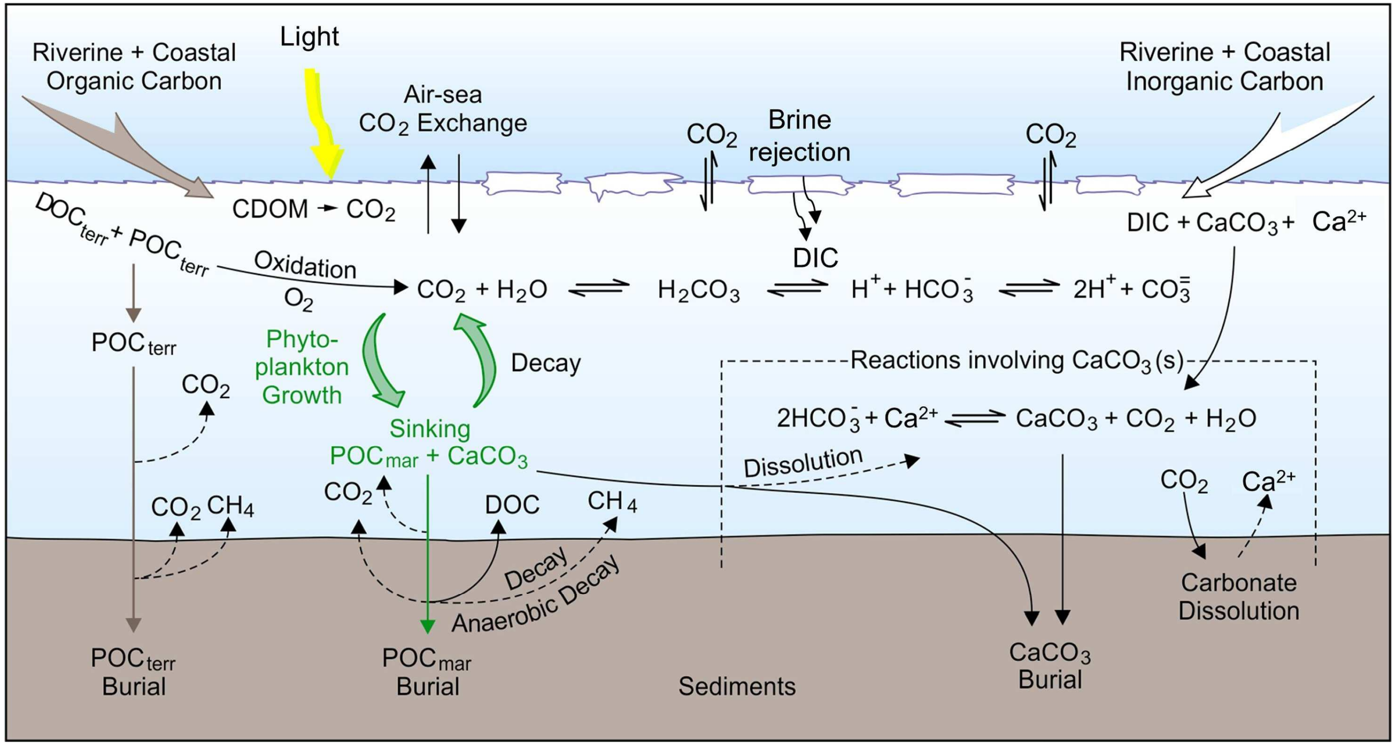
Marine carbon cycle

Carolina Cantoni



The inorganic carbon cycle

Il carbonato $CO_3^{=}$ È la principale molecola utilizzata dagli organismi calcificanti

- Chemistry

- $Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$ → Need to compensate for CO_3^{2-} loss
- $HCO_3^- \leftrightarrow CO_3^{2-} + H^+$ → Proton production
- $HCO_3^- + H^+ \leftrightarrow CO_2 + H_2O$ → Use of H^+ by proton acceptor
- $Ca^{2+} + \cancel{CO_3^{2-}} + HCO_3^- + HCO_3^- + \cancel{H^+} \leftrightarrow CaCO_3 + \cancel{CO_3^{2-}} + \cancel{H^+} + CO_2 + H_2O$
- $Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + CO_2 + H_2O$

