Natural Marine CO_2 Sequestration: How Biological and Solubility Pumps Influence the Sequestration in the Black Sea and in the Eastern Mediterranean?

by
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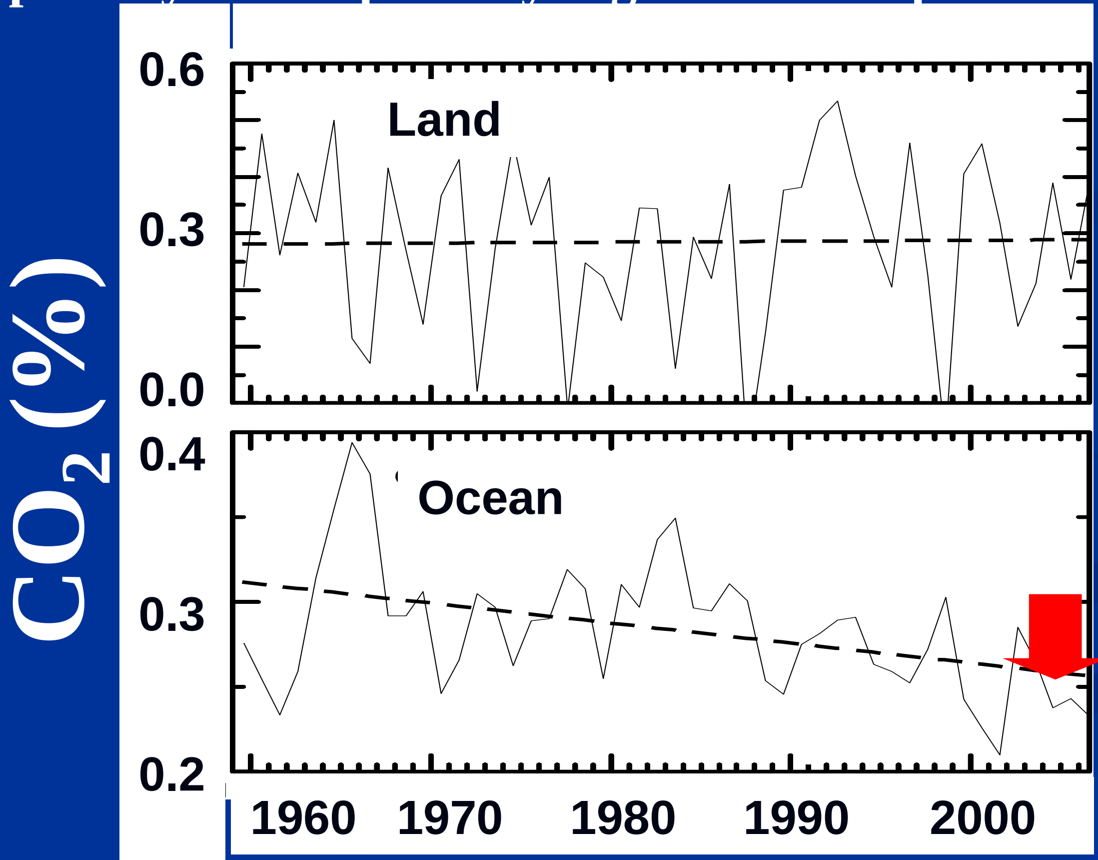
Atmospheric CO_2 is increasing as mankind burns of fossil fuels. This presents serious environmental problems with respect to marine environments.

Forests and oceans naturally sequestrate (capture) about half of the atmospheric CO_2 (5 billions tons of CO_2 globally every year). The oceans portion decreased from 30 % to 25 % since 1960 (till 2006). Reasons:

- Strong winds and storms (Decrease in pCO_2)
- Increase in Sea Surface Temperature (Decrease in dissolution)
- Decrease in photosynthetic/primary organic matter production (Due to stratification)



Canadell et al. 2007, PNAS

Source: Estimated emissions from fossil-fuel combustion and cement production of 9.1 Pg C, combined with the emissions from land-use change of 0.9 Pg C, led to a total emission of 10.0 Pg C in 2010 (Friedlingstein *et al.*, 2010).

Sink: Of the remainder of the total emissions (5.0 Pg C), the ocean sink is 2.4 Pg C, and the residual attributed to the land sink is 2.6 Pg C (Le Quéré, 2009) .

Accumulation in the atmosphere: Half of the total emissions (5.0 Pg C) remains in the atmosphere, leading to one of the largest atmospheric growth rates in the past decade (2.36 ppm) and the concentration at the end of 2010 of 390 ppm of CO_2 (Conway & Tans, 2011).

9.1 Pg C y-1

+

0.9 Pg C y^{-1}

Atmosphere 50 %

5.0 Pg y-1

Land 26 %

2.6 Pg y-1

Oceans 24 %

2.4 Pg y-1

Oceans are natural CO_2 sinks, and represent the largest active carbon sink on Earth. This role as a sink for CO_2 is driven by two processes:

1- The biological pump

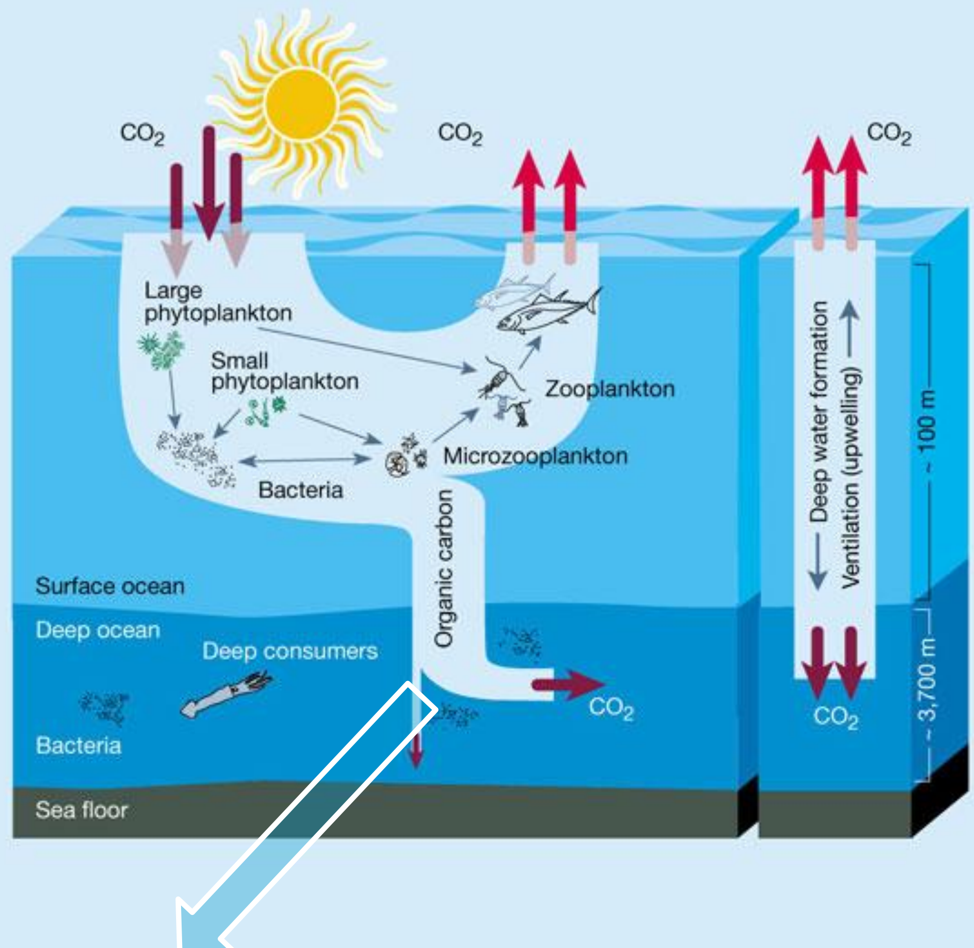
2-The solubility pump

1-The biological pump/Organic Matter Sink

Dissolved CO_2 is taken up by marine phytoplankton driving a CO_2 flux from the atmosphere to surface waters. The organic matter produced is consumed by heterotrophic organisms and remineralized to CO_2 or exported as sinking organic matter.

This sinking fraction is also called as "Export Production", that actuates the removal of CO_2 from the atmosphere.

Biological pump is also important for he food production!



