



Article title: An Assessment of the Potential Value for Climate Remediation of Ocean Calcifiers in Sequestration of Atmospheric Carbon

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An Assessment of the Potential Value for Climate Remediation of Ocean Calcifiers in Sequestration of Atmospheric Carbon

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Abstract: Today's marine calcifiers (coccolithophore algae, Foraminifera [protists], Mollusca, Crustacea, Anthozoa [corals], Echinodermata) remove carbon dioxide (CO₂) from the atmosphere, converting it into solid calcium carbonate (CaCO₃) which is stable for geological periods of time. These organisms could serve as a biotechnological carbon capture and storage mechanism to control climate change. Two criticisms made about this are: (i) ocean acidification has allegedly been shown to cause reduced shell formation in calcifiers; (ii) the calcification reaction that precipitates CaCO₃ crystals into the shells is alleged to return CO₂ to the atmosphere. In this review we assess the evidence concerning such criticisms and find reasons to doubt both. Experiments showing that ocean acidification is damaging to calcifiers have all used experimental pH levels that are not projected to be reached in the oceans until the next century or later; today's oceans, despite recent changes, are alkaline in pH. Claiming precipitation of CaCO₃ during calcification as a net source of CO₂ to the atmosphere is an oversimplification of ocean chemistry that is true only in open water environments. Living calcifiers do not carry out the calcification reaction in an open water environment in equilibrium with the atmosphere. The chemistry that we know as life takes place on the surfaces of enzymatic polypeptides, within organelles that have phospholipid membranes, contained in a cell enclosed within another phospholipid bilayer membrane specifically to isolate the chemistry of life from the open water environment. Ignoring what is known about the biology, physiology, and molecular cell biology of living organisms, calcifiers of all types especially, leads to erroneous conclusions and deficient advice about the potential for calcifier biotechnology to contribute to atmosphere remediation. Net removal of CO₂ from the atmosphere by calcifiers is only achieved by the CaCO₃ stored in the shell, coccoliths, or foram tests that are left when they die. To capitalise on this requires a change in paradigm towards cultivating calcifiers for their CaCO₃ rather than their meat or other products. We conclude that the world's aquaculture industries already operate the biotechnology that, with massive and *immediate* global expansion, can contribute to sustainably controlling atmospheric CO₂ levels at reasonable cost and with several positive benefits in addition to carbon sequestration.

Keywords: aquaculture; biotechnology; carbon sequestration; carbonate biology; carbonate chemistry; climate change; remediation.

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1. Introduction

In several recent publications we have advocated that shellfish farmers should greatly expand their production specifically to generate more shell to sequester atmospheric carbon [1 - 9]. Our core conviction is that humankind must look to the oceans for the solution to the excess CO₂ in the atmosphere that drives climate change, and that marine calcifiers (coccolithophores, Foraminifera, Mollusca, Crustacea, Anthozoa, Echinodermata) are the tools that will provide that solution. We consider that the action plans we have suggested [7] offer the good news message that if we act quickly to change our attitude to calcifier cultivation and, particularly, greatly magnify the global scale of this activity, we could make a serious contribution to ameliorating climate change in the foreseeable future.

Despite the positive messages of our publications referenced above, distinguished marine biologists have cast doubt on our claims by stating (we paraphrase) 'marine shellfish aquaculture could not make a contribution to climate mitigation'; two reasons being offered for this point of view: (i) seawater has become more acidic and shellfish species are shrinking in size and the shells deform and (ii) precipitation of calcium carbonate in shellfish shells is a source of carbon dioxide (CO₂) ...and the major way by which CO₂ is returned to the atmosphere (see 'Frequently Asked Questions' section in [7]).

In this paper, we attempt to provide a different, *biological*, viewpoint of the published data bearing on these two specific issues, which we hope will show why cultivating calcifiers in the short term would be advantageous. We also include some comments about the psychological paradox of why, when we know more than enough about the climate system, we do so little to *control* climate change [11 - 13], being satisfied merely with coping with its outcomes.

Our conclusion remains positive. The most recent Life Cycle Assessments (LCA; described and referenced below) demonstrate that the shellfish cultivation industry offers unique opportunities for permanently sequestering carbon while producing food, but if significant carbon capture is to be achieved, the paradigm (and the business model of shellfish farms around the world) must be changed *from* cultivating shellfish for food *towards* cultivating shellfish for their *shells*. If the level of finance and global effort that are willingly anticipated for forest management and CCS (Carbon Capture and Storage) flue gas treatments was applied to expansion of shellfish (and other calcifiers) cultivation around the world, significant amounts of CO₂ could be removed from the atmosphere with much greater permanence and less cost than any other solution can offer [9]. Start now and by the end of this century the action plan could be contributing to returning the CO₂ level in our atmosphere to its natural, pre-industrial level.

2. Basic Carbonate Chemistry

The chemistry involved in the process of shell-making, whether performed by planktonic algae (coccolithophores), single celled protists (Foraminifera) or multicellular animals (Anthozoa, Crustacea, Mollusca, Echinodermata) is described by the following scheme:

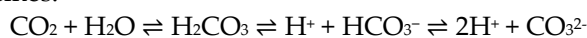


(in words: one divalent calcium ion_(aqueous) + two monovalent hydrogencarbonate ions_(aqueous) \rightleftharpoons calcium carbonate_(solid) + carbon dioxide_(gas) + water_(liquid))

One molecule of CO₂ from the hydrogencarbonate ions of seawater is released, together with a molecule of water, during the calcification (biomineralisation) reaction.

Seawater is over-saturated with calcium ions and its concentration of hydrogencarbonate largely dominates that of carbonate and dissolved free CO₂. In these conditions, the molecule of CO₂ on the righthand side of the above scheme, *if* it is released to seawater during the biomineralisation of shells (which is very doubtful, as explained below), will react with water, forming carbonic acid which will dissociate forming hydrogencarbonate and hydrogen ions (protons) that would be available for marine calcifiers to form more

CaCO₃. Alternatively, the carbonic acid can dissociate to form a carbonate ion and two hydrogen ions. These electrolyte dissociations and associations are described by these schemes:



(in words: one molecule of carbon dioxide + one molecule of water \rightleftharpoons one molecule of carbonic acid \rightleftharpoons one hydrogen ion + one monovalent hydrogencarbonate ion \rightleftharpoons two hydrogen ions + one divalent carbonate ion)

This release of hydrogen ions is usually interpreted as causing potentially damaging seawater acidification. Emerson and Hedges [14] describe carbonate dynamics (their Chapter 4, *Carbonate Chemistry*) in terms that can be paraphrased as:

“As organisms form their shells from Ca and carbonate, alkalinity is being removed. This causes the pH to drop which alters the speciation of the inorganic carbonate system to alter in favor of CO₂. Thus, the CO₂ concentration increases and any gradient driving the gas to the atmosphere increases.”

