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Nicolas Metzl, Jonathan Fin, Claire Lo Monaco, Guillaume Bourdin, Samir Alliouane, et al.. A synthesis of SNAPO-CO₂ ocean total alkalinity and total dissolved inorganic carbon measurements from 1993 to 2022. Earth System Science Data, In press, 10.5194/essd-2023-308 . hal-04292340v2

HAL Id: hal-04292340

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A synthesis of ocean total alkalinity and dissolved inorganic carbon measurements from 1993 to 2022: the SNAPO-CO2-v1 dataset

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1 A synthesis of SNAPO-CO₂ ocean total alkalinity and total dissolved inorganic carbon measurements from 1993 to 2022

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40 **Abstract.** Total alkalinity (A_T) and dissolved inorganic carbon (C_T) in the oceans are important properties
41 to

42 understand the ocean carbon cycle and its link with global change (ocean carbon sinks and sources, ocean
43 acidification) and ultimately find carbon based solutions or mitigation procedures (marine carbon removal). We
44 present a database of more than 44 400 A_T and C_T observations along with basic ancillary data (time and
45 space

46 location, depth, temperature and salinity) in various ocean regions obtained since 1993 mainly in the frame of
47 French projects. This includes both surface and water columns data acquired in open oceans, coastal zones and in
48 the Mediterranean Sea and either from time-series or punctual cruises. Most A_T and C_T data in this
49 synthesis

50 were measured from discrete samples using the same closed-cell potentiometric titration calibrated with Certified

48 Reference Material, with an overall accuracy of $\pm 4 \mu\text{mol kg}^{-1}$ for both A_T and C_T . The data are provided in two
49 separate datasets for the global ocean, and for the Mediterranean Sea (<https://doi.org/10.17882/95414>, Metzl et
50 al., 2023) that offers a direct use for regional or global purposes, e.g. A_T /Salinity relationships, long-term C_T
51 estimates, constraint and validation of diagnostics C_T and A_T reconstructed fields or ocean carbon and coupled
52 climate/carbon models simulations, as well as data derived from Biogeochemical-Argo (BGC-Argo) floats.
53 When associated with other properties, these data can also be used to calculate pH, fugacity of CO_2 ($f\text{CO}_2$) and
54 other carbon system properties to derive ocean acidification rates or air-sea CO_2 fluxes.

55

56 **1 Introduction**

57

58 Since 1750, humans activities have added 700 (± 75) PgC anthropogenic carbon dioxide to the
59 atmosphere by burning fossil fuels, producing cement and changing land use (Friedlingstein et al., 2022) driving
60 up the atmospheric carbon dioxide (CO_2) level and leading to unequivocal global change. The ocean plays a
61 major role in reducing the impact of climate change by absorbing more than 90% of the excess heat in the
62 climate system (Cheng et al., 2020; von Schuckmann et al, 2020, 2023; IPCC, 2022) and about 25% of human
63 released CO_2 (Friedlingstein et al., 2022). However, the oceanic CO_2 uptake changes the chemistry of seawater
64 reducing its buffering capacity (Revelle and Suess, 1957; Jiang et al, 2023a) and leading to a process known as
65 ocean acidification with potential impacts on marine organisms (Fabry et al., 2008; Doney et al., 2009, 2020;
66 Gattuso et al., 2015). With atmospheric CO_2 concentrations, surface ocean temperature and ocean heat content,
67 sea-level, sea-ice and glaciers, the ocean acidification (decrease of pH) is now recognized by the World
68 Meteorological Organization as one of the 7 key properties for global climate indicators (WMO, 2018). In the
69 frame of the 2030 Agenda, the United Nations established a set of Sustainable Development Goals (SDG; United
70 Nations, 2020), including a goal dedicated to the ocean (SDG 14, "Life below water") which calls to "conserve
71 and sustainably use the oceans, seas and marine resources for sustainable development". Ocean acidification is
72 specifically referred in the SDG indicator 14.3.1 coordinated at the Intergovernmental Oceanographic
73 Commission (IOC) of UNESCO. Observing the carbonate system in the oceans and marginal seas and
74 understanding how this system changes over time is thus highly relevant not only to quantify the global ocean
75 carbon budget, the anthropogenic CO_2 inventories or ocean acidification rates, but also to understand and
76 simulate the processes that govern the complex CO_2 cycle in the ocean and to better predict the future evolution
77 of climate and global changes (Eyring et al., 2016; Kwiatkowski et al., 2020; Jiang et al., 2023a).

78 The number and quality of ocean $f\text{CO}_2$, A_T , C_T and pH measurements have increased substantially over
79 the past few decades. Quality-controlled observations are now regularly assembled in global data syntheses such
80 as SOCAT (Surface Ocean CO_2 Atlas, Pfeil et al., 2013; Bakker et al., 2014, 2016) and GLODAP (Global Ocean
81 Data Analysis Project, Key et al., 2004; Olsen et al., 2016, 2019, 2020; Lauvset et al., 2021, 2022). These
82 datasets allow evaluation of properties trends in the global ocean, including the change of the ocean CO_2 sink
83 (e.g. Wanninkhof et al., 2013; Friedlingstein et al., 2022; Watson et al., 2020), anthropogenic CO_2 inventories
84 (e.g. Sabine et al., 2004; Khatiwala et al., 2013; Gruber et al., 2019) and ocean acidification (Lauvset et al.,
85 2015, 2020; Jiang et al., 2019; Feely et al, 2023; Ma et al, 2023). Thanks to publicly available consistent and
86 quality controlled databases new methods were recently developed (Carter et al, 2016; Sauzède et al., 2017;
87 Bittig et al., 2018) to reproduce A_T and C_T distributions from other properties like temperature, salinity and
88 oxygen more often observed in the water column especially from autonomous floats (Claustre et al., 2020;
89 Mignot et al., 2023). These methods (named CANYON-B and CONTENT, Bittig et al., 2018) are now also used

90 to help decisions on GLODAP data quality control or to fill in observational gaps (Olsen et al., 2019, 2020;
91 Tanhua et al., 2019, 2021). The GLODAP data products were also successfully used to construct new global
92 ocean A_T and C_T climatological monthly fields in surface and water column using neural network method (e.g.
93 Broullón et al., 2019, 2020).

