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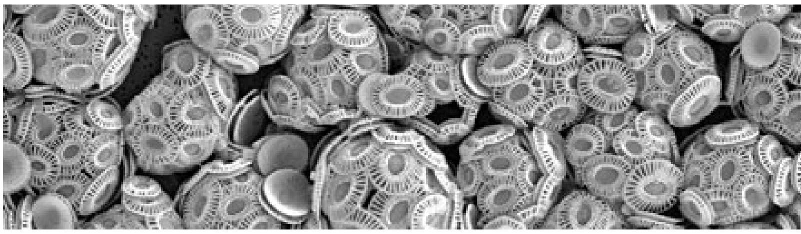
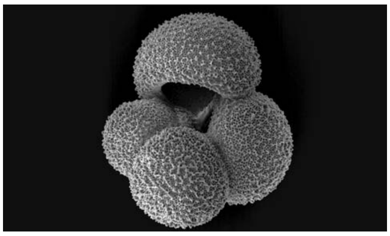
The Significance and Management of Natural Carbon Stores in the Open Ocean

November 2014





We manage land and the coasts for carbon – so why not the ocean as well?

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The Significance and Management of Natural Carbon Stores in the Open Ocean

We manage land and the coasts for carbon – so why not the ocean as well?

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Cover photos (clockwise from top): Antarctic (John Weller); globally distributed coccolithophore *Emiliania huxleyi* (Gustaaf Hallegraeff UTAS); floating *Sargassum* sp. in the Gulf of Mexico (Sylvia Earle); shell of the foraminifera *Globigerina bulloides* (Andrew Moy AAD); and adult Antarctic krill (Rob King).

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IUCN (International Union for Conservation of Nature)
Global Marine and Polar Programme
Rue Mauverney 28
1196 Gland
Switzerland
Tel +41 22 999 0000
Fax +41 22 999 0002
marine@iucn.org
www.iucn.org/publications

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Preface

In 2009 IUCN published a now landmark report[1] that synthesized a significant quantity of new scientific information on coastal ecosystems containing rich, stored carbon resources. At that time we stressed the need for prudent management to ensure that the carbon trapped in these ecosystems remains there – thus serving the triple objectives of mitigating carbon emissions, protecting nature, and supporting livelihoods that depend on such intact ecosystems. This led to global recognition and renewed efforts around the world to safeguard these ecosystems on land.

The question then remains – what about the other half of planet Earth - the open ocean - which is frequently referred to as the largest carbon sink on Earth? In this report we highlight the carbon-critical role of the open ocean by explaining how the system works, and then illustrating the criticality of managing carbon in the sea - as on land - using a number of case studies. Our aim is to bring scientific knowledge together in a way that shows the open ocean in a new light, in a new important context but one with wide resonance, in order to stimulate a global debate on improving the management and protection of the ocean and at the same time ensure the stability of the vast stored carbon resources.

The 2009 report showed that when damaged or destroyed, coastal habitats reduce or stop fixing carbon and can release significant amounts of carbon dioxide (CO_2), derived from the carbon in the living vegetation or below in the sediment, back into the air. Coastal habitats differ from the more readily-recognized terrestrial carbon sinks, such as forests, because they store a higher volume of carbon per unit area, and in some circumstances they are much less affected by emissions of other powerful greenhouse gases, such as methane. There is now consensus that recognition of this so-called coastal "blue carbon" is a major driving force for changes to improve the management, conservation and restoration of coastal ecosystems.

In this current report we set out to answer a series of equally critical questions for the open ocean. What are and where are these open ocean carbon sinks or pools? Are we already impacting them through the consequences of our activities, and is it possible to better manage them to help mitigate against climate change? Does any of this affect how we might seek to mitigate climate change? Is management action even possible, and if so what modifications to human uses of the ocean are needed? Through these questions and others, we would like to stimulate a discussion on the role of oceanic blue carbon in mitigating climate change, just as the 2009 publication did for coastal ecosystems.

It is hoped that this report will add an ocean voice and scientific substance to the urgent need to drastically cut anthropogenic carbon emissions coupled with a twin track approach of rebuilding and sustaining resilience in ocean ecosystems. This could be through, for example, strictly enforced marine protected areas (MPAs) and making our uses of the ocean more truly sustainable, whilst factoring the carbon role of ecosystems and species into day-to-day management, impact assessments and decision making.

Carl Lundin
Director
IUCN's Global Marine and Polar Programme

Dan Laffoley
Marine Vice Chair
IUCN's World Commission on Protected Areas

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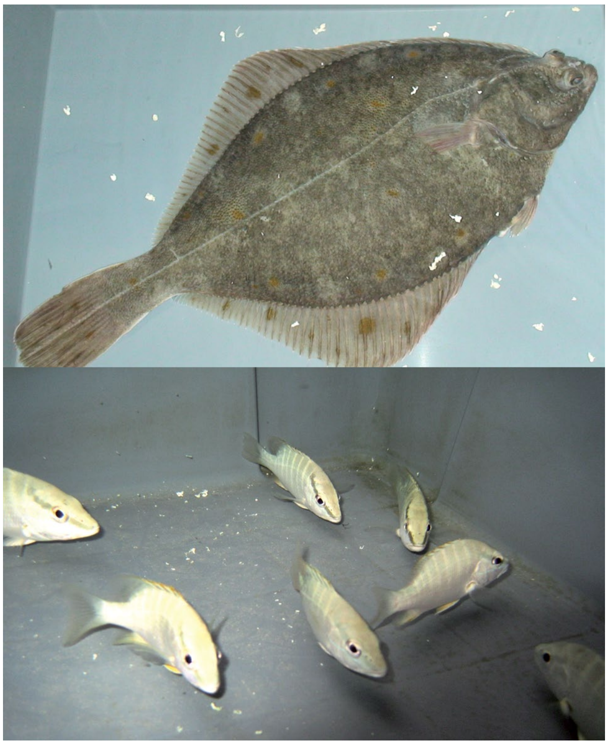
[1] Laffoley, D.d'A. and Grimsditch, G. (eds). 2009. The management of natural coastal carbon sinks. IUCN, Gland, Switzerland. 53 pp.

3.6 Fish

Rod W. Wilson
Biosciences, College of Life
and Environmental Sciences
University of Exeter
Exeter, EX4 4QD, UK
r.w.wilson@ex.ac.uk



Example of a temperate fish species (European flounder) and (sub) tropical fish species (schoolmaster), in tanks showing their white coloured carbonate pellets that have been excreted from their guts.