Which is not so different from the following wording in Gattuso et al. [15]:

“There are three pools of oceanic DIC [Dissolved Inorganic Carbon]: HCO₃⁻ (90%), CO₃²⁻ (9%), and dissolved CO₂ (1%). The latter pool is close to equilibrium with the atmosphere (present pCO₂ ca. 360 μatm). The carbon atom incorporated into CaCO₃ is derived from the HCO₃⁻ pool, with the consequence that H⁺ is liberated and the water gets more acid. The acid pushes an additional amount of HCO₃⁻ across into the oceanic CO₂ pool. There is then a physical equilibration between the seawater and atmosphere CO₂ pools, and this physical equilibration pushes CO₂ into the atmosphere.”

We want to make it clear that we do not doubt, or query in any way these chemical interpretations as they apply to the progress of inorganic chemistry in the open water environment where it is doubtless perfectly true to say that:

“Calcification is therefore a CO₂-releasing process that can make water in equilibrium with the atmosphere degas, against the initial pCO₂ gradient” [15].

But *living* calcifiers do not carry out the calcification reaction in an open water environment ‘*in equilibrium with the atmosphere*’. The chemistry that we know as *life* takes place in a cell enclosed within a phospholipid bilayer membrane specifically to isolate itself from the open water environment. Many of the reaction trains upon which *life* depends take place within organelles that have their own phospholipid membranes within the cell. For example: mitochondria, that generate the chemical energy stored in adenosine triphosphate (ATP) and plastids, in which photosynthesis (or photosynthesis-related special metabolic activity, like starch storage) takes place. Transporters within these membranes control the movement of ions (including protons and inorganic ions), molecules and macromolecules to and from the compartments the membranes enclose. Some metabolites may be allowed simply to diffuse across the phospholipid membrane or through pores in the membrane(s); in other cases, diffusion may be facilitated by highly specific and selective transporters; whilst linking a facilitated diffusion mechanism to an ATPase proton transporter produces an active transport system that can transport molecules against, often considerable, chemical diffusion gradients.

These selectively permeable phospholipid bilayer membranes isolate the cell from its environment and the compartments within the cell from one another as the ion-specific transporters across those membranes control the environments within cellular compartments to the benefit of the organism.

A case in point is that Foraminifera actively pump hydrogen ions (protons) *out from the site of calcification* which is therefore surrounded by a low (acidic) external pH *of their own making* [16]. Foraminifera are amoeba-like, single-celled protists that secrete a protective shell (called a ‘test’ because it is intracellular). The most primitive tests are made from cemented sand grains, but most are made of calcite or aragonite (CaCO₃) crystals. Tests are found in globally-extensive fossilized foraminifera limestones as old as the earliest Cambrian, about 545 million years ago (Mya), and planktonic and benthic Foraminifera are still abundant today, living in marine and brackish waters.

Kawahata et al. [16] focus on the response of two major calcifiers, Foraminifera and corals, which together contribute significantly to global carbon sequestration in sediments and reefs. They demonstrate that the response to acidified seawater today depends on situations, species, community structure and life-cycle stage. Some Foraminifera showed a positive response to low (acidic) pH conditions, while calcification in adult coral branches was not reduced by high CO₂ concentrations. Direct visualization of pH distribution showed that proton (hydrogen ion) *pumping by the cell* which is associated with foraminiferal calcification during chamber formation in the tests is independent of initial seawater CO₂ concentration or pH and produces a high internal pH (more than pH 9 within the site of calcification) and large internal-to-external pH difference (as much as 2 pH units).

Corals also regulate their internal pH at the tissue-to-skeleton interface to levels that could counteract ocean acidification [17, 18]. Salinity, temperature, the amount of light and the amount of oxygen dissolved in the water are the most important factors that control living foraminifera and coral polyps. Higher ocean temperatures *do* induce bleaching of these marine calcifiers because their algal symbionts on which they depend for nutrition are temperature-sensitive (and this applies to corals, giant clams and Foraminifera). Loss of the nutrition contributed by the photosynthetic symbiont to its host animal results in malaise, reduced calcification and ultimately death of the host, although symbiotic Foraminifera are more robust and resilient than coral polyps at higher temperatures.

Given the ability of important calcifying organisms to modify their own internal environments in the ways indicated immediately above, our focus moves from a ‘water in equilibrium with the atmosphere’ viewpoint, to a view guided by what we know about the cellular biology of living things on Earth and in its oceans. It is our hope that we can build upon the work that has already been done on carbonate chemistry in open water environments and extend it to include the biological view of calcification chemistry.

3. Issue 1: Ocean acidification will have a harmful effect on the physiology of calcifying organisms

Acidity is measured in terms of the pH where the pH of a solution = $-\log[H^+]$, which is a logarithmic scale. A neutral solution has a pH of 7 and pH values less than 7 are considered acidic, whilst pH values above 7 are alkaline (or basic). The *Encyclopædia Universalis France* (quoting Tanhua et al. 2015 [19]) states that:

“... Since the industrial era, the ocean’s basic [alkaline] pH has fallen from 8.2 to 8.1. This drop of 0.1 unit corresponds to an increase in acidity of about 25% [because the scale is logarithmic]...” [<https://www.universalis.fr/encyclopedie/acidification-des-oceans/>].

To put these pH values into the context of our common experiences, the pH of fresh orange juice ranges from 3.3 to 4.2, and fresh cow’s milk about 6.7 to 6.9. Most black teas are in the range 4.9 to 5.5, with black coffees averaging pH 4.8 to 5.1. These beverages are considered weakly acidic, whilst the ‘safe’ pH level of drinks to avoid tooth damage is deemed to be 5.5.

Fassbender et al. [20] found that pH changes vary between the many domains of the world’s oceans, being constrained by geographical position, depth, temperature, salinity and current flows. They also highlight that pH provides a relative means for comparison but considered that the absolute hydrogen ion concentrations of areas may help understand actual changes in our ocean better. Nevertheless, the *fact* remains that *today’s oceans are still generally alkaline in pH*.

Mean pH of surface ocean waters is predicted under the IPCC ‘business-as-usual’ scenario [21] to decline by 0.3-0.4 units by 2100 AD [22, 23], and Brewer (1997) [22] tabulated the evolving chemistry of surface seawater under this scenario as shown in Table 1.

This decline in oceanic pH, both predicted and measured, is the very definition of “ocean acidification”. But in our view the description “acidification” (*even though chemically and semantically accurate*) over dramatizes the situation, which can cause a psychological response in individuals leading to group inaction, as the group perception is too

alarming to resolve climate change/climate disruption [12, 13, 24]. When a solution is offered, we should DO something about it rather than dismiss the solution with illogical criticism.

Table 1. Estimated surface oceanic seawater pH between 1800 AD and 2100 AD¹

Year	Predicted oceanic pH
1800	8.19
1996	8.10 (actual value = 8.2)
2020	8.03 (actual value = 8.1)
2040	7.97
2060	7.91
2080	7.85
2100	7.78

¹ Table adapted from Brewer (1997) [22]

The *facts* about ocean acidification are these:

- In 1800 AD the oceanic pH is estimated to have been a decidedly alkaline 8.2.
- In 2020 AD the oceanic pH was measured to be a decidedly alkaline 8.1.
- By 2100 AD the oceanic pH is predicted to be a decidedly alkaline 7.78.