94 Following pioneer works that produced various global-ocean climatologies of the sea-surface carbonate
95 system (Millero et al., 1998; Lee et al., 2000, 2006; Takahashi et al., 2002, 2009, 2014; Sasse et al., 2013; Jiang
96 et al., 2019), the coupling of fCO_2 data (from SOCAT) and A_T data (from GLODAP) now enables reconstruction
97 of the full carbonate system in the surface ocean at monthly scale to investigate temporal trends at decadal scale
98 (e.g. Gregor and Gruber, 2021; Keppler et al., 2023).

99 International projects such as SOCAT and GLODAP offer important way to synthesize ocean carbon
100 data. In these projects, each observation is quality controlled offering to users high quality observations for
101 regional or global analysis, either for processes analysis or to constraint or validate of ocean and coupled
102 climate/carbon models (CMIP6, e.g. Lerner et al., 2021). SOCAT is a publicly available synthesis product
103 initiated in 2007 (Metzl et al., 2007) for quality-controlled, surface ocean fCO_2 (fugacity of carbon dioxide)
104 observations made by the international marine carbon research community (Bakker et al., 2016). The first
105 SOCAT version was released in 2011 (Pfeil et al., 2013; Sabine et al., 2013), followed by 6 SOCAT versions
106 (Bakker et al., 2014, 2016). The last version in 2023 includes more than 40 million fCO_2 data with accuracy
107 better than $5 \mu\text{atm}$ (Bakker et al., 2023). One important product from SOCAT is the use of data to estimate
108 global air-sea CO_2 fluxes based on reconstructed pCO_2 fields (e.g. Surface Ocean pCO_2 Mapping
109 Intercomparison, SOCOM, Rödenbeck et al., 2015). Since 2015, these results are included each year for the
110 global carbon budget (Le Quere et al., 2015; Friedlingstein et al., 2022).

111 On the other hand, following WOCE/JGOFS era in the 90s when almost all observations were started to
112 be synthesized in a specific recommended format (Joyce and Corry, 1994), GLODAP focusses on water-column
113 carbon observations (and other properties). Following the original GLODAP data product (Key et al., 2004), the
114 project accumulated many new quality controlled observations. One important achievement from GLODAP is
115 the use of data to estimate the anthropogenic CO_2 inventory or its change over decades (Sabine et al., 2004;
116 Gruber et al., 2019). Both products, SOCAT and GLODAP, are relevant tools to detect oceanic acidification
117 rates (Lauvset et al., 2015; Jiang et al., 2019; Feely et al, 2023; Ma et al, 2023).

118 Although these projects include many international ocean observations there are ocean CO_2 related
119 observations all around the world (published or not published), such as total alkalinity and dissolved inorganic
120 carbon, that are not included in SOCAT or GLODAP. This is because SOCAT accepts and controls only fCO_2
121 data, whereas GLODAP includes and controls water-columns data mainly from WOCE/GO-SHIP/CLIVAR
122 cruises. It should be noticed that many ocean carbon observations in various formats can be also found in
123 dedicated database such as NCEI/OCADS (former CDIAC-Ocean, Jiang et al., 2023b,
124 <https://www.ncei.noaa.gov/products/ocean-carbon-acidification-data-system>), PANGAEA
125 (<https://www.pangaea.de/>) or Seanoë (<https://www.seanoë.org/>). In this context it is recommended to progress in
126 data synthesis of the ocean carbon observations that would offer new high quality products for the community
127 (e.g. for GOA-ON, www.goa-on.org, IOC/SDG 14.1.3, <https://oa.iode.org/>, Tilbrook et al., 2019).

128 In this work, we present a synthesis of more than 44 400 A_T and C_T observations obtained over the
129 1993-2022 period during various cruises or at time-series stations mainly supported by French projects. This
130 dataset merges observations measured with the same instruments thus being analytically coherent. Most of the
131 data have accuracy better than $\pm 4 \mu\text{mol kg}^{-1}$, i.e. between the climate ($\pm 2 \mu\text{mol kg}^{-1}$) and weather ($\pm 10 \mu\text{mol kg}^{-1}$)

132 ¹) goals (Newton et al, 2015; Bockmon and Dickson, 2015). Hereafter this dataset will be cited as SNAPO-CO2-
133 V1. We describe the data assemblage and associated quality control and discuss some potential uses of this
134 dataset.

135

136 **2 Data collections**

137

138 The time series projects and research cruises from which data were collated are listed in Table 1 with
139 references in the Supplementary file (Table S1) and the sampling locations displayed in Figure 1. Sampling was
140 performed either from CTD-Rosette casts (Niskin bottles) or from the ship's seawater supply (intake at about 5m
141 depth depending the ship and swell). Samples collected in 500 mL borosilicate glass bottles were poisoned with
142 100 to 300 μL of HgCl_2 depending on the cruises, closed with greased stoppers (Apiezon®) and held tight using
143 elastic band following the SOP protocol (Dickson et al., 2007). Some samples were also collected in 500 mL
144 bottles closed with screw caps. After completion of each cruise, discrete samples were returned back to the
145 LOCEAN laboratory (Paris, France) and stored in a dark room at 4 °C before analysis generally within 2-3
146 months after sampling (sometimes within a week). Some samples were also measured for specific processes
147 studies on benthic corals (e.g. Maier et al., 2012; McCulloch et al., 2012) or for mesocosm and culture
148 experiments but the data are not included in this synthesis as they do not represent natural ocean state (e.g.
149 addition of Sahara dust during the DUNE project, Ridame et al., 2014).