Summary points

- Fish make a significant contribution to oceanic carbonate production (0.04-0.33 x 10^{15} g of $CaCO_3$-C per year) in the form of high Mg calcite crystals excreted continuously via the gut.
- The high Mg content suggests rapid dissolution near the ocean surface that would restore surface alkalinity to a greater degree than other biogenic carbonates. This would neutralize much of the CO_2 released as a consequence of the calcification process.
- Temperature and CO_2 forecasts for the next century (+4 °C and 750 ppm) suggest fish carbonate production may become 58% higher than today, contrary to the effect predicted for many calcifiers. Warmer conditions would also increase their Mg content and near-surface dissolution.
- Conversely, there is evidence for preservation of fish carbonates in shallow, tropical sediments. Mid-Cretaceous marine conditions would have massively enhanced production of fish carbonates with much lower Mg content, enhancing their potential for preservation in carbonate sediments and geology.
- Quantitatively, the fate of fish carbonates in the ocean is not yet understood well enough to estimate their role as sources or sinks of CO_2.

3.6.1 Introduction

Marine biogenic calcification has traditionally been attributed solely to those marine organisms that make skeletal material from inorganic calcium carbonate. The major calcifiers in the open ocean are phytoplanktonic coccolithophores, representing about half of global calcium carbonate production (Beardall and Raven, 2013). Microscopic animals such as foraminifera and pteropods also make key contributions (Schiebel, 2002). The role of these species in the open ocean C cycle is discussed in Section 3.1 by Roberts, Hopcroft and Dupont. Of the shallow marine calcifiers, corals are perhaps the most charismatic and well known. However, due to their limited distribution their quantitative significance globally is actually small (<10%; Ware *et al*., 1992; Milliman and Droxler, 1996). More recently the carbonate budget of benthic calcifiers, specifically echinoderms, has been updated and recognized as another major calcifier on a global scale (Lebrato *et al*., 2010). However, fish are perhaps the most surprising addition to the list of quantitatively significant marine calcifiers (Wilson *et al*., 2009), and they are the only marine organisms that make calcium carbonate as a by-product of gut physiological processes as opposed to the need for structural (skeletal) material. A further important distinguishing feature of fish calcification is that their gut carbonates are produced and excreted continuously throughout their lives rather than the very intermittent release associated with either death, moulting or physical erosion of traditional calcifiers.

Fish may turn out to be a major player in both the net production of calcium carbonate minerals and subsequently the control of surface ocean chemistry. In particular the more rapid dissolution of fish carbonates is likely to have a more immediate impact on surface alkalinity and buffering of seawater, enhancing the ability of the ocean to absorb CO_2 from the atmosphere. This chapter will provide the current, though still limited, understanding of the role fish play in the marine inorganic C cycle.

3.6.2 Definition of the key species

Only teleost fish (i.e. those with a bony skeleton) produce gut carbonates, not elasmobranchs (sharks and rays that have a cartilaginous skeleton). However, teleost fish make up ~95% of the global marine fish biomass (8.99×10^8 t), the remaining 5% being elamsmobranchs (Jennings *et al*., 2008). To our knowledge all teleosts produce gut carbonates, as a by-product of their physiological strategy of drinking sea water for osmoregulation (see below for details), whereas elasmobranchs do not drink sea water in significant amounts. The need for drinking sea water is present throughout the lives of teleost fish from hatching to fully mature adult (Tytler and Blaxter, 1988). The production of gut carbonates from this ingested sea water has not yet been explicitly measured across the full size range of teleost fish (<1 mg to > 1000 kg). However, the mass-specific gut carbonate production rate (i.e. μmol-C.kg^{-1} of fish.h^{-1}) has been shown to follow a consistent scaling relationship over a wide range of body sizes and species in tropical teleosts (1 g to 13 kg; Perry *et al*., 2011) in which it doubles for every 10-fold decrease in body mass. This relationship is linked to the overall mass-specific metabolic rate of animals, which is similarly higher in smaller animals (Clarke and Johnston, 1999).

Production and release of gut carbonates by teleost fish is thought to occur throughout their lifecycle and therefore wherever they are found within the oceans. The vast majority of fish biomass occurs around the continental shelves, and this is why Jennings *et al*. (2008) reported that 50 % of fish biomass is restricted to only 17 % of the total area of the ocean. More specifically, high densities of teleost fish biomass are mainly restricted to upwellings and coastal shelves in the mid-latitudes. However, this does not mean that the open ocean is devoid of significant biomass of fish and their carbonate production, just that the density is lower in these regions. It is worth noting that the mesopelagic fish (e.g. lanternfish - small deepwater fish of the Myctophidae family) dominate the global biomass of fish and are the most widely distributed and populous of all vertebrates, let alone fish. Furthermore, Irigoien *et al*. (2014) suggest that their biomass has been previously underestimated by at least an order of magnitude. So despite a much lower density of fish in the open ocean, the potential total contribution of such species to the global production of carbonates should not be ignored, even though it is yet to be measured directly.

3.6.3 The biochemical processes of calcium carbonate production by fish

Teleost fish, unlike other calcifiers, do not produce significant amounts of $CaCO_3$ as part of their skeleton; the bones of vertebrates are made up of the mineral apatite, which is primarily calcium phosphate. The $CaCO_3$ discussed here is produced continuously within the intestines of marine teleosts as a waste product that is excreted on an almost daily basis. For most species examined so far, the crystals of $CaCO_3$ formed in fish guts conform to the mineral type known as high magnesium calcite (Wilson *et al*., 2009). The reason for this high Mg content (up to 40 mole %; Perry *et al*., 2011; Salter *et al.,* 2013) relates to the Mg^{2+} concentration at the site of production (the intestine) and will become clear below.

