



EGUsphere, referee comment RC3
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Comment on egusphere-2022-564

Anonymous Referee #3

Referee comment on "Long-term and short-term inorganic carbon reservoirs in Aegean seawater – an experimental study" by Fabian Matthias Gäb et al., EGU sphere,
<https://doi.org/10.5194/egusphere-2022-564-RC3>, 2022

This manuscript by Gab et al. propose a new classification of seawater dissolved inorganic carbon (DIC) in two reservoirs (background and atmospheric) following a case study on seawater samples from the Aegean Sea. To do so, they proceed to an equilibration of seawater samples with 11 different gas mixtures of CO₂ partial pressure (pCO₂) ranging from near 0 uatm to pure CO₂. The authors propose also an approach to quantify the proportion of anthropogenic DIC in seawater DIC.

The overall manuscript is poorly designed: multiple missing definitions in the introduction, incomplete methodology, discussion with references found in the Result section, results found in the discussion section, misuse and misunderstanding of published literature, inadequate listing of reference. There is also room for improvement regarding to the scientific writing.

That being said, the study merits to be published because the method seems sound and the attempt to quantify the anthropogenic carbon experimentally is welcome considering the numerous indirect methodology applied for this aim. Thus, considering my serious concerns regarding the quality of this submitted manuscript, I request major revisions.

General comments

I did not grasp the scientific interest of identifying and quantifying in seawater, in constant exposure to zero CO₂ artificial atmosphere, the pool of DIC not equilibrating with the atmosphere. What are the interest and perspective of such discovery?

The authors emphasize in the manuscript that their results are valid only for the Aegean

seawater. I suggest adding in the introduction specificities related to Mediterranean and Aegean seawater so that the reader can understand the context of the study samples.

The literature review provided in the introduction about estimates of ocean anthropogenic carbon quantification is largely incomplete and shows a misunderstanding of the literature. This serious lack of understanding is very problematic and also appear in the discussion section. I would expect in the introduction a quick review of other previously-published famous methods developed to achieve this aim (Delta C star, TTD, eMLR). Sabine et al. (2004), Tanhua et al. (2007) and Gruber et al. (2019) do not use mass balance calculation as a way to quantify the ocean anthropogenic carbon inventory, contrary to what is stated by the authors. Same for Freidlingstein et al. (2020) that use global ocean biogeochemistry models and observation-based data products to estimate the ocean anthropogenic carbon sink.

The authors find that, for Aegean seawater, the anthropogenic DIC is 26 % of the DIC equilibrating with the atmosphere. In section 4.3, they compare this estimate with estimates from the literature of the percentage of anthropogenic carbon emissions absorbed by the global ocean. It does not make any sense in comparing these estimates with an estimate of the proportion of anthropogenic DIC in seawater.

The reference section is not following Biogeosciences standards, including systematic omission of journal names and intermittent use of DOI.

Specific comments

Abstract:

line 12: The two proposed background DIC and atmospheric DIC reservoirs are not fundamentally different. According to the current knowledge, both are composed of DIC with similar composition, unless otherwise proven.

line 12: Please remove all unnecessary quotes for background, atmospheric and anthropogenic.

line 12: Please replace ; by :

line 14: Please define pCO₂ in the abstract and in its first instance in line 70.

line 16: What is the interest of knowing the N₂-O₂ gas composition in the abstract? If there is not any, I suggest:

"We equilibrate the pCO₂ of Aegean seawater samples using (idealized?) gas mixtures with pCO₂ from < 10 to 100,000 μatm, as well as pure CO₂ gas."

Line 18: IR is not defined.

Intro:

line 36: In Biogeosciences, references are separated with ";" and a comma is placed before the reference year. Please proceed to the change systematically throughout the manuscript.

line 38: Please define CaCO₃

line 43: I have never seen the notation CO₂(aq) with a "o" such as CO₂o(aq). Please remove this "o".

line 44-45: No need to use the aqueous notation (aq) for CO₃²⁻ and HCO₃⁻.

line 45: replace CO₂(atm) by CO₂gas as usually annotated in seawater carbonate chemistry, e.g.:

Middelburg, J.J. (2019). Biogeochemical Processes and Inorganic Carbon Dynamics. In: Marine Carbon Biogeochemistry . SpringerBriefs in Earth System Sciences. Springer, Cham. https://doi.org/10.1007/978-3-030-10822-9_5

line 46: Ph and Alkalinity are not defined.

line 50,67,155,169,178,284,301,334,: Biogeosciences use the abbreviation Eq. (x) for equation, not "eqn. (x)".

line 70: Missing reference for the pCO₂ of around 280 uatm in the 1860s.