Sinking Organik Material

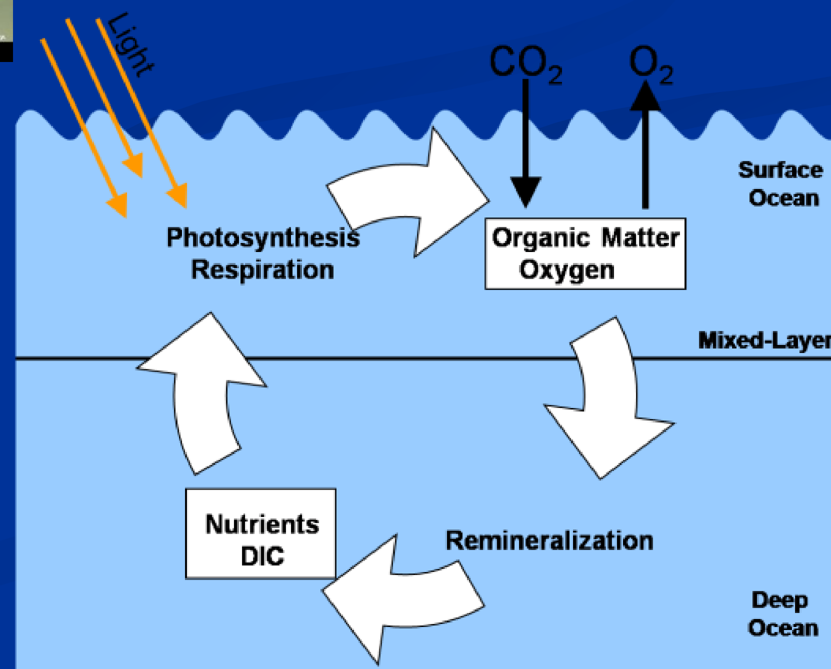
Image of typical Sediment Trap sample from subtropical Atlantic (Honjo, 1997).

Production of organic matter

Dissolved constituents

$$106CO_2 + 16NO_3^- + HPO_4^{-2} + 139H_2O \leftrightarrow C_{106}H_{261}O_{109}N_{16}P + 138O_2 + 18OH^-$$

Suspended Organic Particles (Phytoplankton)

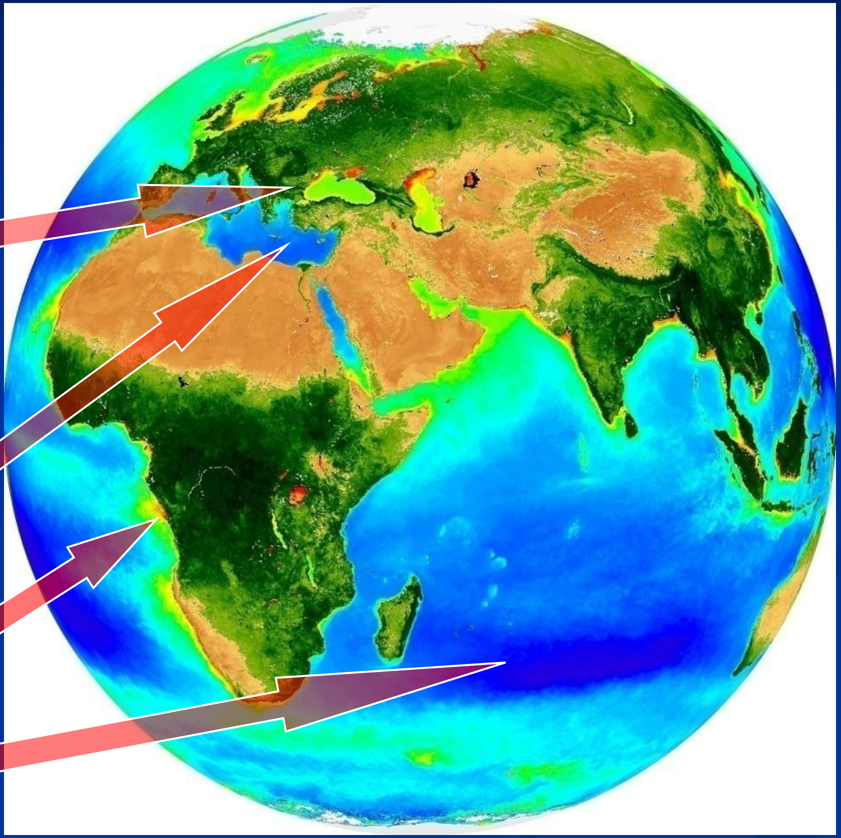


Export production of organic carbon is the engine that drives the biological pump, but it is also modulated by the export of inorganic carbon in the form of $CaCO_3$ particles and shells produced by a variety of marine organisms (like *Coccolithophorids)*.

Export of calcium carbonate increases the alkalinity of surface water, thereby partially compensating for the CO_2 drawdown driven by the export of organic matter.

The efficiency of the biological pump is thus very much dependent on the relative proportion of organic and inorganic carbon leaving the surface mixed layer, which is controlled by ecological, biogeochemical and physical factors.

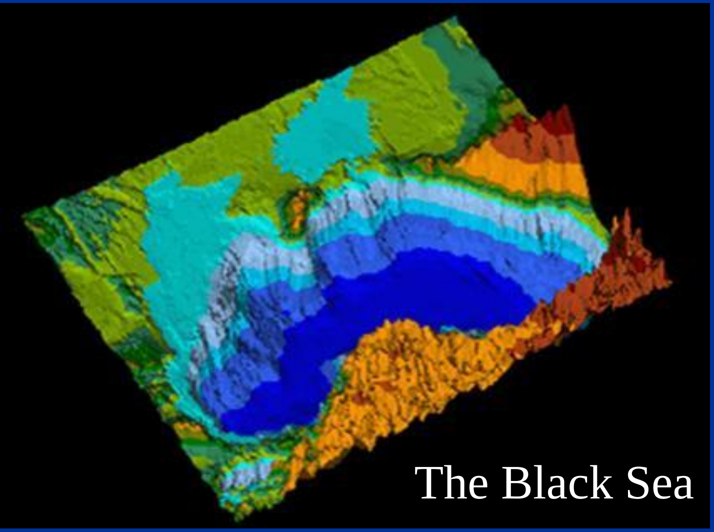
Region	Primary Production $mgCm^{-2}d^{-1}$
Black Sea (Open waters) Black Sea (NW and Shelf/Coastal Waters) (1960-2001)	112 - 587 405 - 2140
Eastern Mediterranean	<100
Upwelling Areas	800-1000
Open Ocean	<100



A distinguishing feature of the Black Sea is the high biological activity in the lower trophic food web structure as compared to neighboring Aegean and Eastern Mediterranean basins.

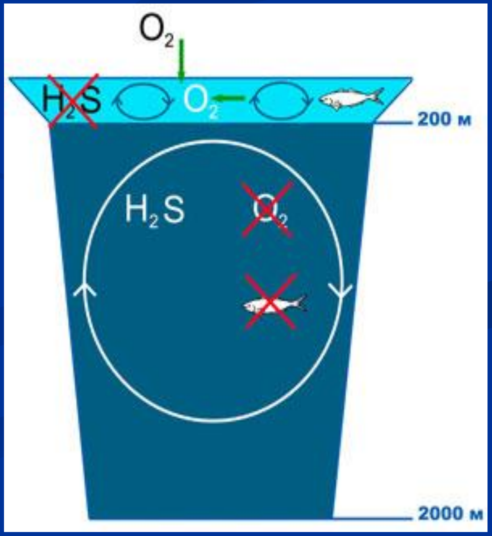
Black Sea: A unique marine environment

The Black Sea is a unique marine environment representing the largest land-locked/semi-enclosed and deep (~2000 m) anoxic basin in the world. Its shelf region (<200m) is generally narrow and it enlarges at the north western corner. It has a very large catchment area, receiving extraordinary amount of nutrients, pollutants as well as fresh water from the rivers draining half of the Europe and some parts of Asia. The major rivers are the Danube, the Dniper and the Dniestr, all concentrated along the north western coast.