The decreasing alkalinity of the oceans represented in these figures is not diminished in importance, and decreasing alkalinity on this scale is still

“... a powerful reason, in addition to that of climate change, for reducing global CO₂ emissions. Action needs to be taken now to reduce global emissions of CO₂ to the atmosphere to avoid the risk of irreversible damage to the oceans” [25].

Our point is that the descriptive phrase “decreasing alkalinity” does not provoke wild fears of the White Cliffs of Dover fizzing away in an acid ocean by the end of the century like a lump of chalk thrown into a bowl of vinegar (try *Googling* “chalk in vinegar experiment”). It is important to control the phraseology to avoid thoughts that we might be faced by a circumstance we are powerless to control.

According to Marshall (2015) [12]:

“There is some research evidence that people stop paying attention to climate change when they realize there is no easy solution for it.” [12, p. 79 of chapter 16].

This is because of a subconscious human mechanism whereby we avoid uncomfortable emotions by rejecting facts that are too unpleasant to act on [13, 26]. A more positive conclusion is implied in the following quotations from Stoknes (2015) [13]:

“Evolutionary psychology highlights that imitating others is [an] efficient [strategy]. Among social animals, following the majority is good for learning and survival. ... But imitation isn’t fate. We can choose differently. So maybe there are smart ways to start harnessing the evolutionary force for imitation for climate action rather than the opposite.” [13, chapter 3, p. 31].

We maintain that humanity is not powerless to control climate change. It is an historical fact that we humans had the power to cause our current circumstance as we developed our global industrial muscle; and now, with the aid of 200 years of accumulated scientific knowledge, we have the power bestowed by that knowledge to apply our industrial muscle to change our current circumstances to alleviate some of the future consequences.

There is a readily implemented contribution to efforts to regulate climate change by combining two proven special natural talents - the ability of calcifiers to remove carbon from the atmosphere immediately and permanently, and the ability of humans to get things done quickly. We can use the oceans of the planet to navigate our way out of the climate crisis of which we are now so aware [10, 27, 28].

Coccolithophores are the most prolific producers of CaCO₃ in the oceans, accounting for almost half of the total CaCO₃ produced in today's oceans annually [29 - 31]. Evidence from the deep ocean indicates that over the past 220 years there has been a 40% *increase* in coccolith mass in the deep sea sediments [32]. Clearly, the coccolithophores have already reacted to the anthropogenic rise in atmospheric CO₂ partial pressures by doing what they have done before: detoxifying their environment. The difference this time is that they are providing humanity with the service of detoxifying atmospheric CO₂.

Study of subantarctic populations of the most abundant coccolithophore calcifying phytoplankton species, *Emiliania huxleyi*, found highly calcified morphotypes in more acidified high-CO₂ conditions. Such observations challenge any claim that ocean acidification will *necessarily* be detrimental to algal calcifiers [33] even though it is also clear that ocean acidification and elevated temperatures in relatively shallow tropical waters adversely impact the viability of the symbiotic algae of Foraminifera, corals and giant clams alike.

Challenging this positive notion, Doney et al. (2009) [34] state that:

"... Many calcifying species exhibit reduced calcification and growth rates in laboratory experiments under high-CO₂ conditions..."

This is a fact that cannot be denied; but in laboratory experiments the pH used is in the hands of the experimenter and *all have chosen pH values representative of the end of this century (or even later) rather than the present day*. For example, Orr et al. (2005) [23] reported that when live pteropods were exposed to conditions *predicted for 2100 AD* in a two-day shipboard experiment, their shells showed notable dissolution. Pteropods are planktonic molluscs that contribute to pelagic food webs worldwide, so this is bad news for ocean biodiversity *in 80 years time*. Orr et al. (2005) [23] use these data to argue that conditions detrimental to ocean "... ecosystems *could develop within decades*, not centuries as suggested previously..." (the emphasis is ours) but this detail may not be appreciated by those with deep fears for the here and now.

Other examples are experiments studying the effect of different pH treatments on shell properties of the blood cockle (or blood clam), *Tegillarca granosa*, that used experimental pH values of 7.1 and 7.5 and a pH of 7.81 as a control [35]. This clam occurs in the intertidal zone throughout the Indo-Pacific region, from South Africa through to Southeast Asia, Australia, and Japan. It is widely harvested in coastal and estuarine mudflats so the finding that "...The shell weight and shell density of *T. granosa* was significantly reduced at pH 7.10..." [35] could have severe economic consequences for the industry. However, this reduction in weight and density is in comparison with a control pH value (of 7.81) *which is not expected to be reached in our oceans until 2100 AD*. Further reassurance for the blood clam aquaculture industry for at least the next 300 years is that (again, the emphasis in this quotation is ours):

"...However, the ocean acidification level of pH 7.50 which is predicted to occur by the year 2300 showed no significant decrease in shell weight and shell density of *T. granosa* compared to the control pH treatment (pH 7.81)" (Nithiyaa et al. 2021 [35]).

Fitzer et al. (2016) [36] have demonstrated significant changes in the hydrated and dehydrated forms of amorphous CaCO₃ in the crystalline layers of shells of the blue (or 'common') mussel (*Mytilus edulis*) cultured under experimental acidification conditions. This could be an important experimental observation as this edible marine bivalve mollusc has a global range and is the subject of a multi-million dollar intensive aquaculture industry. However, these experiments used CO₂ concentrations that were *2½ times higher* than today's observed natural levels. It is unreasonable to predict *present day* detrimental consequences for calcifiers on the basis of such extreme experimental procedures.

Another study with *Mytilus*, which used a similarly extreme upper CO₂ level, found that the resultant acidification (or, as we prefer, *reduced alkalinity*) suggests a complex relationship between calcification and the various active components of climate change that might ease the negative effects of increased sea temperatures on biomineralisation in the

mussel [37]. Even greater complexities become evident in organisms, like calcifying phytoplankton (coccolithophores), that bring photosynthesis into the mix of variables [38].

The publications reviewed so far illustrate the general trends in a fairly copious literature into which we do not intend to delve further. Kroeker et al. (2013) carried out a comprehensive meta-analysis of 155 studies examining biological responses to a 0.5 unit reduction or less in mean seawater pH, which approximates projected acidification by about 2100 AD. They found "... decreased survival, calcification, growth, development and abundance in response to acidification when the broad range of marine organisms is pooled together ..." but stressed *variability*:

"...in species' responses ... in multi-species assemblages, suggesting that it is important to consider indirect effects and exercise caution when forecasting abundance patterns from single-species laboratory experiments. Furthermore, the results suggest that other factors, such as nutritional status or source population, could cause substantial variation in organisms' responses. Last, the results highlight a trend towards enhanced sensitivity to acidification when taxa are concurrently exposed to elevated seawater temperature ..." [39].

An additional unmentioned source of variability is that a broad range of calcifiers, particularly molluscs, have lifestyles and physiologies that have evolved to cope with tidal changes in their coastline habitats. At low tide the seawater within closed shells and, for mobile animals, remaining seawater in rock pools and crevices, increases in temperature, becoming anoxic and CO₂-rich, *conditions not far removed from those predicted for the wider ocean in the distant future*. This emersion being a twice-daily occurrence, the animals have evolved adaptations to suit.