Methods:

line 74-75: Missing details regarding to the seawater sampling. The presence of microorganisms and detritus in the seawater could affect the seawater carbonate chemistry and influence CO₂ parameters during the storage and the experiments (30 to 50 hours to reach equilibrium). Please give the geographical coordinates and the depth of the sampling, and any treatments applied during/after sampling such as filtration.

line 75: Practical salinity should be provided and the later is unitless. See Unesco (1981). The Practical Salinity Scale 1978 and the International Equation of State of Seawater 1980. Tech. Pap. Mar. Sci., 36

line 75: Please remove aq from Ca₂+aq

line 76, 77, 78, 83, 123, 145, 164, 170, 209 222, 256, 267 : Please remove the dot between mmol and kg⁻¹ (and other units). No special need of a "x", "*" or a dot before the 10^x as well. More information: <https://www.bipm.org/en/publications/si-brochure/>

Line 76: TA already defined line 46-47.

line 77: Please add an explanation why you choose 400 uatm for equilibration. Was it the current surface atmospheric pCO₂ at the sampling date and location? Is it coming from a reference or did you measure it? If measured, how?

line 77: I suggest to rephrase: "The total DIC after equilibrium with a pCO₂ of 400 μatm is determined...".

line 75-78: Please precise the seawater temperature when these measurements have been performed and if these measurements are all performed directly after sampling or just before the laboratory experiment with gas exposures.

line 80: A partial pressure is not a concentration...

line 80: Please remove "CO2".

line 81: "Uncertainties in the gas mixtures' pCO2"

line 82: Please develop the abbreviation "vol.". Missing unit of 1. If I understand correctly, I suggest "below 1 % of relative volume."

line 84: Missing space after +- and before the unit.

line 85: The seawater carbonate system is highly sensitive to temperature (Weiss, 1974). The values measured from this seawater sample in equilibrium with near-zero CO2 gas at 17 °C should not be used with values from samples at 25 °C.

Weiss, R. F.: Carbon dioxide in water and seawater: the solubility of a non-ideal gas, *Marine Chemistry*, 2, 203–215, [https://doi.org/10.1016/0304-4203\(74\)90015-2](https://doi.org/10.1016/0304-4203(74)90015-2), 1974.

Table 1: Table titles should be above the table, not below.

line 97: Considering my comment on line 85, I have serious doubts that such calculation is valid using seawater samples at different temperatures (25°C and 17°C). Temperature changes CO2 solubility.

line 97-99: This belongs to the text body in the methods section, not to a table title.

line 98: What does "(*)" refer to? I suggest removing it.

line 98-99: Please use sentences such as : "Carbon speciations are calculated [...]. Abbreviations are included for not analyzed (n/a) and not calculated (n/c)."

line 99: By the way, the abbreviation "n/a" is not used. Why is it needed to introduce it?

line 100: TA already defined line 46-47.

line 119: IR has been defined previously so you could use IR instead of infrared.

line 122: Please replace "μmol DIC per kg water" by "umol DIC kg⁻¹".

line 121: 410 utam is defined here as ambient pCO₂. I am curious of what the 400 uatm refers to line 77.

Results

line 130: The mention "dashed line in Fig. 1)" is not needed and already mentioned in the caption's figure.

Figure 1: Please introduce in the captions the abbreviation "arg prec."

Figure 1: The dashed line/arrow that drops vertically at low pCO₂ is not from PHREEQC. I suggest using another line type.

Figure 1: You put 25°C in the figure for log CO₂ uatm >2. Please add "17°C" on the grey shaded area.

Figure 1, 2 and 3: Theses figures are copyrighted, coming from Gäb et al. (2017) but they have been slightly modified so I don't know if the following is valid: Please keep in mind that you might have to obtain a license through Elsevier/ScienceDirect Copyright Clearance Center's RightsLink® service to publish this preprint even if the original article is the same first author. If so, you might have to include an acknowledgement to the copyright. Or not?

Gäb, F., Ballhaus, C., Siemens, J., Heuser, A., Lissner, M., Geisler, T., and Garbe-Schönberg, D.: Siderite cannot be used as CO₂ sensor for Archaean atmospheres, 214, 209–225, <http://dx.doi.org/10.1016/j.gca.2017.07.027>, 2017

line 142: TA abbreviation is already defined.

line 143: I would expect comparison with the literature in the discussion section.

Figure 2: Please introduce in the captions the abbreviation "extr. by arg".

