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Long-term and short-term inorganic carbon reservoirs in Aegean seawater – an experimental study

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Abstract. The relevant literature does not explicitly address the fact that there are two fundamentally different inorganic carbon (DIC) reservoirs in seawater; (1) a long-term "background" DIC reservoir that is not in net-transfer equilibrium with the atmosphere, and (2) a short-term "atmospheric" DIC reservoir that is fed by atmospheric pCO_2. In addition, we may define a third "anthropogenic" DIC reservoir that quantifies the increase in DIC since industrialization.

We perform experiments to quantify these reservoirs. We equilibrate Aegean seawater with N_2-O_2 (79:21) gases with variable pCO_2 from < 10 to 100,000 µatm, and pure CO_2 gas. We quantify electrochemically the changes in pH *and, by* titration and IR spectroscopy, total alkalinity (TA) and dissolved inorganic carbon (DIC) that occur with variations in pCO_2. About 78% of the Aegean DIC is *"background"*, introduced into the Aegean sea by the long-term carbon cycle, i.e. riverine input, remineralization of organic carbon, and hydrothermal CO_2. In terms of concentration and in the short term, this reservoir is independent of atmospheric pCO_2. About 22% of DIC is atmospheric in origin and is in exchange equilibrium with atmospheric pCO_2. The anthropogenic contribution to the atmospheric DIC reservoir is derived by measuring the increase in DIC between 280 (pre-industrial) and 410 µatm (present-day) pCO_2 and quantified at around 26%.

Our experiments also allow projections into the future. It has been suspected that increasing

https://doi.org/10.5194/egusphere-2022-564
Preprint. Discussion started: 26 July 2022

atmospheric pCO_2 lowers the CO_2 absorption capacity of ocean surface water. Our data confirm this assessment. When the pCO_2 increases, the pH and the CO_3^{2-}-concentration fall, and with them the ability of seawater to hydrolyze CO_2. Without measures to limit anthropogenic CO_2 emissions, the absorption capacity of Aegean seawater in the year 2100 will be only about one half of the absorption capacity of today.

1. Introduction

Emissions of anthropogenic CO_2 not only enhance greenhouse effects in the atmosphere and contribute toward global warming. Atmospheric CO_2 also reacts with ocean surface waters and causes ocean acidification (Caldeira and Duffy 2000, Caldeira and Wickett 2000, Andersson et al. 2005, Andersson et al. 2008, Andersson and Mackenzie 2012, Doney et al. 2009), to an extent that marine organisms may face difficulty in sequestering $CaCO_3$ to assemble their calcareous shells (Wolf-Gladrow et al. 1999, Riebesell et al. 2000, Caldeira and Wickett 2000, Orr et al. 2005, Guinotte and Fabry 2005).

Thermodynamically it can be calculated how increased CO_2 emissions affect the pH of ocean water (Zeebe and Wolf-Gladrow 2002) and how much CO_2 is exchanged with the atmosphere. Atmospheric CO_2 is physically dissolved, following Henry's law, as $CO_2°$ (aq) in seawater and then reacts with CO_3^{2-} (aq) of seawater to HCO_3^- (aq), according to the equilibria

$$CO_2(atm) \rightleftharpoons CO_2^0(aq) + CO_3^{2-}(aq) + H_2O \rightleftharpoons 2\,HCO_3^-(aq) \quad (1)$$

The hydrolysis of 1 mol $CO_2°$ releases 1 mol H_3O^+. If pH and another parameter such as total alkalinity (TA) of seawater are known and the anthropogenic fraction of CO_2 of the atmosphere is quantified, then with knowledge of the dissociation constants of H_2CO_3 (Mehrbach et al. 1973; Roy et al. 1993; Dickson and Millero 1987; Wanninkhof et al. 1999, Millero et al. 2006; Millero 2007) we may calculate from eqn. (1) the anthropogenic fraction of dissolved inorganic carbon (DIC) (Zeebe and Wolf-Gladow 2001, Zeebe and Ridgwell 2011). The practice, however, is more complex since many other factors complicate a quantification. Among them are the mixing rates between shallow ocean water and deep water that is not in equilibrium with atmospheric CO_2, temperature effects

https://doi.org/10.5194/egusphere-2022-564
Preprint. Discussion started: 26 July 2022

(warm water dissolves less CO_2 than cold water), regional differences in the mixing rates, photosynthesis, and remineralization of organic carbon. The most widely used methods to quantify anthropogenic DIC are performed by mass balance calculations (e.g. Sabine et al. 2004, Tanhua et al. 2007, Gruber et el. 2019, Friedlingstein et al. 2020) and comparative analysis of DIC of deep ocean water that has not yet seen ingression of anthropogenic CO_2 and other anthropogenic gas species (Gruber et al. 1996, Na et al. 2022).