→ Shows that calcification PRODUCES CO_2

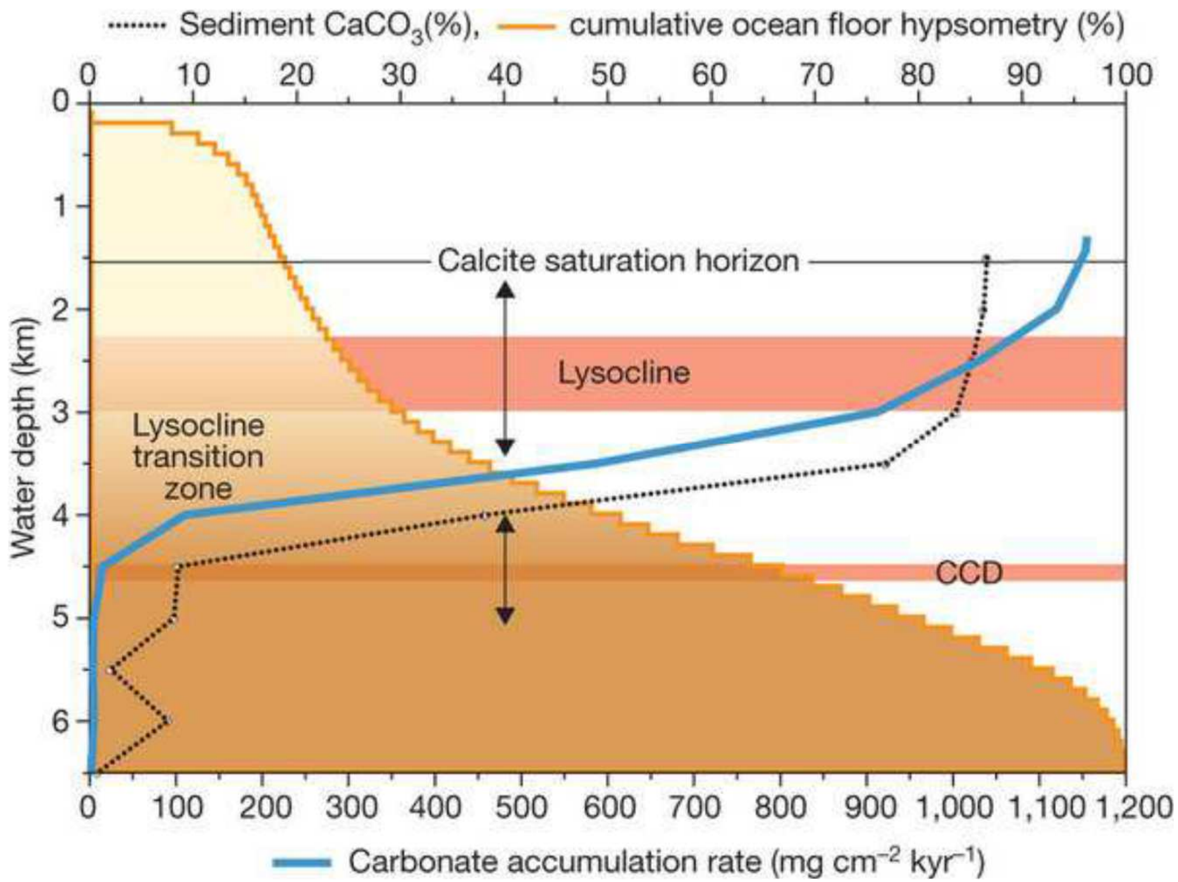
Lisoclino:

Profondità alla quale aumenta rapidamente la velocità di dissoluzione dei sedimenti carbonatici

CCD:

Calcium Carbonate Compensation depth.