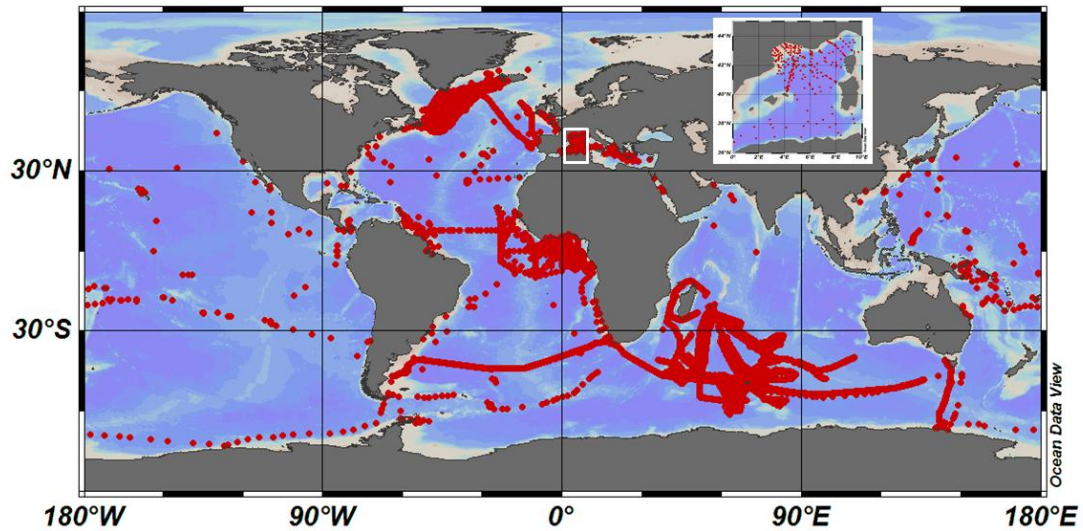
150 As opposed to $p\text{CO}_2$, surface A_T or C_T observations are generally obtained from discrete sampling
151 (measured onboard or onshore). Few cruises offer sea-surface semi-continuous A_T or C_T observations (e.g. Metzl
152 et al., 2006) but new instrumental developments (Seelmann et al., 2020) now enable A_T measurements on Ship of
153 Opportunity Program lines (SOOP). In addition to discrete samples analyzed for various projects conducted
154 mainly in the North Atlantic, Tropical Atlantic, Tropical Pacific, Mediterranean sea and coastal regions (Table
155 1), we complemented this synthesis with A_T and C_T surface observations obtained in the Indian and Southern
156 oceans during the OISO cruises in 1998-2018 (Metzl et al., 2006; Leseurre et al., 2022; data also available at
157 NCEI/OCADS: www.nodc.noaa.gov/ocads/oceans/VOS_Program/OISO.html) and the recent CLIM-EPARSESES
158 cruise conducted in the Mozambique Channel in April 2019 (Lo Monaco et al., 2020, 2021). For OISO cruises
159 the water-column observations are part of the CARINA (CARbon IN the Atlantic) and GLODAP synthesis
160 products (Lo Monaco et al., 2010; Olsen et al., 2016, 2019, 2020) and not included here. Excepted when
161 specified, all data in this synthesis were obtained using the same technique used either in laboratory or at sea (for
162 OISO 1998-2018 and CLIM-EPARSESES 2019 cruises).

163

164 **Table 1:** List of cruises in the SNAPO-CO2-v1 dataset. This is organized by region: Global Ocean and coastal
 165 zones, and Mediterranean Sea (MedSea). See Tables S1, S2, S4 and S4 in the Supplementary Material for a list
 166 of laboratories, of CRMs used, for references and for DOI of cruises. Nb = the number of data for each cruise or
 167 time-series. * indicates the measurements at sea (surface underway)

168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216
Cruise/Project	Start	End	Region	Sampling	Nb																																											
AWIPEV	2015	2021	Arctic	Surface and sub-surface	195																																											
SURATLANT+RREX	1993	2017	North Atlantic	Surface	2832																																											
OVIDE	2006	2018	North Atlantic	Surface, Water Column	397																																											
STRASSE	2012		North Atlantic	Water Column	205																																											
EUREC4A-OA	2020		North Atlantic	Surface, Water Column	135																																											
PROTEUS	2010		North Atlantic	Water Column	27																																											
CHANNEL	2012	2015	English Channel	Surface	696																																											
SOMLIT-Brest	2008	2019	Coastal North Atl	Surface	1174																																											
SOMLIT-Roscoff	2009	2019	Coastal North Atl	Surface and 60m	801																																											
ECOSCOPA	2017	2019	Coastal North Atl	Surface	67																																											
PENZE	2011	2020	River Brittany	Surface and sub-surface	148																																											
AULNE	2009	2010	River Brittany	Surface	27																																											
ELORN	2009	2009	River Brittany	Surface	28																																											
BIOZAIRE	2003	2004	Trop Atlantic	Water Column	87																																											
EGEE	2005	2007	Trop Atlantic	Surface	199																																											
PIRATA-FR	2009	2017	Trop Atlantic	Surface, Water Column	513																																											
PLUMAND	2007		Trop Atlantic	Surface	38																																											
OUTPACE	2015		Trop Pacific	Water Column	240																																											
PANDORA	2012		Solomon Sea	Water Column	178																																											
TARA-Pacific	2016	2018	Trop Pac North Atl	Surface and sub-surface	325																																											
TARA-Ocean	2009	2012	Global Ocean	Surface + 400m	123																																											
TARA-Microbiome	2021	2022	Atlantic	Surface, Water Column	216																																											
ACE	2016	2017	Southern Ocean	Surface, Water Column	135																																											
MOBYDICK	2019		Southern Ocean	Water Column	64																																											
CLIM-EPARSES *	2019		Indian	Surface	790																																											
OISO *	1998	2018	South Indian	Surface	24950																																											
DYFAMED	1998	2017	MedSea	Water Column	2118																																											
BOUSSOLE	2014	2019	MedSea	Surface + 10m	172																																											
SOMLIT-PointB	2007	2015	MedSea Coastal	Surface + 50m	2397																																											
ANTARES	2010	2016	MedSea	Water Column	502																																											
MOLA	2010	2013	MedSea Coastal	Water Column	66																																											
SOLEMIO	2016	2018	MedSea Coastal	Water Column	212																																											
MOOSE-GE	2010	2019	MedSea	Water Column	1847																																											
LATEX	2010		MedSea	Water Column	51																																											
CARBORHONE	2011	2012	MedSea	Water Column	706																																											
CASCADE	2011		MedSea	Water Column	218																																											
DEWEX	2013		MedSea	Water Column	367																																											
SOMBA	2014	2014	MedSea	Water Column	203																																											
AMOR-BFLUX	2015		MedSea Coastal	Water Column	6																																											
PEACETIME	2017	2017	MedSea	Water Column	233																																											
PERLE	2018	2021	MedSea	Water Column	805																																											

