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Luminescence light collection technology in the aragonite of stone corals

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Abstract

Stone corals do not use calcium carbonate in the form of calcite, which has a calculated energy gap of 3.93 eV, but in the form of aragonite, which has a calculated energy gap of 2.88 eV (here experimentally determined to amount to 2.46 eV) as a building material. This enables the coral to harvest blue light, which is penetrating and filtering deep into the surface water of the ocean. White luminescence, which is composed of different wavelength lengths, is generated, and then conducted and redistributed within the aragonite structure to be supplied to the symbiotic photosynthetic algae. This mechanism of light concentration and adaptation via the aragonite structure leads to a smaller amount of light-absorbing phosphorescent pigments being required for the symbionts to survive. The resulting advantages are a significantly smaller exposure to photo-degradation, less effort for chemical synthesis and higher efficiency for solar energy conversion. The mechanism of luminescence light collection in the aragonite network is discussed on the basis of spectroscopic measurements on thin coral slices and in context with its architecture and the coral’s living activities. The relevance of the stone coral’s fractal geometry, both for broadband solar light harvesting and luminescence light collection within non-imaging optics, is emphasized. It is proposed that synthetic aragonite should be developed as a solar energy material.

1. Introduction

Stone corals are sessile marine animals, which live in symbiosis with light-harvesting photosynthetic algae. These algae are called zooxanthellae and typically reside in the coral polyp’s gastrodermis in close proximity to the topmost outer surface of the coral’s CaCO₃ skeleton, as shown in figure 1. They provide important additional nutrients to the stone corals (Scleractinia). Typically, stone corals are found up to 30–100 m deep in sea water, where they depend on solar energy, filtered to this depth [2]. The light reaching these depths is predominantly light from the short wavelength region of visible solar light [3].

1.1. The fractal structure

While stone corals occur in a large variety of different manifestations, forming shapes of branches, sheets, leaves, plates, boulders, mounds, flowers, cups and pillars or even brain-like structures. A striking common denominator is the organization in self-resembling functional units on different levels of hierarchy—the so-called fractality.

Smaller branches mimic larger ones and there are exponentially more small branches than larger ones. Each point of the structure provides qualitatively and to some extent quantitatively identical physical and chemical conditions. Fractal structures are applied in many natural systems [4, 5] and often lead to complex and sophisticated functionality.

They are scale invariant and thereby exhibit a quite robust structure, balanced between order and chaos. Examples are tree structures with their branch and root system, neuron geometries, the brain, the respiratory system or the circulatory system.

It has to be noted that no biological system is self-resembling at all scales. In the example of staghorn corals, this organization starts at the level of elongated single aragonite fibres with a length of approximately 15 µm, which are growing from calcification centres to sclerodermites. These sclerodermites form tube-like structures called trabeculae with a diameter...
of approximately 100–200 µm, which are the building material for the corallites, which in the process form the branches of the coral skeleton. The different levels of hierarchy in staghorn corals are illustrated in figure 2.

Stone corals capture light extremely efficiently. Even though the coral’s symbiotic algae contain three to six times less chlorophyll in direct comparison to the green leaves found in land plants, their absorption efficiency is roughly the same [7].

One possible conclusion might be that stone corals are much more efficient in harvesting solar energy. However, this is not a satisfactory answer, since quantum efficiency in plant photosynthesis is known to be close to a hundred per cent and the energy conversion efficiency cannot be three to six times more efficient in algae. Is an additional light-harvesting technology involved?

This study proposes that the functional mechanism behind it is luminescence solar concentration (LSC) via the CaCO₃ structure, which supports light-harvesting in stone corals. In technology, such LSC systems collect incident sunlight radiation over a wider area via parallel plates of doped glass or dye containing polymers. The dye particles then convert the incident light inducing luminescence (fluorescence), and direct it via total reflection within the glass plate towards a smaller area at the edges. Here, it is utilized and typically converted into photovoltaic electricity via deployed solar cells [8].

Due to the large surface area, the principle works even with diffuse light, and no reorientation of the system is needed to follow the path of the sun throughout the day.