The Black Sea

Catchment Area



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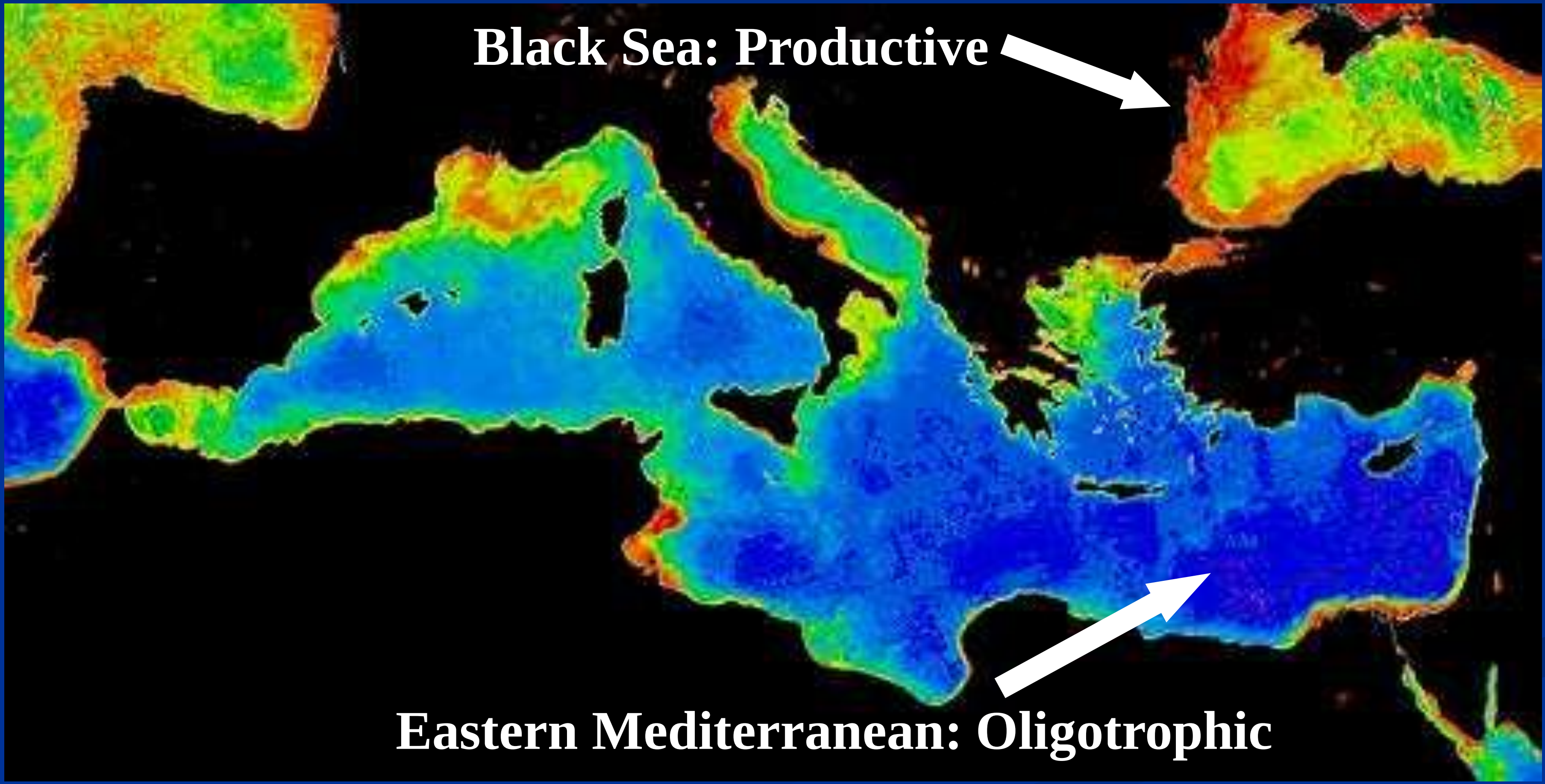


Use of satellite images of phytoplankton concentration from NASA's Goddard Space Flight Center to examine the productivity of the ocean.

Basin	Area (%)	Global Production* Gt C y^{-1}	% of Global Production
Pacific Ocean	45	21	44
Atlantic Ocean	23	12.8	27
Indian Ocean	17	9.9	21
Southern Ocean	13	2.6	5.5
Arctic Ocean	1.2	0.33	0.7
Mediterranean	0.8	0.45	0.95
Black Sea	**0.12**	**0.106****	**0.22**

- **Although Black Sea is a small basin, it is highly productive area and unique area for effective natural sink for carbon!**

Carr et al., DSR, 2006

*****Yılmaz et al., 1998; Yayla et al., 2001; Yunev et al., 2002; Sorokin, 2002; Yılmaz et al., 2006***

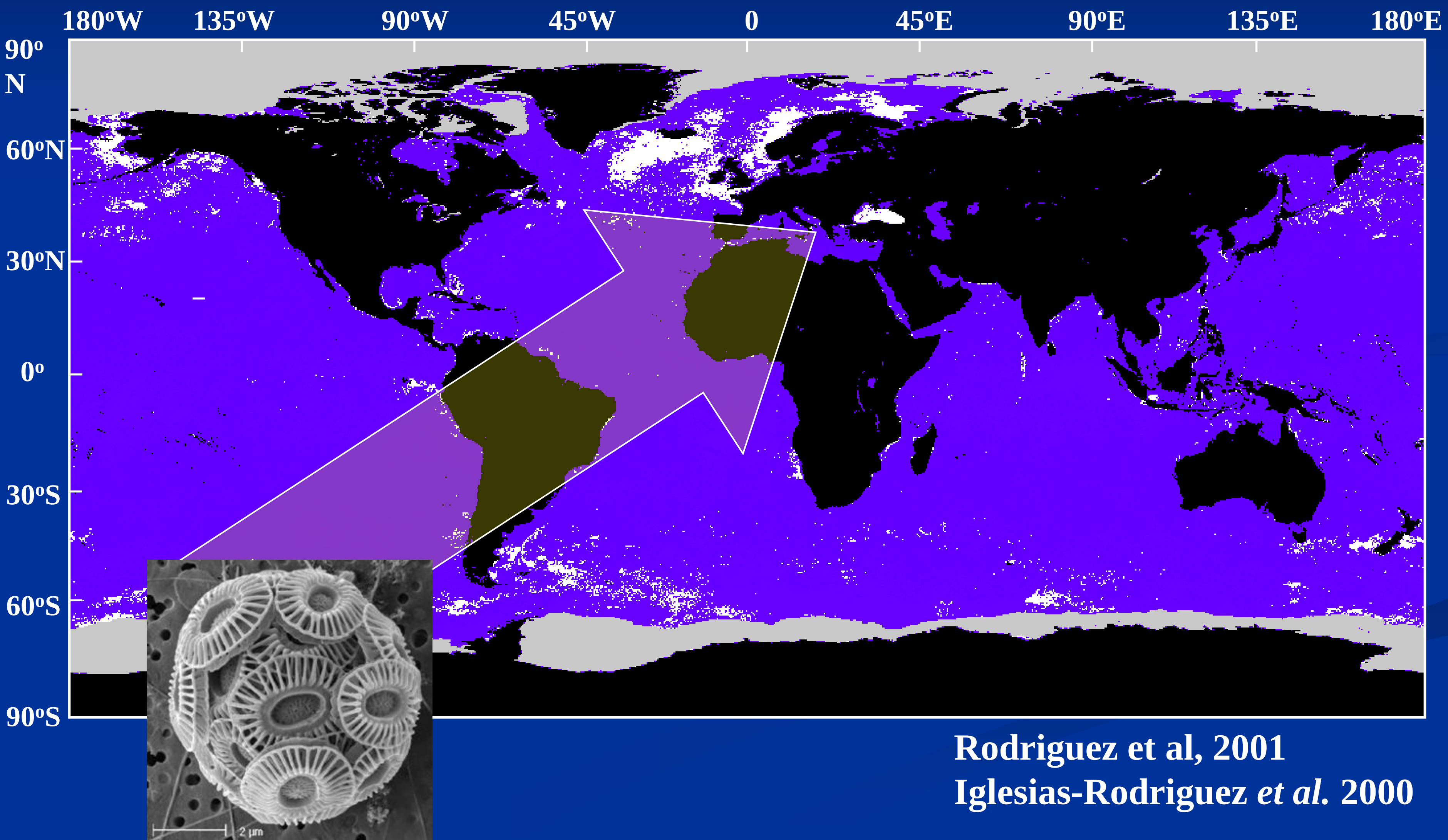
Export Production ~33 % in the Black Sea, which means ~35 tonnes C is exported anualy. Approximately the same amount (~32 tonnes C y^{-1}) produced by chemoautotrophic activity at mid-water depths sinks down to bottom.

The flux of organic matter is the key element of the biological pump that eliminates carbon (CO_2) from the euphotic zone and delivers it to deeper layers.

Oxidation of organic matter results in consumption of oxygen and production of nitrate, phosphate, and CO_2 below the euphotic zone. This results in natural sequestration of CO_2 from the surface water and natural acidification (decreasing pH) of the suboxic zone and deeper layers.

Konovalov and Murray (2001) demonstrated that the observed decline in the content of oxygen in the 1970’s to 1990’s was stoichiometrically equivalent to oxidized organic matter that was produced in increasing quantities due to eutrophication and potentially due to increasing concentrations of CO_2.

Some phytoplankton taxa (*Coccolithofores*) are more abundant at some locations and impacts the CO_2 exchange between oceans and atmosphere (e.g. Black Sea).