In this contribution we apply an experimental approach to the problem. We let react natural seawater with N_2-O_2 (79:21) gases with known quantities of CO_2. We show for the first time that only a small fraction of the DIC in seawater is in net-transfer equilibrium with the CO_2 of the atmosphere. By far the largest DIC reservoir in ocean water, around 78%, is inorganic carbon that was (and is being) derived from the long-term carbon cycle (Berner 1992, 1999), added by weathering reactions, submarine hydrothermal activity, and re-mineralization of organic material. We refer to this DIC reservoir as "background DIC". The remainder, i.e. ca. 22%, is derived from the CO_2 exchange between atmosphere and seawater via eqn. (1) and referred to here as "atmospheric DIC". The anthropogenic fraction of the atmospheric DIC is about 26 ±3%, here termed "anthropogenic DIC". It corresponds to the DIC fraction added since 1860, the beginning of industrialization, when the pCO_2 was around 280 µatm. We emphasize that all our data and interpretations are valid only for Aegean seawater.

2. Methods

The seawater used for the equilibration experiments comes from the Aegean sea near the island of Sifnos. Its salinity is determined by ICP-OES analysis at 38‰ NaCl equiv. The $Ca^{2+}aq$ concentration is analyzed at 12 mmol • kg^{-1}. The total alkalinity (TA) is titrated at 2687 ±27 µmol • kg^{-1} (2σ). The total DIC (equilibrium with 400 µatm CO_2 partial pressure) is determined by infrared (IR) spectroscopy (see below) at 2515 ±16 µmol • kg^{-1} (2σ).

The gases to simulate atmospheric exchange are N_2:O_2 (79:21) gas mixtures with CO_2 concentrations of < 10, 200, 280, 410, 1000, 2,000, 5,000, 20,0000, and 100,000 µatm CO_2. In

https://doi.org/10.5194/egusphere-2022-564
Preprint. Discussion started: 26 July 2022

addition, one experiment was performed with pure CO_2 gas. Uncertainties in CO_2 contents are certified by the gas supplier (AirLiquide®) to < 1 relative vol.%. The gases are bubbled through the seawater in 280 ml reaction flasks with gas flow rates of ~ 0.1 L • min^{-1} (Fig. 1). Temperature is buffered at 25 ±0.2°C by suspending the flasks in temperated water baths. Equilibration experiments with a near-zero CO2 gas are carried out at 17°C, in order to suppress, or at least delay, aragonite nucleation (see below). The electromotive force (emf) is monitored with hydrogen ion sensitive glass electrodes using a 3n KCl standard solution as reference electrolyte. The precision is ±0.02 units in pH. The pH values reported in Table 1 are given on the free hydrogen scale (Dickson 1993). Equilibration between gas and water is assisted by stirring solutions with a magnetic stirrer while they are bubbled with their equilibrium gases. Typical run times are 30 to 50 h. Hydrolysis equilibrium with the gas is considered reached when the pH has remained constant around ±0.02 pH units for at least 8 hours.

Table 1

pCO_2	pH values		Total alkalinity		HCO_3^-	CO_3^{2-}	$CO_{2,aq}$	Total CA	Total DIC	
µatm	(n runs)		µmol kg^{-1}		µmol kg^{-1}			µmol kg^{-1}	µmol kg^{-1}	
< 10	> 9 (see text)	(11)	1630 ± 30	(3)	n/c	n/c	n/c	n/c	1974 ± 27	(11)
200	8,44 ± 0,03	(5)	2714 ± 28	(3)	1798	461	5	2720	2263 ± 19	(9)
280	8,3 ± 0,02	(4)	2631 ± 5	(2)	2019	375	8	2769	2400 ± 8	(11)
410	8,21 ± 0,02	(3)	2687 ± 14	(3)	2177	329	10	2835	2515 ± 16	(36)
700	8,08 ± 0,01	(3)	2634 ± 29	(3)	2392	268	15	2928	2674 ± 38	(9)
1000	7,87 ± 0,07	(10)	2717 ± 24	(6)	2510	174	26	2858	2708 ± 38	(6)
2000	7,55 ± 0,04	(4)	2690 ± 24	(4)	2587	87	55	2761	2727 ± 61	(6)
5000	7,24 ± 0,05	(5)	2732 ± 39	(2)	2642	44	115	2730	2800 ± 78	(6)
20000	6,66 ± 0,01	(4)	2714 ± 7	(11)	2639	13	437	2665	3087 ± 29	(6)
100000	5,97 ± 0,02	(5)	2618 ± 6	(10)	2788	4	2263	2796	5054 ± 52	(6)
1000000	4,94	(1)	1666	(1)	3148	2	27384	3152	30530 ± 300	(3)

Table 1. Summary of the experimental data. Uncertainties quoted are either the analytical ranges (pH and TA) or reflect two standard deviations of the mean (DIC). In parentheses the number of trials (pH), the number of titrations (TA), or the number of samples and aliquots analyzed (DIC). Atmospheric

https://doi.org/10.5194/egusphere-2022-564
Preprint. Discussion started: 26 July 2022

contributions to DIC are calculated by subtracting from the total DIC at the pCO_2 of interest the DIC at < 10 µatm CO_2. Carbon speciations (*) calculated from TA and the pH averages with the stoichiometric constants by Millero et al. (2006). n/a not analyzed, n/c not calculated.