Bivalves need to maintain a large volume of water inside the mantle cavity, which is enclosed by the shell, because the cavity functions as a respiratory chamber. The shell is secreted by the outer epidermal layers of the mantle tissue and during the adverse conditions of emersion there is survival advantage in continuing to calcify the now firmly-closed, and possibly exposed-to-air, shell to reinforce the shell's valves against predation.

The mantle cavity also contains the main body tissues of the animal (gills, foot and visceral mass of digestive tissues, reproductive organs, etc). In contrast to the shell, there is survival advantage in reducing the rates of body tissue growth under prolonged emersion. If the soft tissue continued to grow steadily and came to occupy a larger part of the space, there would be less water inside the shell to support the metabolic needs of the increased tissue mass [40 – 42]. The tidal effects of the Moon are thought to have been a key environmental factor in the evolution of life on Earth since the Moon was formed [43]. These are not recent adaptations of shore-dwellers, but they have within them the physiological tools to cope with at least some of the more recent environmental challenges.

Remembering that all this concern about acidification applies to the *future-relevant pH levels of the next century*, the commonly held view that anthropogenic CO₂ in the world's oceans have reduced the pH of seawater to levels likely to have a harmful effect on the physiology of calcifying organisms is not the case yet.

For oceans a lifetime into the future, acidification is a legitimate concern; but this is irrelevant for the present day and its dire predictions should not be allowed to influence our choice of mechanisms to control climate change today, nor our intent to put them into effect immediately. We are not alone in this conclusion. Connell et al. (2017) [44] tested the effects of ocean acidification on a calcifying gastropod herbivore in a volcanic CO₂ vent ecosystem with local CO₂ levels close to those predicted for the world's future oceans. They found that:

"... contrary to predictions, the abundance of this calcifier was greater at vent sites (with near-future CO₂ levels). Furthermore, translocation experiments demonstrated that ocean acidification did not drive increases in gastropod abundance directly, but indirectly as a function of increased habitat and food (algal biomass) [44]."

They concluded:

“...the effect of ocean acidification on algae (primary producers) can have a strong, indirect positive influence on the abundance of some calcifying herbivores, which can overwhelm any direct negative effects [44].”

The review paper entitled *Rebuilding marine life* [45] indicates that achieving the UN’s Sustainable Development Goal 14 (“... to conserve and sustainably use the oceans, seas and marine resources for sustainable development ...”)

“... will require rebuilding the marine life-support systems that deliver the many benefits that society receives from a healthy ocean ...”. But they finally conclude that “... Rebuilding marine life represents a doable Grand Challenge for humanity, an ethical obligation and a smart economic objective to achieve a sustainable future ...[45]”.

In the opinion of Duarte et al. (2020) [45], recovery rates seen in past studies of conservation interventions suggest that:

“... substantial recovery of the abundance, structure and function of marine life could be achieved by 2050, if major pressures - including climate change - are mitigated ...[45].”

In their brief letter to the journal *Science*, Gordon et al. (2020) [46] asserted that “... Marine restoration projects are undervalued ...” and in their final paragraph they concluded:

“The pessimistic view of marine restoration as a fruitless exercise differs from attitudes about the rehabilitation of forest habitats that suffer equivalent large-scale degradation. Generally, socioeconomic, ecological, and cultural values are appreciated in tree planting, whether it involves a few saplings or millions ... Political agreements for global reductions in atmospheric carbon have been slow to emerge. Relying on their implementation as the only solution to the degradation of tropical habitats is a major gamble. In the meantime, restoration projects could help maintain species survival and ecosystem services, ultimately providing humanity with the breathing space to stabilize the climate [46].”

There is clearly a widely held view that protecting ocean health is important and overdue. If the roles that ocean calcifiers could play in atmospheric carbon capture and storage were to be factored into these arguments it might increase the urgency with which ocean health is addressed.

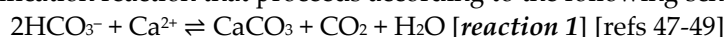
Marshall (2015) [12] points out that science uses words like ‘uncertainty’ in a different way to the lay public. To avoid any thoughts of scientific uncertainty becoming a primary issue in this debate, we wish to emphasise that in relation to ‘ocean acidification’:

- The uncertainty lies in the doubts that exist about the future date at which the oceans will become acidified to the point at which calcifiers are grossly adversely affected by oceanic pH. Will it be 2050 AD, 2100 AD or 2150 AD?
- In contrast, it is certain that calcifiers in their natural environments will be adversely affected when the general ocean pH levels do reach the extreme levels that the experimenters choose to use in their laboratory experiments on the topic;
- It is equally certain that today’s ocean pH has no general adverse effect on the behaviour of our principle calcifiers, animal, plant, unicellular or multicellular, which in many cases where the tests have been done, showed a positive response to today’s less alkaline (but described as acidified) pH conditions.

Consequently, today’s calcifiers *can be put immediately* to the tasks of providing us with nutritious food, numerous ecosystem services (filtration, biodeposition, denitrification, enhanced biodiversity, reef building for shoreline stabilisation, wave management and coastal protection), whilst, incidentally, permanently sequestering CO₂ from the atmosphere to the extent of at least half their mature body weight and depositing in the oceans as present day fossilised limestone.

4. Issue 2: calcification makes a net return of CO₂ to the atmosphere

CaCO₃ and CO₂ are produced from calcium ions and hydrogencarbonate ions by the calcification reaction that proceeds according to the following scheme:



This calcifying reaction scheme shows that two hydrogencarbonate ions (which originally were both derived from the atmosphere, photosynthetic fixation of atmospheric CO₂ being the only source of metabolic carbon) react with a Ca²⁺ ion and one of them is precipitated as CaCO₃, and the other released as CO₂.

It is the ongoing interpretation of this by marine inorganic chemists “as a net return of CO₂ to the atmosphere” that is a concern. We want to emphasize at this point that the immediately following discussion does not deal with the ‘carbon footprint’ of bivalve farming (for which see Subsection 4.4 ‘Life cycle assessments (LCA) of bivalve farming’ below) but deals specifically with the ‘carbon footprint’ of the formation of the shell material.

The proposition that shellfish offer no net removal of carbon from the atmosphere starts to worry us at the lunch table, when we discard all those CaCO₃ shells that are left after our meals of *moules marinière* (see Figure 1). Many of us enjoy shellfish foods, especially oysters, clams, mussels, lobster and crab, and all the other seaside treats, too. So, we must be aware from our own experiences of the amount of shell left over after the meal. For example, our average *moules marinière* for two (Figure 1), which uses 810 g fresh weight of mussels and, after the meal, leaves shells with a dry weight of 296 g.



Figure 1. The main ingredient of a lunchtime *moules marinière* for two. Mussels fresh weight of 810 g; after the meal, shell dry weight of 296 g. Photograph by David Moore.

If we assume that this shell ‘waste’ is all CaCO₃, then this calculates to these two plates of food permanently removing about 36 g of carbon from the atmosphere. That may not be very much, but it is just two plates of food in one dining room on one occasion. Can you think of any other plate of food that demonstrably removes *any* carbon from the atmosphere, *permanently*? If we could arrange for every person on Earth to enjoy such a meal on just one day every week, about 7.5 million metric tonnes of carbon would be removed permanently from the atmosphere each year. We will think about scaling up these numbers more realistically a little later.

