I - EXECUTIVE SUMMARY OF CIESM WORKSHOP 36

“Impacts of acidification on biological, chemical and physical systems in the Mediterranean and Black Seas”

by


This synthesis was drafted under the coordination of Aysen Yilmaz by all workshop participants, with special thanks to Scott Fowler and Marion Gehlen. The Monograph Series Editor, Frédéric Briand, reviewed and edited the entire volume, assisted by Valérie Gollino for the physical production process.

1. INTRODUCTION

The Workshop took place from 1 to 4 October 2008 at the Hotel Royal Westminster in Menton, within walking distance of the border separating France from Italy. Seventeen researchers from ten countries (see list at the end of this volume) attended this exploratory meeting at the invitation of CIESM. Frédéric Briand, Director General of the Commission, did warmly welcome the participants, reminding them that the workshop had been scheduled deliberately on the eve of the 2nd SCOR International Conference on 'Ocean in a high CO₂ World' - due to open in Monaco on the following week - so as to draw attention to this issue for the Mediterranean Sea, a region where the impact of acidification is still hardly known. A challenge for the participants would be to draw a much needed inventory of major gaps in, and priorities for, acidification research within the specific regional context. Professor Briand then introduced Professor Aysen Yilmaz, Chair of the Committee on Marine Biogeochemistry, who presented an overview of the scientific background and key objectives of the meeting, which would seek to take optimal advantage of the original mix of chemical and biological expertise brought along by the invited participants.

As a result of human activity, the chemistry and biology of the marine world are fast changing. This is particularly notable in terms of carbon emissions: since the beginning of industrialization, between 1800 and 1999, mankind has emitted 361 Gt C to the atmosphere of which the ocean has absorbed approximately 155 Gt C (Sabine et al., 2004). This makes the world ocean the largest sink of anthropogenic CO₂.
The uptake of CO₂ by the ocean is primarily a physico-chemical process. As CO₂ penetrates seawater, it behaves like a weak acid dissociating according to:

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + 2\text{H}^+
\]

which leads to an increase of [H⁺] and thus a drop in pH. This process, now well documented, results in acidification of marine waters on a global scale. It is referred to as ‘Ocean Acidification (OA)’ (Caldeira and Wickett, 2003; Orr et al., 2005).

Acidification of ocean water occurs in tandem with a decrease in carbonate ion concentration and the saturation state with respect to carbonate minerals (CaCO₃), which directly impacts its formation and dissolution. In the marine environment, carbonate formation is largely a biotic process (Milliman, 1993). Marine organisms form shells and skeletons composed of a variety of carbonate minerals: high-Mg calcite (coralline algae), aragonite (pteropods and corals, some foraminifera and bivalves), calcite (coccolithophores, foraminifera, some bivalves), as well as mixed-layered calcite and aragonite (certain bivalves). The solubility of a carbonate mineral depends on its composition and structure; it increases in the order of calcite, aragonite and high-Mg calcite. One can easily envision that these differences in solubility translate into variable susceptibility to dissolution of these minerals. Likewise one can also expect differing degrees of vulnerability of calcifying organisms to ocean acidification. In addition to changes in the carbonate system, OA is expected to influence ocean chemistry, affecting the availability and speciation of nutrients and toxins to marine organisms.

The general impact of OA on water chemistry is well understood but regional data and models are needed. An even more urgent need is to assess the impact on ecosystems. Study of the impact of OA at the biological level is in its infancy and there is little known about present and future impacts on marine organisms and ecosystems. This is particularly true for the Mediterranean and the Black Seas since these mid-latitude, semi-enclosed water bodies are not projected to experience the first effects of acidification such as occur in high latitude seas. The scant available data reveal contradictory results (increased and decreased calcification) (e.g. coccolithophores, Ziveri et al., this volume) and apparent paradoxes (e.g. corals, Fine and Mordechay, this volume; early life history, Dupont and Thorndyke, this volume). Furthermore the eastern and western basins of the Mediterranean Sea are significantly different environments, both chemically and biologically, so that the potential effects of OA on their chemistry and biology could substantially differ. At this early stage, based on limited present knowledge, it would be risky to extrapolate from one species to another and from one region to another. There is clearly an urgent need to predict the near future consequences of OA in Mediterranean and Black Sea species and ecosystems and to determine what species/ecosystems are most at risk.

Given the potential of OA to appreciably affect marine biodiversity, it is important as well to make initial evaluations of the possible negative socio-economic impacts, related for example to the fisheries and tourism industries.

This report presents the outcome of our discussions on where there are gaps in our knowledge, which data are needed urgently so as to predict potential impacts of OA on marine ecosystems in the near future. Based on available data, we will define priorities and suggest guidelines for future work.

2. IMPACTS OF HIGH \( p\text{CO}_2 \) ON MEDITERRANEAN AND BLACK SEA CHEMISTRY

2.1. Impacts of high temperature and \( p\text{CO}_2 \) on the chemistry of the Mediterranean and the Black Seas: emphasis on carbon cycle, carbonate chemistry, aragonite and calcite saturation horizons, and on pH

As the seawater temperature rises, we expect a slight decrease in the air-sea CO₂ fluxes due to the change in CO₂ solubility. On the other hand, as CO₂ rises in the atmosphere, we can expect a slight increase in the air-sea CO₂ fluxes due to the larger difference in \( p\text{CO}_2 \) between the air and the surface seawater. Consequently, the increase or decrease of CO₂ penetration into the Mediterranean and Black Seas will strongly depend upon the rate of CO₂ rise in the atmosphere. However since the temporal response of the CO₂ air-sea flux is relatively slow (one year), the CO₂ increase in the
atmosphere would probably be more rapid than in the sea-surface and will mitigate the temperature effect, which would tend to decrease the penetration of anthropogenic carbon in seawater.