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231 **Figure 1:** Locations of A_T and C_T data (1993-2022) in the Global Ocean and the Western Mediterranean Sea
232 (white box, insert) in the SNAPO-CO2-v1 dataset. Figure produced with ODV (Schlitzer, 2018).
233

234 3 Method, accuracy, repeatability, inter-comparison and quality control

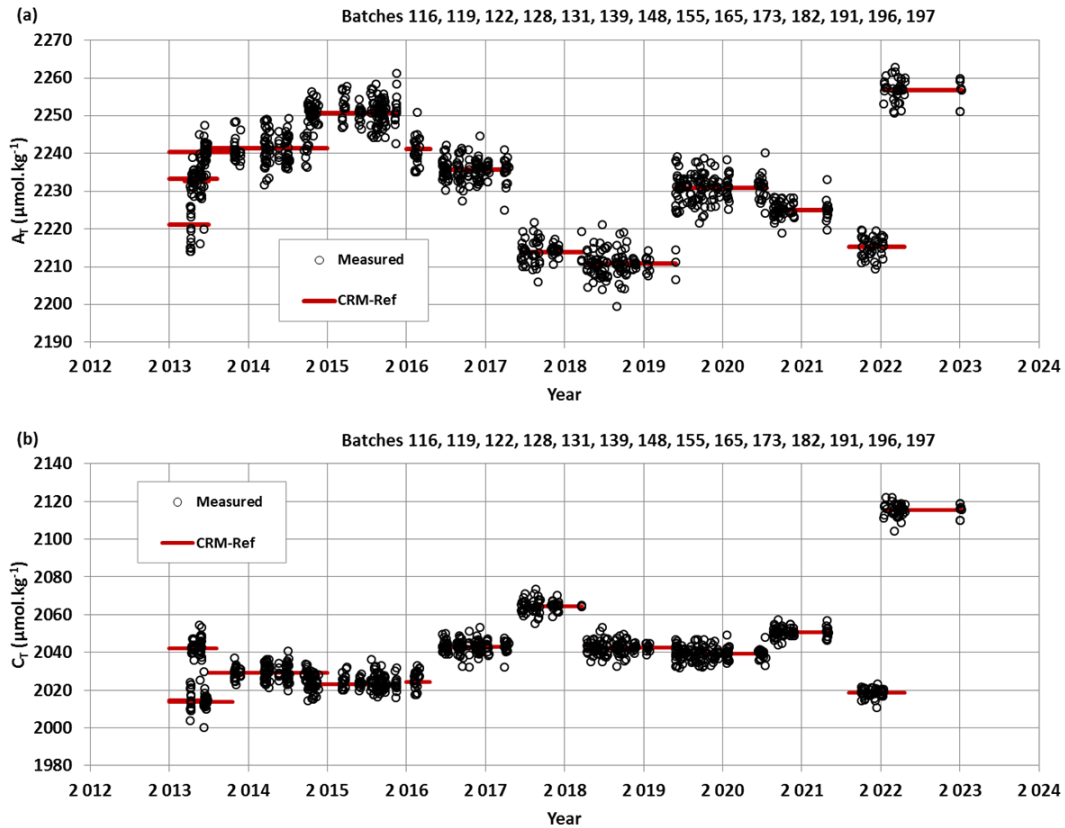
235 3.1 Method and accuracy

236 Since 2003, the discrete samples returned back at SNAPO-CO2 Service facilities (LOCEAN, Paris),
237 were analyzed simultaneously for A_T and C_T by potentiometric titration using a closed cell (Edmond, 1970;
238 Goyet et al., 1991). The same technique was used at sea for surface water underway measurements during OISO
239 and CLIM-EPARSEES cruises (indicated by * in Table 1). For two time series, the dataset also includes
240 measurements obtained before 2000 using other techniques: the DYFAMED time-series observations measured
241 between in 1998 and 2000 in the Mediterranean Sea (Copin-Montégut and Bégovic, 2002; Coppola et al., 2020;
242 Lange et al., 2023) and the SURATLANT time-series values acquired from 1993 to 1997 in the North Atlantic
243 subpolar gyre (Reverdin et al., 2018). We also include A_T data in the river Penzé (Brittany) in 2019-2020 (Yann
244 Bozec, SBR/Roscoff, pers. comm.).
245

246 In the late 1980s the so-called “JGOFS-IOC Advisory Panel on Ocean CO₂” recommended the need for
247 standard analysis protocols and for developing Certified Reference Materials (CRMs) for inorganic carbon
248 measurements (Poisson et al., 1990; UNESCO, 1990, 1991). The CRMs were provided to international
249 laboratories by Pr. A. Dickson (Scripps Institution of Oceanography, San Diego, USA), starting in 1990 for C_T
250 and 1996 for A_T , respectively. These CRMs were thus always available to us and used to calibrate the
251 measurements (CRM Batch numbers used for each cruise are listed in Supplementary file (Table S2). The
252 concentrations of CRMs we used vary between 2193 and 2426 $\mu\text{mol kg}^{-1}$ for A_T and between 1968 and 2115
253 $\mu\text{mol kg}^{-1}$ for C_T corresponding to the range of concentrations observed in open ocean water. The CRMs
254 accuracy, as indicated in the certificate for each Batch, is around $\pm 0.5 \mu\text{mol kg}^{-1}$ for both A_T and C_T
255 (www.nodc.noaa.gov/ocads/oceans/Dickson_CRM/batches.html).
256