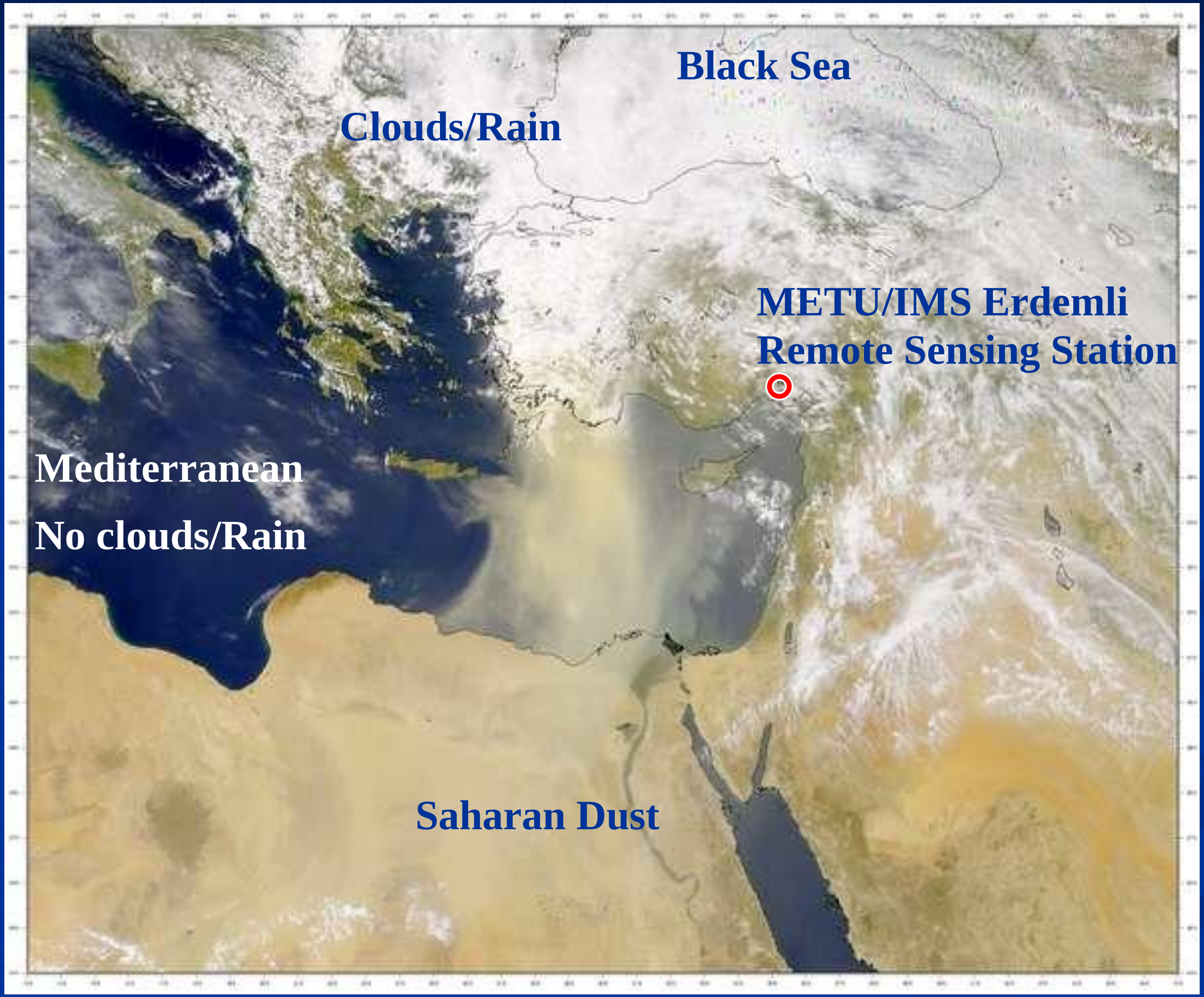
Rodriguez et al, 2001
Iglesias-Rodriguez *et al.* 2000

SeaWiFS data analyzed for the 1997-2000 period (Çokacar *et al*., 2001) provided new details on the duration, persistence, spatial extent of the *Emiliania huxleyi (Coccolithofores)* blooms in the Black Sea. A marked change in the appearance of the water is observed, and the colour turns a milky turquoise during intense blooms.

Black Sea, R/V Bilim April, 1998

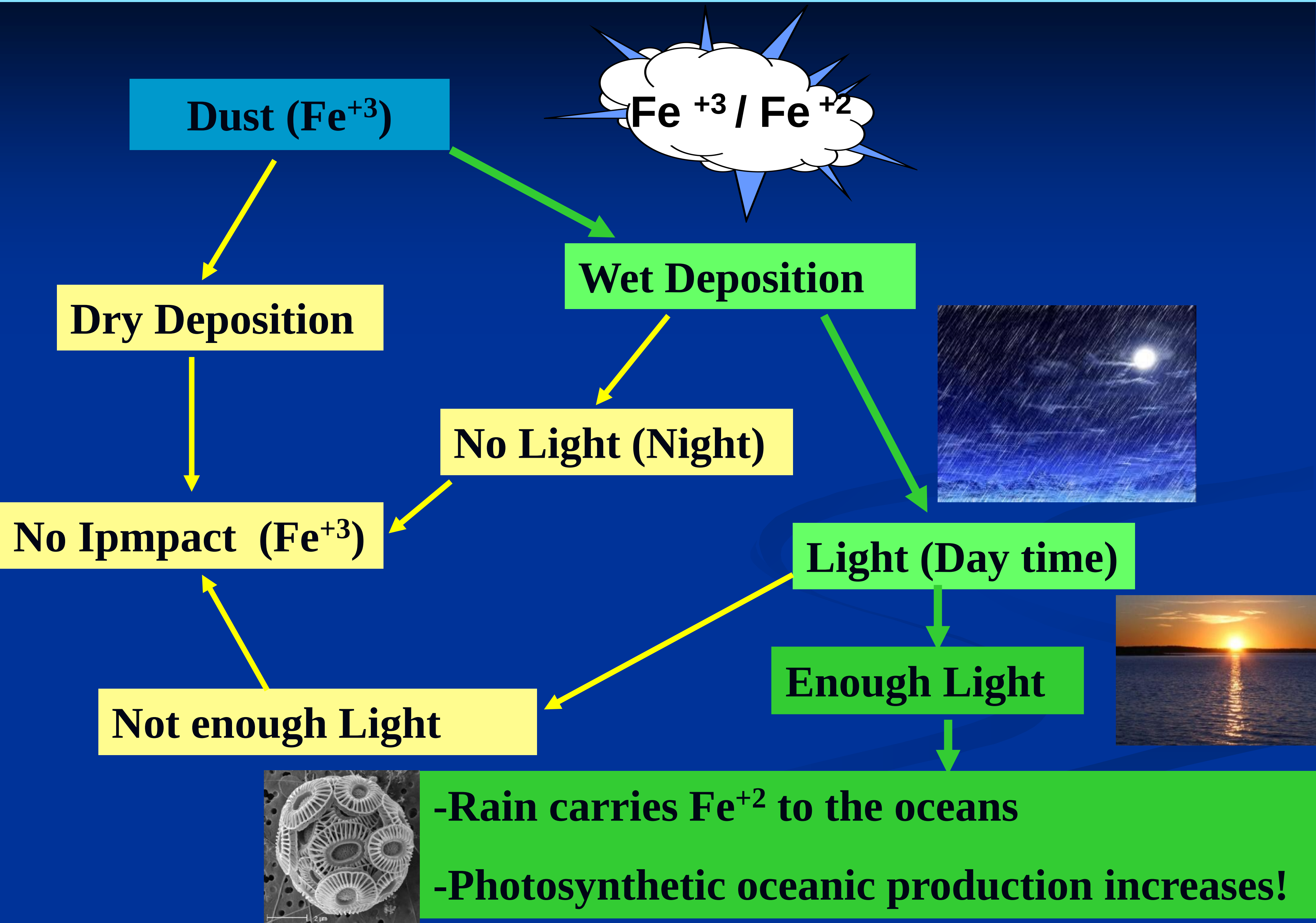
Photo by Ayşen Yılmaz

Saharan dust, rich in nitrogen, iron and phosphorus, helps to fertilize the phytoplankton blooms that occur in the Black Sea.



April 18, 2001 (SeaWiFS)

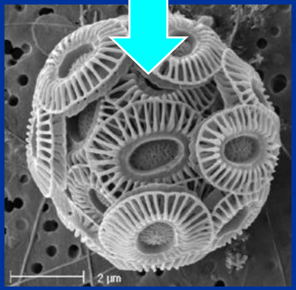
Availabilty of Iron for the Fertilization of the Oceans



Emiliania huxleyi (Coccoliths) blooms

All phytoplankton (also *Coccoliths*) removes CO_2 to form organic matter and reduces atmospheric CO_2 by photosynthesis. However, *Coccoliths* also take up bicarbonate (HCO_3^-) to form their calcium carbonate ($CaCO_3$) shells and during this reaction CO_2 is released!.

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2$$



In this way, *coccolithophore* blooms may affect global warming negatively (by causing increased atmospheric CO_2).

However;

$$\rho_{coccolith\ calcite} = 2.7\ kg/L$$
$$\rho_{sea\ water} = 1.024\ kg/L$$

Coccoliths sink very rapidly!

