and calcification in the scleractinian coral, *Galaxea fascicularis*: active internal carbon cycle. J. Exp. Mar. Biol. Ecol. 288, 1–15.

Al-Horani, F.A., Al-Moghrabi, S.M., De Beer, D., 2003b. The mechanism of calcification and its relation to photosynthesis and respiration in the scleractinian coral *Galaxea fascicularis*. Mar. Biol. 142, 419–426.

Al-Horani, F.A., Ferdelman, T., Al-Moghrabi, S.M., De Beer, D., 2005. Spatial distribution of calcification and photosynthesis in the scleractinian coral *Galaxea fascicularis*. Coral Reefs 24, 173–180.

Allemand, D., Furla, P., Bénazet-Tambutté, S., 1998. Mechanisms of carbon acquisition for endosymbiont photosynthesis in Anthozoa. Can. J. Bot. 76, 925–941.

Allemand, D., Ferrier-Pagès, C., Furla, P., Houlbrèque, F., Puverel, S., Reynaud, S., Tambutté, E., Tambutté, S., Zaccola, D., 2004. Biomineralisation in reef-building corals: from molecular mechanisms to environmental control. C.R. Palevol 3, 453–467.

Allemand, D., Tambutté, E., Zoccola, D., Tambutté, S., 2011. Coral calcification, cells to reefs. In: Dubinsky, Z., Stambler, N. (Eds.), Coral Reefs: An Ecosystem in Transition. Springer Press, New York, pp. 119–150.

Barnes, D.J., Lough, J.M., 1993. On the nature and causes of density banding in massive coral skeletons. J. Exp. Mar. Biol. Ecol. 167, 91–108.

Bertucci, A., Tambutté, É., Tambutté, S., Allemand, D., Zoccola, D., 2010. Symbiosis-dependent gene expression in coral–dinoflagellate association: cloning and characterization of a P-type H^+-ATPase gene. Proc. R. Soc. London, Ser. B 277, 87–95. doi:10.1098/rspb.2009.1266.

Brown, B.E., Hewit, R., Le Tissier, M.A.A., 1983. The nature and construction of skeletal spines in *Pocillopora damicornis* (Linnaeus). Coral Reefs 2, 81–89.

Chamberlain Jr., J.A., Graus, R.R., 1975. Water flow and hydromechanical adaptations of branched reef corals. Bull. Mar. Sci. 25, 112–125.

Cohen, A., Holcomb, M., 2009. Why corals care about ocean acidification. Oceanography 22, 118–127.

Cohen, A.L., McConnaughey, T.A., 2003. Geochemical perspectives on coral mineralization. In: Dove, P.M., Weiner, S., deYoreo, J.J. (Eds.), Biomineralization. : Reviews in Mineralogy and Geochemistry, vol. 54. The Mineralogical Society of America, Washington, DC, pp. 151–187. doi:10.2113/0540151.

Colombo-Pallotta, M.F., Rodríguez-Román, A., Iglesias-Prieto, R., 2010. Calcification in bleached and unbleached *Montastraea faveolata*: evaluating the role of oxygen and glycerol. Coral Reefs 29, 899–907.

Crossland, C.J., Barnes, D.J., 1974. The role of metabolic nitrogen in coral calcification. Mar. Biol. 28, 325–332.

Enns, T., 1967. Facilitation by carbonic anhydrase of carbon dioxide transport. Science 155, 44–47.

Enrıquez, S., Méndez, E.R., Iglesias-Prieto, R., 2005. Multiple scattering on coral skeletons enhances light absorption by symbiotic algae. Limnol. Oceanogr. 50, 1025–1032.

Fang, L.-S., Chen, Y.-W.J., Chen, C.-S., 2004. Why does the white tip of stony coral grow so fast without zooxanthellae? Mar. Biol. 103, 359–363.

Fine, M., Oren, U., Loya, Y., 2002. Bleaching effect on regeneration and resource translocation in the coral *Oculina patagonica*. Mar. Ecol. Prog. Ser. 234, 119–125.

Furla, P., Galgani, I., Durand, I., Allemand, D., 2000a. Sources and mechanisms of inorganic transport for coral calcification and photosynthesis. J. Exp. Mar. Biol. Ecol. 203, 3445–3457.

Furla, P., Orsenigo, M.N., Allemand, D., 2000b. Involvement of H+-ATPase and carbonic anhydrase in inorganic carbon absorption for endosymbiont photosynthesis. Am. J. Physiol. 278, R870–R881.

Galloway, S.B., Work, T.M., Bochsler, V.S., Harley, R.A., Kramarsky-Winters, E., McLaughlin, S.M., Meteyer, C.U., Morado, J.F., Nicholson, J.H., Parnell, P.G., Peters, E.C., Reynolds, T.L., Rotstein, D.S., Sileo, L., Woodley, C.M. 2007. Coral disease and health workshop: coral histopathology II. NOAA Technical Memorandum NOS NCCOS 56 and NOAA Technical Memorandum CRCP 4. National Oceanic and Atmospheric Administration, Silver Spring, MD. 84p.