Total alkalinities (TA) are titrated in situ, that is, while a seawater sample is bubbled with its respective equilibrium gas. Titrations are performed with a Metrohm titrator and 0.1 n HCl MerckTM standard solution. The amount of acid used is equivalent to the TA of the sample, which is set equal to $[HCO_3^-] + 2 \cdot [CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + 2 \cdot [PO_4^{3-}] + [HPO_4^{2-}] + [SiO(OH)_3^-] - [H_3O^+] - [HSO_4^-]$. Titration is continued until a pH of 4.5 is reached. At this pH, all anionic carbon species are considered neutralized to CO_2,aq and exchanged with the experimental gas. In seawater, between 95 and 97% of the TA are carbonate alkalinity CA (Morse and Mackenzie 1990; Zeebe and Wolf-Gladrow 2001), defined as $[HCO_3^-] + 2 \cdot [CO_3^{2-}] - [H_3O^+]$, but it is the total alkalinity that is quantified by titration.

Following attainment of pH equilibrium, 10 ml aliquots of each solution are siphoned off and analyzed for total DIC. Samples are taken by moving bubble-free solution from the reaction flasks into rubber-sealed glass vials via PE tubing, using the slight gas overpressure inside the reaction flasks as driving force. Before samples are taken, the ejection system and the glass vials are vented with the experimental atmosphere for several minutes and flushed with the equilibrium seawater solution at least once, to avoid contaminating the water sample with ambient atmosphere. The DIC concentrations are determined with a TOC-VCPH analyzer (Shimadzu Corp.) by extracting solution from the sealed vials with a headspace-free syringe into a reactor. An aliquot of 25% H_3PO_4 is injected into the reactor while sparging it with a CO_2-free carrier gas (purified artificial air). At the pH imposed by H_3PO_4 (~ 1), all DIC of the sample is liberated as gaseous CO_2. The CO_2 content in the carrier gas is then quantified by infrared spectroscopy. The IR spectrometer is calibrated before and after each block of DIC analyses (usually three aliquots of two runs) with four H_2O-$NaHCO_3$-Na_2CO_3 standard solutions containing 10, 25, 50, and 100 mg C, respectively 833, 2082, 4163, and 8326 µmol DIC per kg water. The blank is the DIC in milli-Q water in equilibrium with ambient (410 µatm) pCO_2, which is calculated with a Henry constant of 3.38×10^{-2} mol $\cdot$ L^{-1} $\cdot$ atm^{-1} at 13.5 µmol kg^{-1} DIC. The detection limit is set at three times that blank. For further analytical details see

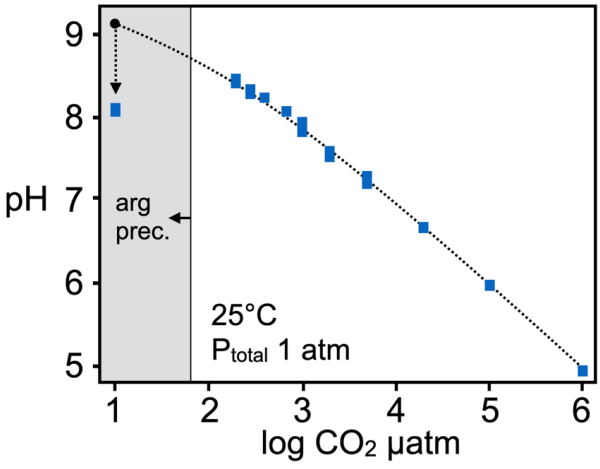
https://doi.org/10.5194/egusphere-2022-564
Preprint. Discussion started: 26 July 2022

125 Siemens et al. (2012).

3. Results

3.1. Relations between pCO_2 and pH

The pH falls as pCO_2 increases (Fig. 1), in much the same fashion as predicted by
130 thermodynamic models (Parkhurst 1995, dashed line in Fig. 1). However, there is a pCO_2 - pH space, shaded in gray in Fig. 1, where the experiments do not follow the thermodynamically calculated trend. The reason is that at a pCO_2 below ca. 50 to 100 µatm CO_2 aragonite is precipitated from Aegean seawater, lowering the pH. The issue of aragonite precipitation under low pCO_2 will be discussed below.



135 **Figure 1. The pH of seawater after equilibration with N_2:O_2 (79:21) artificial gases with variable CO_2 contents in µatm. The blue symbols are the experimentally determined pH-pCO_2 pairs, the dashed line is the pH dependence calculated with PHREEQC (Parkhurst 1995). Symbol lengths reflect the pH range of n determinations (cf. Table 1). Uncertainties in terms of pCO_2 as quoted by the gas supplier are ±10 µatm in CO_2. (modified after Gäb et al. 2017)**

140

https://doi.org/10.5194/egusphere-2022-564
Preprint. Discussion started: 26 July 2022

3.2. Relations between pCO2 and total alkalinity (TA)

Total alkalinity (TA) in Fig. 2 averages around 2687 ±27 µmol kg^{-1} (2σ) and is slightly higher than the alkalinity of Mediterranean seawater reported by Schneider et al. (2007) at 2600 µmol kg^{-1}.