If organic matter sinks faster than the time period necessary for bacterial decomposition, causes the depletion of the surface CO_2.

This co-transport of organic matter with coccoliths offsets the atmospheric CO_2 increase. This makes coccolithophore blooms act to oppose global warming, rather than to intensify it.

Carbon fluxes to Deep Oceans

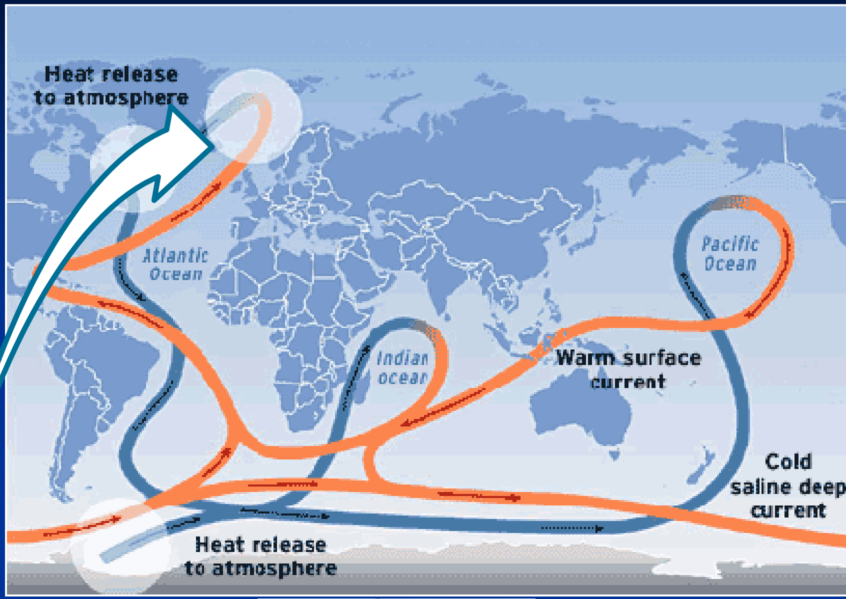
The export of carbon through the biological pump from the surface to the deep ocean has a direct influence on the removal of CO_2 from the atmosphere. This is because the carbon is sequestered for only a few days to months in the surface while the carbon removed from the surface to deep waters takes hundreds of years to re-enter the atmosphere (Sarma et al., 2007).

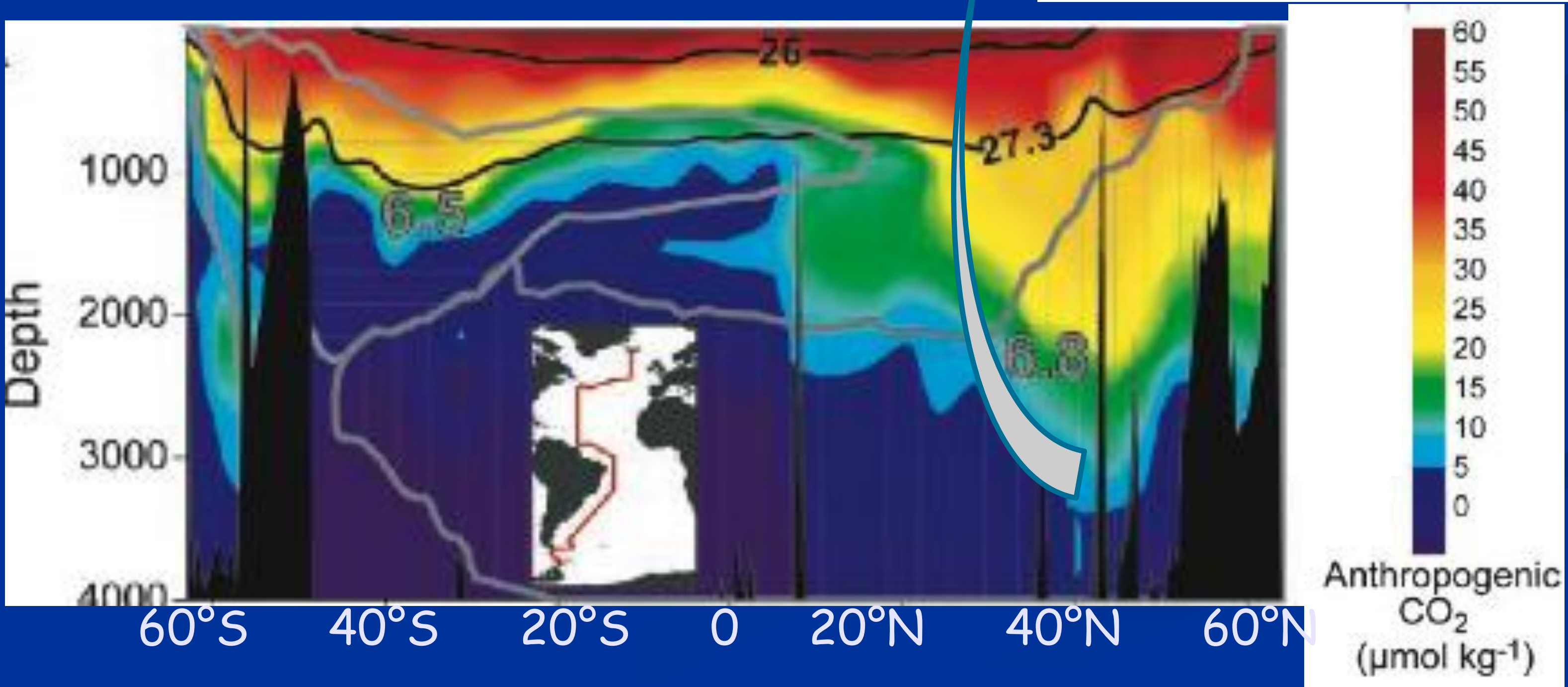
Carbon Removal Processes:

- **CO_2 absorption by surface ocean: ~1 yr ($CO_2 + H_2O \longrightarrow H^+ + HCO_3^-$)**
- **Mixing to deep ocean: ~300 yr**
- **Carbonate dissolution: ~6000 yr ($CO_2 + CaCO_3 + H_2O \longrightarrow Ca^{2+} + 2HCO_3^-$)**
- **Silicate-rock weathering: ~300,000 yr ($CO_2 + CaSiO_3 \longrightarrow CaCO_3 + SiO_2$)**

Carbon Transport to Deep Sea

Solubility pump: CO_2 is more soluble in cold, saline waters, such as those that sink in the NorthAtlantic. Thermohaline Circulation (THC) takes carbon out of surface and transfer into deep (Sinking waters hold lots of CO_2!!!)





Sabine et al. 2004, *Science*

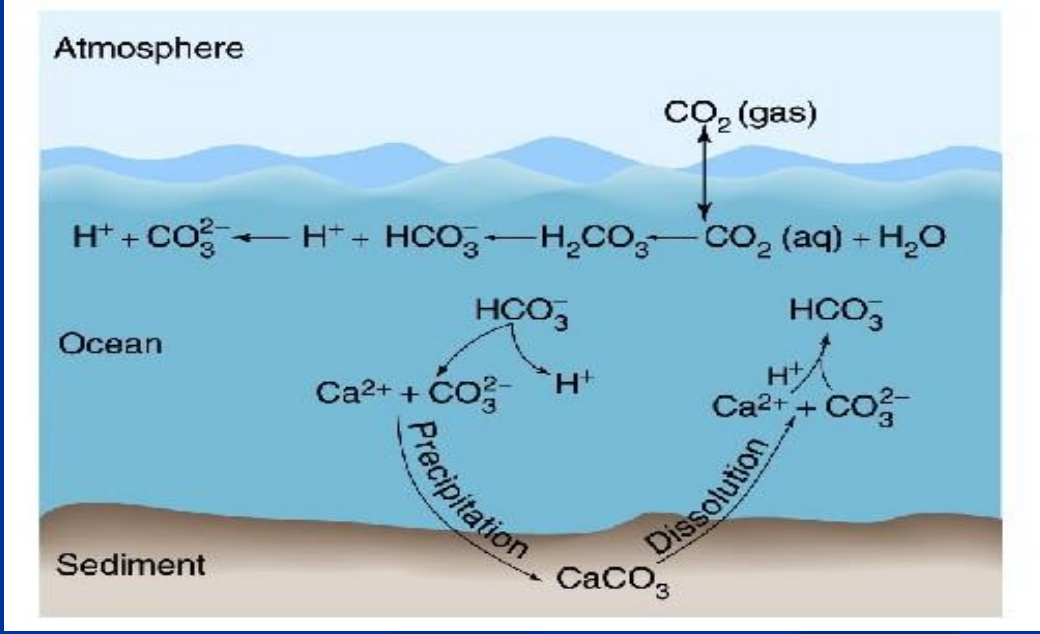
2-Solubility Pump: Surface waters uptake of CO_2 by dissolution.