For arithmetic convenience in what follows we will adopt the convention that the bivalve’s shell represents 50% of the fresh weight of the animal, though this is undoubtedly a gross underestimate of the amount of shell in shellfish harvests. The “shell to flesh” ratio is extremely variable between different cultivated bivalves. In addition, the shell, which is mineralised CO₂ from the atmosphere, is the animal’s protective armor, of course, so a component of the variability lies in the individual animal’s response to its local environment by managing the physical density of its shell. Waldron (2019) [50] reminds us that the shell of the “... Gulf oyster *Crassostrea virginica*, which has evolved to repel oyster drills, drumfish, oyster flatworms, raccoons, and crabs, can armor itself with 5 to 6 times its body weight in shell ...”. and he describes and illustrates a single individual “... healthy, mature oyster, whose flesh weighed 3 ounces [85 g], and whose shell weighed 1.1 lbs [499 g] ...” that appeared in a dredge sample during an oyster lease survey of bedded leases in Terrebonne Parish of Louisiana, USA, in September of 2018.

Shellfish tonnage (comprising oysters, mussels and clams) *marketed* in the European Union (EU) in 2019 had a live weight of 580,044 tonnes and yielded 458,700 tonnes of (waste) shells [51]. This Aquaculture Advisory Council (AAC) *Recommendation* to the European Commission and Member States quotes the average *meat percentages* of harvested bivalve live weight as 8.5% (oysters), 25% (mussels) and 14% (clams). Importantly, the AAC report points out that in addition “to the volume of shells at consumer level, the volume of farmed shell debris must be added” [51]. This shell debris is part of the harvest and results from bivalve mortality during cultivation and, expressed as a percentage of live weight of the harvest, is estimated as 25% for oysters, 20% for mussels and 4% for clams. The total *farmed shell debris* harvested during 2019 being estimated as 118,230 tonnes. This makes the total farmed bivalve shell tonnage harvested in the EU in 2019 equal to 576,930 tonnes, which is further estimated to represent the sequestration of 45,124 tonnes of *atmospheric carbon* [51]. As the shells of dead molluscs are not digested and are chemically stable, they can contribute to offshore reefs that can persist for geological periods of time.

Mulling this over after lunch, we realised that there are five major scientific reasons for doubting that shell calcification is “a net return of CO₂ to the atmosphere”, so we decided to audit what has been described as the *Blue Carbon Account*.

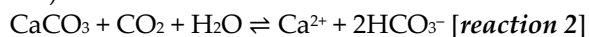
4.1. Two minus one cannot be a net return to atmosphere

In shallow waters, where most shellfish are cultivated, CaCO₃ is essentially insoluble and totally stable (limestone). Consequently, the biological calcification reaction removes from any further chemistry or biochemistry one of its two initial reactant hydrogencarbonate ions. As the ocean absorbs about 30% of the CO₂ released into the atmosphere [52], the source of both of those hydrogencarbonate ions is atmospheric CO₂, either through CO₂ reacting with water to form carbonic acid (which dissociates), or from metabolism of food-derived organic carbon (*ALL* of which on this planet is derived from photosynthetic fixation of atmospheric CO₂). Hence, *reaction 1* can be expressed as 2 atmospheric carbons + calcium \rightleftharpoons one precipitated carbon + one potentially atmospheric carbon. Arithmetically, this cannot be claimed as a net return of CO₂ to the atmosphere. Using only the stoichiometry of *reaction 1* to evaluate carbon fluxes gives a false impression and merely tells part of the story [51].

4.2. The calcification reaction is reversible in oceanic waters

We must also recognise the fact that *reaction 1* is *chemically* reversible (we deal with its enzymology below), the position of the equilibrium changing according to local, open water oceanic, conditions. The equilibrium shown above as the scheme for *reaction 1* refers to the chemistry of shallow waters. As water depth increases, changes in local conditions gradually change the causality to favour the reverse scheme, shown as *reaction 2*, below.

Solid shells of dead calcareous plankton and other calcifiers occur in the water column of the ocean, to depths of about 3,500 to 5,000 metres, which is the Calcite Compensation Depth (CCD) that separates calcareous from noncalcareous sediments [53]. At the depth of the CCD all CaCO₃ dissolves to form hydrogencarbonate ions. High hydrostatic pressure at these depths, coupled with decreasing temperature and increasing amounts of dissolved CO₂ derived from the respiration of organisms living in the habitat drives the equilibrium in the direction of hydrogencarbonate formation according to the following equation (because gaseous CO₂, as the only compressible reactant, cannot outgas from the solution):



CO₂ is taken up in this reaction but the carbonate ion (CO₃²⁻) remains intact. If the seabed is above the CCD, bottom sediments consist of calcareous ooze, which accretes into a type of limestone or chalk in (geological) time. If the exposed seabed is below the CCD the sea floor sediment will be a layer of siliceous ooze or abyssal clay [54], because

CaCO₃ dissolves before reaching the ocean bottom, but this is a solvation, not a dissociation; *the carbonate ion remains intact*.

Note that **reaction 2** (dissolution at high hydrostatic pressure) is the exact reverse of **reaction 1** (calcification). The gaseous atmosphere is not directly involved in either equilibrium direction, this calcification/dissolution equilibrium being a balanced oceanic CO₂ cycle that depends on water depth. In the extreme case the solubilised hydrogencarbonate ions will be carried by the global thermohaline circulation and could take a thousand years to surface and interact again with the atmosphere.

4.3. Calcifying organisms use a highly conserved biomineralization toolkit to make the shell

So far, we have dealt only with the reversible calcification reaction as though the chemical reactions were taking place in laboratory glassware. In the *living* cell, calcium has a key role in signalling and calcium homeostasis is strictly maintained. In coccolithophores calcium is transferred in vesicles, containing calcium-loaded particles, that fuse with another “coccolith vesicle” in which coccolith calcification occurs [55]. Thus, to be returned to the seawater (one step prior to the atmosphere), CO₂ molecules released by **reaction 1** would have to be transported across *at least* two ion-selective phospholipid membranes. Though, as we explain below, in all calcifying cells, **reaction 1** takes place on the surface of an evolutionarily conserved polypeptide complex, not in free solution.

If this CO₂ is released from the calcification assemblage, it will dissolve in the first aqueous compartment it encounters in a matter of seconds [56] becoming a hydrogencarbonate ion which is a candidate for another round of calcification, and in illuminated coccolithophores, would most likely be harvested for photosynthesis. Even “dissolving in a matter of seconds” is too slow for *metabolic* processes. Waldron (2019) [50] has indicated that most of these debates about CO₂/ HCO₃⁻/ H⁺ ignore the fact that the cascade of reactions giving rise to biogenic calcification is mediated by the enzyme **carbonic anhydrase** [57]. This indifference occurs despite the fact that this enzyme family is figuring increasingly in civil engineering biomimetic designs using immobilized enzymes for CO₂ capture for industrial carbon capture and storage (CCS) processes from flue gases, where it is called *microbially induced carbonate precipitation* or MICP technology [58-63].