While the approach itself is promising, major challenges are still the long-term stability of the dye and the polymer and a sufficient spectral separation of absorption and emission of radiation to avoid reabsorption of luminescence. While various prototypes and some smaller applications were demonstrated, a broader thrust towards commercial industrial application has not yet occurred. More modern efforts concentrate on innovative materials such as quantum dots or photonic materials. However, again with the difficult challenges of long-term stability and reasonably high efficiency.

2. Experimental method

Examinations were conducted on samples cut from skeleton branches of Acropora spec., collected from coral fragments in June 2012 on Pulau Perhentian, Malaysia. They were kept at ambient conditions for four months prior to examination. Additional experiments were performed on dead corals of the species Pocillopora collected in Kenya near Mombasa.

2.1. Optical microscopy

Examinations were conducted using a SteREO Discovery.V12 light microscope manufactured by Carl Zeiss Microscopy GmbH, Jena, Germany to gain insight into the macrostructure of the coral skeleton. Images were recorded to a PC using a digital camera of the type AxioCam ICc 1 Rev. 4 (Carl Zeiss Microscopy GmbH, Jena, Germany) with a resolution of 1388 × 1038 pixels, a spectral sensitivity of approximately 400–700 nm and an IR-blocking filter. Further processing and analysis were then done with
the Software AxioVision 4.8 (Carl Zeiss Microscopy GmbH, Jena, Germany). For analysis, the integrated interactive measurement module was activated. Apart from the integrated light source, a blue laser-emitting light at 405 nm was utilized for illumination of the samples.

### 2.2. UV–visible photography

UV–visible photography was used to get a deeper visual impression of the luminescence properties of the coral specimens. The UV photos were taken using a Panasonic Lumix DMC-FZ40 digital camera with 12 megapixels and f-stops between 2.8 and 3.6, shutter speeds between 1/125 and 1/4 s, ISO levels between 100 and 800 and a focal length of 4.5 mm. For UV illumination, a UV hand lamp of the type VL-215.LC with a power output of 15 W was used at two different wavelengths, 254 and 365 nm. The lamp was manufactured by Vilber Lourmat, Marne La Vallée, France. Distribution observations of laser-induced luminescence from corals of the species *Pocillopora* collected in Kenya near Mombasa were recorded with a Sony DSC-HX10 digital camera (laser specifications: 405 nm, 1 mW). The photo illustrating preferential light transmission in figure 13 was taken in RAW format with a Canon 600D digital camera at ISO 400, f/6.3 and 0.3 s exposure.

### 2.3. Scanning electron microscopy (SEM)

The examinations were conducted at the Institute for Electron Microscopy and Fine Structure Research (FELMI) in Graz, Austria, using an environmental scanning electron microscope of the type Quanta 600 FEG, manufactured by FEI Company, Hillsboro, Oregon, USA. Backscattered electrons were used to increase the material contrast at an operation voltage of 10 kV, and secondary electrons to increase the topography contrast at an operation voltage of 5 and 10 kV.

### 2.4. Energy-dispersive x-ray spectroscopy (EDX)

Energy-dispersive x-ray spectroscopy (EDX) and infrared spectroscopy were used to clarify the molecular composition of the specimens. These EDX examinations were conducted using a digital x-ray microanalysis system of the type Vantage,
2.5. Infrared spectroscopy
Infrared spectroscopy was used as a supplement to the EDX to gain further insight into the specimen’s elemental composition. The examinations were conducted at the Institute for Electron Microscopy and Fine Structure Research (FELMI) in Graz. A spectrometer of the type Equinox 55 in combination with an infrared microscope of the type Hyperion 3000 was used, both manufactured by the Bruker Corporation, Billerica, USA. The transmission measurements were conducted in a diamond cell with a measuring area of approximately 20–50 μm. For the measurements, the absorption in the middle IR-area (wavelength 2.5–15 μm) was used.

2.6. Fluorescence spectroscopy
Fluorescence spectroscopy was used to gain detailed insight into the fluorescence properties of the coral specimens, namely Stokes shift, excitation and emission spectra. The fluorescence measurements manufactured by Thermo NORAN Instruments Inc., Middleton, USA, combined with the above environmental scanning electron microscope.