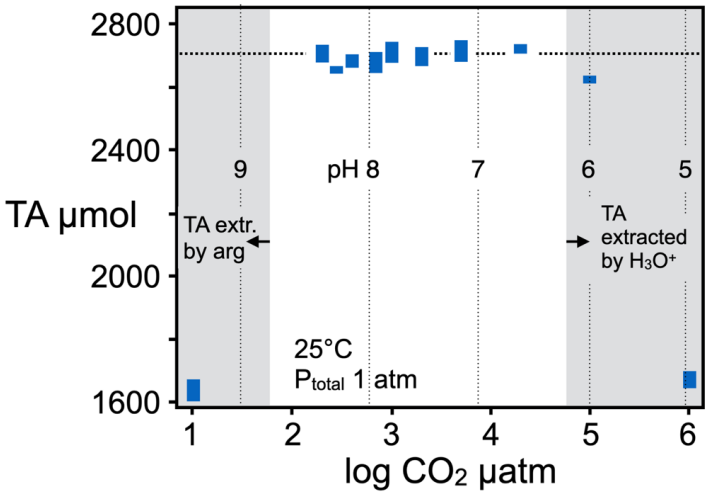


Figure 2. Total alkalinity (TA) of the seawater in µmol · kg^{-1}, titrated with 0.1 n HCl while each water sample was kept in exchange equilibrium with its respective gas. Blue symbols experimental data, dashed line (Parkhurst 1995) to illustrate that TA is considered independent of pCO_2 (Millero 2005, Zeebe and Wolf-Gladrow 2001). Numbers next to symbols are the pH values from Table 1. Error bars are the ranges of n titrations. (modified after Gäb et al. 2017)

Contrary to statements in the literature (Morse and Mackenzie, 1990; Zeebe and Wolf-Gladrow 2001), the TA of seawater is not strictly independent of pCO_2: below a CO_2 of ca. 50 to 100 µatm, the pH and the HCO_3^-/CO_3^{2-} ratio in solution adopt values so high (respectively so low) that Aegean seawater precipitates aragonite, lowering TA by $CaCO_3$ extraction to 1630 ± 30 µmol kg^{-1}. At very high pCO_2, that is, when CO_2 exceeds 100,000 µatm, the H_3O^+ concentration generated by the hydrolysis of CO_2 (eqn. 1) is high enough to neutralize some HCO_3^- to CO_2 (aq) and drive it out with the experimental gas. In Fig. 2, the two regions where TA is not independent of pH are shaded in grey. Obviously though, these two regions are of theoretical interest only, for neither in the past nor in the foreseeable future were (or will) $CO_2 < 50$ to 100 and $CO_2 > 100{,}000$ µatm be reached. Nonetheless, the statement that the TA is independent of pCO_2 (Zeebe and Wolf-Gladrow 2001) is

https://doi.org/10.5194/egusphere-2022-564
Preprint. Discussion started: 26 July 2022

not strictly valid for the entire range of possible CO_2 partial pressures.

3.3. Relations between pCO_2 and dissolved inorganic carbon (DIC)

Total DIC as analyzed with IR spectroscopy is shown in Fig. 3. For comparison we also display the DIC of fresh water at 25°C calculated with Henry's law and a K_H of 3.38 • 10^{-2} mol • L^{-1} • atm^{-1} (dashed line).

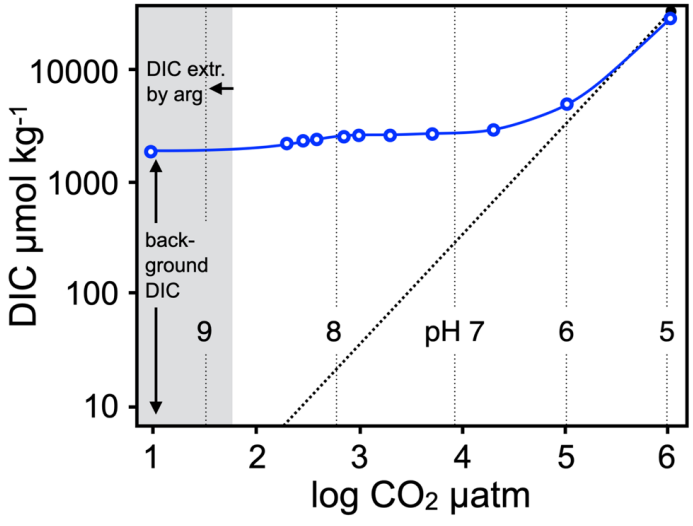


Figure 3. Total dissolved inorganic carbon (DIC) versus the CO_2 partial pressures of the experimental gases, in Aegean seawater (blue curve 1) and in fresh water (dashed line). At low pCO_2, CO_2 is dissolved by hydrolysis via eqn. (1) while above a pCO_2 of ~ 5,000 µatm dissolution is increasingly physical by CO_2,atm ⇌ CO_2,aq. The CO_2 uptake by pure water is calculated with a Henry constant K_H = 3.38 * 10^{-2} mol kg^{-1} atm^{-1}. (modified after Gäb et al. 2017)