257 Results of analyses performed on 965 CRM bottles (different Batches) in 2013-2023 are presented in
258 Figure 2. The standard-deviations of the differences of measurements were on average around $\pm 3.5 \mu\text{mol kg}^{-1}$ for

259 both A_T and C_T . For unknown reasons, the differences were occasionally up to 10-15 $\mu\text{mol kg}^{-1}$ (0.8% of the
 260 data, Figure S2). These few CRM measurements were discarded for the data processing. On average, and
 261 excluding some outliers, standard-deviations of the differences for 1090 CRM analyses were $\pm 2.71 \mu\text{mol kg}^{-1}$ for
 262 A_T and $\pm 2.86 \mu\text{mol kg}^{-1}$ for C_T , respectively. We did not detect any specific signal for CRM analyses (e.g., larger
 263 uncertainty depending on the Batch number or temporal drifts during analyses, Figure 2) but for some cruises the
 264 accuracy based on CRMs could be slightly better than 3 $\mu\text{mol kg}^{-1}$ (e.g. Marrec et al., 2014; Touratier et al.,
 265 2016; Ganachaud et al., 2017; Wimart-Rousseau et al., 2020a).

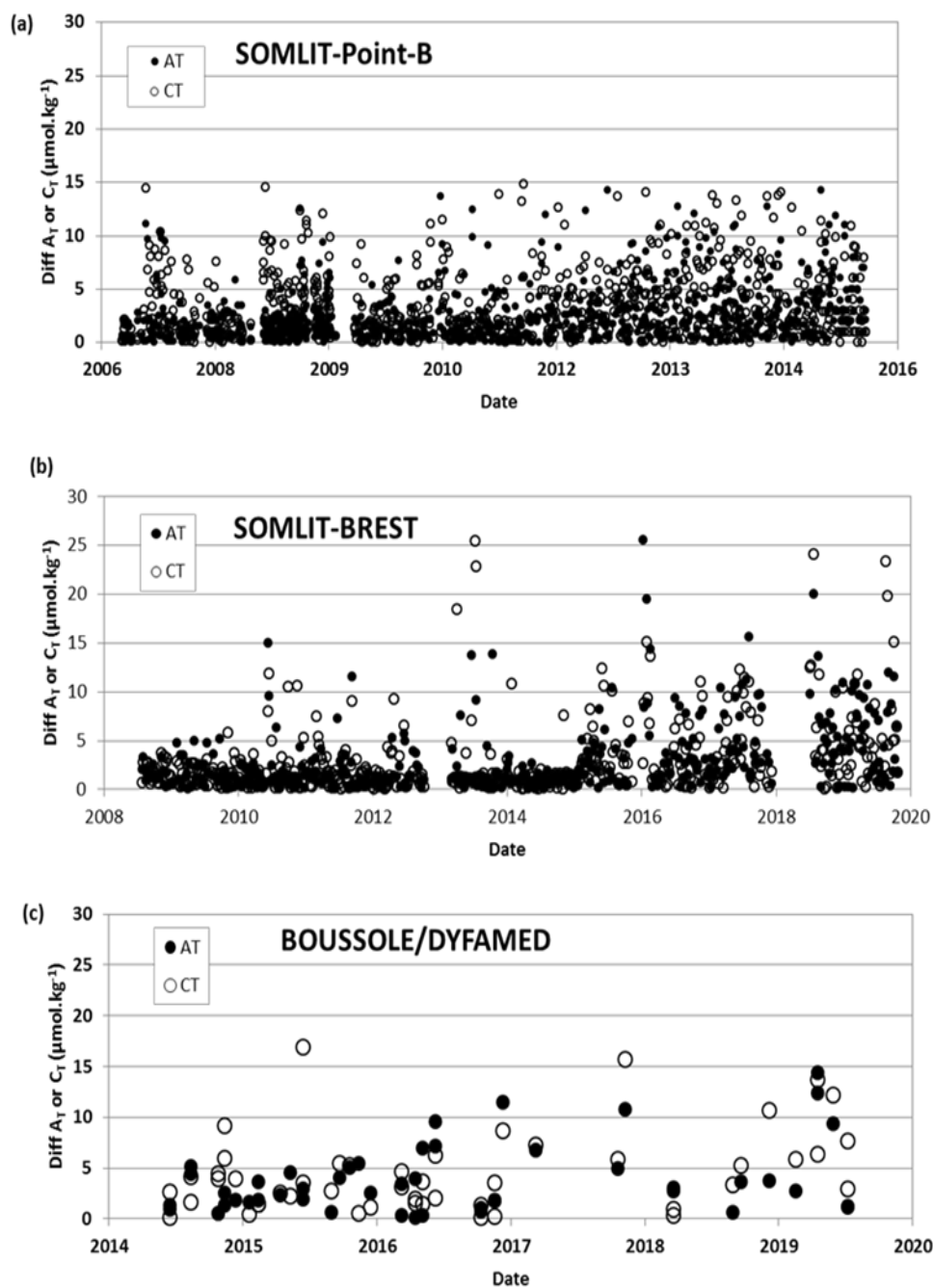


288 **Figure 2:** A_T (a) and C_T (b) analyses for different CRM Batches measured in 2013-2023. For these 965 analyses
 289 the mean and standard-deviations of the differences with the CRM reference were $-0.1 (\pm 3.4) \mu\text{mol kg}^{-1}$ for A_T
 290 and $0.1 (\pm 3.7) \mu\text{mol kg}^{-1}$ for C_T .