Teleost fish need to drink substantial quantities of sea water to avoid dehydration. This is because their blood-salt content is approximately one third that of the ambient sea water, resulting in substantial osmotic loss of water across their permeable outer surfaces (Marshall and Grosell, 2005). For example, a typical seawater ingestion rate in marine fish is equivalent to an adult human drinking about 7 litres of fluid per day. Drinking a fraction of this volume of sea water would be lethal to most vertebrates, due to the high concentrations of salts, particularly the dominant sodium and chloride ions. Such high intake of Na^+ and Cl^- ions would exceed the salt-excretion capacity of human kidneys and actually lead to even worse dehydration, but teleost fish have evolved extra-renal mechanisms to exclude the ingested and absorbed Na^+ and Cl^- ions, primarily via the gills. Sea water also has high levels of divalent ions, specifically calcium (Ca^{2+}), magnesium (Mg^{2+}), and sulphate (SO_4^{2-}) that may also be absorbed once ingested and require additional mechanisms of regulation (Wilson *et al*., 2002; Wilson and Grosell, 2003; Marshall and Grosell, 2005). To limit their dehydration problem, marine fish produce very little urine that consists almost entirely of Mg^{2+} and SO_4^{2-} ions. Excretion of excess Ca^{2+} ions via the kidney of marine fish is limited, as this would risk the precipitation of kidney stones (Wilson *et al*., 2002; Wilson and Grosell, 2003). The majority of ingested Ca^{2+} actually remains within the intestinal fluid and, after passage through the (usually acidic) stomach, it is precipitated within the intestine as carbonate crystals.

The cause of gut precipitation is the highly alkaline (pH 8.2-9.2) and bicarbonate-rich (30-100 mM) nature of intestinal fluids (Grosell, 2011). To put this into perspective the bicarbonate concentration/alkalinity of the intestinal fluids is 15 to 50 times higher than the ambient sea water (~2 mM). Intestinal epithelial cells use metabolic CO_2 to generate bicarbonate ions that are transported at very high rates into the intestinal fluid (Figure 3.6.1).

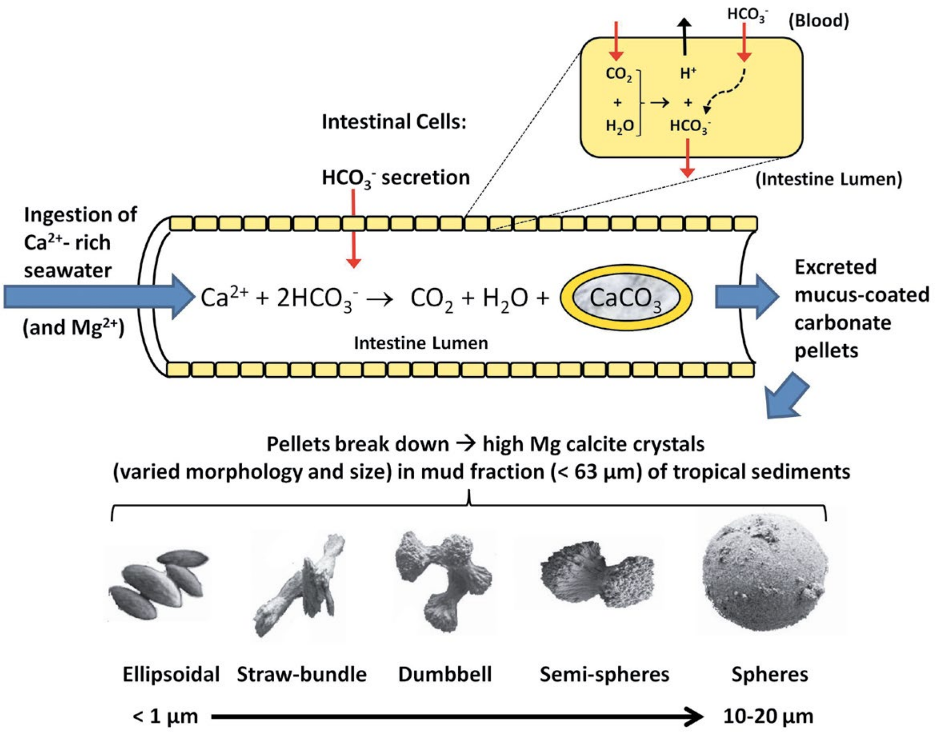


Figure 3.6.1. A schematic diagram of the mechanism of alkaline precipitation of carbonates (high Mg calcite) in the intestine of marine teleost fish. The intestine is shown as a simple tube. Epithelial cells that line the whole length of the intestine continuously secrete HCO_3^- ions at high rates. This is fuelled by either a) respiratory CO_2 (either produced within the cell itself or from the blood) being hydrated under the catalysis of carbonic anhydrase, or b) via uptake of HCO_3^- ions from the blood. The resulting cellular HCO_3^- ions are then transported into the intestinal lumen. Details of the transport processes involved are provided by Grosell (2011). The net effect is very alkaline pH (typically 8.2–9.2) and high HCO_3^- concentration (30-100 mM) within intestinal fluid, substantially higher than in sea water (pH ~8.1 and $[HCO_3^-]$ ~2 mM). This promotes rapid precipitation of most of the Ca^{2+} ions (and some of the Mg^{2+}) ingested with sea water as crystals of high Mg calcite that aggregate in mucus-coated pellets which are regularly excreted into the external environment. The mucus and pellets rapidly disaggregate once released yielding crystals with a wide range of morphologies and a high magnesium content (e.g. 4–40 mol% as $MgCO_3$; Perry *et al*., 2011; Salter *et al.,* 2012).