If the chemistry of the CO2/carbonate system in seawater is well known, the amplitudes of variation of temperature and anthropogenic CO2 penetration that will influence the chemical equilibrium are not. For instance, it is known that as anthropogenic CO2 penetrates into the surface water by air-sea gas exchange, it raises both the concentration of total CO2 (CT), and the partial pressure of CO2 (p CO2). As p CO2 in sea-water increases, CO2 fluxes from the atmosphere into the sea surface decrease. In addition, p CO2 is very sensitive to temperature increase (~ 4,3 % per °C). Thus, both the increase in sea-surface temperature and the penetration of anthropogenic carbon into the sea-surface will increase the sea-surface p CO2, reducing the penetration of anthropogenic carbon into seawater. As the Mediterranean Sea is relatively more alkaline than the open ocean, during a given time-period it can absorb relatively more anthropogenic CO2 than the open ocean. In other words its potential pH change (decrease) is relatively large compared to that of the Atlantic Ocean. As Mediterranean seawater is warmer (> 13°C) and more alkaline than the open ocean throughout the water column (Touratier and Goyet, in press), its saturation state (Ω) with respect to calcium carbonate will remain saturated throughout most of the water column for many years to come.

Total alkalinity (A T) concentrations measured in the Mediterranean Sea are high (2,600 μmol kg⁻¹), which was attributed to evaporation coupled with high freshwater A T inputs into coastal areas (Schneider et al., 2007). Mediterranean waters are supersaturated with respect to calcite and aragonite; the excess alkalinity likely reflects alkalinity inputs to coastal areas close to regions of deep and intermediate water formation. An alkalinity budget shows that the main alkalinity inputs come from the Black Sea and from rivers, whereas the Strait of Gibraltar is a net sink (Schneider et al., 2007). The major sink appears to be carbonate sedimentation. The basin-average net calcification rate and CaCO3 sedimentation was estimated to be 0.38 mol m⁻² yr⁻¹. The estimated residence time of A T is 160 yr (Schneider et al., 2007).

In the late 1980s and early 1990s, abrupt changes in salinity and in temperature caused a continuous increase of density and massive deep water formation in the south Aegean Sea that altered the thermohaline circulation of the eastern Mediterranean with consequences also in the distribution of other environmental parameters (Roether et al., 1996; 2007; Malanotte-Rizzoli et al., 1999; Klein et al., 1999). Deep water formation areas in the Mediterranean may be responsible for setting the air-sea CO2 balance and act to sequester CO2 and increase the sink capacity in such areas.

There are less data on the carbonate chemistry of the Black Sea (Tyrrell et al., 2008). Goyet et al. (1991) measured total inorganic carbon (C T) and total alkalinity (A T), plus other carbonate system parameters derived from them at a single station in 1988. Surface water concentration of carbonate ion was 250 µmol kg⁻¹, and calcite saturation state was 7.5, that is, similar to the data collected in the central Black Sea in 2001 by Hiscock and Millero (2006). Data on the present calcium carbonate saturation state for the Black Sea surface waters are limited, but appear to remain strongly supersaturated year-round.

### 2.2. Impacts of acidification on biogeochemical cycling: emphasis on nutrients, trace elements and primary production

Robust information on the flux of nutrients and biogeochemical cycles under the influence of enhanced p CO2 is scarce at global level, and appears to be non-existent for the Mediterranean. Following a review of published information and a number of small scale experiments, we tentatively propose that ocean acidification will act to increase the oligotrophic nature of the Mediterranean Sea and increase the degree of phosphorus limitation currently found which, almost by definition, will contribute to reduced productivity and carbon export.

Theoretical considerations of nutrient equilibria with pH (Zeebe and Wolf-Gladrow, 2001) would suggest significant reductions in PO4 concentration and alteration of the NH4 ⇔ NH3 equilibrium at a pH decrease of 0.3, although two independent studies in northern waters have recorded little or no change in both PO4 and NO3 under this altered pH regime (Tanaka et al., 2007; Rees et al., this volume).
Two studies in Pacific (Hueseman et al., 2002) and Atlantic coastal waters (Rees et al., this volume) have indicated that nitrifying bacteria may be sensitive to OA. Reductions in nitrification rate of 20 – 30% have been suggested, which may have implications for the balance of new to regenerated productivity in surface waters and in the balance of the nitrification: denitrification couple in sediments and anoxic waters. Changes in the ammonium:nitrite:nitrate ratios may alter microbial species activity and diversity, with consequences on ecosystem function and the release of nitrous oxide.

Denitrification and sediment nutrient fluxes are also liable to be impacted by OA (Widdicombe and Needham, 2007; Rees et al., this volume). This has the potential to change microbial activity and both the type of bioturbatory organisms present and the intensity of their activities in the transport of nutrients across the sediment-water interface. There is evidence to suggest that under current reduction scenarios for ocean pH, NO3 removal from, and NH4 release to, overlying waters may be enhanced. This would further alter the NO3:NH4 stoichiometry, with implications for ecosystem function and algal community composition.

Recent laboratory studies with cultured Trichodesmium have shown that N- and C-fixation rates increased significantly with elevated CO2 (Hutchins et al., 2007; Levitan et al., 2007; Barcelos e Ramos et al., 2007). Particularly relevant to the P-impoverished Mediterranean is the study of Hutchins et al. (2007) who found that higher CO2 enhanced nitrogen fixation and growth rates even under severely phosphorus-limited steady-state growth conditions. However, our knowledge of the distribution and activity of diazotrophs under natural conditions in the Mediterranean is limited, and the dangers of extrapolating from a single species to the level of community effects need to be considered.

Decreases in ocean pH generally increase the proportion of free dissolved trace metals (Royal Society, 2005), thereby increasing metal solubility. This could in theory lead to substantial increases in the total bioavailable fraction of many trace elements, perhaps resulting in toxic concentrations. Micronutrients (e.g. Fe, Co, Zn, Cd and Cu) are essential components of numerous metalloenzymes, which ultimately regulate microbial activity, productivity and thus carbon export in the oceans. The variable sporadic supply of atmospheric Saharan dust is considered perhaps the most significant source of many essential metal nutrients such as Fe to the eastern Mediterranean (Statham and Hart, 2005). The present view is that Fe is highly unlikely to be limiting in the Mediterranean basins (Ozsoy and Saydam, 2001; Statham and Hart, 2005). Thus changes or increases in the bioavailable fraction of many trace metals due to ocean acidification of the Mediterranean are more likely to result in changes in the composition of microbial assemblages and/or toxic effects. Increased local regional variability in the manifestation and magnitude of these changes will be of paramount importance, e.g. potentially to the fishing industry.