293 3.2 Repeatability

294
 295 For some projects, duplicates have been regularly sampled (SOMLIT-Point-B, SOMLIT-BREST,
 296 BOUSSOLE/DYFAMED) or replicate bottles sampled at selected depths at fixed stations during the cruises (e.g.
 297 OUTPACE-2015, SOMBA-2014). Results of A_T and C_T repeatability are synthesized in Table 2 and Figure 3
 298 shows example of regular duplicates from the times-series SOMLIT-Point-B in the coastal Mediterranean Sea,
 299 SOMLIT-Brest in the Bay of Brest, coastal Iroise Sea and BOUSSOLE/DYFAMED in the Ligurian Sea. For the
 300 26 OISO cruises conducted between 1998 and 2018 and the CLIM-EPARSEES cruise in April 2019, the
 301 repeatability was evaluated from duplicate analyses (within 20 minutes time) of continuous sea surface
 302 underway sampling at the same location (when the ship was stopped). Similarly to what was found for the CRM
 303 measurements (Figure S2), differences in duplicates are occasionally higher than 10-15 $\mu\text{mol kg}^{-1}$ (Figure 3) but
 304 most of the duplicates for all projects are within 0 to 3 $\mu\text{mol kg}^{-1}$. Based on the CRM analyses and replicates for

305 different projects, different regions and different periods, we estimated A_T and C_T data to be consistent to better
306 than $4 \mu\text{mol kg}^{-1}$.



347 **Figure 3:** Results of duplicate A_T and C_T analyses from the time-series (a) SOMLIT-Point-B in the coastal
348 Mediterranean Sea (Kapsenberg et al., 2017), (b) SOMLIT-BREST in the Bay of Brest, coastal Iroise Sea (Salt
349 et al., 2016 and unpublished) and (c) BOUSSOLE/DYFAMED in the Ligurian Sea (Merlivat et al., 2018; Golbol
350 et al., 2020). The plots show differences in duplicates for both A_T (filled circles) and C_T (open circles). Standard-
351 deviations of these duplicates are listed in Table 2.

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Table 2: Repeatability of A_T and C_T analyses for cruises with duplicate analysis. The results are expressed as the standard-deviations (Std) of the analysis of replicated samples. Nb = the number of replicates for each Time-series or Cruise (a). For the 26 OISO cruises (1998-2018) and for simplicity we list the mean repeatability obtained for all cruises.

Cruise	Nb	Std A_T $\mu\text{mol kg}^{-1}$	Std C_T $\mu\text{mol kg}^{-1}$	Reference
OUTPACE	12	3.64	3.68	Wagener et al. (2018)
SOMBA	13	2.00	3.30	Keraghel et al. (2020)
SOMLIT-Point-B	786	2.63	3.10	Kapsenberg et al. (2017)
SOMLIT-Brest	446	3.34	3.67	Salt et al. (2016) + unpub
BOUSSOLE	48	3.47	4.02	Merlivat et al. (2018); Golbol et al. (2020)
CLIM-EPARSES	122	2.20	2.30	Lo Monaco et al. (2020, 2021)
OISO 1998-2018	1162	2.06	2.28	Metzl et al. (2006) and (b)

(a) See Figure 3 for the results of regular duplicates for 3 time-series (SOMLIT-Point-B, SOMLIT-BREST, and BOUSSOLE).

(b) Metadata and data available at www.nodc.noaa.gov/ocads/oceans/VOS_Program/OISO.html

3.3 Inter-comparisons

Inter-comparisons of measurements performed with different technics help to evaluate the quality of the data and detect potential biases when merging the data in the same region obtained by different laboratories at different periods. This is especially important to interpret long-term trends of A_T and C_T as well as for $p\text{CO}_2$ and pH calculated with A_T/C_T pairs. For ocean acidification studies, this also refers to the “climate goal” for which an accuracy for A_T and C_T better than $\pm 2 \mu\text{mol kg}^{-1}$ is needed (Newton et al., 2015; Tilbrook et al., 2019). For the projects in this data synthesis, inter-laboratory comparisons were performed occasionally and summarized below.

3.3.1 CHANNEL project

As part of the time-series CHANNEL (2012-2015) in the Western English Channel, Marrec et al. (2014) analyzed surface samples collected bi-monthly in 2011-2013. A_T analyses were performed with a TA-ALK-2 system (Appolo SciTech.) while C_T measurements were acquired with an AIRICA system (Marianda Inc.) Based on CRM analyses (Batch #92) the accuracy was estimated $\pm 3 \mu\text{mol kg}^{-1}$ for A_T and $\pm 1.5 \mu\text{mol kg}^{-1}$ for C_T (Marrec et al., 2014). When comparing with the samples measured at LOCEAN/Paris for the year 2012, Marrec et al. (2014) concluded that between the two methods the concentrations were within $\pm 2 \mu\text{mol kg}^{-1}$ and $\pm 3 \mu\text{mol kg}^{-1}$ for A_T and C_T respectively. This is close to the “climate goal” offering confident results for long-term trend analysis of the carbonate system in this region.

3.3.2 SURATLANT project

In the frame of the SURATLANT project in the subpolar North Atlantic gyre, some samples collected at the same time (in 2005, 2006, 2010, 2015, and 2016) were also analyzed onshore for A_T and/or C_T by other

laboratories using different technics (e.g. coulometric method) and the results summarized by Reverdin et al. (2018). For C_T , the mean (and STD) differences between LOCEAN values and from 4 other laboratories range between $-0.7 (\pm 4.6)$ and $-6.5 (\pm 3.4) \mu\text{mol kg}^{-1}$ depending on the cruise. For A_T the mean differences with 2 other laboratories range from $-0.6 (\pm 4.1) \mu\text{mol kg}^{-1}$ to $+2.3 (\pm 4.8) \mu\text{mol kg}^{-1}$.