- **Gas diffusion between ocean and atmosphere: Depends on concentration gradient between CO_2 (g) and CO_2 (aq).**
- **Solubility = f (Temperature, Salinity, Pressure)**
- **Key role of winds in determining (pCO_2) and rate of exchange.**
- **Key reactions:**

  $CO_2 + H_2O = HCO_3^- + H^+$

  $HCO_3^- = CO_3^{2-} + H^+$

  $Ca^{2+} + CO_3^{2-} \Rightarrow CaCO_3$



- **If atmospheric CO_2 increses, pH decreases (waters becomes more acidic) and CO_3^{2-} decreases.**

Anthropogenic CO_2 :

While the increase in surface ocean dissolved CO_2 is proportional to that in the atmosphere (equilibration after ~1 y), the increase in TCO_2 is not. This is a result of the buffer capacity of seawater.

As a consequence, the man-made increase of TCO_2 in surface seawater (ocean acidification) occurs not in a 1:1 ratio to the increase of atmospheric CO_2. Rather, a doubling of pCO_2 only leads to an increase of TCO_2 of the order of 10%.

There are also dramatic changes in the carbonate system in the Black Sea. The pH decreases from ~8.2 in the surface layer to 7.4 in the upper suboxic zone, while alkalinity remains constant (Goyet et al., 1991; Hiscock and Millero, 2006). The pH increases slightly through the suboxic zone and then decreases steadily in the deep water to a low value of 7.3.

None of the existing models for the Black Sea account for the carbonate system, even though it is an extremely important component of the Black Sea biogeochemistry. The changes in the carbonate system of the Black Sea have not been numerically simulated, leaving an open question on the evolution due to human- and climate-driven changes in CO_2 and other boundary conditions in the Black Sea.

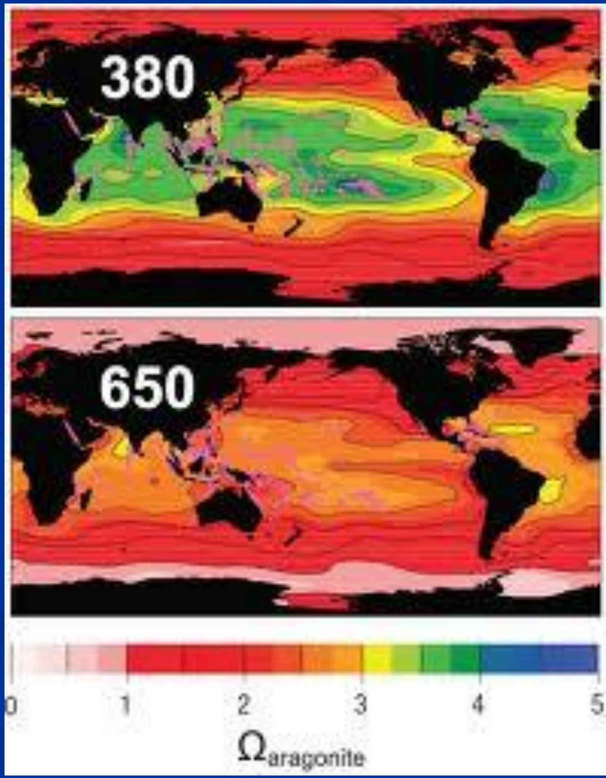
Carbonate Saturation

$Ca^{2+} + CO_3^{2-} \longleftrightarrow CaCO_3$

- Saturation state, Ω : A measure of how saturated the surface ocean is with respect to $CaCO_3$.

$\Omega = [Ca][CO_3] / K_{sp}$

(K_{sp}:Solubility Product)



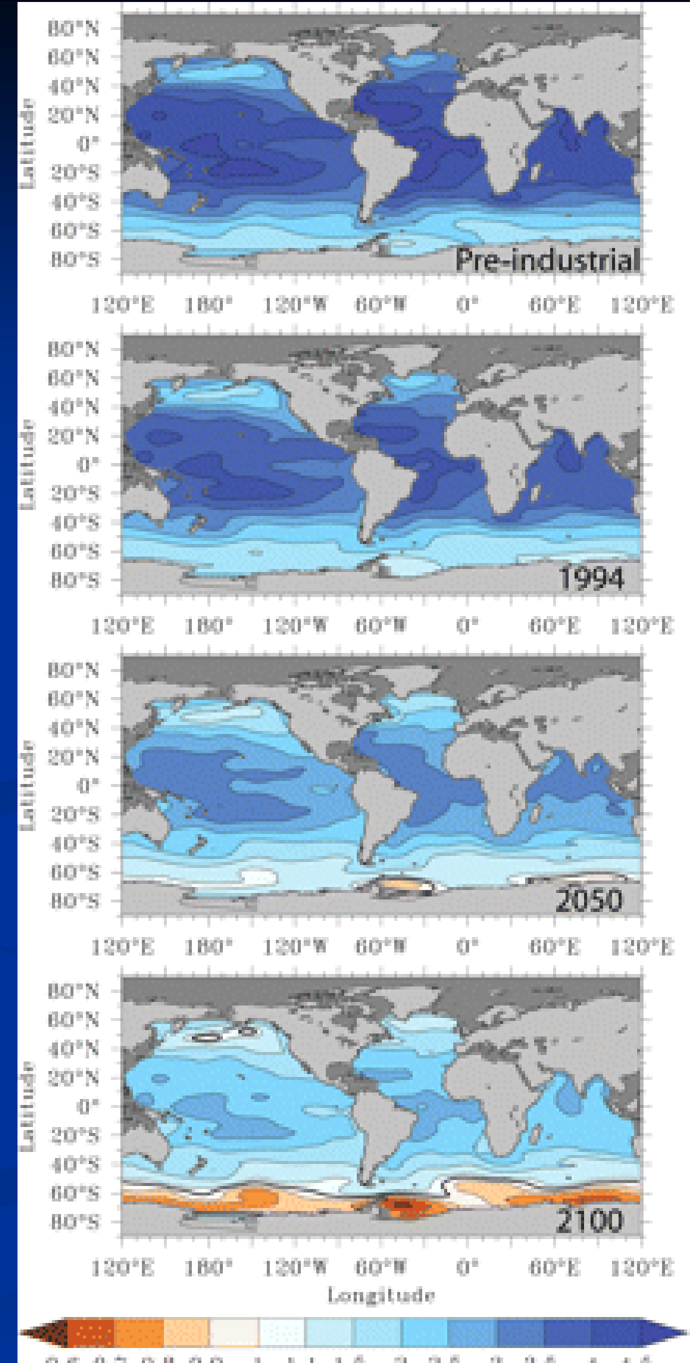
- If Ω > 1, supersaturated: precipitation
- If Ω < 1, undersaturated: dissolution

- Increase of atmospheric CO_2 causes the reduction in CO_3, so Ω decreases.

Climate Change and Carbonate Saturation Trends

$CO_{2\,(g)}$ ⇅ Gas exchange

	Glacial	Pre-industrial	Present	$2XCO_2$	$3XCO_2$	Change from pre-industrial to $3XCO_2$
pCO_2	180	280	380	560	840	200%
$CO_{2\,(aq)} + H_2O \rightleftharpoons H_2CO_3$ Carbonic acid	7	9	13	18	25	178%
$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ Bicarbonate	1666	1739	1827	1925	2004	15%
$HCO_3^- \rightleftharpoons H^+ + CO_3^{-2}$ Carbonate	279	222	186	146	115	- 48%
DIC	1952	1970	2026	2090	2144	8.8%
$pH_{(sws)}$	8.32	8.16	8.05	7.91	7.76	- 0.4
$\Omega_{calcite}$	6.63	5.32	4.46	3.52	2.77	- 48%
$\Omega_{aragonite}$	4.26	3.44	2.90	2.29	1.81	- 47%



Fabry et al., 2008

At present surface waters of the Black Sea are supersaturated with respect to calcite and aragonite and the degree of saturation decreases with depth.