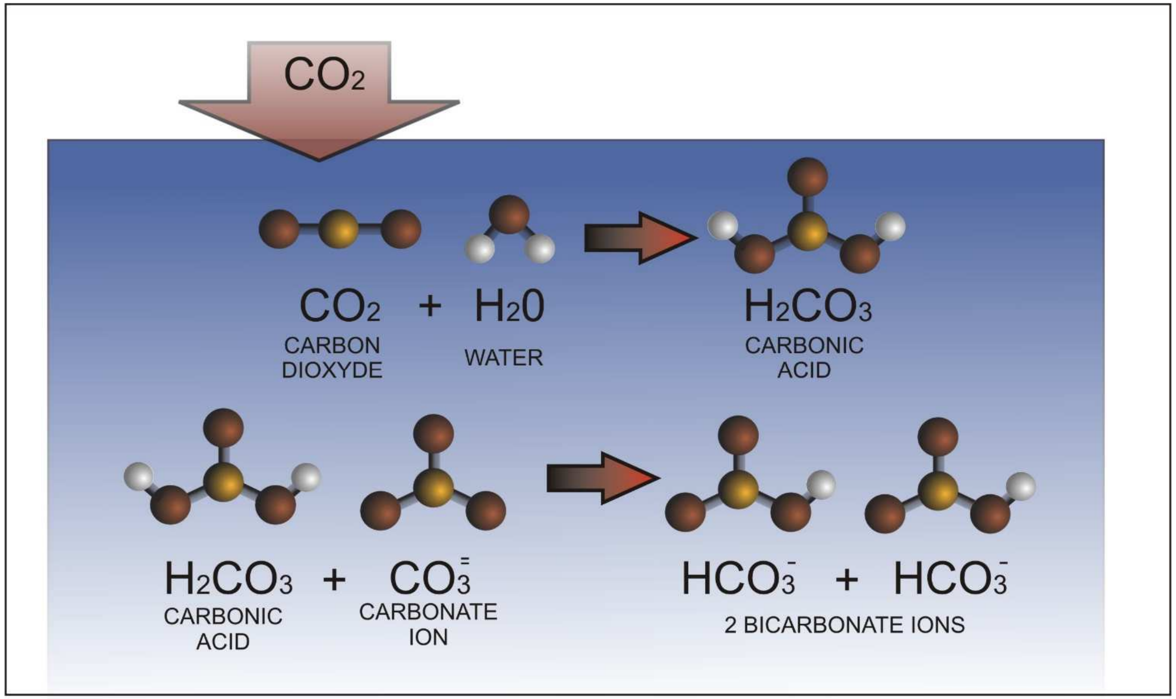
Profondità alla quale i sedimenti sono privi di carbonati



Ocean Acidification

Carbonate chemistry equilibria.

CO_2 (gas) ⇆ CO_2 (aq)
CO_2 (aq) + H_2O ⇆ H_2CO_3 (aq)
H_2CO_3 (aq) ⇆ H^+ (aq) + HCO_3^- (aq)
HCO_3^- (aq) ⇆ H^+ (aq) + $CO_3^=$(aq)



pH and carbonate ion decrease "Ocean Acidification"

Stati di saturazione dei minerali carbonatici: Calcite and Aragonite

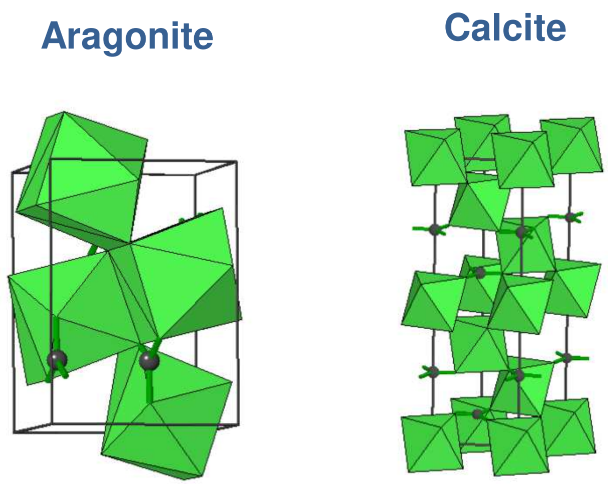
$CaCO_{3\ (s)} \rightarrow Ca^{2+}{}_{(aq)} + CO^{3=}{}_{(aq)}$