The response of primary producers to OA is currently contentious and should be given priority for research activity. Whilst there have been a number of reports of enhanced organic carbon fixation at elevated CO2, the opposite has also been reported. At present coccolithophores are the main calcifying group in the Mediterranean and Black Seas. Published culture results show prevailing uncertainties regarding the controls on coccolithophore calcification response to anthropogenic OA. Adaptation to changes in carbonate ion concentration (e.g. basic building block of skeletons and shells for a large number of marine organisms) is also unknown. It is worth noting that the phytoplankton population of the modern eastern Mediterranean is dominated by picoplankton (Li et al., 1993) and nannoflagellates, including coccolithophores (Ziveri et al., 2000; Cros, 2001; Malinverno et al., 2003).

The strong uptake of anthropogenic CO2 by the Mediterranean Sea is significantly altering its seawater chemistry, particularly in the coastal zones. Acid-base imbalance and reduced oxygen transport capacity are some of the high CO2 influences on the physiology of marine organisms (Fabry et al., 2008; Widdicombe and Spicer, 2008). Today, one of the main limits to quantify and predict the impacts of ocean acidification is the scarcity of temporal observations of CO2 penetration in seawater. The first results of such observations in the Mediterranean Sea are from the DYFAMED time-series station. The main results (Touratier and Goyet, in press) indicate that:

1) The concentrations of anthropogenic CO2 in the Mediterranean are much higher than those found in the Atlantic Ocean (the minimum concentration at the DYFAMED site is ~50
µmol.kg-1). Consequently, the Mediterranean seawater already presents significant pH drops. Furthermore, the Mediterranean Sea is a source of anthropogenic CO$_2$ for the Atlantic Ocean.

2) Anthropogenic CO$_2$ is decreasing with time, especially in the intermediate and the deep layers of the water column at the DYFAMED site. This decrease of anthropogenic CO$_2$ in deep waters is significantly correlated with a decrease in the dissolved oxygen and with an increase in both salinity and temperature. The decrease of anthropogenic CO$_2$ resulted from an invasion of old water masses. In order to better understand the origin of this reduction, several hypotheses - such as increased stratification limiting the nutrient supply and high anthropogenic CO$_2$ penetration - are currently investigated.

2.3. How Mediterranean and Black Sea environmental conditions have changed due to changes in pH in the past: “Ocean Acidification” and lessons from history

To assess the impact of future effects of changing environmental conditions in the Mediterranean, we need to explore what lessons can be learned from the past. Subsequently this information can serve as a basis for validating model simulation studies on future impacts.

Abrupt climate changes are known to have occurred in the Mediterranean in the past, resulting in major changes not only in the accumulation of C$_{org}$ but also in that of calcium carbonate. Assessments of ocean acidification usually refer to the Mediterranean as being supersaturated with respect to carbonate, thus not a potentially impacted basin. However, the short water mass ventilation time of ~100 years suggests a rapid potential response to changing environmental conditions. When looking into past records, rapid variations in the Mediterranean acidification state appear to have occurred. These are most clearly expressed during periods of formation of organic-rich units (sapropels), often coinciding with considerably reduced sedimentary carbonate contents. Such observations may be related to changes in ecosystem, surface water biogeochemical processes, calcification of planktonic calcifying organisms, and partly also to dissolution events. These variations must be related to the very subtle balance in the eastern Mediterranean where slight environmental/climatic disturbances have resulted in major and abrupt system perturbations with dramatic consequences (Figure 1; De Lange, unpublished data). Not only do we find such major changes on the ~ 20 kyr scale, distinct but, more minor variations also appear to have occurred at higher frequency. Such major perturbations do not seem to govern the Western Mediterranean in the same way. In the present and in the past as well, environmental conditions apparently were different between the eastern and western Mediterranean resulting in distinct ecological responses. These differences are at least partly related to differences in thermohaline circulation and to the overall circulation pattern, the latter being more restricted and more sensitive to changes related to environmental forcing. The present-day situation is forced by the increasingly rapid rise of anthropogenic carbon into the atmosphere (Goyet and Touratier, this volume), thus provoking numerous impacts on the physical, chemical and biological properties of the Mediterranean Sea. The fast increasing rate of these changes makes them now observable over only a few decades, making continual observations essential.

Figure 1. Illustration of major rapid changes in eastern Mediterranean sedimentary carbonate contents over (a) the last 1.2 million years, and (b) the 160-200 kyr time interval. Sample resolution is ~ 500 years. (De Lange, unpublished data).
No published data are yet available for the carbonate response of planktonic calcifying organisms to past changes in sea surface water carbonate chemistry in the Mediterranean (Ziveri et al., this volume). The rate of calcium carbonate burial and the contribution of coccoliths to this amount can, however, be evaluated by estimates of species-specific coccolith weight (Young and Ziveri, 2000; Beaufort, 2005). The morphology and thickness of individual coccoliths help to evaluate past calcite production.