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407 3.3.3 OVIDE project

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409 During OVIDE cruises conducted since 2002 in the North Atlantic along a section from Greenland to
410 Portugal (Lherminier et al., 2007; Mercier et al., 2015) samples have been taken (since 2006) to complement, for
411 summer, the SURATLANT time-series in the North Atlantic subpolar gyre (NASPG). The OVIDE samples at
412 the surface and along the water-column at a few stations were measured back at LOCEAN for A_T and C_T (Metzl
413 et al., 2018). This enables us to compare our data with the measurements performed on-board by the IIM group
414 in Vigo/Spain (e.g. Pérez et al., 2010, 2013, 2018; Vazquez-Rodriguez et al., 2012). The OVIDE data have been
415 regularly quality controlled in CARINA and GLODAP data products (Velo et al., 2009; Key et al., 2010; Olsen
416 et al., 2016, 2019, 2020). The results of inter-comparisons are gathered in Table 3. For OVIDE in 2006 we
417 identified (for unknown reason) a large difference between our original A_T values compared to the A_T data
418 qualified in GLODAP and we thus corrected our A_T data by $+7.2 \mu\text{mol kg}^{-1}$. However, no correction was applied
419 for C_T . For other OVIDE cruises, differences for A_T range between $-4.5 (\pm 4.11) \mu\text{mol kg}^{-1}$ and $-0.05 (\pm 3.43)$
420 $\mu\text{mol kg}^{-1}$ depending on the cruise (i.e. A_T measured at LOCEAN was always slightly lower than onboard
421 measurements). For C_T , we compared our measurements onshore with C_T values calculated with A_T and pH
422 measured onboard. Most of the mean C_T differences are slightly positive (i.e. C_T measured at LOCEAN was
423 always higher, except for 2010). Taking into account all errors associated with the sampling, the transport of
424 samples, the instrumentations, the data processing, or the calculations for C_T using A_T /pH pairs (around $8.8 \mu\text{mol}$
425 kg^{-1} , Orr et al, 2018), the comparisons between LOCEAN and IIM data for OVIDE cruises are deemed
426 acceptable and large differences for both A_T and C_T ($> 4 \mu\text{mol kg}^{-1}$) are far from being systematic (Table 3). The
427 data from SURATLANT and OVIDE can then be merged to complete the time-series in the NASPG in summer
428 and to better describe the seasonality of the oceanic carbonate system. For example, in 2010, when the North
429 Atlantic Oscillation (NAO) was strongly negative, the SURATLANT data showed a rapid decrease of C_T
430 concentrations in the NASPG between early June and August (Figure 4), with C_T concentrations in August much
431 lower than other years (Racapé et al., 2014). This leads to a rapid drop in $f\text{CO}_2$ in 2009-2010, such that the
432 NASPG was a strong CO_2 sink (Leseurre et al., 2020). The winter-to-summer seasonal decrease of C_T in 2010 in
433 the north NASPG was on average $-77 \mu\text{mol kg}^{-1}$ (Figure 4) much larger than in the climatology (range -50 to -55
434 $\mu\text{mol kg}^{-1}$, Takahashi et al., 2014; Reverdin et al., 2018). The OVIDE data in late June 2010 and SURATLANT
435 in August 2010 confirmed this signal that was linked to a pronounced primary productivity in that period (Figure
436 4, Henson et al., 2013; Racapé et al., 2014; Mc Kinley et al., 2018). Notice that for this period no $f\text{CO}_2$
437 observations were available in July-September 2010 in SOCAT data product and the A_T/C_T data presented here
438 could be used to calculate $f\text{CO}_2$ to complement the $f\text{CO}_2$ dataset in this region like was done for other periods
439 (Mc Kinley et al., 2011).

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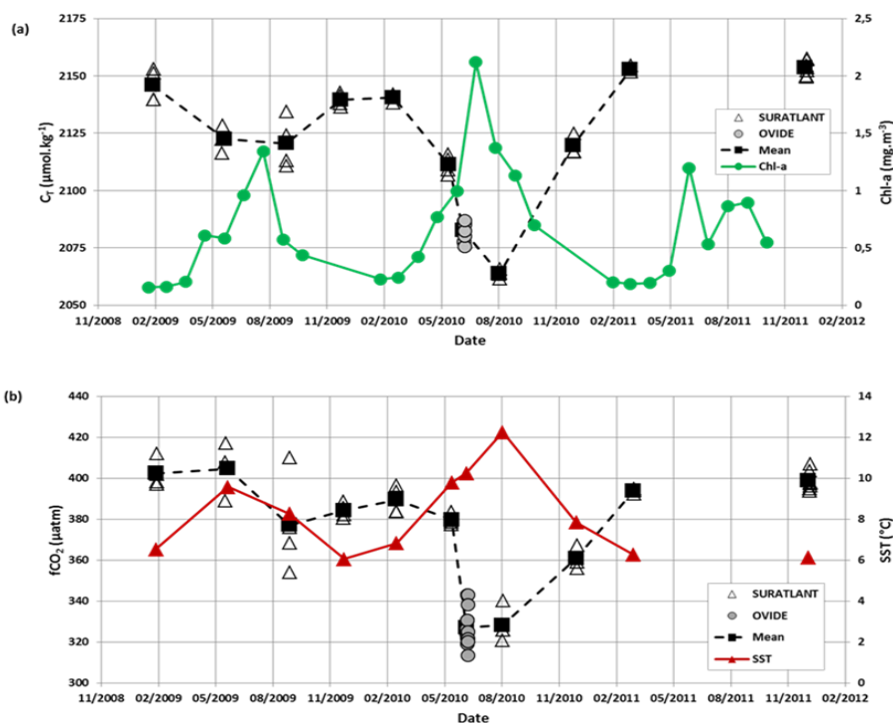


Figure 4: (a) Time-series of C_T concentrations ($\mu\text{mol.kg}^{-1}$) for 2009-2011 in surface waters in the North Atlantic subpolar gyre (zone 59°N - 33°W) based on SURATLANT (open triangles) and OVIDE-2010 (grey circles) data. In 2009, SURATLANT data were available in February, June, September and December, while in 2010 data available in March, June, August and December and in 2011 data only available for March and December. The OVIDE data in late June 2010 completed the temporal cycle and confirmed the strong seasonal signal and low C_T concentrations in summer 2010 not seen in 2009 (or in 2011 as there is no data in summer). The mean observations for each period describe the C_T seasonal cycles in 2009 and 2010 (Black squares, dashed line). The monthly surface chlorophyll-a concentrations (Chl-a, mg.m^{-3}) averaged in the same region based on MODIS are also shown (Green dots and line) highlighting the high productivity during the summer 2010. Chl-a monthly data extracted from MODIS (Giovanni/NASA, last access 3/5/19). (b): Time-series of $f\text{CO}_2$ (μatm) for the same cruises (same symbols) calculated with A_T/C_T and using the K1, K2 constants from Lueker et al (2000). Mean SST ($^\circ\text{C}$) indicated (red triangles). In June 2010 oceanic $f\text{CO}_2$ decreased by $53 \mu\text{atm}$ in 2 weeks.