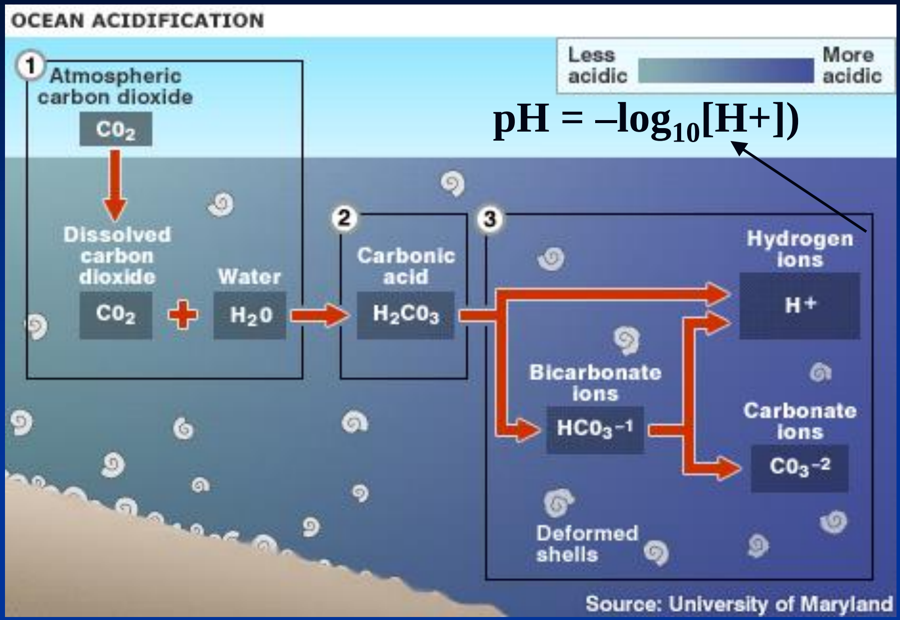
In the suboxic zone calcite is just above saturation while aragonite is just under saturation. However, the degree of saturation is not the only indicator of stress as experimental studies have shown that biological impacts are observed with decreasing saturation, even though a state of supersaturation persists in the Black Sea (Fabry et al., 2008).

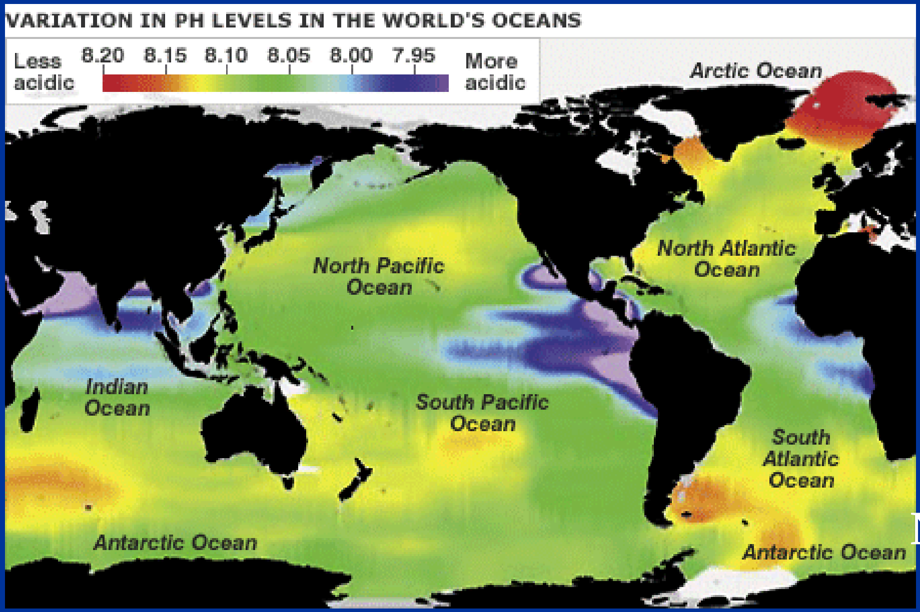
Ocean Acidification

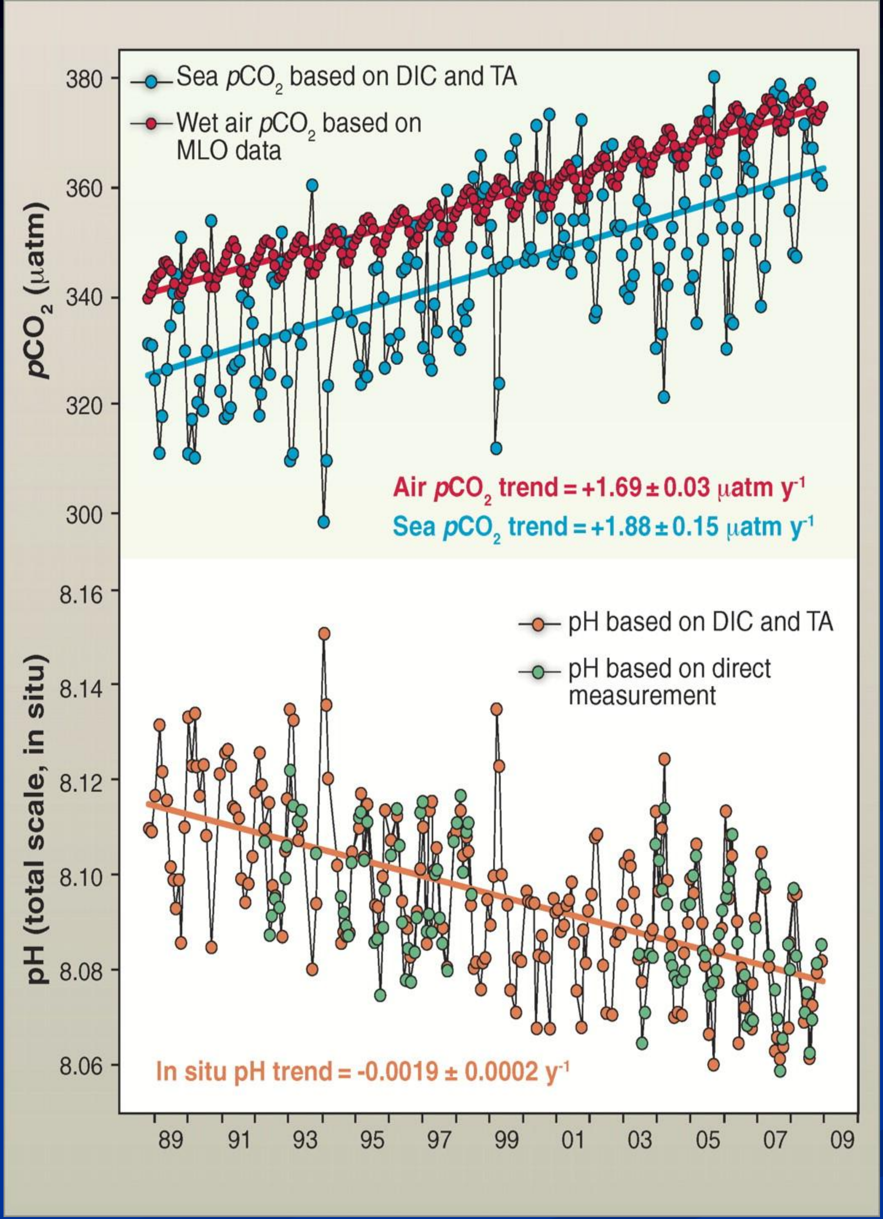
• The ocean absorbs antrophogenic CO_2 at a rate of 22 million tons per day, thus removing about 25 % of CO_2 emitted to the atmosphere each year and mitigating the harmful impact of this “greenhouse gas” on climate!

• This valuable service provided by the ocean, however, may have a high ecological cost. When CO_2 dissolves in seawater, carbonic acid is formed. This phenomenon, called as “Ocean Acidification (OA)”, decreases the availability of carbonate (CO_3^{2-}), making it more difficult for many marine organisms to construct their hard parts (shells) out of calcium carbonate minerals.