Figure 2 and 3: The pH isolines and the line from PHREEQC (or freshwater for Fig.3) are both dashed lines. Please use different line types to avoid confusion.

line 146: Please write sentences such as ""blue symbols represents..." or "Experimental data are depicted as blue symbols", "The dashed line illustrates...".

line 148: I suggest "Dashed isolines are depicting pH values calculated from PHREEQC (Parkhurst, 1995)". One could remove the pH label in the middle of the figure.

line 147-148, 150-151, 159-160: Gäb et al's statements stating that Zeebe and Wolf-Gladrow (2001) consider TA as independent of pCO₂ are wrong. The Figure 1.1.3 page 7 of Zeebe and Wolf-Gladrow (2001) disqualifies these statements (copyright figure so I don't dare to include it here). The figure clearly shows a dependency of Alkalinity to dissolved CO₂. According to Zeebe and Wolf-Gladrow (2001), alkalinity is only independent to the invasion or release of CO₂ from/to the atmosphere, but not to the physical dissolution of CO₂. I do not have the book of Morse and Mackenzie (1990) to verify the statements but I am expecting the same misunderstanding from Gäb et al.

line 147-148, 150-151, 159-160: If it happens that these statements are kept, I suggest to move them to the discussion section.

line 165: Please move the freshwater and dashed line description to the figure 3 caption.

line 168-170: This is a copy-paste from the text body. Please remove it from the figure caption.

line 164, 170: If pure water is freshwater, please be consistent and use only pure water or fresh water throughout the manuscript.

line 163-165: These lines are not useful. They are only repeating the figure captions. I suggest removing them and begin line 172 with "In Fig. 2,".

line 175-176: Here it is hypothesized that this fraction is not extractable by changing pCO₂ on a 30-50 hours duration (daily timescale). I would expect such statement in the discussion with some explanation on what is preventing it to be extracted on monthly or yearly time scales, considering that DIC_{back} has fundamentally the same composition as DIC_{atmo}.

line 176-177: See my comment for line 85.

line 189: Please describe XRD and SEM in the methods section.

line 192-194: The whole sentence "This is not to say..." is a bit out of scope. Please remove it.

line 204: metastable

line 202-203: See comment line 85.

line 207: Please remove "One such time series is shown in Fig. 5. "

line 208-209: I would expect an equation here rather than a wordy explanation of it.

line 210: Please add "In Fig. 5, as expected, ..."

line 212: semiquantify

line 214: No need to repeat what is explained in the text.

line 220: Missing space after the +- sign.

line 225: I am not sure if intuition has its place in science. Please remove or change the wording.

line 227-231: This should belong to the discussion section.

Discussion

line 242: You stated line 71 that "all our data and interpretations are valid only for Aegean seawater." and here, you state for seawater in general?

line 257: Please define SO₂.

line 255-260: I am not convinced by the sulfate analogy. The authors just compare a preindustrial atmospheric [SO₂] concentration with, I guess, a contemporary seawater [SO₄²⁻] concentration (global average?) to support the fact that a supposed background DIC reservoir is not reacting to the atmosphere. The speculation done in line 258 ("probably") does not help.

line 264-270: This should belong to the result section. This is not a discussion but only a presentation of results.

line 275-277: If you refer to the estimate of 30 % of the anthropogenic carbon absorbed by the global ocean (and not only northern and tropical Atlantic waters) that Gruber et al. (1996) refers in their first introduction sentence, the 30 % comes from Schimel et al. (1994), not Gruber et al. (1996) itself.

line 277-278: This is a very vague, if not incorrect, description of the Delta C star methodology.

line 279: Sabine et al. (2004) do not use mass balance calculation but Delta C star.

line 282: Gruber et al. (2019) do not use mass balance calculation but eMLR.

line 282-284: The 34 PgC found by Gruber et al. (2019) relates to an increase of anthropogenic carbon inventory during a recent ~14 year period, not a share. It cannot be compared to your estimate that is supposed to encompass a period beginning from preindustrial conditions. Freidlingstein et al. (2020) uses global ocean biogeochemistry models and observation-based data products to deduce the ocean anthropogenic carbon sink.

This section 4.2 does not make sense at all. The authors are misunderstanding all the literature cited. Comparing their anthropogenic carbon quantification in Aegean seawater with estimates of proportion of anthropogenic carbon emissions absorbed by the global ocean does not make sense.

line 297-298: This is neglecting the Atlantic deep water formation and the Southern Ocean subduction permitting to transport large amount of anthropogenic carbon to the deep ocean (Sabine et al., 2004).

line 306-309: I would expect an introduction to the Revelle factor in the introduction or in the method section, including the Revelle equation (please write it as a proper equation). I would expect the Figure 6 in the result section.

line 311: Please give the function used for extrapolation. This is highly speculative. Please see my suggestion below.

line 314: Why not using atmospheric pCO₂ in 2100 from the literature? Such as the northern hemisphere value of SSP5-8.5:

Meinshausen et al.: The shared socio-economic pathway (SSP) greenhouse gas concentrations and their extensions to 2500, *Geosci. Model Dev.*, 13, 3571–3605, <https://doi.org/10.5194/gmd-13-3571-2020>, 2020.

line 345-348: There is high speculation without reference on line 343-343 discrediting the entire paragraph.

Code availability

You might have to provide a Code availability section providing the link to download the PHREEQC software.

Reference

Numbers before each references are not needed.

line 411-414, 467-472: References are repeated.