$K_{sp} = [Ca^{2+}][CO^{3=}]$ sat

$\Omega = [Ca^{2+}][CO^{3=}]/\ K_{sp}$

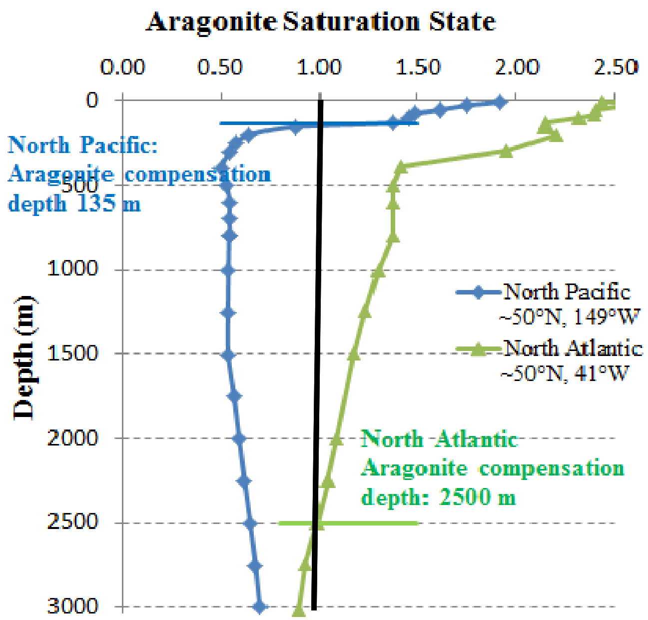
Ω<1 sottosaturazione

La dissoluzione è termodinamicamente favorita

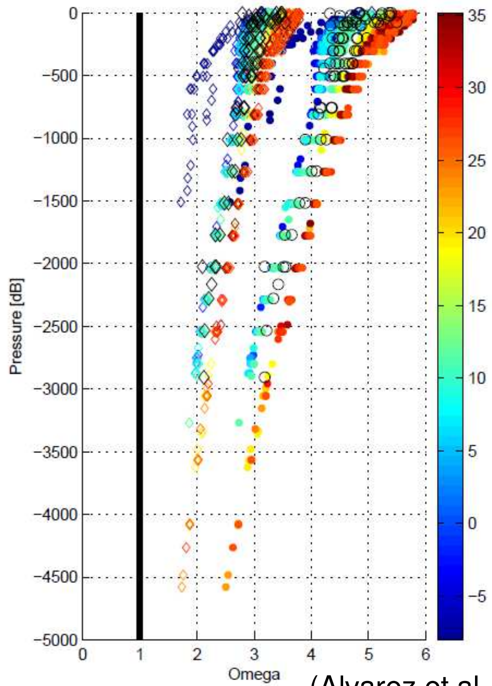


Due forme polimorfe di carbonato di calcio

Saturazione di calcite (ΩCa) ed aragonite (ΩAr) nel Mediterraneo



Distribuzione verticale di ΩAr negli oceani



(Alvarez et al. 2014)

Fig. 9. Vertical distribution of the carbonate saturation state for calcite (circles) and aragonite (diamonds). Data from the EF11 cruise are shown as black circles (saturation of calcite) and diamonds (aragonite). The colour code stands for longitude.

Total Alkalinity

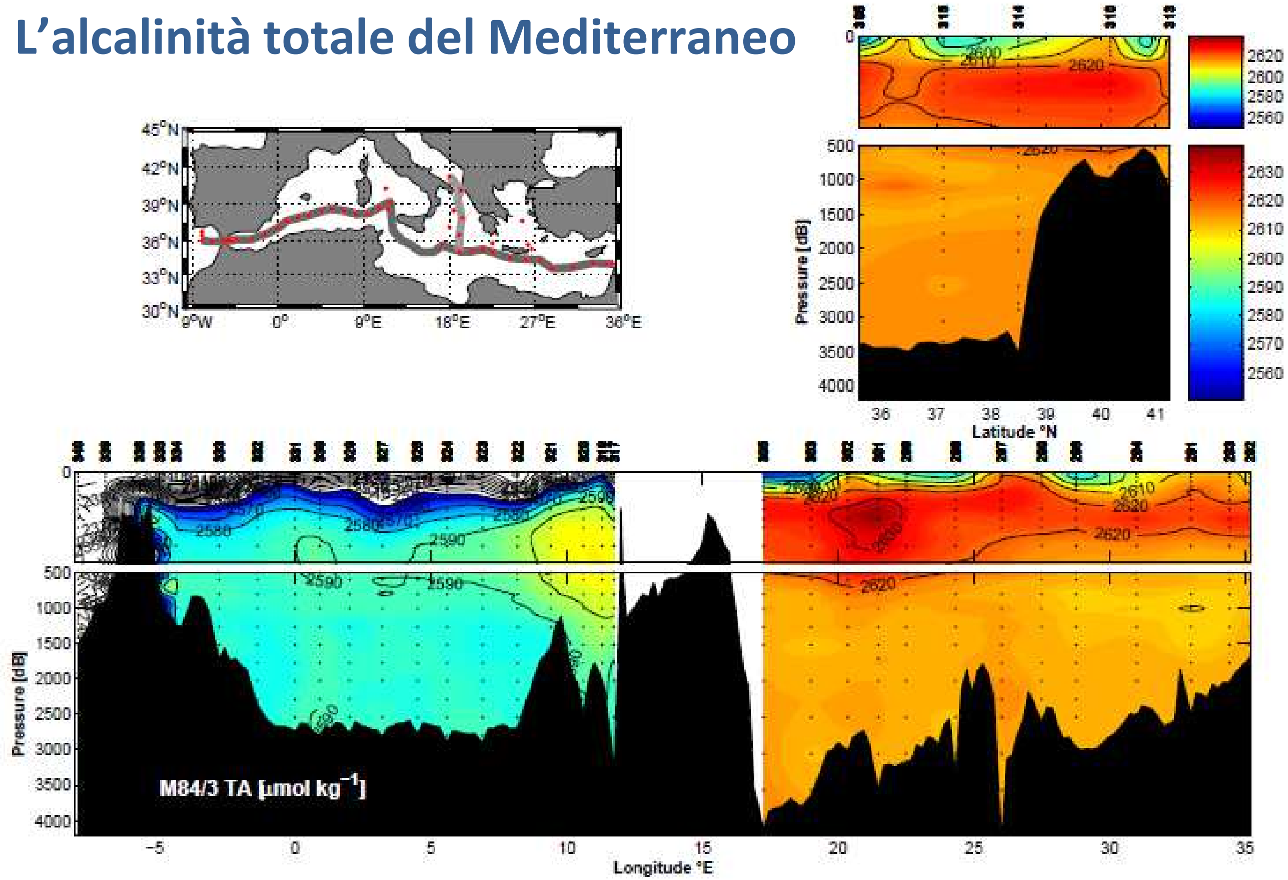
A chemical measurement of water's ability to neutralize acids
And also…
A measure of a water's buffering capacity to resist changes in pH upon the addition of acids or bases