In living organisms, prokaryotes and eukaryotes alike, *carbonic anhydrases* (CAs) are so widely distributed that it is probably true to say they are universal enzymes. These zinc-containing polypeptides catalyse the reversible hydration of CO₂ to hydrogencarbonate (‘bicarbonate’). At least five distinct CA families are recognized: α , β , γ , δ and ζ . These families have no significant similarity in amino acid sequence (implying their *convergent* evolution) and vary in distribution across different organisms. Each family usually has numerous isoforms that may be differentiated for different functions in the cell, between organelles or between tissues and organs in more complex organisms. Sequence diversity of this magnitude demonstrates that *enzymic control* of the hydration of CO₂ has been, and remains, of such crucial importance to life on this planet that the function has been endowed with exceptionally high positive selection pressure.

Physiologically the CA reaction contributes widely to normal metabolism: to control the acid-base balance of the cell, organelle or tissue; to metabolic respiration in aerobes (as well as gas transport and gas exchange ‘respiration’ in the complex organisms that ‘breathe’), and, in a chemically different environment, to anaerobic metabolism. CA is also essential in photosynthesis (for more information, view *Science Direct* at this URL: <https://tinyurl.com/4h3thahn>).

The *essential* contribution of carbonic anhydrase to calcification reactions of calcifier organisms is well documented. CA plays a key role in biomineralization by the benthic foraminiferan, *Amphistegina lessonii* [64] and ten α -CAs were found in the mantle tissues of the Mediterranean mussel [65]. Comparative genomics of the sequence of the most abundant form (named, MgNACR) grouped MgNACR with oyster nacreins, suggesting to these authors that, like nacrein, the MgNACR protein “likely regulates mussel shell

production" (Cardoso et al 2019 [65]). Miyamoto et al (1996) [66] had already demonstrated that nacrein, a soluble organic matrix protein in the nacreous layer of oyster pearls, contained two functional domains: a carbonic anhydrase domain which was split into two subdomains with what was suggested to be a calcium-binding domain between them. Seemingly, these domains participate in calcium carbonate crystal formation of the nacreous layer [66] and are components of a highly conserved biomineralization toolkit in shell-bearing bivalves [67] that has been described as "a complex bioceramic assembly process" [68].

For several reasons, therefore, but principally the wide distribution of carbonic anhydrases and the intimate connection of molecules having this enzymic activity with the structural assembly of the shell material, calcifying organisms will make no return of CO₂ to the open atmosphere from their calcifying activities, but only controlled emissions of metabolic wastes, like CO₂, to their local aqueous environment. Mussels on their rocky shore would fizz like sparkling wine if such calcification-related atmospheric emission really happened [52].

4.4. Life cycle assessments (LCA) of bivalve farming

A growing amount of detailed and comprehensive data bearing on 'shellfish for carbon sequestration' has appeared in recent years, though use of quantitative units was confusingly variable in the early years [50, 69-76]. The most recent of these studies make use of life cycle assessments (LCA) of mussel and clam farming in Mediterranean waters and conclude that the activity is a sustainable aquaculture practice as well as a carbon sink [57, 77-80].

Alonso et al. (2021) [81] estimated that the CO₂ sequestration potential of bivalve aquaculture, using the then current value of 1 metric tonne of CO₂ in the carbon market, to be over 25 € per tonne fresh weight of shellfish, which would represent a value of around 125 to 175 million € yr⁻¹ to the European Union's *current* bivalve aquaculture industry alone. A global overall assessment of the economic value of non-food ecosystem services provided by today's bivalve aquaculture [76] estimated this to be worth about \$US 6.5 billion per annum. This estimate did not include carbon sequestration, but the authors do claim that oyster shells have an *additional* global potential worth of \$US 5.2 billion, as they are widely seen as having great potential as a CaCO₃ feedstock [51, 82] primarily, perhaps, for the cement industry in which:

"Between calcination and energy use, the production of one metric ton of cement results in the approximate emission of 1 metric ton of CO₂ into the atmosphere ... and according to the Zurich Polytechnic, something like 900 billion metric tons of it have been cast since the beginning of the industrial revolution..." [83].

Data from FAO Fisheries and Aquaculture Information and Statistics Branch (as of 25 May 2019; <https://www.fao.org/fishery/en/statistics/en>) show that over the years 2010–2017 aquaculture harvests across the globe totalled 53,512,850 metric tonnes of crustaceans and 122,527,372 metric tonnes of molluscs (a combined total of 176,040,222 metric tonnes in 8 years. If the shells represent an average 50% of the animal's mass, total shellfish shell produced globally was 88 million tonnes over 8 years. An average of 11 million tonnes of shell per year [10].

Molluscan shell is composed of about 95%-99% CaCO₃ with very small amounts of matrix proteins (responsible for directing species-specific crystal growth), whilst arthropod (crab, shrimp, lobster) exoskeletons are composed largely of chitin, but this is hardened after molting by heavy depositions of calcium-magnesium carbonate nanocrystals. In either group of organisms, mature shellfish shell is about 95% crystalline calcium/calcium-magnesium carbonate. So, not much arithmetic precision is lost by assuming that the shells are made entirely from CaCO₃. On a molar mass basis, carbon represents 12% of the mass of calcium carbonate. So, 11 million tonnes of shell per year is equivalent to 1.32 million tonnes of carbon per year being captured from the atmosphere *by current aquaculture activities*.

Moore et al. (2022c) [10] point out that global carbon emissions from fossil fuel use were 9.8 billion tonnes in 2014 (equivalent to 35.9 billion tonnes of carbon dioxide) [source: <https://www.co2.earth/global-co2-emissions>], thus, the carbon captured by world aquaculture is a very small contribution to compensating these emissions. However, these authors also calculated:

“... we estimate that 4.84 million tonnes of CO₂ per year is being captured, and mineralised, from the atmosphere by current aquaculture activities around the world. In carbon-offset terms, that’s equivalent to one million business class return flights between London Heathrow and JFK New York (6 billion miles of flying per year, every year)...” and that a single shellfish farm “... designed to produce 10,000 tonnes of mussels per year ... would permanently remove from the atmosphere an annual total of 1,606 metric tonnes of CO₂ ... [which could] offset 740 return business class tickets LHR-JFK, or offset driving 7,300,000 miles [in a 1.5 l petrol-engine family car]...” [10].

Unfortunately, so little credence is given to the ability of shellfish calcifiers to sequester atmospheric carbon that none of this offsetting is possible. Aquaculture is not presently considered to be a valid carbon-offsetting scheme (for the reasons mentioned in the second paragraph of our Introduction, above), and the yield of captured atmospheric carbon by the world’s current aquaculture industry is considered pitifully small in the face of the annual emissions of CO₂ through continued fossil fuel use. But the world’s current aquaculture industry is devoted to *food* production, and its scale, and the organisms cultivated are governed by the market forces applicable to a food delicacy; the atmospheric carbon the activity captures and stores in the shells is a by-product (and too often treated as a food waste needing some form of disposal).