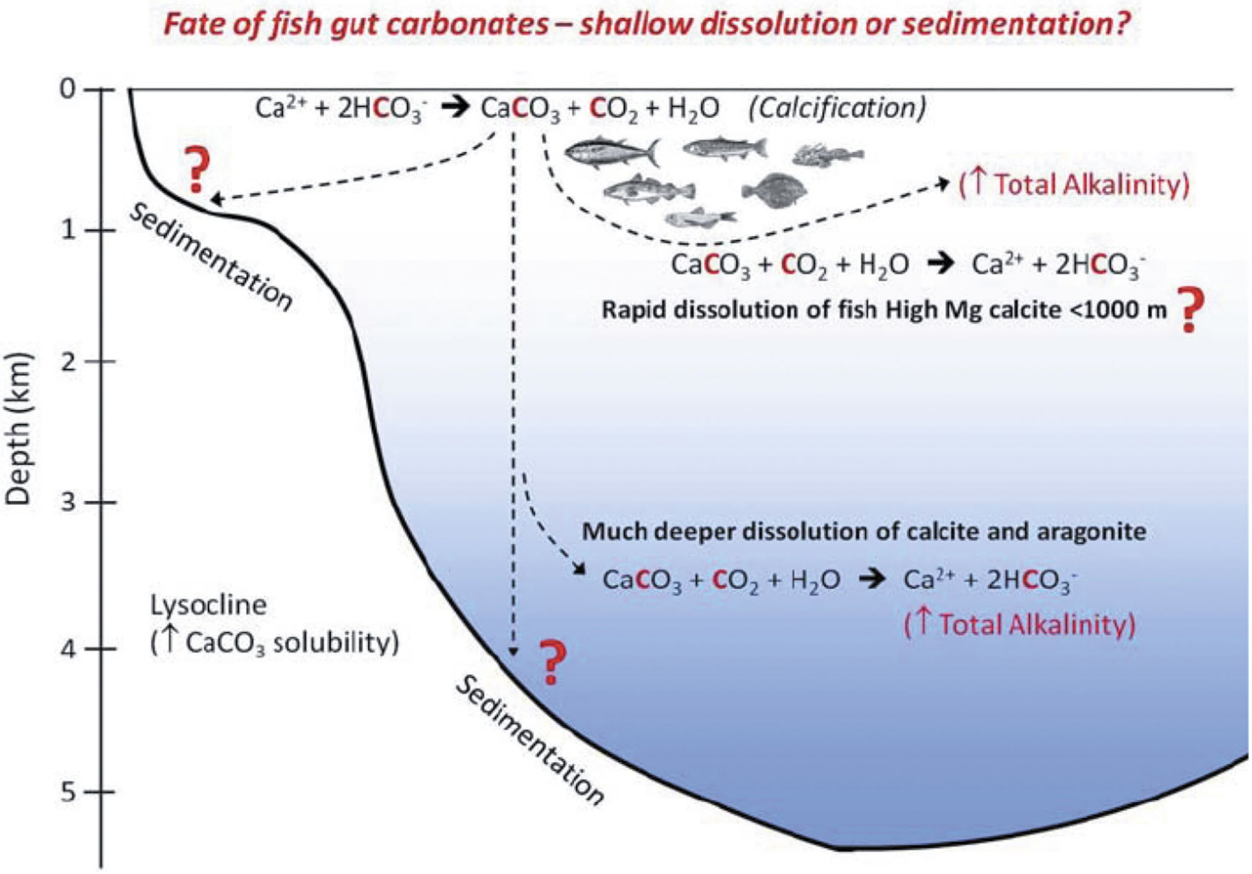


Figure 3.6.2. A schematic diagram of the potential fates of high Mg calcites produced by marine teleost fish. Chemical reactions show carbon atoms highlighted in bold and red. The original calcification process acts as a sink for carbon by 'consuming' one carbon molecule from the first HCO_3^- ion. However, an issue that often causes confusion is that this reaction also transfers carbon from a second HCO_3^- ion into CO_2. Therefore calcification actually contributes to enhanced seawater (and atmospheric) CO_2 and ocean acidification. Sedimentation of any carbonates results in their removal from the inorganic carbon cycle, and hence a net acidifying effect on ocean chemistry. However, relatively shallow dissolution of high Mg calcites from fish (based on expected high solubility; Wilson *et al.,* 2009; Woosley *et al.,* 2012), would result in restoration of total alkalinity and pH in the surface ocean. Dissolution of carbonates (e.g. calcites and aragonites from other calcifiers) in the deeper ocean will also restore seawater alkalinity and pH, but, owing to the slow vertical mixing from such depths, this will not affect the surface ocean for hundreds of years.

This creates super-saturated conditions with respect to $CaCO_3$, resulting in at least 80 % of ingested Ca^{2+} ions being precipitated prior to their ultimate defaecation in mucus-coated pellets (Wilson and Grosell, 2003). Precipitation occurs along the entire length of the intestine with the transit time for intestinal fluid ranging from a few hours to days, decreasing as temperature (and metabolic rate) increases. Ingested sea water has about 52 mM Mg^{2+} which becomes more concentrated (i.e. >150 mM) as fluid is absorbed along the intestine (Wilson and Grosell, 2003). This explains why the gut carbonate crystals of fish often incorporate such high proportions of magnesium giving rise to the collective description as high Mg calcite (Wilson *et al*., 2009; Perry *et al*., 2011; Salter *et al*., 2012; Woosley *et al*., 2012). It is worth highlighting that although these carbonates pass via the guts of marine fish, they are produced *de novo* from calcium ions in the ingested sea water rather than representing undigested food items. Indeed, marine fish produce gut carbonates at very high rates even when starved (Wilson *et al*., 2002, 2009).

As pointed out in Section 3.2 of this report, the role of biogenic $CaCO_3$ producers in carbon cycling is complicated by the fact that the calcification reaction is simultaneously a sink for carbon and a source of CO_2 gas (Figure 3.6.2), with ~0.6 mol of CO_2 being generated for each mol of $CaCO_3$ precipitated (Ware *et al*., 1992). At first glance this is counterintuitive and it is therefore important to make clear the distinction between carbon sinks and CO_2 gas sinks. The latter are the most relevant regarding our understanding, and potential management, of atmospheric CO_2 levels.

3.6.4 Local, regional and global significance of calcifiers as carbon pools

Global $CaCO_3$ production by fish

Laboratory based physiological studies of marine fish have produced data on mass-specific calcium carbonate excretion rates (i.e. quantity of HCO_3^- C excreted per kg of fish per unit time) in a variety of fish species over a wide range of temperatures (Wilson *et al*., 1996, 2002, 2009; Perry *et al*., 2011). Walsh *et al*. (1991) were the first to raise the possibility of fish as an environmentally relevant source of carbonates. However, until 2008 no models of global fish biomass were available such that a global estimate of fish $CaCO_3$ production was previously impossible. Then two separate approaches using ecological computer simulations of fish populations provided the first ever models of fish biomass across the full range of body sizes and habitats globally (Jennings *et al*., 2008; Christensen *et al.,* 2009). By combining the physiological data from lab experiments with population modelling a conservative estimate of the global contribution of fish to the marine inorganic carbon cycle yielded values between 40 and 110 million tonnes (0.04 to 0.11 x 10^{15} g) of $CaCO_3$ - C per year (Wilson *et al.,* 2009). This represents 3 to 15 % of the previous estimates of new calcium carbonate production in the surface ocean globally. To put this into perspective, 0.11 x 10^{15} gC.y^{-1} is equivalent to the carbon emissions (from fossil fuels) of countries like Brazil, UK or Australia (Schmitz *et al*., 2013). However, the proportion from fish could potentially be as much as 45 % (0.33 x 10^{15} gC.y^{-1}) if less conservative but realistic assumptions are used in the model (Wilson *et al.,* 2009).