In general, at seawater pH (8.1)…

$$AT = [HCO_3^{-}] + 2[CO_3^{2-}] + [B(OH)_4^{-}] + [OH^{-}] - [H^{+}]$$

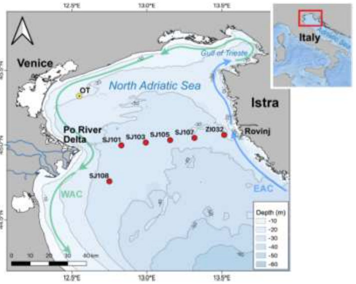
…expressed in units of concentration (mg/L $CaCO_3$)

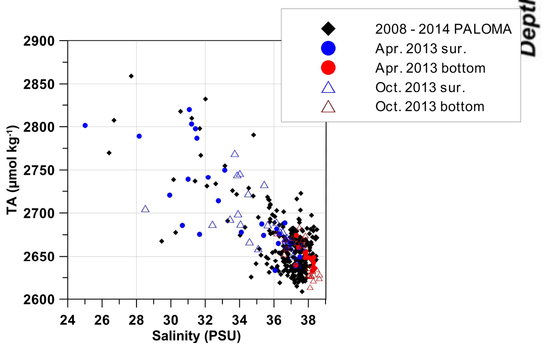
L’alcalinità totale del Mediterraneo



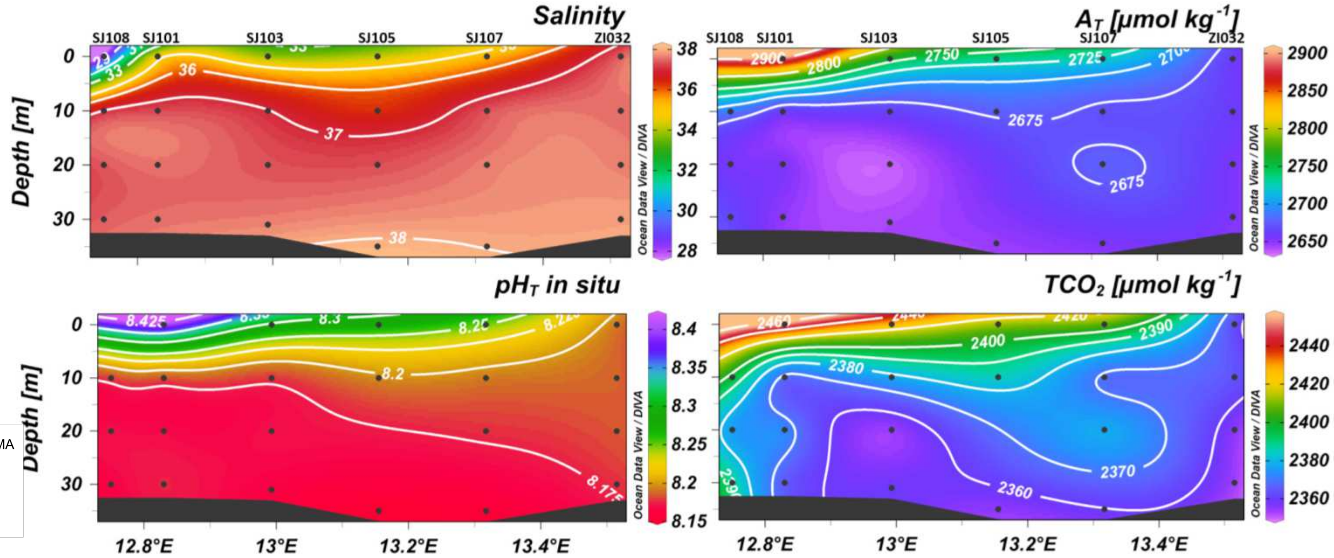
Alvarez et al. 2014

L’alcalinità totale nel Nord Adriatico