Figure 3. Tauc plot for aragonite sample for n = 2, indicating an indirect band gap of ΔE = 2.46 eV.

Figure 4. (a)–(c) Bleached (a) and tinted (b) specimen. Scale bars in (a) and (b): 10 mm. (c) Pocillopora skeleton above a mirror in daylight illustrating the setup for laser illumination (figure 11). Amplifications display the corallite marks on the aragonite structure.
were conducted on a bleached slice cut from a branch of *Acropora spec.* with a thickness of approximately 7 mm using a PerkinElmer LS55 Fluorescence spectrometer. Excitation wavelengths ranged from 200–390 nm with a step width of 10 nm. Emission wavelengths were recorded from 400–900 nm with a step width of 0.5 nm. The results were analysed using a demo version of the software BL Studio v1.01.02 beta by BioLight Luminescence Systems Ltd, Stockton-on-Tees, UK.

For the reflection measurements, a PerkinElmer Lambda 950 UV/VIS/NIR Spectrometer with an Ulbricht sphere was used. The range of measurement was set to 250–200 nm, with a step width of 5 nm. Emission baseline correction was generated by applying a Teflon standard to both outlet openings of the attached Ulbricht sphere.

As light sources, a tungsten-halogen lamp (with continuous spectral output) and a 15 W UV lamp were used. Both devices are manufactured by PerkinElmer Inc., Waltham, Massachusetts, USA. The results were analysed using the software Spekwin32 v1.71.6.1 by Dr Friedrich Menges, available at www.effemm2.de/spekwin (last access 5.1.2013).

### 3. Results and discussion

The approach developed in this contribution presupposes that the inorganic CaCO$_3$ material of stone corals, aragonite, collects luminescence light and is actually a semiconductor with a band gap allowing absorption of visible blue light. An experimental determination of the aragonite band gap therefore turned out to be an important aim, since the only available data on aragonite is a theoretically calculated value of $\Delta E = 2.88$ eV, which could involve an error of 0.5 eV. This challenge was met based on the spectroscopic measurements on thin slices of coral aragonite shown further below.

#### 3.1. Aragonite bandgap determination

To determine the optical band gap of aragonite experimentally, the Tauc plot method was applied. In this method, the product of the optical absorption coefficient $\alpha$ and the photon energy $hv$ is raised to an...
The optical absorption $a$ was approximated from reflectance measurements using the Kubelka–Munk function. It can be presumed that inhomogeneous media are scattering light when it is interacting with them and passing through them. Their optical behaviour thus differs significantly from homogeneous media that do not scatter. The resulting diffuse reflection from such light scattering media can approximately be calculated. For this purpose, the Kubelka–Munk function is the most commonly used formula, which relates the diffuse reflection with the absorption constant. The Kubelka–Munk function is as follows:

$$f(\nu) = \frac{(1 - R)^2}{2R}.$$  

The intersection of the extrapolation of the linear slope with the axis of abscissae yields the approximation of the band gap (see figure 3). From our measurements, it was determined to be around $\Delta E = 2.46 \text{ eV}$, which coincides reasonably well with the theoretical $\Delta E$ calculations from the literature [9]. In addition, visible light actually induces significant luminescence in the aragonite samples. This proves that visible light is indeed absorbed to a larger extent after multiple light scattering. In addition, the bandgap measurement shows that the aragonite structure of CaCO$_3$ is actually a semiconductor absorbing blue light, which penetrates into deep water. A more profound study of luminescence light technology in stone corals is thus justified.

### 3.2. The macroscopic structure of stone corals

Figure 4 shows the structure of a completely bleached (a) and yellow-tinted ((b)—still polluted with organic material typical for stone corals) coral of *Acropora spec*.