The key assumptions within the model centre around the influences of temperature, body size, feeding, activity and lifestyle on the individual rates of carbonate production by fish. Current research is providing more precise data on these influences and will lead to a refinement of the estimates of global production by fish. The suggestions so far are that the influence of the most important variables, temperature and body size, on fish carbonate production are much greater than previously assumed in Wilson *et al*. (2009). The estimate of global $CaCO_3$ production by fish therefore seems likely to increase as a proportion of the global inorganic carbon cycle.

The shallow dissolution of fish carbonates in the ocean

Perhaps equally important to the quantity of high Mg calcite produced by fish is the fate of this carbonate material once excreted by the fish. Its high magnesium content compared to most biogenic calcite or aragonite is thought to increase the rate of dissolution within sea water (Morse *et al*., 2003). This suggests that fish carbonates may go into solution at shallower depths (< 1000 m) than carbonates from better-studied planktonic calcifiers (especially coccolithophores, the dominant producers of calcite) (Wilson *et al*., 2009). Dissolution of pelagic calcite and aragonite particles is only expected to occur once they sink below the chemical lysoclines for these carbonate minerals (i.e. depth where undersaturation becomes critical and the rate of dissolution increases dramatically; Milliman *et al.*, 1999). The lysocline for calcite ranges from 750 to 4,300 m in the north Atlantic and Pacific oceans, respectively. The equivalent lysocline depths for the more soluble aragonite mineral are 500 and 1,500 m, respectively. However, even the latter cannot explain consistent reports of dissolution of the majority of exported surface carbonates at depths much shallower than 500 m (Milliman and Droxler, 1996; Lee, 2001; Sabine *et al*., 2004), resulting in a parallel and striking increase in total alkalinity between the surface and 500 m depth (Feely *et al*., 2002; Chung *et al.,* 2003; Millero, 2007). This contradiction has been the source of a long-standing debate (Milliman, 1999). The simplest explanation is a significant source of much more soluble carbonates in the surface ocean. High Mg calcite excreted by fish would fit this scenario, and Wilson *et al*. (2009) suggested fish may therefore explain at least a quarter of the observed alkalinity-depth profile phenomenon, based on the original conservative estimates of fish production. A key factor in this being a correct hypothesis lies in the solubility of high Mg calcite from fish being much greater than that of calcite and even aragonite. The only published estimate of the solubility of fish gut carbonates suggests this is the case (Woosley *et al.,* 2012) with the value for high Mg calcite from the Gulf toadfish (*Opsanus beta*) being twice that of aragonite. However, it is worth noting that the method used by Woosley *et al.* (2012) did not actually measure dissolution, but instead measured the precipitation of new carbonates in super-saturated sea water stimulated by the presence of toadfish excreted carbonates. Direct measurements of the dissolution of fish carbonates remain unpublished, but certainly their consistently high Mg content should favour the potential for rapid dissolution at relatively shallow depths. The phenomenon of rapid dissolution of sinking carbonates is clearly important to understand because it reverses the original calcification reaction (which is a CO_2 source). In doing so it helps replenish the surface ocean alkalinity (Figure 3.6.2) which both buffers against further ocean acidification and enhances the absorption of further atmospheric CO_2 (Feely *et al.,* 2002).

Preservation of fish carbonates in shallow marine sediments

In warm shallow areas of the ocean, like the Bahamas, fish have recently been established as a significant source of carbonate sediment (Perry *et al.,* 2011; Salter *et al.,* 2012), suggesting that their dissolution is not always rapid. The potential for preservation of fish carbonates in such habitats is most likely explained by the high carbonate saturation states of surface waters. Based on lab experiments and ecological surveys of 11 fish species across a variety of different habitat types, Perry *et al.* (2011) estimated that fish contributed 14 % to the total quantity of carbonate mud (i.e. particles <63 µm) across the Bahamas, with values as high as 70 % of the fine-grade $CaCO_3$ particles produced in specific areas such as mangrove habitats. Perry *et al.* (2011) also identified identical crystals to those excreted by fish in sediments from all seven habitats surveyed in the Bahamas. Thus, in contrast to the potential for rapid dissolution of fish carbonates in the open ocean, at least in warm, shallow habitats (i.e. resulting in high carbonate saturation states) burial and preservation of high Mg calcites from fish is also a plausible fate.

Carbonate sediments generally provide important records of changes in ocean chemistry and climate throughout Earth's history (Elderfield, 2002; Riebesell, 2004; Ridgwell and Zeebe, 2005). Despite the occurrence of seemingly fish-derived crystals in modern shallow sediments, key questions remain about their long-term preservation potential. Specifically, how long do fish carbonates last in the sedimentary record before either dissolving or undergoing a chemical transformation to more stable mineral forms (i.e. diagenesis) within sediments. Revealing these unknowns is important to understanding the long-term fate of fish carbonates. However, it is too early in this field of research to provide a truly quantitative analysis of the global role of fish in both the calcification and dissolution fluxes of the marine inorganic carbon cycle. Nevertheless, the size of the estimated global carbonate production by fish, together with their global distribution, suggests that this information will be vital to accurately predict the impact of fish on the surface chemistry and potential of the oceans as a sink or source of atmospheric CO_2. In essence, fish appear to be a big player in the fluxes of marine inorganic carbon but at present it is not possible to be confident of the quantification of their short and long-term impacts.

3.6.5 Evolutionary aspects of fish as calcifiers – Lessons from the geological past and predictions for the future

Cretaceous marine fish carbonates?

Given that fish-derived carbonates are significant components of modern carbonate production it is of interest to consider how this source of carbonate production may have varied in the geological past. Modern marine bony fish (Osteichthyes) evolved from freshwater bony fish in the Jurassic (Fyhn *et al.,* 1999) and are considered to have undergone several major radiations that began in the early Cretaceous ~150 My ago (Benton, 2005) and include a particularly spectacular radiation during the Cretaceous that is unprecedented in its rapidity amongst the vertebrates (Finn and Kristoffersen, 2007). The precipitation of $CaCO_3$ in the intestine provides a key advantage in the osmoregulation of marine bony fish. It is an adaptation that probably arose very early in the evolution of vertebrates, even prior to the emergence of marine bony fish. This is because it can be induced in chondrostean and chondrichthyan fishes (sturgeon and sharks) when they are experimentally manipulated to drink seawater by transfer to a hyper-osmotic medium (Taylor and Grosell, 2006). So it seems likely that marine bony fish were excreting gut carbonates from very early in their evolutionary history. A key question therefore concerns how the prevailing environmental conditions over this timescale may have influenced the quantity produced, its mineralogy and fate, and hence the inorganic carbon cycle through Earth's history.