Gattuso, J.P., Allemand, D., Frankignoulle, M., 1999. Photosynthesis and calcification at cellular, organismal and community levels in coral reefs: a review on interactions and control by carbonate chemistry. Am. Zool. 39, 160–183.

Gladfelter, E.H., 1982. Skeletal development in *Acropora cervicornis*: I. Patterns of calcium carbonate accretion in the axial corallite. Coral Reefs 1, 45–51.

Gladfelter, E.H., 1983. Circulation of fluids in the gastrovascular system of the reef coral *Acropora cervicornis*. Biol. Bull. 165, 619–636.

Goreau, T.F., 1959. The physiology of skeleton formation in corals. I. A method for measuring the rate of calcium deposition by corals under different light conditions. Biol. Bull. 116, 59–75.

Goreau, T.F., 1963. Calcium carbonate deposition by coralline algae and corals in relation to their roles as reef-builders. Ann. N.Y. Acad. Sci. 109, 127–167.

Goreau, T.F., Goreau, N.I., 1959. The physiology of skeleton formation in corals. II. Calcium deposition by hermatypic corals under various conditions in the reef. Biol. Bull. 117, 239–250.

Graham, D., Smillie, R.M., 1976. Carbonate dehydratase in marine organisms of the Great Barrier Reef. Aust. J. Plant Physiol. 3, 113–119.

Graus, R.R., MacIntire, I.G., 1976. Light control of growth form in colonial reef corals: computer simulation. Science 193, 895–897.

Horne, R.A., 1969. Marine Chemistry. Wiley-Interscience, New York.

Hughes, T.P., 1987. Skeletal density and growth form of corals. Mar. Ecol. Prog. Ser. 35, 259–266.

Hurd, C.L., Cornwall, C.E., Currie, K., Hepburn, C.D., McGraw, C.M., Hunter, K.A., Boyd, P.W., 2011. Metabolically-induced pH fluctuations by some coastal calcifiers exceed projected 22nd century ocean acidification: a mechanism for differential susceptibility? Glob. Chang. Biol. 17, 3254–3262. doi:10.1111/j.1365-2486.2011.02473.x.

Jaubert, J., 1977. Light metabolism and growth forms of the hermatypic scleractinian coral *Synaraea convexa* (Verrill) in the lagoon of Moorea (French Polynesia). Proceedings of the 3rd International Coral Reef Symposium. Miami, Florida, 1, pp. 483–488.

Jokiel, P.L., 1978. Effects of water motion on reef corals. J. Exp. Mar. Biol. Ecol. 35, 87–97.

Jokiel, P.L., 2011. Ocean acidification and control of reef coral calcification by boundary layer limitation of proton flux. Bull. Mar. Sci.. doi:10.5343/bms.2010.1107

Jokiel, P.L., Morrissey, J.I., 1986. Influence of size on primary production in the reef coral *Pocillopora damicornis* and the tropical macroalga *Acanthophora spicifera*. Mar. Biol. 91, 15–26.

Kaandorp, J.A., Sloot, P.M.A., Merks, R.M.H., Bak, R.P.M., Vermeij, M.J.A., Maier, C., 2005. Morphogenesis of the branching reef coral *Madracis mirabilis*. Proc. R. Soc. London, Ser. B 272, 127–133.

Kaandorp, J.A., Filatov, M., Chindapol, N., 2011. Simulating and quantifying the environmental influence on coral colony growth form. In: Dubinsky, Z., Stambler, N. (Eds.), Coral Reefs: An Ecosystem in Transition. Springer Press, New York, pp. 177–185.

Kajiwara, K., Yokoch, H., Nagai, A., Ueno, S., 1997. Growth patterns of white-tipped and brown-tipped branches of the reef building coral, *Acropora pulchra* from Amitori Bay, Iriomote Island. Bull. Inst. Ocean Res. Dev, Tokai Univ 18, 1–10.

Kawaguti, S., Sakumoto, D., 1948. The effects of light on the calcium deposition of corals. Bull. Oceanogr. Inst. Taiwan. 4, 65–70.

Kühl, M., Cohen, Y., Dalsgaard, T., Jørgensen, B.B., Revsbech, N.P., 1995. Microenvironment and photosynthesis of zooxanthellae in scleractinian corals studied with microsensors for O_2, pH and light. Mar. Ecol. Prog. Ser. 117, 159–172.

Lamberts, A.E., 1974. Measurement of alizarin deposited by coral. Proceedings of the 2nd International Coral Reef Symposium. Brisbane, Australia, 2, pp. 241–244.

Lesser, M.P., 2011. Coral bleaching: causes and mechanisms. In: Dubinsky, Z., Stambler, N. (Eds.), Coral Reefs: An Ecosystem in Transition. Springer Press, New York, pp. 405–419.