With increasing pCO_2, DIC increases as expected, although the actual dependence between the two parameters is found relatively small. While pCO_2 of the gas phase increases from 200 to 1,000,000 µatm by a factor of 5000, the DIC in the equilibrium seawater is only raised by a factor of 15.5. That is due to the high background DIC, i.e. that fraction that is no extractable by changing pCO_2. The amount of background corresponds to the difference in DIC between Aegean seawater

https://doi.org/10.5194/egusphere-2022-564
Preprint. Discussion started: 26 July 2022

and fresh water (arrow in Fig. 3). In the low pCO_2 region, below a pCO_2 of ~ 5,000 µatm, carbon is dissolved by hydrolysis (eqn. 1), while above a pCO2 of ~ 10,000 µatm dissolution is increasingly physical by CO_2,gas ⇌ CO_2,aq.

Considerable effort went into determining experimentally the background DIC fraction, entrained into the oceans by processes governing the long-term carbon cycle (Berner 1999). Experimentally, it would seem straightforward to determine that fraction by difference, once all exchangeable DIC is extracted from the water by equilibration of with a zero-CO_2 gas. However, this involves experimental problems. When a seawater solution is exposed to near-zero pCO_2 (here < 10 µatm CO_2, Table 1), the pH and the ion concentration product $[Ca^{2+}] \cdot [CO_3^{2-}]$ of the water rise with exposure time until a pH is reached where the supersaturation in $CaCO_3$ of Aegean seawater becomes so high that aragonite precipitates, extracting both TA and DIC.

When solid $CaCO_3$ is stabilized, the solutions become turbid, precipitating a whitish phase. Phase analysis by XRD characterizes the precipitate as aragonite, and SEM imaging identifies star-shaped aragonite aggregates with µm-sized aragonite crystals arranged radially around a nucleus (Fig. 4). Aggregates similar in morphology may be seen in the cores of aragonite ooides observed at the Bahama banks (Dravis 1979; Rankey and Reeder 2009; 2010). This is not to say that whitenings in the Bahamas are triggered by a drop in pCO_2 but unusually high water temperatures could have a similar effect, since warmer water cannot dissolve as much CO_2.

https://doi.org/10.5194/egusphere-2022-564
Preprint. Discussion started: 26 July 2022

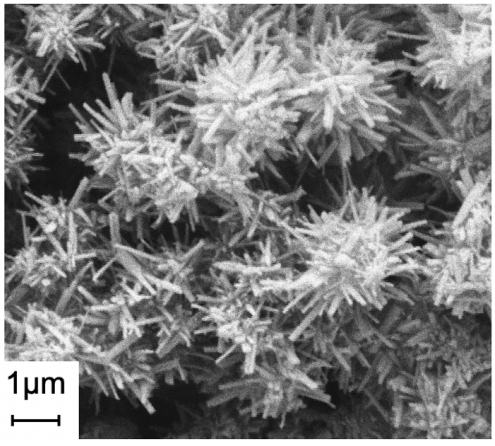


Figure 4. Secondary electron image of aragonite aggregates, precipitated from Aegean seawater while it is reacted with a zero-CO_2 (pCO_2 < 10 µatm) gas.

Given those results, it is clear that reliable pH, TA or DIC values can no longer be determined with aragonite in suspension. We try to overcome the problem of aragonite precipitation with time series runs. While a water sample is reacted with a near-zero (< 10 µatm) CO_2 gas, 10 ml water samples are taken from the reaction flasks in regular intervals (several hours) until aragonite precipitation is observed. To delay aragonite precipitation, these time series experiments are carried out at 17 instead of the usual 25°C equilibration temperature. The expectation is that a slightly lower temperature may help keep aragonite metastably in solution, hence may delay the onset of aragonite nucleation to a higher pH and extend the pH-pCO_2 range within which aragonite-free low-pCO_2 water samples can be taken.

One such time series is shown in Fig. 5. The degree of aragonite saturation is computed in terms of Ω_{arg}, which is defined as the $[Ca^{2+}] \cdot [CO_3^{2-}]$ ion concentration product in seawater divided by the stoichiometric solubility product of aragonite ($6.65 \pm 0.12 \cdot 10^{-7}$ mol^2 kg^{-2}, Mucci 1983). As expected, Ω_{arg} increases with exposure time to a near-zero CO_2 gas. When pH rises, the HCO_3^-

https://doi.org/10.5194/egusphere-2022-564
Preprint. Discussion started: 26 July 2022

/CO_3^{2-} ratio falls and Ω_{arg} increases.