Cantoni unp. Res.



Urbini et al. 2020

Conseguenze dell'elevata alcalinità

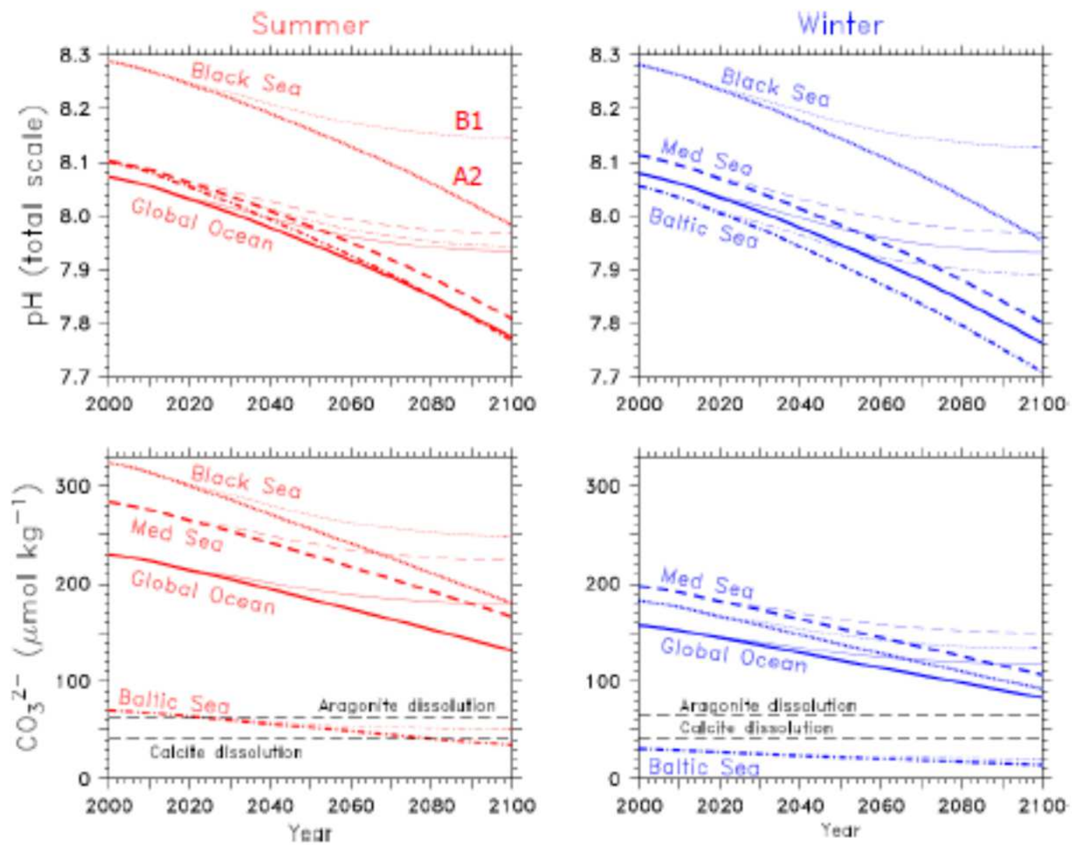
SURFACE	Salinity	TA $\mu mol\,kg^{-1}$
Aegean	39.20 ± 0.01	2628 ± 2
Levantine	39.05 ± 0.13	2612 ± 10
Ionian	38.73 ± 0.21	2607 ± 16
Adriatic	38.70 ± 0.12	2616 ± 1
Tyrrhenian	38.32 ± 0.29	2570 ± 26
Western	37.79 ± 0.51	2522 ± 46
Atlantic	36.75 ± 0.89	2423 ± 83