Suppose we change the paradigm and cultivate shellfish *for their shells*, taking the meat produced as a nutritious byproduct. Then the market forces might dictate enhancing the scale of production towards a level that removes *very significant* quantities of carbon from the atmosphere. Moore et al. (2022c) [10] put it this way:

“...a million mussel farms would permanently remove about 4.5% of the global CO₂ emissions in each year. The call for a million mussel farms is by no means an extreme or unrealistic proposition. Imagine a mussel farm on every offshore wind turbine, every oil and gas rig, every pier, wharf and jetty, every breakwater or harbour wall; imagine cultivating cockles (and other clams) in every shallow sandy/muddy bay. Imagine restocking and extending every fished-out oyster fishery, every fished-out scallop fishery. We could start tomorrow” [10 and see ref 7]. To this, we would add that colocation of a range of aquaculture farming activities with wind farm installations has been demonstrated to be feasible and rewarding [84-86].

Another important point is that the LCAs show that as far as the aquaculture fishery industry is concerned, the diesel fuel consumption of diesel powered fishing vessels and the electricity consumption of onshore industrial plant (refrigeration, processing plant, warehousing, road transport, etc) are the major contributors to the environmental burden (the carbon cost) of cultivating calcifiers like bivalves. This is no different from any other maritime industry and will be steadily reduced as fossil fuel energy is replaced by renewable resources across this sector.

We have dispelled the notion that the calcification reaction itself is a net CO₂ source for the atmosphere earlier in this Section (above). But any adverse contribution of the *respiratory* flux of CO₂ to promote production of the shell that might be suggested is also doubtful. This environmental burden is true for all living organisms and is an inescapable part of the natural carbon cycling generated by *all* the life processes of those organisms. Designs for atmospheric amelioration must concentrate on net additions of CO₂ to the atmosphere resulting from use of fossilised resources. For an LCA about the aquaculture industry, although the carbon footprint of the boat’s diesel fuel is undoubtedly relevant, the release of CO₂ as a metabolic waste by the shellfish is no more relevant to their ability to sequester carbon than the respiratory flux of CO₂ of the boat’s crew; or even the respiratory flux of CO₂ of those who write and read about it.

None of these caveats about the ability of cultivated molluscs to contribute to carbon trading schemes have any parallel in discussions about including forest trees in carbon trading schemes. The common mantra there is ‘plant a tree to save the atmosphere/ biodiversity/ world’ and nobody seems to worry about the fact that *trees also release respiratory CO₂*. Photosynthetic organisms only sequester carbon when illuminated. When the light goes out, they are net CO₂ emitters. Indeed, analysis of forest carbon accounting indicates that, because of this, for more than two decades commercial forest carbon protocols have *overestimated* the carbon trading value of forest carbon by about 2½ times [87]. Another negative aspect for expectations that tree planting schemes can make a serious contribution to amelioration of our atmosphere is that “tree numbers have declined to nearly half since the start of human civilisation and over 15 billion trees are lost on an annual basis” [88].

The *key aspect* in any comparison between mariculture and forestry, though, is that photosynthetic organisms only sequester carbon whilst they remain alive; calcifier shells sequester atmospheric carbon permanently. Plant a billion trees [<https://www.nature.org/en-us/get-involved/how-to-help/plant-a-billion/>], and even though this number is only 7% of what is required to compensate for annual tree losses, and all the carbon is returned to the atmosphere after the plant dies, being digested by the legions of animals, bacteria and, especially, fungi that are just waiting for the chance to consume the forest’s biomass and convert it back to atmospheric CO₂ as quickly as possible. Cultivate a billion bivalves and when the animals die, they leave their shells as a legacy of solidified atmospheric carbon that can demonstrably stay sequestered for 500 million years. That’s a legacy worth cultivating.

4.5. Middens to be proud of!

Continuing the audit analogy, an audit trail (a sequential record of the history and details around an event) finds intact shellfish shells through the whole of early human evolution [4, 5], and into the deeper history of planet Earth as illustrated by the global reorganisations of carbonate accumulations from the Cretaceous to the Miocene (between 125 and 9 million years ago) [89-91].

Sedimentary limestone rocks derive all their CaCO₃ from the biological activities of bryozoa, corals, crinoids, microscopic algae, Foraminifera in the plankton and/or benthos of the day, as well as shellfish shells. And the fossils from really deep time that can all be described as calcifying shellfish include ammonites (extinct heavily calcified cephalopod molluscs that lived 65 to 240 million years ago), trilobites (heavily calcified marine arthropods of 520 million years ago), brachiopods (animals with upper and lower shells hinged at the rear end, while the front can be opened for feeding or closed for protection) fossils of which extend to 550 million years ago, and though the majority of their 15,000 species are extinct, about 300 species remain today.

There may well be doubts about the relevance to the current state of climate change of paleo-processes that occurred many millions of years ago. Yet we maintain that the fossil record clearly illustrates that the ancestors of today’s marine calcifiers possessed the physiological tools to flourish with both acidified oceans and great excesses of atmospheric CO₂. These organisms have regulated extremes of atmospheric CO₂ and ocean pH earlier in Earth’s history; we should empower them to provide these services again [2, 6, 8, 10].

Comparing the potential of this blue carbon biotechnology with artificial/industrial CO₂ Capture and Storage (CCS) solutions [8-10] we find that industrial CCS facilities deliver, at considerable cost, nothing more than captured CO₂, for which safe, reliable, *long term* storage, so far untested, of course, must be engineered at even further cost. Whereas aquaculture enterprises cultivating shell to capture and store atmospheric CO₂ permanently also provide nutritious *food* and perform many *ecosystem services* like water filtration, biodeposition, denitrification, enhanced biodiversity, reef building, shoreline stabilisation and wave management.

Most cultivated bivalves are capable, in nature, of building reefs of sufficient size that they provide coastal protection through their wave-calming effects [92]. Comparing terrestrial natural solutions, such as afforestation, we estimate that a mussel farm sequesters three times as much carbon per unit area as terrestrial ecosystems retain. However, blue carbon farming does not need irrigation or fertiliser, nor does it conflict with the use of scarce agricultural land [93]. Further, blue carbon farming can be combined with restoration and conservation of overfished fisheries contributing the potential social co-benefits of ecosystem conservation, reclamation, and restoration, e.g., restoration of the European and US oyster beds that were dredged-out in the 18th and 19th centuries, and coral reef restoration with cultivation of giant clams [93, 94]. The portfolio of benefits from bivalve cultivation and the ecosystem conservation value of restoring these exhausted fisheries is being recognised around the world. Just three examples will suffice to show the variety of approaches that can be used: in Louisiana, USA [*“Louisiana Oyster Management and Rehabilitation Strategic Plan”* download PDF from <https://tinyurl.com/5azjs7ee>], Scotland’s ‘*Review of the contribution of cultivated bivalve shellfish to ecosystem services*’ [download PDF from <https://tinyurl.com/3umymbnt>], *Native Oyster Restoration Alliance* [<https://tinyurl.com/bep4ckzm>] and the ‘*Maorach Beag*’ *Scottish Shellfish Company* website [<https://scottishshellfishcompany.com> & <https://tinyurl.com/38pn967z>], the Chesapeake Bay Program [<https://tinyurl.com/4khe7cds>] and the *Billion Oyster Project*, which is restoring oyster reefs to New York Harbor in collaboration with New York City communities [website: <https://www.billionoysterproject.org/>].