The setup for the laser illumination of the *Pocillopora* specimen is illustrated in figure 4(c) and also shows the special structure of this coral. Figures 5(a)–(d) shows SEM images of the characteristic fine structure of the stone coral’s CaCO$_3$ material. A young polyp secretes six radial stripes of CaCO$_3$ via its foot disc, which grow and also develop an external circular rampart. A CaCO$_3$ column is also growing in the centre. The polyp itself sits on the structure like a lemon on a lemon squeezer. The CaCO$_3$ structure of stone corals is thus a systematically perforated material which also provides abundant scattering centres for light. The photosynthetic zooxanthellae are residing close to the surface of this perforated structure within the gastrodermis of the polyp [1].

### 3.3. The aragonite nature of CaCO$_3$ in stone corals

In this contribution, a peculiar path to answer the question why stone corals are so efficient for capturing solar light is followed. The CaCO$_3$, which stone corals apply, is not supplied in the form of the abundant calcite, but in the form of the more unstable aragonite, which is, as shown in section 3.1, a visible-light-absorbing semiconductor with an energy gap of $\Delta E = 2.46 \text{ eV}$.

Aragonite is a polymorph of calcite. Its crystal chemistry is identical, but its structure, symmetry and crystal shape differ. While calcite exhibits a cube-like crystal structure, aragonite forms an orthorhombic conformation with acicular crystals showing a needle-like, slender form [10]. Its crystals have an approximate geometry of hexagonal close packing.
and they consist of triangular, non-planar carbonate ion groups. The carbon atom is located in the centre of the triangle, while the three oxygen atoms reside at the corners. The carbon atoms project on top of each other [11–14].

Pure aragonite typically has a pale appearance and exhibits transparent to translucent optical properties. Doping with trace elements occurs frequently in nature and may change the optical properties, giving a tint of various colours. Aragonite is also known to exhibit various forms of luminescence, depending on the type of doping.

Usually, aragonite is considered a high-pressure polymorph; still, *Scleractinia* corals manage to synthesize it biogenically under ambient conditions. In comparison with its polymorph calcite, aragonite has, as already indicated, a calculated energy gap, which is approximately 1 eV smaller than the one found in calcite and amounts to around $\Delta E = 2.88$ eV (theoretical value from [9]) and $\Delta E = 2.46$ eV (experimentally, as determined here, see above). In figure 6, a simplified energy-band diagram of Aragonite is drawn, which depicts the position of the allowed energy states. The difference between the occupied ground states and unoccupied excited states is visible and makes up the band gap, which is recognizable for both calcite and aragonite. Only light quanta with energies corresponding to the difference between the ground state and excited state can be absorbed. It can be recognized that thanks to its smaller energy gap, aragonite can absorb blue and near UV light, which penetrates deep into sea water (shown in the form of parallel arrows on spectral colours within the appropriate energy range of aragonite and calcite, respectively, in figure 6, considering its approximate energetic distribution). By selecting the aragonite structure instead of the calcite structure of calcium carbonate, evolution made it apparently possible to harvest blue light for energy conversion.

The effect of short-wavelength light on luminescence light emission becomes apparent by focussing a laser point with a wavelength of 405 nm, a width of 2 mm and power of 1 mW onto dry, dead stone coral pieces (see figure 11).

### 3.4. Optical experiments with dead coral structures

Since Aragonite is not available as a synthetic material, experiments were performed with dead stone corals and slices cut out from dead stone corals. First, infrared measurements were taken to determine the purity of the dead stone coral material. The skeleton of living stone corals is known to be built up of aragonite crystals combined with a chitin fibril network forming a composite material. The infrared spectrum of dead coral material has been compared with a reference spectrum of pure aragonite in a range.

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**Figure 7.** IR spectra of a completely bleached specimen of *Acropora spec.* (a) and of a pure aragonite reference (b).

**Figure 8.** Transmission spectrum of the fully bleached slice of *Acropora spec.* with a thickness of 7 mm.
between 500–5000 cm$^{-1}$ and no significant differences were found (see figure 7). This means that when studying completely bleached dead stone corals we are essentially dealing with pure aragonite. The situation is different when stone coral specimens with a yellow tint are studied. In this case, spectroscopic evidence for organic impurities is found [15].