Deep- and intermediate water formation – and therefore ventilation – may have been much more variable in the eastern basin than in the western basin. Consequently, much larger perturbations are observed in the deep eastern Mediterranean sediment record. Such past perturbations have resulted in more acidic deep water characteristics, in the enhanced preservation of organic matter and dissolution of carbonate, and thus in enhanced sequestration of CO₂. One way to assess the differences in the past deep-water ventilation among the Mediterranean basins is through the investigation of the geochemical signals in natural marine archives, such as the deep-water corals inhabiting the intermediate and deep-waters. Cold-water corals are among the most promising archives for intermediate and bathyal water depths, generally providing higher resolution (although more discontinuous with time) than sediment cores (e.g. sub-decadal vs. 100-500 years for sediments), and not being affected by bioturbation. Moreover, cold-water corals can be radiometrically dated using both high precision U-series and ¹⁴C methods. By coupling radiocarbon data with P/Ca ratios – a technique which has been recently demonstrated to be a proxy for nutrients in azooxanthellate corals (Montagna et al., 2006) – from the same absolutely dated sample (U/Th) it will be possible to calculate the ventilation rate for specific time-windows in the past. The P/Ca encoded in the skeletal aragonite provides information on the phosphate content of individual water masses in the past and represents a water mass tracer, giving constraints on the mixing ratio between distinct compositional end-members. Further, ⁴P/Ca micro-analyses (Montagna et al., this volume) will allow us to quantify the fluxes of nutrients to intermediate and deepwater environments and assess the past ocean productivity, thereby furthering our understanding of the biological functions of the Mediterranean Sea in regulating atmospheric CO₂. Suggested future changes, i.e. in deep-water formation, thus in residence times for deep and intermediate water masses, will influence all of these properties.

3. MODELING STUDIES FOR BETTER UNDERSTANDING AND PREDICTIONS OF FUTURE IMPACTS

The Mediterranean basin is a potential hotspot for environmental change. Anthropogenic stressors such as increasing river nutrient loads, atmospheric inputs, pollution, fishing and aquaculture activities combine with climate change-induced temperature increase and changes in seawater chemistry. High alkalinity and high levels of super-saturation of surface waters are distinct features of the Mediterranean Sea (Schneider et al., 2007). Taken together these characteristics have led to the conclusion that impacts of ocean acidification would be less severe in the Mediterranean Sea than in other oceanic regions (e.g. Arctic Ocean). While a growing number of studies address changes in seawater carbonate chemistry in response to rising atmospheric CO₂ at the global or regional scale, we are not aware of studies targeting the Mediterranean or Black Sea. It is tempting to turn towards state-of-the-art coupled climate carbon models for a first order evaluation of effects. However these models lack the appropriate spatial resolution and process representation for deriving a realistic description of the Mediterranean and Black Seas. A typical model output is shown here (Figure 2) depicting the saturation state of the upper 100 m of the water column with respect to aragonite ($\Omega_a$) in the global ocean and the Mediterranean Sea respectively. Model results are from the French (IPSL) coupled climate carbon cycle model for a standard IPCC business as usual scenario (SRESA2). The model projects a decrease in surface ocean $\Omega_a$ from ± 4 in pre-industrial times to ± 2 at the end of the scenario. Therefore Mediterranean surface waters would remain oversaturated with respect to aragonite.

Studies of the calcification response of various organisms (Kleypas et al., 2006 and references cited there) suggest a reduction of calcification rates before undersaturation is reached. Similarly, saturation states of $\leq 2$ are referred to as marginal for tropical corals. Recent results (Iglesias-Rodriguez et al., 2008) challenge the straightforward relationship between calcification and
saturation. The biological impacts of changes in carbonate chemistry projected by the model need to be addressed through studies targeting Mediterranean calcifying organisms, both benthic and pelagic.

\[\Omega_{\text{aragonite}}\]

Figure 2. Saturation state with respect to aragonite averaged over top 100 m of water column in the global ocean (left panel) and Mediterranean Sea (right panel), computed for the preindustrial (top), present day (middle) and 21st century (bottom) by a coupled coarse resolution climate carbon cycle model.
While such a coarse resolution model allows a first assessment of changes in Mediterranean Sea carbonate chemistry in response to global change and rising atmospheric CO₂ levels, it does not resolve the complexity of Mediterranean hydrodynamics (e.g. rates and sites of deep water formation and variability). An improved representation of Mediterranean hydrodynamics is obtained from regional coupled atmosphere ocean models (Somot et al., 2006; 2008), which predict a decrease in deep water formation and thus a slowing down of the Mediterranean thermohaline circulation in response to climate change. A slowing down of deep water formation will isolate intermediate and deep waters from exchange with the atmosphere. This event could have consequences for anthropogenic carbon sequestration and for deep water chemistry. Such impacts need to be quantified on a Mediterranean basin scale and across the Mediterranean Sea outflow into the North Atlantic.

4. Biological impacts of ocean acidification in Mediterranean and Black Sea ecosystems

4.1. A rich biodiversity at risk

The Mediterranean maintains overall low biological productivity and a high species diversity with an estimated 8,560 species (between 4 - 18% of all described marine species), many of which are endemic. This is primarily because it is a warm sea in temperate latitudes and therefore hosts both temperate and subtropical species. There is a notable east to west gradient in increasing species richness which closely reflects climate gradients. Over the last few decades a northward migration of certain species associated with warming waters has been demonstrated in several areas of the western Mediterranean (CIESM, 2008).

The number of species in the Black Sea is around one third of that in the Mediterranean. Despite recent changes in absolute numbers, the ratio remains close to 2.3, with approximately 8,500 species in the Mediterranean versus 3,700 in the Black Sea. There have been dramatic changes in species diversity, particularly in the northwestern portion of the shelf, caused by eutrophication and subsequent hypoxia and anoxia conditions observed in the late 1980s and early 1990s. For example, between 1961 and 1994 the number of macrozoobenthic species on the Romanian shelf fell from 70 to 14 (Zaitsev and Mamaev, 1997) and there was mass mortality of benthic species (between 100 and 200 tonnes of organisms per km² of shelf) because of oxygen depletion. Recently, there has been some relaxation from the pressure of eutrophication on the Black Sea ecosystem. The first signs of recovery have been seen in the pelagic communities, while the zoobenthic communities are responding more slowly.

Functioning of the Black Sea ecosystem has profoundly changed since the early 1970s under cumulative effects of excessive nutrient enrichment (eutrophication), strong cooling/warming events (climate change), over-exploitation of pelagic fish stocks, and a population explosion of gelatinous species.