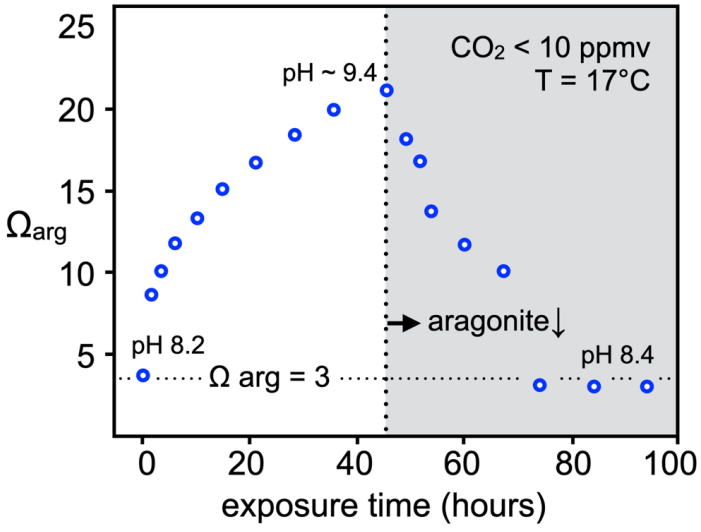


Figure 5. Time series experiments with pCO_2 < 10 µatm at 17°C, carried out to semi-quantify the background DIC. Region where macroscopic aragonite saturation is observed is shaded in grey. Note that after aragonite precipitation, Ω_{arg} finds back to a value near 3, identical to Ω_{arg} of pristine Aegean seawater (see text).

Spontaneous precipitation is usually observed when the pH has reached a value near 9.4, which for Aegean seawater corresponds to a HCO_3-/CO_3^{2-}concentration ratio of ~ 2.5 : 1 calculated with PHREEQC (Mehrbach et al. 1973; Dickson and Millero 1987; Pankhurst 1995; Table 1). After aragonite has settled out and the solution has cleared, the TA of the remaining solution is titrated at ~ 1630 ±30 µmol kg^{-1}. The pH also falls when aragonite is extracted, from ca. 9.4 to 8.4. The loss in TA after aragonite precipitation compared to pristine Aegean seawater at pCO_2 = 410 µatm (TA = 2687 µmol • kg^{-1}) is about 40%.

We note with interest that following aragonite precipitation, the residual solution finds back to an Ω_{arg} of ~ 3, near-identical to the Ω_{arg} of pristine Aegean seawater prior to exposure to a near-zero pCO_2 gas (Fig. 5). Intuitively, one would expect Ω_{arg} to drop to unity when macroscopic aragonite falls, i.e. that the intrinsic aragonite oversaturation of Aegean seawater would be degraded as well. However, this does not seem to be the case. Perhaps the study by Gebauer et

https://doi.org/10.5194/egusphere-2022-564
Preprint. Discussion started: 26 July 2022

al. (2008) provides an explanation: these authors found that Ca^{2+} and CO_3^{2-} tend to form stable prenucleation clusters even when a solution is $CaCO_3$ undersaturated. Apparently, this fraction of cluster $CaCO_3$ in seawater is not affected by the precipitation reaction in Fig. 5, but is retained even when macroscopic aragonite precipitates.

The average DIC of 11 zero-CO_2 analyzed seawater samples, reacted at 17°C and drawn just before aragonite precipitation set in, is analyzed at 1974 ±27 (2σ) µmol C per kg seawater (Table 1). This is our best estimate as to the background DIC in Aegean seawater, added by processes of the long-term carbon cycle. Note that despite all experimental efforts in delaying aragonite precipitation, this DIC concentration may still be a maximum. In $CaCO_3$ oversaturated seawater, DIC equilibrium with a zero-CO_2 gas can only be approached but never precisely reached.

4. Discussion

4.1. The inorganic carbon inventory of Mediterranean seawater

Our data allow to differentiate for the first time quantitatively among the inorganic carbon contributions to Aegean seawater and seawater in general. Around 1974 ±27 µmol kg^{-1}, or 78% of the total DIC at ambient pCO_2, are background DIC. That fraction is quantified by reacting seawater with near-zero CO_2 gas and recording the pH at which aragonite precipitation begins (pH ~ 9.4). The background DIC value resulting must be a maximum, for we cannot rule out the possibility that samples are contaminated by small amounts of suspended aragonite crystals. To determine an accurate value, equilibrium with a zero-CO_2 gas would be needed, but this is not possible since Aegean seawater is supersaturated with respect to $CaCO_3$. In the land-locked Aegean sea without active spreading ridges, the principal sources are surface weathering and remineralization of organic carbon, less so hydrothermal input.