In order to get information about the energy-band structure on aragonite from stone corals (evaluated in figure 3), transmission measurements were taken with a slice of completely bleached Acropora spec. (figure 8). It shows strong absorption between 350–550 nm and quite good transmission below and above until 1400 nm. According to figure 8, the calculated transmission is in the order of 5%. This seems to be a low value, but in fact it is quite significant due to the scattering properties of the material and the thickness of the tested sample (7 mm). The measured value for the aragonite energy gap of $\Delta E = 2.46$ eV (corresponding to 504 nm) coincides reasonably well

**Figure 9.** Excitation and luminescence light emission of a fully bleached sample of Acropora spec. Excitation spectrum monitored with 495 nm light, emission spectrum activated with 397 nm light. Emission peak is at 504 nm, Stokes shift is 106.5 nm.

**Figure 10.** (a) and (b) EDX analysis of aragonite structure of yellow-tinted stone coral showing a pure aragonite surface (a) and areas with additional organic components (b).
with the calculated value of $\Delta E = 2.88$ eV by Aydinol et al [9].

Aragonite is highly luminescent. The approximate position of the conduction band of coral aragonite can also be deduced from the excitation spectrum of luminescence. This is shown in figure 9. Its peak is positioned between 390–420 nm and confirms that UV and blue light can well be absorbed to result in luminescence light emission in the visible spectral region between 400–650 nm.

In order to examine the degree of complexity in the structure of the conduction band of aragonite, and in order to understand the width of the emitted luminescent light distribution, luminescence measurements were taken for different excitation wavelengths. Three different excitation wavelengths, 254, 385 and 395 nm yielded a similar peak around 500 nm followed by a gradual decrease of luminescence towards 700 nm. This could also be confirmed for a yellow-tinted sample of Acropora spec. containing organic remnants [15].

In semiconducting materials, luminescence centres are typically determined by impurities, which introduce electronic levels supporting electron recombination via luminescence (symbolically visualized in figure 6). For this reason, the coral samples were examined in regard to possible doping elements. EDX spectra were taken from a yellow-tinted coral sample, which was still contaminated by its organic components (photograph shown in figure 4(b)). Figure 10 shows that areas of essentially pure aragonite (Ca, C, O) with traces of sulphur were found, but also areas with organic components (N, P, K, S). No clear hint at possible dopants in biologically grown aragonite became evident, even though N, S, P and K should be considered more closely, since they may substitute elements present in aragonite.

Figure 11 visualizes an experiment intended for demonstrating luminescence light transmission and distribution via the aragonite of a dead stone coral (Pocillopora sp., collected at the seashore in Kenya, Africa). A 405 nm violet laser beam with a power of less than 1 mW was reflected from a mirror to illustrate its cross-section (elongated by 41% because it is incident at an angle of approximately 45° on the mirror, seen at the bottom of figure 11) and aimed at a piece of dead coral. Comparing the (elongated) violet laser spot in front of the coral (2 mm wide) and the wide distribution of white light generated within the coral (approximately 40 mm wide), the effect of luminescence light distribution via aragonite is perceivable. The 405 nm laser light induces numerous luminescence emissions with different wavelengths (lower than 405 nm), which combine giving the impression of white light (compare figure 9).

The stone coral fragment and its position on the mirror are shown in figure 4(c). The lower part of the coral fragment is seen from below where the reflected 2 mm wide, 405 nm laser beam is entering the coral structure. The upper part of the 40 mm coral is showing the distribution and emission of the luminescence light, which is basically white (as figure 9 shows). Inset in figure 11 are amplifications.

Figure 12 shows the visible fluorescent light, which is mainly emitted from the 0.75 mm wide corallite structures seen as white patches. To reach them, fluorescence light must have travelled up to several centimetres. However, as the contrast to the dark back and the entirely white area shows, also between corallites luminescent light is emitted from the aragonite structure. There must, however, be a mechanism which allows a preferential light conduction towards the zooxanthella-covered polyp environment, which generates photosynthesis.
When a coral structure is illuminated as in figure 13 with a 405 nm laser spot, a large and bright, white-yellowish illuminated area is observed, which first indicates that luminescent light is emitted, and second, that this light is propagating to a certain distance. The fact that white-yellowish light is emitted indicates that more than one luminescence light transition is possible in aragonite. Luminescence light of different wavelengths obviously combines to yield the impression of white light. Since this light is able to propagate within the aragonite of the stone coral, it will thus reach the location of the algae on the end plates of the individual corallites to induce photosynthesis. What mechanisms are involved in solar and luminescence light transduction?