The effects of past marine conditions on fish carbonate production

The ocean environmental conditions have varied greatly during the ~200 million years of marine teleost inhabitation. From the current understanding of the physiology of gut carbonates it is likely that many of these variables would have resulted in major differences in $CaCO_3$ production by marine fish and its fate compared to today. In the mid-Cretaceous period, environmental conditions should have been particularly favourable for fish carbonate production and its preservation in sediments. In some cases the predicted effect of individual seawater variables are as great as an order of magnitude increase (see below). The combined effects of several of these variables have never been tested, but additive and possibly synergistic effects on $CaCO_3$ production can be hypothesized. The warmer temperature, higher Ca^{2+} and CO_2 levels, but lower Mg^{2+}, SO_4^{2-} and potentially O_2 in sea water, suggest that during the mid-Cretaceous fish may have peaked in terms of a truly massive contribution to the inorganic carbon cycle of the ocean. Its preservation was also much more likely given the considerably lower magnesium content under such conditions (see below). Thus Cretaceous fish could have been a major sink of inorganic carbon and a major source of CO_2 via the calcification process.

The effects of the above environmental variables on fish carbonate production are all linked to how they affect the delivery of seawater divalent ions (Ca^{2+}, Mg^{2+} and SO_4^{2-}) to the gut via ingestion, and/or the supply of secreted HCO_3^- ions from the intestinal epithelial cells. The variables known or predicted to affect these processes are discussed below:

A: Factors affecting seawater drinking rate in marine fish – salinity, temperature and oxygen

Gut carbonate production in fish is directly linked to the rate at which they drink sea water in order to osmoregulate. Ultimately this depends on the rate of osmotic water loss via their permeable outer surfaces. Obviously ambient salinity affects this directly by changing the osmotic gradient between the blood and external environment. Seawater drinking rate increases in proportion to this osmotic gradient, and gut $CaCO_3$ production actually increases exponentially with ambient salinity (Genz *et al*., 2008; Cooper *et al*., 2010). This is because as salinity rises, so do all the individual ion concentrations being ingested. So if salinity doubles, the ingestion of seawater Ca^{2+} ions would increase ~4-fold (double the volume × double the concentration) and ould subsequently all be precipitated by the super-saturated conditions within the intestine (Cooper *et al*., 2010). Palaeo-salinity proxies suggest that Cretaceous surface oceans were saltier than today's mean salinity of 35 (Rohling, 2007) with some suggesting values in the low 40s (Wagner *et al*., 2008) not dissimilar to the current Red Sea. Based on the above relationships a salinity of 40 in mid-Cretaceous should have generated $CaCO_3$ production rates that were 40-50% greater than today.

Temperature and oxygen affect seawater ingestion rate indirectly; rising environmental temperature or falling O_2 cause fish to increase gill ventilation so the osmotic loss of water via the gills increases in parallel. Gut $CaCO_3$ production increases at least 2.3-fold for every 10°C rise in temperature (i.e. $Q_{10} = 2.3$; Wilson *et al.,* 2009), which compares well with the Q_{10} of 2.5 for drinking rate in marine fish (Takei and Tsukada, 2001). Cretaceous temperatures were substantially warmer than today, the global average sometimes by as much as 10°C and deep ocean at least 10°C warmer (Huber *et al.,* 2002) with the mid-Cretaceous being one of the best examples of "hot greenhouse" climate conditions. Although the precise temperature differences relative to today are debated, fish in a Cretaceous surface ocean that was 7-8°C warmer on average (Friedrich *et al.,* 2012) would be expected to produce at least two thirds more $CaCO_3$ based on a Q_{10} of 2.3 (Wilson *et al.,* 2009).

Similar to temperature, atmospheric O_2 (currently ~21%), and hence dissolved O_2 in the surface ocean, is known to have undergone major changes over geological time. Most fish maintain normal metabolic rates (i.e. O_2 uptake) in the face of hypoxia. This is achieved by increases in gill ventilation (Perry *et al*., 2009) that in turn induce proportional changes in passive water fluxes across fish gills (Wood and Randall, 1973; Loretz, 1979). To compensate for the dehydrating effect of hypoxia-induced hyperventilation, marine fish must increase their drinking rate. Preliminary data on European flounder exposed to half the current atmospheric O_2 levels suggest that gut $CaCO_3$ excretion also increases more than 2-fold under such chronic hypoxic conditions (Rogers and Wilson, unpublished). Commonly cited scenarios for early-Cretaceous (~145 Mya) based on chemical proxies suggest that atmospheric O_2 was around 15% and subsequently rose to the modern level of 21% (Falkowski *et al.,* 2005; Berner, 2006; 2009). Under the mild hypoxia of early-Cretaceous it is estimated that gut $CaCO_3$ production would have been 50-60% higher than today.

Of additional relevance is the impact of the above variables on the mineralogy of biogenic carbonates. Magnesium content typically increases with temperature in marine calcifiers (Dickson, 2002) that in turn should enhance its solubility and thus reduce its preservation potential in carbonate sediments. However, the effects of salinity and oxygen on the carbonates produce by fish are not known and not obvious to predict.

B: Seawater Ca^{2+}, Mg^{2+} and SO_4^{2-} variations over geological time - influence on $CaCO_3$ precipitation and mineralogy

Modern oceanic sea water has a molar Mg/Ca ratio (*m*Mg/Ca) of 5.2 (Mg^{2+} = 52 mM, Ca^{2+} = 10 mM). However, this has varied greatly during the Phanaerozoic

Eon (i.e. the last 542 My) between about 1.0 and the present value (Horita *et al.,* 2002; Lowenstein *et al.*, 2003; Brennan *et al.*, 2004; Hönisch *et al.,* 2012). These secular variations in marine *m*Mg/Ca are considered responsible for major changes observed in the mineralogy of marine carbonates throughout this timeframe (Sandberg, 1983). A particularly low *m*Mg/Ca (<2) overlapped with the Cretaceous explosion of marine bony fish when the predominant form of abiotic carbonate mineral produced in shallow seas was low Mg calcite. Stanley and Hardie (1998) reported that the carbonate mineralogy of calcifying organisms correlates well with changes between "aragonite-sea" (when high seawater *m*Mg/Ca ratios >2 were prevalent) and "calcite-sea" conditions (low seawater *m*Mg/Ca ratios) throughout the Phanerozoic. Ries (2009) provides a thorough review of lab studies that explore the effects of experimental manipulation of seawater *m*Mg/Ca on extant marine calcifying organisms, although notably this did not include fish.