While very little published information is available on the effects of ocean acidification on specific marine organisms inhabiting the Mediterranean and Black Seas, many taxonomic groups present in these two semi-enclosed seas are also found in high latitude regions where many OA studies are presently focused. Thus lessons learned there will assist the design of experiments in Mediterranean and Black Seas. It is also agreed that one of the main consequences of an elevated pCO₂ in seawater will be a reduction in the rate of biogenic calcification in many marine species (e.g. corals, coccolithophores, pteropods, foraminifera, benthic molluscs, echinoderms and crustaceae). Research on warm water corals and calcifying phytoplankton (coccolithophores) indicated controversial responses of calcification rate with increased atmospheric CO₂ concentrations and concomitant decreased CaCO₃ saturation state in seawater. Beyond these two groups of organisms, there is very little published information about potential impacts on other calcifying species of ecological (pteropods, foraminifera) and additional economic (molluscs, echinoderms and crustacea) importance. Similar studies in the Mediterranean and Black Seas are only in their infancy.

4.2. Biological response to OA (based on experiments in the laboratory or in mesocosms

4.2.1. Pelagic organisms

*Coccolithophores:* Coccolithophores are responsible for approximately half of the global CaCO₃ production and can cause feedbacks to atmospheric CO₂ cycling (Milliman, 1993; Ridgwell et al.,...
They have a well documented continuous fossil record since the Mesozoic and in the Mediterranean provide a unique tool for Cenozoic paleo-reconstructions. Coccolithophores can also serve as mineral ballast which plays a role in the export of particulate organic matter to the deep ocean (Klaas and Archer, 2002; Ziveri et al., 2007). The effects of changes in coccolith calcification on carbon export in the Mediterranean and Black Seas are completely unknown but deserve attention: for pelagic benthic organisms, coccolithophores provide a major mechanism for food transfer from the surface to depth.

There have been controversial results from culture experiments (Riebesel et al., 2000; Langer et al., 2006; Iglesias-Rodriguez et al., 2008) on the impact of increased CO₂ on coccolithophores calcification. Experimental studies suggest a species-specific response of coccolithophores most probably due to artificial conditions used in the laboratory and this may not be relevant for field extrapolation. As only four species have been tested so far, the question of how many types of responses coccolithophores display, and whether these types are related to phylogenetic relationships, geographical distribution or life cycle phases, remain open. While *Emiliania huxleyi* is the dominant coccolithophore species in the Mediterranean Sea, the coccolith carbonate production is dominated by several other species depending on the individual mass of the coccolithophores (Young and Ziveri, 2000). To date no study has investigated the effect of OA on a Mediterranean coccolithophore species. However the large variability observed in size, morphology and carbonate mass of some key species (Ziveri et al., this volume) suggests a calcification response to the wide range of carbonate ion and CO₂ concentrations in surface waters (Schneider et al., 2007).

While no detailed studies have been performed on coccolith carbonate production in the Black Sea, preliminary studies have shown very low species diversity, with *Emiliania huxleyi* again largely dominating. SeaWIFS data for 1998-2002 suggest that the Black Sea consistently experiences high reflectance patches of *Emiliania huxleyi* throughout the basin each year during the May-July period (Cokacar et al., 2001; 2004). How OA can affect the major bloom activity in this basin is still unknown. However, the presence of a thick layer of coccoliths in surface sediments of the Black Sea (Hay, 1988) demonstrates that coccolithophores have also been present over the last few thousand years.

**Pteropods:** these planktonic molluscs are very common in the Mediterranean. Some species of pteropods produce a calcareous shell made of aragonite. Because of the higher solubility of aragonite in comparison to calcite – the constituent of foraminifera and coccolithophores calcareous structures – they are believed to be among the first planktonic organisms that will be threatened by ocean range (Orr et al., 2005). Because of the difficulty to culture these organisms, no published studies are available to date on the impact of low pH on their growth and calcification rates. Ongoing research in high latitudes areas and in the Mediterranean Sea will hopefully fill this gap in coming years.

**Planktonic foraminifera:** to the best of our knowledge, the effect of OA on foraminifera that are present in the Mediterranean and Black Seas has not been investigated. Most of the work on foraminifera in the Mediterranean Sea has been obtained from the fossil record. Interestingly, previous studies have shown changes of foraminifera shell mass during periods of sapropel formation (Principato et al., 2006) when a lower saturation state of the deep photic zone with respect to calcite has been suggested. Changes in foraminifera shell weight due to changes in surface water carbonate chemistry have also been suggested by several studies in other regions (Barker and Elderfield, 2002).

**Jellyfish:** there is some evidence (Attrill et al., 2007), which is controversial (Haddock, 2008; Richardson and Gibbons, 2008), that OA in conjunction with increasing temperature may lead to higher abundances of jellyfish over the next century. During the last two to three decades, jellyfish blooms have increased throughout the Mediterranean Sea, but the lack of adequate time-series on pH and jellyfish blooms frequencies prevents the resolution of this question.

### 4.2.2. Benthic organisms

The Mediterranean Sea hosts a high biodiversity and a relatively high number of endemic species (Fowler, this volume), together with a number of unique benthic ecosystems characteristic of its subtropical and temperate basins. Among these are the vermetid reefs, *Posidonia oceanica*...
meadows, coralligenous reefs, deep sea coral assemblages and _Cladocora caespitosa_ bioherms, all of which are biodiversity hot-spots that might undergo dramatic changes under ocean acidification conditions.

**The coralligenous reefs:** coralligenous reefs are characterized by numerous calcareous algae (Corallinaceae and Peyssonneliaceae, red algae) whose thalli are linked together, building a hard and heterogeneous structure of a few centimeters to a few meters in thickness, extending over rocky substrates between the _Posidonia oceanica_ meadows and the muddy bottoms of the continental shelf. This remarkable landscape harbors some 650 invertebrate species and at least 30 fish species. A number of studies have shown that calcareous algae are highly sensitive to ocean acidification conditions (Hall-Spencer _et al._, 2008; Hall-Spencer and Rodolfo-Metalpa, this volume; Kuffner _et al._, 2008). Coralline algae were absent from most experimental OA systems as well as from the nearshore CO2 vent zone off Ischia. Inability of calcareous algae to form bio-constructions might result in loss of the many species dependent on it. As photosynthetic organisms, these algae may benefit from increased pCO2, but their role as framework builders is crucial for the well-being of many other organisms. Failure to do so, together with natural eroding processes by physico-chemical forces and bio-eroding organisms, may shift the present balance from net buildup to net dissolution.