3.5. The role of fractal structure for light harvesting and luminescence light collection

Corals have evolved fractal structures [16–18]. The striking feature of fractal organization in stone corals has been mentioned before (see section 1—Introduction). An obvious advantage of this fractal structure concerning light management is the avoidance of self-shading. But it is not the only advantage. Fractal structures offer many elegant opportunities for growth, reorganization and change. Apart from that and most importantly, they can easily provide efficiently communicating interfaces for connecting to other systems: to energy sources, nutrient supplies or recipients of entropy products in the form of released gases and chemicals.

In the case of stone corals, the fractal aragonite structure may be involved in life-sustaining energy supply, both by collecting filtered, bluish solar light, and by re-directing luminescence light towards the algae, sitting on the basal end plates of individual corallites.

Several optical processes turn out to be largely enhanced in fractal structures, due to the generation of strong localized electromagnetic fields. These fields are interacting with the dipoles responsible for electronic transitions and are generating strongly enhanced phenomena such as light absorption and luminescence emission [19]. Also, unique light localization and transport properties in fractal structures have been identified.

How do stone corals deal with the effects of their fractal structures in relation to photon energy turnover, and what significance do these structures have for non-imaging luminescence energy harvesting?

In several publications, the behaviour of energy in time-dependent phenomena has been investigated [20–24]. Assuming excited states subject to different types of interaction (exchange interaction, dipole–dipole interaction, dipole–quadrupole interaction), a time-dependent relation has been obtained. The formula can also be applied to energy transfer via luminescence collection and has the form

\[ f(t) = e^{-\frac{\Delta d^4}{4}}, \]

Here \( f(t) \) is the time-dependent decay function for excited states. \( A \) is a time-independent constant, \( d \) is the Euclidean dimension and \( s \) accounts for the type of multipolar interaction \( (s = 6 \) for dipole–dipole, \( s = 8 \) for dipole–quadrupole and \( s = 10 \) for quadrupole–quadrupole interaction). It can be derived that for fractal geometries the Euclidean dimension \( d \) can simply be replaced by the fractal dimension \( \tilde{d} \). This means that for a 3D structure, the Euclidean dimension \( d \) of 3 has to be replaced by a number between 2 < \( \tilde{d} \) < 3. The consequence is that the decay of the energy as described by equation (3) is always slower when the Euclidean dimension \( d \) is replaced by the fractal dimension \( \tilde{d} \).

Hence, the lifetime of the luminescence light transfer phenomena becomes longer in fractal structures. Since a faster decay means a faster loss of energy in the form of heat, luminescence transfer in fractal structures is more efficient.

3.6. The role of light scattering and fractal dimensions in the harvest of luminescence

It has already been demonstrated that stone corals of the three genera *Pocillopora*, *Porites* and *Acropora* use fractal dimension between 2 and 3 (Basillais et al calculated the fractal dimensions of stone corals of the three genera *Acropora*, *Pocillopora* and *Porites* to amount to around 2.64 [17]) or for 2D thin layers between 1 and 2 [25]. It has also been shown that fractal structures may be used for the tailoring of scattering light [16, 26].

Due to its peculiar material structure combining layers of pure aragonite with layers of aragonite
containing organic inclusions (which is the consequence of genetically controlled mineralisation at ambient temperature), light-scattering centres occur in the stone coral CaCO₃ material. The sizes of the scattering centres range from 50–200 nm nanostructures of CaCO₃ nanograins to 5 mm microstructures of fibre bundles according to Marcelino et al [16]. In this paper, the authors examined the light-scattering properties of skeletons from several coral species. A correlation between fractal complexity, light transmission and light-scattering properties was found. This indicates that light scattering is an important property of stone coral aragonite, which is also related to the bleaching properties of individual species of stone corals.