There is also a growing awareness that “seafood is climate friendly” [95] and even that bivalve shells have value over and above their present day categorization as “food waste” [96] but all this research and all these conservation projects maintain the established categories that *bivalve meat is food* and *bivalve shell is food waste*.

This conservatism is no real surprise given the long history of humanity’s dependence on shellfish. Shellfish have been a critically important resource for coastal human populations [97] since the genus *Homo* first emerged “out of Africa” [93]. Shell middens made by these ancient peoples map their migrations around the world, being one of the most widespread archaeological deposits in the world which inform about human adaptations to coastal environments, the evolution of coastal economies, ritual practices, and prehistoric architecture [98, 99]. Shell mounds are the most recurrent and conspicuous evidence of prehistoric populations, and other examples are the intertidal rock-walled terraces, or clam gardens, developed by Indigenous Peoples of the Northwest Coast of North America. These ancient mariculture engineering features managed the resources of their shoreline habitats by creating shallow sloping intertidal shelves where clam productivity was enhanced [100, 101].

In recorded history, exploitation of marine resources was greatly increased to support an ever-growing human population. By the end of the nineteenth century oysters had become a cheap staple food on both sides of the Atlantic. The working man could get a decent meal of oysters at any street corner for a few cents in New York or a penny or two in London. The price we all paid for this bounty was that oyster dredging around the coasts of Europe and North America destroyed at least 85% of the world’s oyster beds [93, 102, 103].

The paragraphs above demonstrate the crucial contribution that shellfish have made to human development in the past and there is growing appreciation of the continuing role that mariculture can play in food production in the future [95]. We wish to go much further and convey the potential value to humanity of a marine environment properly managed as a carbon capture facility, which many recent reports suggest to us to be a viable and worthwhile activity [51, 104-108].

4.6. Solution for today: Cultivate shellfish on industrial scale for their shells

Shellfish shells, coccolithophore coccoliths and foram tests are all left behind in the ocean when calcifying organisms die and it is only this legacy of the long-term sequestration of CaCO_3 produced by calcifiers that will **remove net CO_2 from the atmosphere**. And this is why our argument demands a change in paradigm towards cultivating calcifiers for their CaCO_3 . It is also why we believe that this change in paradigm would transcend the current vogue for carbon accounting that integrates into the account all possible carbon flows, even those that do not contribute directly to sequestration. Good commercial economic practice this may be, but it ignores the basic biology of the biotechnologies it seeks to analyse and has led to inflation of the carbon trading value of forest carbon [87] and, in our view, critically underestimates, and undervalues, shellfish shells and the CaCO_3 produce by planktonic calcifiers in **permanent net carbon sequestration**. Marine sediments already sequester a great deal of carbon. Indeed one recent study states clearly that "...a lot of carbon is already stored away in Welsh marine sediments, at least 113 Million tonnes (Mt) in the top 10 cm. This represents almost 170% of the carbon held in Welsh forests" [107].

We calculate that the paradigm shift (from 'shellfish as food' to 'shellfish for carbon sequestration') makes bivalve mollusc farming and microalgal farming enterprises, viable, profitable, and sustainable, alternatives to *all* industrial carbon capture negative emissions technologies [109] and terrestrial biotechnologies in use or in development today. Aquaculture can be scaled from supporting indigenous subsistence communities [93, 104] through to industrial facilities like offshore platforms (re-purposed oil/gas-rigs) and/or factory ships producing nutritious human food/animal feed in massive quantities as a by-product of their carbon sequestration service [110].

To encourage change of the paradigm from cultivating shellfish for food to cultivating shellfish for their shells we must make the shells a valuable resource that can be traded. So, the most urgent need is to have shellfish cultivation recognized as a carbon offsetting scheme for other people's carbon footprints. Carrying through the principle that the polluter pays, CO_2 producers (from holiday jets to heavy industry and the fossil fuel industries) could fund cultivation of shell quite legitimately as a permanent *biotechnological* removal of carbon from the atmosphere. The shellfish farmers could then take the shellfish meat-protein as a profitable by-product.

Biotechnological research on all forms of aquaculture, including shellfish processing, is very well documented [111-115] and it is important to appreciate *as a fact* that fears that action to deal with climate change is impossibly costly are not true for the biotechnology of aquaculture [116-118]. Clearly it will take time, perhaps several decades, to amplify calcifier cultivation globally to levels that remove decisive quantities of CO_2 from our atmosphere on an annual basis but gains from this activity are not restricted to some far off uncertain future. Every tonne of live shellfish that is harvested *today* provides half a tonne of nutritious meat. When the corresponding half-tonne of dead shell is returned to the seabed to contribute immediately to a growing reef habitat that fosters biodiversity, shoreline stability and make its contribution to CaCO_3 accumulation in ocean sediments [119-122]. In particular cases (oysters and giant clams, for example), such restoration repairs the losses caused by generations of overfishing. And from the very first harvest, every metric tonne of live shellfish harvested removes a quarter-tonne of CO_2 from the atmosphere, permanently [7, 10].

5. Conclusions

On the basis of the varied research referenced above we conclude that dire warnings to the effect that acidification of the oceans can cause adverse effects on the activity of marine calcifiers do not apply to *present day* oceanic calcifiers and *present day* oceanic conditions. Such warnings about acidification relate to projected future events if the IPCC

IS92a ‘business-as-usual’ scenario [21] is played out. Even then, the high levels of atmospheric carbon dioxide (CO₂) accumulation and change in ocean pH of a magnitude likely to cause marine calcifiers to suffer are a *lifetime in the future*; being projected for 2100 AD.

We believe that the most commonly held views of the present day about ocean chemistry arise from too much weight being given to carbonate chemistry in circumstances in which water surfaces are in equilibrium with the open atmosphere. Alongside this, there is too little consideration of **biological** carbonate chemistry that is organised to take place within and between membrane-bound organelles located within membrane-bound cells. Yet the latter evolved from the former and this evolutionary connection should enable recognition that marine shellfish of our present day oceans *do* have a physiology and lifestyle that is daily, as the tides ebb and flow, experiencing and *living with* stressful conditions within their own shells. Indeed, conditions that are far more stressful than even the most pessimistic of predictions do not anticipate for the wider oceanic environment for more than 100 years. We hope that this view of marine calcifiers will show the value and promise of the contribution that aquaculture could make to bringing equilibrium to the atmosphere.

Whatever we humans decide to do, it remains the case that in today’s oceans there is, and there will continue to be, a constant rain of the solid CaCO₃ shells of dead calcareous plankton and other calcifiers sedimenting through the water column of the ocean to contribute to the calcareous ooze of the sea floor. Which, in due time will create the next layer of fossiliferous limestone. If we make the right decisions *now*, there may be humans around in ten-thousand years to admire our actions. This outcome is much less certain if we continue to hesitate.

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