**Posidonia meadows:** _Posidonia oceanica_ is a seagrass endemic to the Mediterranean Sea and it constitutes meadows which are the basis of a highly diverse and productive ecosystem. The _Posidonia_ ecosystem is threatened by anthropogenic perturbations such as OA. Under increased pCO2, _P. oceanica_ reaches a higher density, with a lower epibiont coverage (Hall-Spencer and Rodolfo-Metalpa, this volume), which may be advantageous for a photosynthetic engineering organism. On the other hand within the low pH zone _P. oceanica_ appears more susceptible to grazing due to lack of calcareous epiphytes.

**Vermetid reefs:** vermetids are sessile gastropods distributed in tropical and subtropical seas. The vermetids have a tubular, irregularly uncoiled shell cemented (in the adult organisms) to hard substrates. In the Mediterranean, two reef-building vermetids, _Vermetus triqueter_ and _Dendropoma petraeum_, thrive in intertidal or shallow subtidal zones forming dense aggregates of colonial individuals with very high densities. Vermetid reefs have been described from rocky shores in the southern Mediterranean, from the Gibraltar Strait and southeastern Spain to the Levantine Basin. The importance of these reefs lies in the species richness they sustain, in their rarity, and in the physical protection from erosion they give the shoreline. Ocean acidification may affect both the calcifying abilities of vermetid gastropods and affect buildup to balance dissolution. Furthermore, the coralline algae involved in consolidating the vermetid's buildup are very sensitive to decreased pH as discussed above, and this may also reduce buildup rates. To date, no study is available on the effect of OA on this important bio-constructor in the Mediterranean Sea.

**Deep water corals:** in the Mediterranean Sea the deep-water corals community is like an oasis in the desert. In fact, the complex three-dimensional structure built by corals provide distinct ecological niches for a great number of species (Rogers, 1999), including crustacea and fish species of economic interest, such as _Aristeus antennatus_ and _Helicolenus dactylopterus_ (Tursi _et al._, 2004). The white azooxanthellate coral reefs may function as nurseries for many deep-water species and as centres of spreading for the associated fauna, having positive “spill-over” effects on the deep-water demersal resources (Fossa _et al._, 2002). This unique assemblage has developed in a very stable environment, leading to a relatively low resilience of these organisms to change. While it is expected that changes in seawater temperature or pH in deep water environments will lead to the demise of the high biodiversity through various mortality events, both the effects of OA and environmental factors on deep water corals are unknown, especially for Mediterranean species.

**Cladocora banks:** _Cladocora caespitose_, perhaps the most important constructional species in the Mediterranean Sea, can form structures comparable to tropical reefs (Schuhmacher and Zibrowius, 1985; Kružic and Požar-Domac, 2003). Some large banks are found in the Ligurian (Morri _et al._, 1994), Adriatic (Kružić and Požar-Domac, 2003) and Aegean seas (Kühlmann, 1996). Several informal reports suggest a decrease in the population size and spatial distribution of this species in the Mediterranean. Possible causes of this decrease may be global processes such as global
warming and acidification, or more local causes such as competition with invading species (algae and invertebrates).

**Benthic molluscs**: several studies have shown significant negative impacts of decreasing pH on mollusc species, including reduced growth and calcification rates as well as metabolic depression (Gazeau, this volume). Recent studies also revealed health and immune system deterioration following several weeks exposure to moderate hypercapnia, observations which suggest the incapacity of these ecologically and economically important species to adapt to low pH conditions. Such long-term investigations of moderate hypercapnia are obviously lacking for Mediterranean and Black Sea species.

**Echinoderms**: echinoderms play major ecosystem roles as keystone predators and grazers (Paine, 1966; Estes and Palmisano, 1974), in bioturbation and remineralisation (Ambrose et al., 2001), and as food sources for commercial fish (e.g. *Limanda limanda*; Duineveld and Noort, 1986; Mattson, 1992) and crustaceans (e.g. *Nephrops norvegicus*; Baden et al., 1990). Studies have shown a negative OA impact on growth, survival and physiology of adult sea urchins (e.g. Shirayama and Thornton, 2005; Miles et al., 2007; Dashfield et al., 2008); controversial results such as increased regeneration ability in brittle stars (Wood et al., 2008); or species-specific response (see below). However, the impact of OA on Mediterranean species remains poorly investigated. Only Hall-Spencer and Rodolfo-Metalpa (this volume) reported a drastic decrease of echinoderms abundance in the Mediterranean under acidified conditions. More experiments are needed.

**Larval stages**: whereas some species spend their entire life cycle in the plankton (holoplankton), many organisms are planktonic for only a part of their life cycle, usually during the larval stage (meroplankton). Larval stages are the most sensitive to environmental stresses (Pörtner and Farrell, 2008), but surprisingly only few studies have focused on early developmental stages. In the Mediterranean region, data are available only for the sea urchin *Paracentrotus lividus* (Dupont and Thorndyke, this volume), showing an overall positive impact (higher metamorphosis success), and for cephalopods and fishes, reflecting both a morphological and physiological impact (Jeffree et al., this volume). Nevertheless, data available for other regions (Dupont et al., 2008; Dupont and Thorndyke, this volume; Gazeau, this volume; Havenhand et al., 2008; Kurihara et al., 2004) clearly demonstrate that OA impact on early developmental stages is difficult to predict, and is species-specific even in closely related taxa. For example, sea urchins show positive, neutral or negative survival responses to OA depending on the species. If OA induces calcification problems in some species (e.g. brittle stars), other calcifying larvae do not have difficulty constructing a normal skeleton (e.g. sea urchins) under near future pH conditions. Both positive (e.g. better survival in tunicates) and negative (e.g. delay in development in sea stars) impacts are also observed on non-calcifying species (Figure 3).