Light scattering may also be responsible for inducing or amplifying luminescence in coral skeletons. Stimulated luminescence may occur due to multiple interactions of light within the imperfect crystal lattice with defects that involve trapped electrons and missing electron holes, as shown by Modreski [27]. This author observed luminescence in aragonite powder samples induced by stamped holes, and concluded that luminescence in the aragonite is more likely to result from the skeletal structure than from the inclusion of humic substances as was widely accepted before. The fractal structure of the coral skeleton apparently offers multiple ways of light interaction and is thus very likely to contribute to the luminescence in the coral skeleton.

Apart from that, it should be emphasized that highly scattering systems are subject to non-imaging optics. This discipline of optics, which was essentially developed by Ploke [28], Winston [29] and O’Gallagher [30], aims only at pure light concentration and is hence more effective than imaging optics, which can also deal with images. Non-imaging optics mostly uses light deflection, light refraction and light scattering in special geometries [31]. Non-imaging optics is now applied in a wide range of fields, ranging from solar light collection with Winston collectors to modern thin-layer solar cells, where the non-imaging optics is integrated via light-scattering structures. The obtainable light concentration C is proportional (proportionality factor B) to the square of the refractive index n (n = 1.529–1.686 for aragonite), divided by the half angle θ of light incidence:

\[ C = B \frac{n^2}{\sin \theta} \]  (4)

The proportionality factor B depends on the geometry of the light-collecting system and can reach values up to 4. For the highly light-scattering fractal aragonite structure, the magnitude of coefficient B determines the degree of light concentration both for incident filtered solar light, as well as for outgoing luminescence light from aragonite. It must be related to the fractal dimension of the stone coral structure, so that the overall performance of light-collecting corals should involve both non-imaging and fractal mechanisms.

### 3.7. Combination of non-imaging light collection and luminescence energy transport

Scattered and reflected light is collected via equation (4), but when luminescence light is generated energy will be transmitted in fractal structures via equation (3).

It follows that the overall efficiency for light collection will be the multiplication of equation (4), which is scattered and reflected light collection, with equation (3), which is proportional to luminescence light harvesting. The resulting equation for total light harvesting \( L \) via luminescence light collection in the aragonite of stone corals would then be

\[ L \sim \frac{Bn^2}{\sin \theta} \times e^{-\frac{\theta^2}{2}}. \]  (5)

In this equation, the Euclidian dimension \( d \) is replaced by the fractal dimension \( D \) as explained in section 3.5.

In conclusion, efficient light harvesting in stone corals obviously only became possible because evolution has exchanged the calcium carbonate building material from insulating calcite to semiconducting aragonite, enabling the efficient harvesting of blue filtered solar light—a technologically crucial step. In addition, nature used non-imaging optics via light scattering and reflection for non-imaging optical light concentration and enhanced the efficiency further via implementing fractal dimensions.

Apparently, nature has reached a high level of optical performance in stone corals. It could be a rewarding approach to copy nature in a bio-mimetic way, to create artificial fluorescence harvesting systems on the basis of highly structured aragonite for light collection. As for the crucial downside in current luminescence collectors, the longevity of such systems—stone corals live from 5–10 years (e.g. *Favia fragum*) to several centuries (e.g. *Montastraea annularis*) [32, 33]. This seems to be sufficient evidence for the long-term photostability of aragonite.
4. Conclusions

This survey of light-collecting properties of stone corals focuses attention on the following facts, which should be further investigated:

- Aragonite is a promising material for artificial luminescence light collection. Its solid-state physics including doping possibilities for luminescence generation should be studied in detail, since it promises long-term stability and possibly low-temperature preparation techniques.

- Fractal geometries of light-harvesting materials appear to be favourable structures for energy harvesting and energy transmission. A more detailed theoretical description and more effort towards experimental verification of this phenomenon should be attempted.

- The application of non-imaging optics for solar light concentration combined with luminescence light collection and concentration should be explored for improved light-collecting devices.

- An in-depth elucidation of the optical performance of stone corals will also shed more light on the fascinating world of energy turnover and the survival strategies of coral reefs.

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