Preliminary studies with various seawater-acclimated fish species have revealed some remarkable responses to experimental manipulations of marine chemistry that mimic those within the Cretaceous period (Wilson, Rogers, Bill, Whittamore and Reardon, unpublished). For example, tripling seawater Ca^{2+} concentration alone from 10 to 30 mM (by addition of $CaCl_2$) produces a predictable 3-fold increase in $CaCO_3$ excretion by the gut of European flounder. However, a more realistic Cretaceous scenario is elevated Ca^{2+} concentration but with simultaneously reduced Mg^{2+} and SO_4^{2-} concentrations. Both latter ions are individually known to inhibit $CaCO_3$ precipitation (Morse *et al.,* 2007), and so Cretaceous seawater conditions should enhance $CaCO_3$ precipitation. The most extreme variation occurred around 130-100 Mya, when Ca^{2+} concentration was at least 3x higher than today (≥30 mM), with Mg^{2+} and SO_4^{2-} concentrations approximately half their current levels (about 26 and 9 mM, respectively; Lowenstein *et al.*, 2003; Ries *et al.,* 2009; Bots *et al.,* 2011). When these conditions were recreated in the lab, gut $CaCO_3$ excretion by three different species of fish (flounder, rainbow trout, sheepshead minnow) increased by 4- to 10-fold, i.e. much more than predicted simply by 3-fold greater Ca^{2+} ions available. This enhanced $CaCO_3$ excretion may be partly due to the lower Mg^{2+} and SO_4^{2-} levels in gut fluid and hence less inhibition of $CaCO_3$ precipitation. However, these lower seawater Mg^{2+} and SO_4^{2-} levels may also increase the osmotic permeability and water loss via the gills (Isaia and Masoni, 1976). In turn this would require elevated drinking rates to restore water balance thus supplying even more Ca^{2+} to the gut for precipitation.

As well as producing far more carbonate in total, the above three fish species exposed to Cretaceous seawater conditions all produced crystals with a much lower Mg content (half to a quarter of their carbonate crystals produced in modern seawater carbonates). Although warmer Cretaceous temperatures alone would yield higher magnesium content, the much lower availability of Mg^{2+} ions in Cretaceous sea water is likely to have much greater influence on the gut products from fish at that time. So the chances of being preserved, and so acting as both a carbon sink and a CO_2 source, would have been much higher during the Cretaceous period.

C: Factors affecting intestinal HCO_3^- secretion - seawater pCO_2

The permeability of fish gills to all respiratory gases is obviously essential and means that blood pCO_2 parallels external pCO_2 in fish (Heisler, 1984). Increased seawater pCO_2 therefore raises blood pCO_2 and causes an initial blood acidosis. However, fish are very good acid-base regulators and undergo compensatory accumulation of HCO_3^- ions in the blood to restore normal blood pH within 10-24 hours (Melzner *et al.*, 2009). The combined elevation in blood pCO_2 and HCO_3^- ions fuels further HCO_3^- production and secretion by intestinal cells (Esbaugh *et al.*, 2012). Unpublished data (Cobb, Whittamore and Wilson) shows that increasing seawater CO_2 from 470 to 4600 ppmv doubled the excretion of precipitated carbonates in European flounder, with no effect on their magnesium content. Atmospheric and marine CO_2 was elevated during the Cretaceous relative to today, but estimates of by how much vary from 1500 to 3000 ppmv during the peak at around 110 Mya (Royer *et al.,* 2007; Zeebe, 2012). Gut carbonate production is expected to respond to rising CO_2 in a linear manner, for the reasons explained above. So ocean CO_2 values of 1500 to 3000 ppmv would be expected to increase production by about 30 to 60%, but with no effect on its magnesium content and hence dissolution potential.

3.6.6 Predictions for the fish $CaCO_3$ production in the near future

Marine conditions during the Cretaceous will not be repeated in the near future. In particular no major changes in salinity, individual seawater ion concentrations, alkalinity or oxygen that are likely to affect fish carbonate production are predicted. However, both temperature and CO_2 are rising exponentially and at an unprecedented rate, and both these factors individually are known to accelerate $CaCO_3$ production in fish by different means (seawater ingestion rate and intestinal HCO_3^- supply, respectively). Based on the assumption of simple additive effects of these climate change variables in fish a 58% increase under a +4°C and 750 ppmv scenario would be predicted with a 40% increase being due to temperature alone (assuming a Q_{10} of 2.3 for carbonate production; Wilson *et al.*, 2009).

This contrasts with many other calcifiers that are predicted to decrease carbonate production at higher levels of seawater CO_2. Thus, if global fish biomass and distribution remain the same, their role in $CaCO_3$ production seems likely to increase as a proportion of all marine calcifiers. In addition the effect of warmer temperatures increasing the magnesium content suggests that their high Mg calcite products will have higher dissolution potential than today. However, precise data on solubility and magnesium content of fish carbonates are not yet available, and so the relative contribution of fish carbonates to future near-surface dissolution (i.e. neutralizing the effect of calcification) versus long-term preservation in sediments (i.e. a net carbon sink but CO_2 source) is currently impossible to predict.

Marine fish biomass is declining through over-fishing and there may be good reason to consider how this will also affect their role in carbonate production and subsequently ocean chemistry (Jennings and Wilson, 2009). This issue is complicated by the fact that fishing tends to remove larger individuals, leaving fewer predators for smaller fish, and these smaller individuals have a much larger contribution to global $CaCO_3$ production than larger fish (Jennings and Wilson, 2009; Wilson *et al.,* 2009). Predicting the future ocean carbon budget therefore becomes difficult when considering both the population effects of over-fishing, and the expected effects of climate change on individual fish highlighted above. Thus fish carbonate production in the future is difficult to forecast, and there are not enough data currently to allow confirmation of the combined effects of population restructuring by overfishing together with rising temperatures and CO_2. Further research into how the interaction of these various factors affects the role of fish in the global inorganic carbon cycle is therefore important, given the quantitative significance of fish as a major source of marine calcium carbonate.