In terms of bulk concentration, the background DIC fraction is not in net-transfer exchange with the atmosphere and independent of short-term variations in atmospheric CO_2. This means that short-term variations in pCO_2 to not alter the concentration of background DIC. In terms of speciation, however, the background fraction does respond to changes in pCO_2 by changing its

https://doi.org/10.5194/egusphere-2022-564
Preprint. Discussion started: 26 July 2022

HCO_3^-/CO_3^{2-} ratio when pCO_2 and pH fluctuate. An analogue to this behavior is the sulfate SO_4^{2-} concentration in seawater (~ 29 mmol • kg^{-1}; Millero 2005). Sulfate is also out of net transfer equilibrium with the SO_2 of the present-day pristine atmosphere (Berner 2004) which carries ~ 0.0036 µatm SO_2 (DWD 2022). Sulfate in seawater probably originates from oxidative weathering of sulfide, just as background DIC is contributed by surface weathering, hydrothermal input, and remineralization of organic matter. In the long term though, background DIC is not inert to atmospheric CO_2, as this reservoir is influenced by processes like $CaCO_3$ solution-precipitation and photosynthesis. However, these processes operate on much longer time scales of up to millions of years (Berner 2003) than CO_2 air-sea exchange (cf. Sabine and Tanhua 2010).

The DIC fraction in Aegean seawater that is exchangeable with the atmosphere at present-day atmospheric CO_2 level is quantified analytically at 540 µmol kg^{-1}, or 22% of the total DIC. This fraction is given by the DIC difference between the background DIC and the DIC analyzed at 410 µatm CO_2 (Table 1). The anthropogenic fraction of this exchangeable DIC is 115 µmol • kg^{-1}. This fraction is calculated by measuring the DIC increase between 280 and 410 µatm CO_2 and relating it to the bulk atmospheric DIC at 410 µatm CO_2. The result is that 26 ±3% of the atmospheric DIC must be anthropogenic in origin.

4.2. Comparison with other studies

Our anthropogenic DIC fraction (26 ± 3%) compares quite favorably with other quantifications from the literature, although it is valid only for Aegean seawater. Gruber et al. (1996) approximate the uptake of northern and tropical Atlantic waters between 1980 and 1989 with ca. 30% of anthropogenic CO_2. They derive that fraction by comparing the DIC of deep water uncontaminated by anthropogenic CO_2 with the DIC of surface waters. Sabine et al. (2004) calculate via mass balance that global oceans absorbed from 1800 to 1999 ca. 48%, and from 1980 to 1999 ca. 30% anthropogenic CO_2. The difference implies that with increasing CO_2 and time the absorption capacity may diminish (see below). Sabine and Tanhua (2010) quote the oceanic uptake

https://doi.org/10.5194/egusphere-2022-564
Preprint. Discussion started: 26 July 2022

as ~ 25% CO_2. Gruber et al. (2019) calculate via mass balance the anthropogenic share of DIC for the time interval from 1994 to 2007 as 34 ±4 Gt via mass balance which corresponds to ~ 31 ±4% of total emitted CO_2. Friedlingstein et al. (2020) calculate, again by mass balance (cf. eqn. 1 in their paper) that from 2010 to 2019 about 22% of the anthropogenic CO_2 emissions were absorbed by ocean water. We do not wish to imply that our value is more accurate than that of previous studies, especially since it is only valid for Aegean seawater. However, it does give credence to our purely experimental approach when we derive, without the intrinsic uncertainties in quantifying all terrestrial carbon reservoirs, an anthropogenic fraction that agrees well with literature data.

4.3. Future development

Our data also allow an assessment of whether the percent uptake of CO_2 by ocean water will remain constant or change with time and increasing pCO_2. There is already the suspicion that the uptake capacity decreases with time with increasing anthropogenic pCO_2 (Sarmiento et al. 2000, Knorr 2009; Orr 2013). Sabine and Tanhua (2010) note that "the rate of ocean carbon uptake does not seem to be keeping pace with the rate of growth in CO_2 emissions". We support this assessment. For once, it is only the top several 100s of meters of ocean water above the thermocline that is an effective CO_2 sink, and that reservoir could "fill up" over time because the mixing rate with deep water does not keep pace with CO_2 uptake by hydrolysis (cf. Sabine et al. 2004). Second, as pCO_2 increases, the HCO_3^-/CO_3^{2-} rises, thereby reducing the uptake capacity of CO_2 via eqn. (1). Third, with increasing pCO_2 due to anthropogenic emissions, the average temperature of seawater (above the thermocline) will increase, and thus the capacity to absorb CO_2 will diminish since warm water dissolves less CO_2 than cold water.

https://doi.org/10.5194/egusphere-2022-564
Preprint. Discussion started: 26 July 2022

We concur with Sarmiento et al. (2000), Sabine et al. (2004), Knorr (2009), Sabine and Tanhua (2010), and Orr (2013) that with time and increasing CO_2 emissions, the uptake capacity of seawater will degrade. In Fig. 6a, we show the change in DIC with CO_2 of the atmosphere. In effect, the vertical axis of Fig. 6a is the inverse of the Revelle factor (Revelle and Suess, 1957; Egleston et al. 2010), defined as $(\Delta CO_2/CO_2)/(\Delta DIC/DIC)$ where ΔCO_2 and ΔDIC denote the differences in pCO_2 and DIC from today's values (410 µatm CO_2; Table 1).