Air-sea CO_2 gas exchange
$\Delta DIC = +10\ \mu mol\,kg^{-1}$

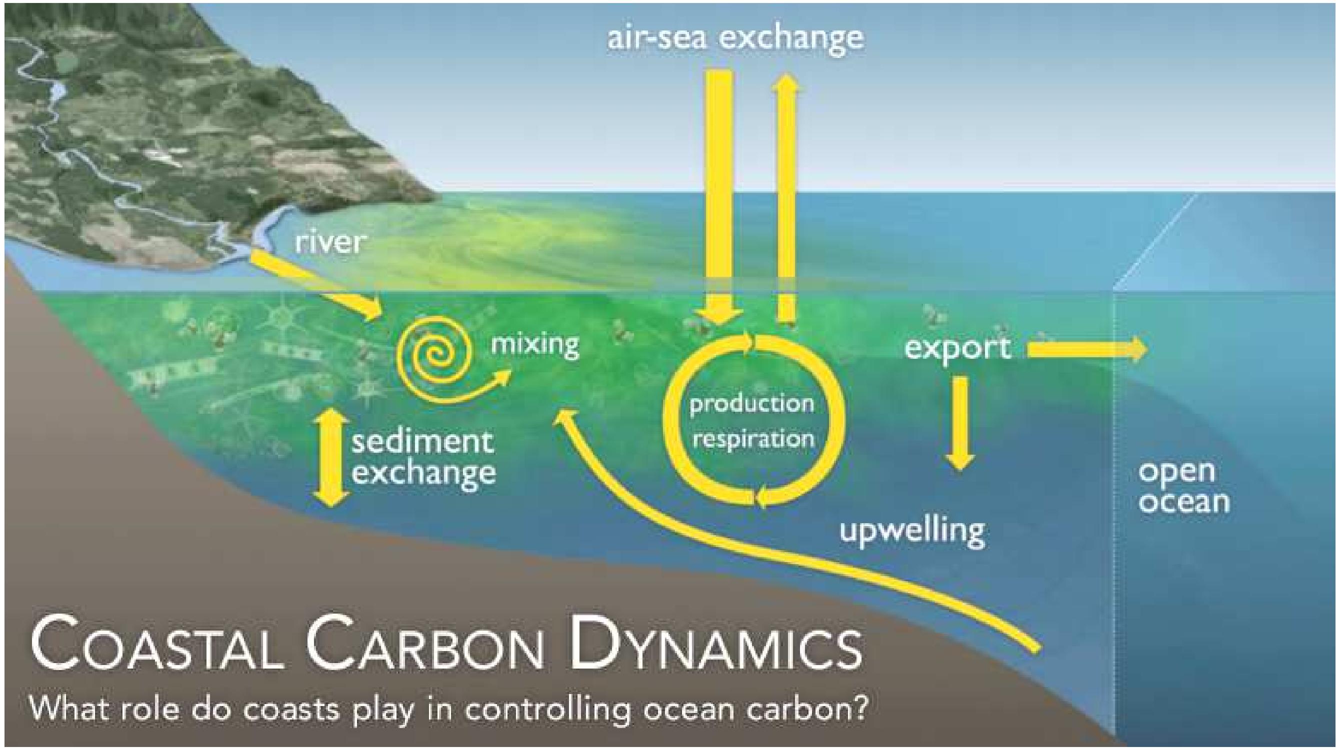
	$\Delta[CO_2]$	ΔpH	ΔOmega
Aegean	0.56	−0.016	−0.10
Levantine	0.57	−0.016	−0.10
Ionian	0.62	−0.017	−0.07
Adriatic	0.62	−0.016	−0.10
Tyrrhenian	0.77	−0.018	−0.10
Western	0.76	−0.018	−0.10
Atlantic	0.78	−0.020	−0.10