![Figure 3](https://example.com/figure3.jpg)

**Figure 3.** (A) Development abnormalities in larvae of the brittlestar *Ophiothrix fragilis* raised at different pH (polarized light is used to highlight skeletal malformations). At low pH, larvae are smaller and more asymmetric, leading to 100% mortality after 8 days (Dupont et al., 2008). (B) Comparison of two-days old larvae of the tunicate *Ciona intestinalis* raised in control (pH 8.1, left) and acidic (pH 7.7, right) conditions. At low pH, larvae are larger and show a faster developmental rate.

[photos by Sam Dupont, Department of Marine Ecology, Göteborg University, Sweden]

The main conclusion from all available biological data is that OA impact is species-specific, showing apparent contradictions and paradoxes. Adequately predict the impact of future ocean
acidification on organisms and ecosystems in the Mediterranean and Black Seas will require investigating consequences on a wide range of local species and ecosystems and so better understand the reasons for such paradoxical results.

4.3. Field studies on community and ecosystem responses

The response of marine ecosystems to increased atmospheric CO₂ levels has been extrapolated mainly from results of short-term laboratory experiments in which pH or CO₂ levels were manipulated in aquaria and examined over short timescales. Although these experiments have shown species-specific responses, there is a general consensus of an overall detrimental effect of acidification on calcifying marine organisms. The long-term effects of decreasing seawater pH on ecosystems are largely unknown. However, a unique field study using natural submarine CO₂ vents has facilitated assessing OA effects on a shallow water ecosystem. Gas emitted from the sea bottom acidified seawater in the vent zone to levels that are expected to be seen by the end of this century and beyond (Hall-Spencer et al., 2008; and Hall-Spencer and Rodolfo-Metalpa, this volume). Because CO₂ vents at this site have existed for centuries to millennia, benthic species have acclimatized or adapted in their natural ambient to chronic acidified conditions. Preliminary results show that long-term exposure to low pH has dramatic impacts on calcifying organisms, but that a suite of organisms in this vent community are resilient and may benefit from such conditions. This chronic acidification stress may ultimately lead to major shifts in species composition.

Consistent with responses derived from laboratory studies, typical rocky shore communities with abundant calcareous organisms, such as coralline algae, corals and sea urchins, shifted to communities lacking calcifiers. Their sensitivity to decreased pH was consistent with the mineral composition of their shells or skeletons. Therefore, calcifiers like snails, limpets and barnacles were more resilient also at very low pH (<7.7). This shift in the community composition showed no indication of adaptation or replacement of sensitive species by others capable of filling the same ecological niche, and it confirms the need for concern about the future ecology of our seas in a high-CO₂ world.

In general, it seems that photosynthetic, non calcifying species such as green and brown algae, or the sea grass *Posidonia oceanica* that forms one of the most important and rich ecosystem in the Mediterranean Sea, might directly take advantage of the acidified conditions by increasing their photosynthetic rates or, indirectly by the exclusion of other competitors for space. Some invasive alien species, which cause damage to ecosystems worldwide, may also thrive at high CO₂ levels. Although investigations on this topic are at their infancy, it seems that acidified conditions do not affect fish behaviour and abundance. Indeed, adults and juveniles of species like *Sarpa salpa*, *Labrus* sp. and *Scorpaena porcus* were found at very low pH.

This field study indicates that nearly a third of such species might disappear at the lower pH levels predicted for the future, constituting the first evidence of a potential shift in marine community structure due to ocean acidification. This unique and useful natural laboratory will be used extensively to test the response and sensitivity of a large range of benthic species to long-term acidification exposure. Another way to test impact at a larger scale is to use mesocosm experiments, “simple assemblages or even complex substets of whole ecosystems”.

Future research priorities should include other CO₂ vent zones that are abundant in other parts of the Mediterranean Sea (e.g. the Aeolian Islands and Aegean Sea): they can be used as field laboratories to obtain data on ecosystem responses to OA.

5. Socio-economic impacts of ocean acidification — regional aspects

In view of the intensity of aquaculture and artisanal fisheries in the Mediterranean, to any adverse effects of OA on the viability or productivity of living resources could have high socio-economic significance. Based on current knowledge, these adverse effects would be expected first on bivalves, but could also extend to sea urchins and cephalopods. Collaboration between natural resource scientists and economists will be required to assess the scale of possible economic losses associated with seafood depletions due to OA.
Adverse impacts of OA on the geographical extent, structure and biodiversity of coral reef habitats could be expected to affect the species dependent upon them, particularly those fishes that use them as nurseries for their early life stages, with attendant economic losses to regional communities. There is growing evidence that marine benthic communities are subjected to change as a result of local perturbation, over-exploitation and global climate change, primarily global warming and ocean acidification. Mediterranean Sea ecosystems are likely to experience similar processes although we lack long-term data indicating so (Astraldi, 1995; Bianchi, 2007; Fowler, this volume). Mediterranean Sea ecosystems and benthic communities were shaped by long term geological and ecological processes but recent observations such as the occurrence of warm-water species in shallow waters of the northern Mediterranean suggests rapid ongoing changes (CIESM, 2008). This is also supported by records of elevated temperature of deep water (Bethoux et al., 1990) and current warming trends (CIESM Hydrochanges Program <http://www.ciesm.org/marine/programs/hydrochanges.htm>). In light of these changes and the projected increase in carbon dioxide concentration, it is extremely important to understand how ocean acidification might affect Mediterranean Sea ecosystems.

There is some evidence, although controversial, that OA may lead to increases in the abundances of jellyfish over the next century. This effect would further exacerbate the current problems of their occurrences in those coastal regions that are used in the summer as prime tourist destinations. Despite current adaptive approaches at some of these locations to reduce exposure to medusae (e.g. the use of netted barriers), the repeated occurrence in the future of medusae in even higher abundances would be expected to ultimately deter tourists, with the associated losses of revenues and employment opportunities for coastal populations.