Lesser, M.P., Weis, V.M., Patterson, M.R., Jokiel, P.L., 1994. Effects of morphology and water motion on carbon delivery and productivity in the reef coral, *Pocillopora damicornis*

(Linnaeus) — diffusion barriers, inorganic carbon limitation, and biochemical plasticity. J. Exp. Mar. Biol. Ecol. 178, 153–179.
Marshall, A.T., Wright, A., 1998. Coral calcification: autoradiography of a scleractinian coral *Galaxea fascicularis* after incubation in ^{45}Ca and ^{14}C. Coral Reefs 17, 37–47.
Mass, T., Genin, A., Shavit, U., Grinstein, M., Tchernov, D., 2010. Flow enhances photosynthesis in marine benthic autotrophs by increasing the efflux of oxygen from the organism to the water. Proc. Natl. Acad. Sci. U. S. A. 107, 2527–2531.
McConnaughey, T.A., Whelan, J.F., 1997. Calcification generates protons for nutrient and bicarbonate uptake. Earth Sci. Rev. 42, 95–117.
Moya, A., Tambutté, S., Bertucci, A., Tambutté, E., Lotto, S., Vullo, D., Supuran, C.T., Allemand, D., Zoccola, D., 2008. Carbonic anhydrase in the scleractinian coral *Stylophora pistillata*: characterization, location and role in biomineralization. J. Biol. Chem. 283, 25475–25484.
Muscatine, L., Falkowski, P.G., Porter, J., Dubinsky, Z., 1984. Fate of photosynthetically fixed carbon in light and shadeadapted corals. Proc. R. Soc. Lond. B Biol. Sci. 222, 181–202.
Pearse, V., Muscatine, L., 1971. Role of symbiotic algae (zooxanthellae) in coral calcification. Biol. Bull. (Woods Hole) 141, 350–363.
Reef, R., Kaniewska, P., Hoegh-Guldberg, O., 2009. Coral skeletons defend against ultraviolet radiation. PLoS One 4 (11), e7995. doi:10.1371/journal.pone.0007995.
Rinkevich, B., Loya, Y., 1983. Short term fate of photosynthetic products in a hermatypic coral. J. Exp. Mar. Biol. Ecol. 73, 175–184.
Roos, P., 1967. Growth and occurrence of the reef coral *Porites astreoides* (Lamarck) on relation to submarine radiance distribution. Ph. D. thesis, Drukkerij Elinkwijk, Utrecht, Norway.
Rowan, R., Whitney, S.M., Fowler, A., Yellowlees, D., 1996. Rubisco in marine symbiotic dinoflagellates: form II enzymes in eukaryotic oxygenic phototrophs encoded by a nuclear multigene family. Plant Cell 8, 539–553.
Santos, S.R., Toyoshima, J., Kinzie III, R.A., 2009. Spatial and temporal dynamics of symbiotic dinoflagellates (*Symbiodinium*: Dinophyta) in the perforate coral *Montipora capitata*. Galaxea J. Coral Reef Stud. 11, 139–147.
Shashar, N., Cohen, Y., Loya, Y., 1993. Extreme diel fluctuations of oxygen in diffusive boundary layers surrounding stony corals. Biol. Bull. 185, 455–461.
Shashar, N., Kinane, S., Jokiel, P.L., Patterson, M.R., 1996. Hydromechanical boundary layers over a coral reef. J. Exp. Mar. Biol. Ecol. 199, 17–28.
Smith, S.V., Key, G.S., 1975. Carbon dioxide and metabolism in marine environments. Limnol. Oceanogr. 20, 493–495.
Tambutté, É., Allemand, D., Mueller, E., Jaubert, J., 1996. A compartmental approach to the mechanism of calcification in hermatypic corals. J. Exp. Biol. 199, 1029–1041.
Tambutté, É., Allemand, D., Zoccola, D., Meibom, A., Lotto, S., Caminiti, N., Tambutté, S., 2007. Observations of the tissue–skeleton interface in the scleractinian coral *Stylophora pistillata*. Coral Reefs 26, 517–529.
Taylor, D.L., 1977. Intra-clonal transport of organic compounds and calcium in some Atlantic reef corals. Proceedings of the 3rd International Coral Reef Symposium. Miami, Florida, pp. 431–436.
Venn, A.A., Tambutté, E., Lotto, S., Zoccola, D., Allemand, D., Tambutté, S., 2009. Intracellular pH in symbiotic cnidarians. Proc. Natl. Acad. Sci. U. S. A. 106, 16574–16579.
Venn, A.A., Tambutté, E., Holcomb, M., Allemand, D., Tambutté, S., 2011. Live tissue imaging shows reef corals elevate pH under their calcifying tissue relative to seawater. PLoS One 6 (5), e20013.
Vicsek, T., 1989. Fractal Growth Phenomena. World Scientific, London.
Weis, V.M., Smith, G.J., Muscatine, L., 1989. A "CO_2 supply" mechanism in zooxanthellate cnidarians: role of carbonic anhydrase. Mar. Biol. 100, 195–202.