Alvarez et al. 2014

	ΔDIC in $\mu mol\,kg^{-1}$			
	25 µatm	100 µatm	200 µatm	300 µatm
Aegean	13.1	52.4	104.8	157.2
Levantine	13.0	52.1	104.2	156.3
Ionian	12.9	51.6	103.1	154.7
Adriatic	11.9	47.8	95.5	143.3
Tyrrhenian	9.7	38.8	77.7	116.5
Western	9.8	39.1	78.2	117.2
Atlantic	10.8	43.3	86.6	129.9
	$\Delta\Omega -$ Ar			
	25 µatm	100 µatm	200 µatm	300 µatm
Aegean	−0.13	−0.52	−1.05	−1.57
Levantine	−0.13	−0.52	−1.04	−1.56
Ionian	−0.13	−0.52	−1.03	−1.55
Adriatic	−0.12	−0.48	−0.96	−1.43
Tyrrhenian	−0.10	−0.38	−0.76	−1.14
Western	−0.10	−0.38	−0.77	−1.15
Atlantic	−0.11	−0.43	−0.85	−1.28
	ΔpH			
	25 µatm	100 µatm	200 µatm	300 µatm
Aegean	−0.020	−0.088	−0.199	−0.349
Levantine	−0.021	−0.089	−0.200	−0.350
Ionian	−0.022	−0.094	−0.215	−0.383
Adriatic	−0.019	−0.083	−0.186	−0.321
Tyrrhenian	−0.017	−0.073	−0.160	−0.269
Western	−0.017	−0.074	−0.164	−0.278
Atlantic	−0.022	−0.095	−0.216	−0.384

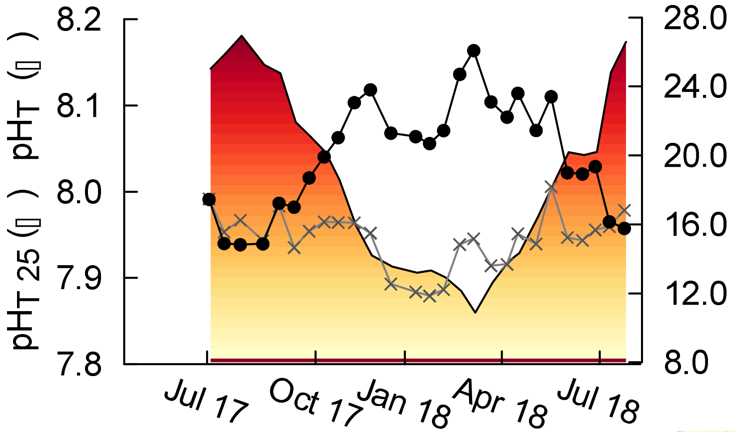


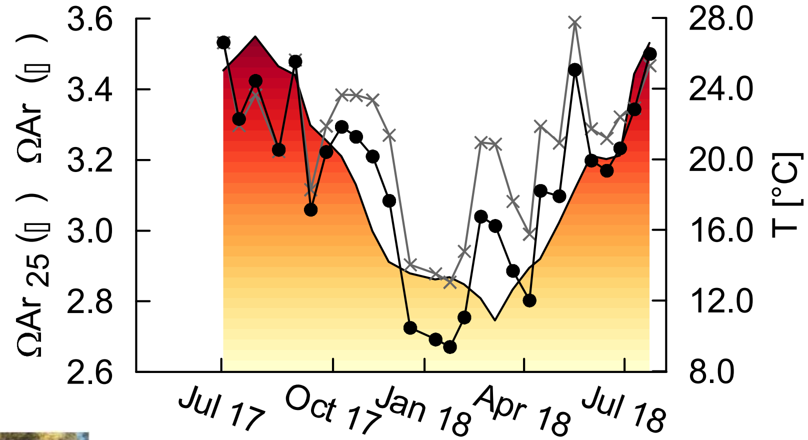
Credits: James Orr, LSCE/IPSL, CNRS, Saclay, France

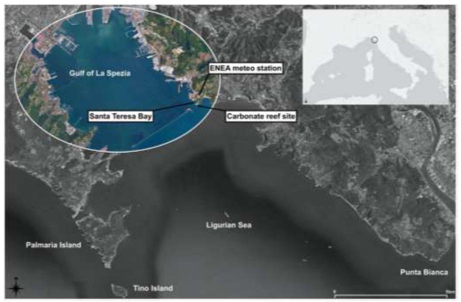


Coastal regions experience complex biogeochemical processes which influence carbon dynamics and can contribute to coastal acidification. Source: NOAA/PMEL.

Temperature and acidification







1 m depth over a "Elisolandia Elongata" reef

Adapted from Ragazzola et al. 2021, «

Strong T influence on pH, lower on ΩAr and decreasing carbonate availability.

Winter is less acidic (Higher pH) but more "corrosive" (lower ΩAr)