3.6.7 Values - goods and services provided by fish

Management recommendations to maintain or enhance feature's ocean carbon role

The study of fish with respect to their quantitative role in the ocean's carbon cycle is in its infancy, having only been recognized as significant global producers of carbonates five years ago (Wilson *et al.*, 2009). The estimates of global carbonate production are in the process of being revised, based on more precise information on the influences of various biotic and environmental factors. However, little is yet known, quantitatively at least, about the fate of fish carbonates within the ocean. Yet this is the most vital component regarding our understanding of their influence on surface ocean chemistry and their net effect as a sink or source of CO_2. Without a better appreciation of the fate of fish carbonates, it is currently not possible to judge or recommend how to influence their role in the ocean carbon cycle. Nevertheless, a number of anthropogenic factors are already influencing fish populations globally, and with these undoubtedly global carbonate production by fish.

The direct impact/responsibilities of human activities on biogenic carbon sink

The only available global estimates of gut carbonate production by fish conservatively suggests a 3-15 % contribution to newly formed surface ocean carbonate, and this could be up to 45 % based on realistic rather than the most conservative assumptions (Wilson *et al.*, 2009). Furthermore, Irigoien *et al.* (2014) have very recently suggested that mesopelagic fish (quantitatively the largest group of fish by biomass) may be 10-30 times more abundant than previously estimated - including the biomass data used by Wilson *et al.* (2009) to estimate global fish carbonate production. So the upper figure of 45 % of surface ocean carbonate production looks likely to be even higher than previously suggested. This would potentially make fish the largest contributor globally. Perhaps more importantly, unlike the calcite and aragonite minerals produced by the better known ocean calcifiers (see Section 3.2), the high Mg calcite produced by fish is thought to dissolve rapidly enough whilst sinking to restore alkalinity to the surface ocean within a timescale of years rather than centuries (Wilson *et al.*, 2009; Woosley *et al.*, 2012). Thus fish carbonates may be a quantitatively substantial offset to the net CO_2 release by other sources of calcification currently, and likely to increase in this role in response to future warming and rising CO_2 levels (see above). Anthropogenic changes in fish populations and biomass therefore have the potential to diminish this neutralising role of fish carbonates in the surface ocean. The most obvious human activity in this respect is over exploitation through fishing.

Wild capture fisheries have already altered fish populations with regard to both total biomass (reduced) and their size distribution being shifted from larger to smaller individuals (Bianchi *et al*., 2000; Shin *et al*., 2005). Jennings and Wilson (2009) considered how fishing could influence the carbonate production by fish as a potential “ecosystem service”. Fisheries managers often aim to take the largest catch that can be removed from a species stock over an indefinite period, i.e. the “maximum sustainable yield” (MSY). Jennings and Wilson (2009) applied modelling of fishing impacts on carbonate production to a North Sea herring population and a coral reef fish community. This modelling suggested that even at exploitation rates that were lower than those deemed sustainable for the fish populations, their carbonate production would be substantially reduced. Thus, if fish carbonate production were to be considered by fisheries managers as an ecosystem service simply on the basis of their carbonate production, then lower rates of fishing mortality (than currently considered to be sustainable) would be required to viably maintain this service (Jennings and Wilson, 2009).

Multiple ocean stressors

Rising temperature and CO_2 are the most obvious combined stressors that are known to influence fish carbonate production, and its potential for dissolution. However, the third major chemical change to the ocean concerns oxygen, with the incidence of hypoxia increasing in coastal regions and the expansion of the oxygen minimum layer (OML) as a result of eutrophication and climate change (Diaz and Breitburg, 2009). As discussed above, any reduction in available oxygen is likely to accelerate the production of carbonates by fish (due to the link between gill ventilation, osmotic water loss, and compensatory drinking of sea water). Thus, all three of the most serious environmental changes afflicting the ocean (warming, carbonation, and deoxygenation) are expected to enhance global carbonate production by fish, with the interactions likely to be additive.

Unknown unknowns

Increasing temperature and CO_2 are predicted to increase gut $CaCO_3$ production by individual fish. In addition, fish are thought to be pre-adapted to coping with the increases in CO_2 forecast for the next century given their very good acid-base regulation capabilities (Melzner *et al*., 2009). However, surprising and unpredicted effects have been reported for such small elevations in CO_2 on fish sensory systems and behaviour of fish early life stages in particular. Specifically, the ability to smell, hear and respond appropriately to ecologically relevant stimuli such as predators and settlement habitat cues may be severely impacted in juvenile fish (Munday *et al*., 2009; 2012; Simpson *et al*., 2011). The negative implications of such behavioural changes for survival and population stability are obvious. So far most of these observations have been on coral reef fishes, but if the same applies to fish in other habitats, and acclimation or adaptation were limited, then this could be a major concern for fish populations as a whole.

3.6.8 Recommendations for policy makers

Fish represent a major source of protein for human populations globally, as well as providing a number of specific dietary health benefits via their oil content (particularly omega-3 fatty acids). In terms of harvesting fish, aquaculture currently provides just under half and continues to expand so will soon outweigh wild-caught fisheries production (FAO, 2012). Of course, the biodiversity loss due to over-fishing has already had an important impact on ecosystem services that fish provide (Worm *et al.,* 2006). Although aquaculture is often heralded as the solution to over-fishing its dependence on wild-caught fish as a source of fishmeal therefore means it is currently still contributing to the problem and is therefore not yet a totally sustainable answer. Fish also provide vital ecosystem services across all their life stages and via a wide range of both fundamental ecological and human “demand-driven” processes (Holmlund and Hammer, 1999). Examples of these services include maintaining healthy habitats (Mumby *et al.,* 2007), and nutrient cycling (Deegan *et al*., 1993; Meyer and Schultz, 1985). Additional socio-economic values of fish include the aquarium trade (Wood, 2001) and tourism (Vianna *et al.,* 2012). It is therefore not the intention of this review to make recommendations for policy makers regarding how we may wish to influence fish populations specifically based on their production of marine carbonates. However, the quantitative significance of fish within the inorganic carbon cycle has only recently been highlighted (and may be even larger). In addition, their carbonates appear to have a very different dissolution potential relative to most other calcifiers, with significance for the chemistry of the surface ocean and its ability to absorb atmospheric CO_2. This suggests that we currently do not fully understand this half of the ocean's carbon cycling and cannot appreciate it properly without substantially more basic information on the role and fate of fish carbonates.

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3.6.10 References

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