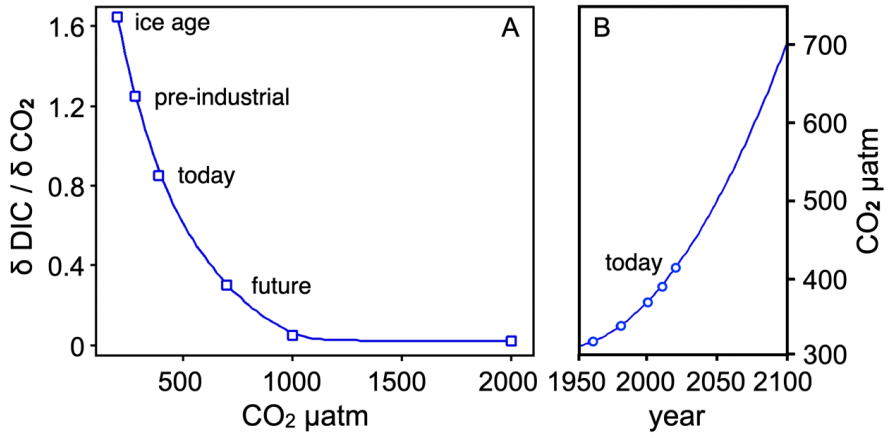


Figure 6. Absorption capacity of anthropogenic CO_2 by Aegean seawater (A) and potential increase in pCO_2 by extrapolation of the monthly Mauna Loa averages to the year 2100 (B). For details see text.

The graph suggests that in the near future the shallow regions of the Aegean ocean in exchange equilibrium with the atmosphere may fill up with respect to anthropogenic DIC. If CO_2 emissions continue to increase as projected in Fig. 6b, the buffering capacity in 2100 (700 µatm) would be reduced by more than half compared to today. In addition, there is a temperature effect with global warming since warm seawater dissolves less CO_2. Not taken into account in Fig. 6a are the mixing rates between shallow water and deep water, but the latter occur at much longer timescales than the equilibration of seawater with atmospheric CO_2 (cf. Caldeira and Wickett 2003).

5. Conclusions and Implications

We have equilibrated natural seawater from the Aegean sea with N_2-O_2 gases with variable

https://doi.org/10.5194/egusphere-2022-564
Preprint. Discussion started: 26 July 2022

pCO_2 and determined pH, TA and DIC as a function of pCO_2. The experiments allow to identify and quantify the different DIC reservoirs in seawater. There are two principal reservoirs; (1) background DIC that is introduced via the long-term carbon cycle and that is not in net-transfer equilibrium with the pCO_2 of the atmosphere, and (2) an atmospheric DIC reservoir that is fed by the pCO_2 of the atmosphere. The percentages of these two reservoirs in Aegean seawater are about 78 and 22%, respectively. To our knowledge, it is the first time that these two reservoirs are explicitly distinguished and quantified.

We quantify the fraction of anthropogenic DIC that has entered Aegean seawater since industrialization. The increase in anthropogenic CO_2 between a pCO_2 of 280 and 410 µatm is 26 ± 3% of the atmospheric DIC. In the future, the uptake capacity may fall if CO_2 emissions continue as before and if the exchange rate between surface ocean water and deep water does not change with global warming. A further increase in pCO_2 decreases the HCO_3/CO_3-ratio and depletes seawater in the carbonate ion, which is essential for the hydrolysis of atmospheric CO_2 (eqn. 1).

Following the studies by Gebauer et al. (2008, 2014) we suggest that some of the Ca^{2+} and CO_3^{2-} in seawater must be present in the form of associated nano-sized pre-nucleation clusters. Even when macroscopic aragonite precipitates, we note that the supersaturation in $CaCO_3$ persists and that the left-over solute after aragonite precipitation reverts to an Ω_{arg} of ~ 3 (cf. Fig. 6). This is more important than its seems. Perhaps we can generalize to the extent by stating that the $CaCO_3$ supersaturation of seawater is due to $CaCO_3$ nano-particles. This could be beneficial for marine calcifying organisms. Normally it is assumed that calcifiers extract Ca^{2+} hydrates ($Ca^{2+}(H_2O)_x$) and CO_3^{2-} ions from seawater to build their $CaCO_3$ skeletons or shells (cf. de Nooijer et al. 2012 and refs therein), but energetically it may be more advantageous to use already existing stable nano-nuclei as building materials rather than ionic species. In this context, it is important that Gebauer et al. (2008, 2014) noted $CaCO_3$ nanoparticles to remain stable even when a solution is $CaCO_3$ undersaturated ($\Omega_{arg} < 1$). By implication, it may follow that carbonate accreting marine organisms can handle ocean acidification better than is widely assumed (cf. Wolf-Gladrow et al. 2001, Gattuso and Hansson 2011, Riebesell and Tortell 2011).

https://doi.org/10.5194/egusphere-2022-564
Preprint. Discussion started: 26 July 2022

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