Ocean Acidification

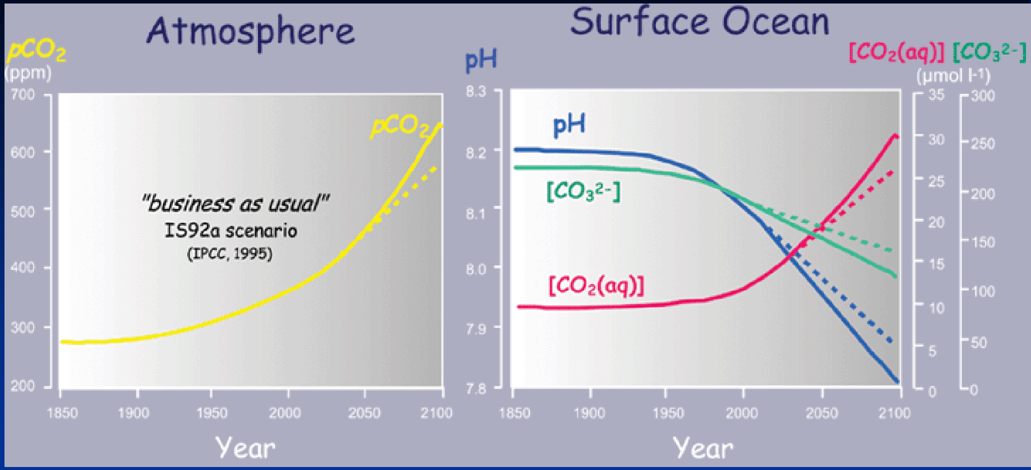




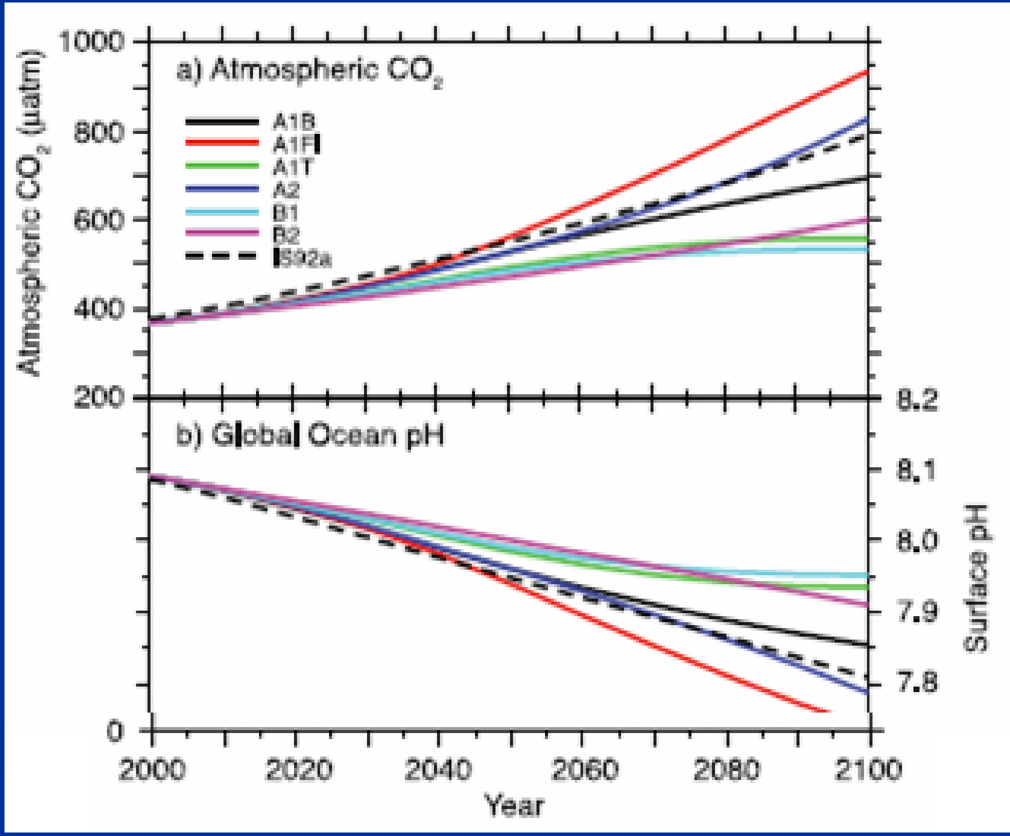


Northern Hawai (ALOHA Stations)-Surface pH (Doney, Science 2010)

Ocean Acidification



If atmospheric CO_2 increases from e.g. 390 ppm today to 900 ppm in 2100, the pH will decrease by 0.4-0.5 units. This will cause 3 times increase in H^+ concentrations in sea water for the first time with in the last 20 x 10^6 years (Raven *et al.*, 2005).



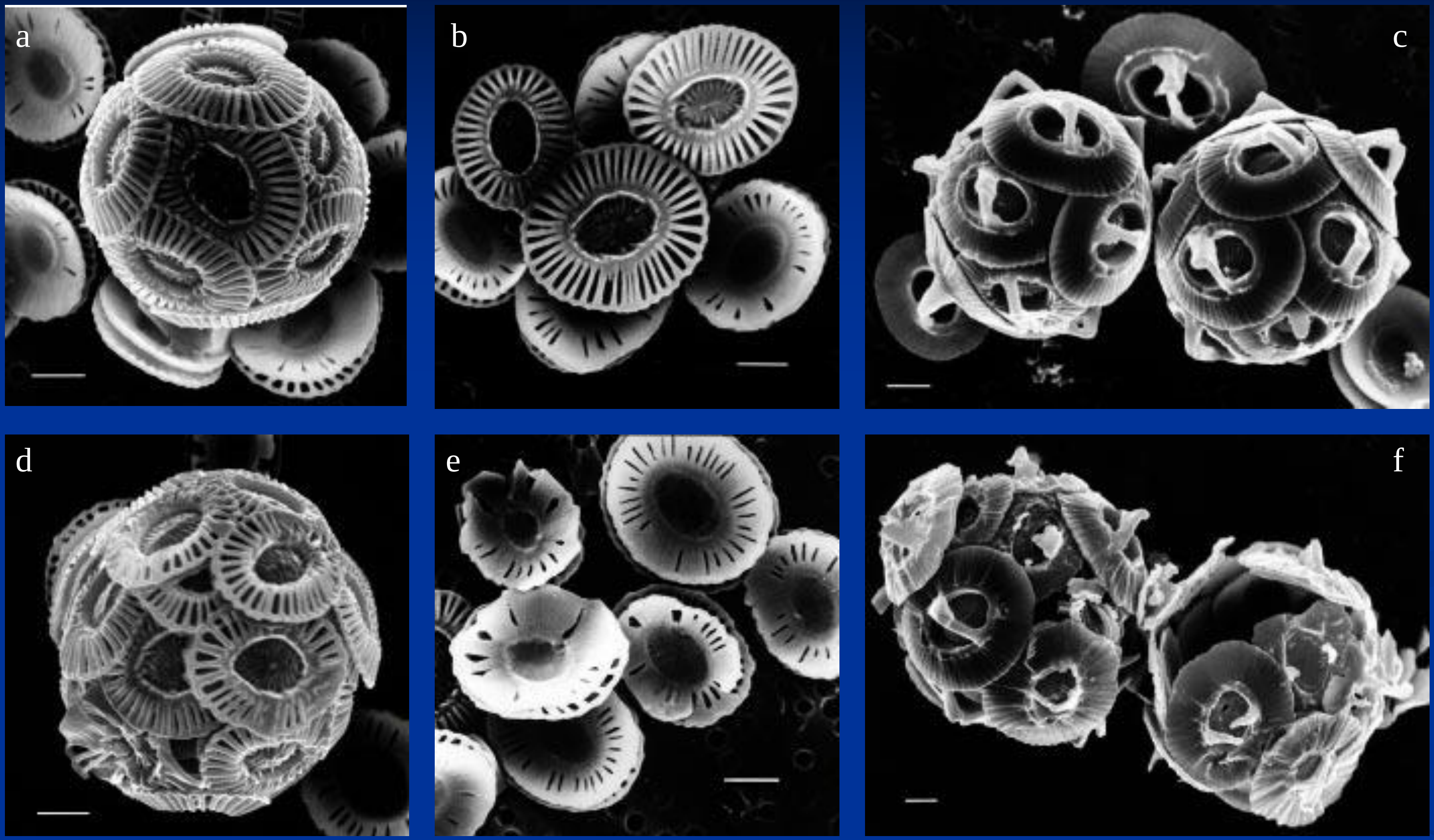
Consequences of Ocean Acidification:

• A decrease in pH causes a decrease in carbonate ion (CO_3^{2-}) concentration, a species used by many organisms to make their $CaCO_3$ shells. Many species of calcifying and non-calcifying organisms are sensitive to higher CO_2 levels. This removal will have a cascading effect, altering the species composition and abundance of phytoplankton in the World's ocean.

• Ocean acidification alters inorganic and organic seawater chemistry beyond the carbonate system (e.g., the concentrations of the major ions of seawater, the C/N ratios of plankton, Burkhardt et al., 1999).

• Decreases in primary productivity are likely to further exacerbate rising CO_2 levels in the Earth's atmosphere by creating a positive feedback. If productivity is reduced, less CO_2 will be removed from the atmosphere, resulting in an increase in atmospheric CO_2 concentration. This increase will enhance ocean warming and acidification, both of which may lead to further reductions in primary productivity.

Effect of higher CO_2 on *Coccolithophores*



300 ppm

750 ppm

- Increased calcification at low CO_2
- Increased deformation at high CO_2 (Due to decrase in CO_3^{2-} concentration)

Riebesell et al. 2000

Ocean acidification due to the flux of CO_2 from the atmosphere is a problem. This will result in a lower carbonate mineral saturation state and impact the biological community structure all the way through the Black Sea fisheries industry (Orr et al., 2005).

In addition, recent studies (Brewer and Peltzer, 2009) have suggested that increasing atmospheric CO_2 has the potential to result in expansion of the suboxic zone.

The Black Sea has a high CO_2 assimilation capacity because of its high alkalinity and long residence time. Both of these problems represent potentially serious Environmental Security problems with consequences are very difficult to predict.

Brewer and Peltzer (2009) recently showed that the domain of low oxygen waters, which is controlled by the ratio of pO_2/pCO_2, can be expanded due to increasing CO_2 as well as increased consumption of O_2.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