Additionally, the outbreaks of harmful algal blooms (HAB) in the Mediterranean and Black Seas that have been linked to climate change and eutrophication effects may be further exacerbated by OA. There are no HAB species that are calcifiers, and they may obtain a relative ecological advantage by OA over their calcifying algal competitors. Accordingly, enhanced harmful algal blooms would adversely affect tourism as well as regional fisheries and aquaculture production, consumption and export potential.

In addition to direct effects on particular high-value seafood species, any effect of OA on organisms necessary or important in the diet of seafood species, for example calcified pteropods, would also adversely affect their abundances.

Loss or degradation of coral reef environments due to OA could also have negative socio-economic impacts in those regions that particularly attract tourists for recreational diving, bathing and viewing from underwater observatories or glass-bottom vessels.

6. **WORKSHOP RECOMMENDATIONS: GAPS AND FUTURE WORK**

6.1. Main gaps

- lack of long term data (monitoring studies, in particular enhanced time-series studies) on impacts of OA on marine organisms and ecosystems;
- understanding of cumulative and combined stresses of environmental factors including OA on marine ecosystems;
- changes in the chemistry and biogeochemical cycling of carbon and carbonate;
- standardization of the experimental methods used for measuring the basic parameters, and employing AQM analyses;
- examination of issues related to OA using a multidisciplinary approach;
- in general data and research on OA in the Mediterranean Sea are very recent, while comparable data and published material for the Black Sea are presently lacking;
- socio-economic impact and public awareness (what is the perception of the problem among citizens and decision makers, and how to improve that?).

6.2. Recommendations for future research

*Data availability*: targeted research on OA impacts in the Mediterranean Sea is quite recent and robust data are very few. There is a need for basic data on survival, reproduction, fitness, etc.,
in a variety of Mediterranean species. In particular, more focus should be placed on ecologically and economically important and relevant species such as pelagic tunicates (salps), jellyfish, bivalves, crustacea, echinoderms and fish. Data and published information are lacking for the Black Sea, where a thorough review of relevant information should first be carried out, followed by initiation of scientific studies on OA.

**Time series:** long time-series studies are too few for an area like the Mediterranean Sea under high anthropogenic and environmental pressure. It is particularly important to have time-series data on the seawater carbonate chemistry: some data are available for the Western Mediterranean but they are scant or basically lacking for the Eastern Mediterranean and the Black Sea. Essential basic parameters such as T, S, O₂, DIC, and TA are recommended to be measured on a biweekly/monthly basis. Therefore, new directions and developments for monitoring the changes due to ocean acidification should be undertaken.

**Biological aspects:** there is an urgent need for basic biological data (survival, reproduction, fitness) on the impacts of OA on Mediterranean and Black Sea species. To give a realistic overview and allow future prediction, it is important to:

- Be not too prescriptive in species/ecosystem selection. Biological impact of OA is species-specific, and it is therefore inappropriate to extrapolate from a few model species or from one region to another. A wide range of keystone species should be investigated. For example, it is time to move beyond assessing only calcification effects and also investigate non-calcifying species such as tunicates (e.g. salps) and jellyfish that may benefit from OA.
- Assess the long term impact. To understand the real impact of OA on species, it is essential to embrace the whole life cycle and not just focus on the direct impact on one facet of the life history (e.g. adult stages). For example, multigeneration studies should be performed to assess microevolution and adaptation.
- Use realistic conditions for experiments. Relevant abiotic (e.g. pH, temperature) and biotic (e.g. food concentration, density) conditions should be taken into account in experimental designs to give a realistic view of the impact of OA in the field. The synergetic impact of these parameters with other stressors (e.g. pollutants) should also be investigated.
- Take intraspecific variability into account. Species and population adaptive potential should be investigated. More ecophysiology studies are needed. OA can impact organisms at many different physiological levels, not only calcification but also ion transport, neural and muscle activity, calcium transport and signalling, ciliate movement, etc. These functional aspects should be correlated with ecological parameters (habitat, life-history, etc.).
- It is dangerous to extrapolate from laboratory experimental results on few species to community level where there is an overall lack of evidence of OA impact. To take into account ecosystem processes such as biotic interactions, large scale experiments (mesocosm, FOCE approach, etc.) and field studies in natural environments under the influence of acidification (e.g. CO₂ vents) should be performed.
- Amongst marine calcifiers the calcification mechanisms differ considerably. For example, some organisms produce their skeleton as an epidermal secretion with direct contact to the environment (e.g. molluscs, crustacea, worms) while others have enclosed skeletons with at least one epithelium integument (e.g. echinoderms). To better understand the effects of pH and the saturation state of carbonate on calcifiers, there is a need for more information on the basic calcification mechanisms in many different taxa, including corals for which these mechanisms are poorly known.

**Methodology:** one must refine already established tools and develop new geochemical ones (e.g. δ₁₁B, B/Ca ratios) to study biogenic carbonate in order to reconstruct the chemistry of CO₂ during the pre-industrial period at different depths in the water column. Understanding historical changes in ocean chemistry will greatly assist in predicting future oceanic conditions.

**Modeling:** assessing future changes in Mediterranean and Black Sea biogeochemistry in response to climate change and increasing atmospheric CO₂ levels calls for an integrated
modeling approach at the regional scale. Such models should also include the synergistic effects of multiple stressors (e.g. pH, temperature, nutrient loads, etc.).

**Socio-economic perspective**: the economic implications at regional and local scales should be investigated by way of collaboration between natural resource economists and scientists so as to evaluate potential economic detriment resulting from OA impacts on the fisheries and tourism industries.

### ACRONYMS:

- **OA**: Ocean Acidification
- **HAB**: Harmful Algal Bloom
- **CT**: Total Inorganic Carbon; $C_I = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$
- **AT**: Total Alkalinity
- **pCO_2**: Partial Pressure of CO$_2$
- **C$_{org}$**: Organic Carbon
- **IPCC**: Intergovernmental Panel on Climate Change