Table 3: Comparisons of A_T and C_T samples measured back at LOCEAN with measurements onboard by IIM Laboratory (F. Pérez, Vigo, Spain) for OVIDE cruises in the North Atlantic. Nb= Number of samples. ND= No Data. The results listed indicate the mean and standard-deviations of the differences (LOCEAN-IIM). For A_T , IIM values were measured on-board. For C_T , IIM values were calculated from A_T and pH both measured onboard. The IIM data were quality controlled and here taken from the GLODAP data products (Olsen et al, 2016, 2019).

Cruise Year	Nb A_T	A_T (LOCEAN) - A_T (IIM) $\mu\text{mol.kg}^{-1}$	Nb C_T	C_T (LOCEAN) - C_T (IIM) $\mu\text{mol.kg}^{-1}$
OVIDE-2006	14	-2.0 (\pm 5.9) (*)	14	1.1 (\pm 2.5)
OVIDE-2008	29	-4.5 (\pm 4.1)	29	3.8 (\pm 3.1)
OVIDE-2010	41	-2.0 (\pm 2.3)	41	-2.4 (\pm 3.3)
OVIDE-2012	37	-0.1 (\pm 8.8)	ND	ND
GEOVIDE-2014	57	-0.1 (\pm 3.4)	54	2.4 (\pm 7.9)

(*) for the OVIDE 2006 cruise original difference for A_T was $-9.0 (\pm 5.8) \mu\text{mol.kg}^{-1}$ and LOCEAN A_T data were corrected by $+7.2 \mu\text{mol.kg}^{-1}$ based on the mean concentrations in deep layers. No corrections were applied for A_T and C_T for other cruises.

497 3.3.4 PENZE river

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499 The comparisons described above concern the open ocean region with A_T and C_T concentrations in a
500 range of concentrations close to the CRM references (used by the different laboratories). Another example of
501 comparison is presented here for samples obtained along a river and thus for waters with low salinity and A_T
502 concentrations (river Penzé in North Brittany). In 2019-2020, A_T was measured at SBR laboratory (Station
503 Biologique de Roscoff) by a potentiometric method (using a Titrino-847 plus Metrohm) calibrated with CRM
504 (Batch #131) for a final accuracy of $\pm 2.1 \mu\text{mol kg}^{-1}$ (Gac et al., 2020). Although the samples were measured
505 with different technics the A_T /Salinity relationships are very coherent for both datasets (Figure 5). The
506 regressions for each period are for A_T (in $\mu\text{mol kg}^{-1}$):

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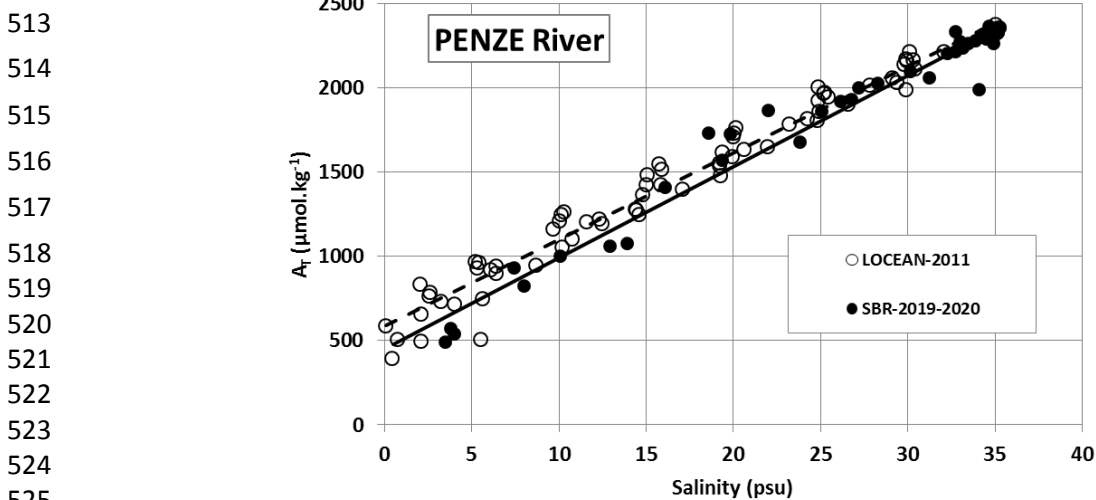
508 In 2011 (78 samples): $A_T = 51.525 (\pm 0.944) S + 583.95 (\pm 19.94) (r^2 = 0.975)$

509 In 2019-2020 (70 samples): $A_T = 54.022 (\pm 1.018) S + 450.23 (\pm 31.53) (r^2 = 0.976)$

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511 Therefore we added the A_T data measured in 2019-2020 to complete the synthesis for this location (river Penzé).

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513

514 **Figure 5:** Total alkalinity (A_T) versus salinity for samples measured in 2011 and 2019 in the river Penzé, North
528 Brittany (Gac et al., 2020). A_T samples were measured at LOCEAN in 2011 (open circles, dashed-line) and at
529 SBR laboratory (Roscoff) in 2019 (filled circles, black line).

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531 3.4 Quality control assigned flags

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533 Identifying each data with an appropriate flag is very convenient for selecting the data (good,
534 questionable or bad). Here we used 4 flags for each property (flags 2 = good, 3= questionable, 4=bad, and 9= no
535 data) following the WOCE program and used in other data products such as SOCAT (Bakker et al., 2016) or
536 GLODAP (Olsen et al., 2016, 2019, 2020; Lauvset et al., 2021). During the data-processing, we first assigned a
537 flag for each A_T and C_T data based on the standard error in the calculation of A_T and C_T concentrations (non-
538 linear regression, Dickson et al. 2007). By default, if the standard-deviation on the regression is $> 1 \mu\text{mol kg}^{-1}$,
539 we assigned a flag 3 (questionable) although the data could be acceptable and then used for interpretations. Flag
540 3 was also assigned when salinity was doubtful or when differences of duplicates were large (e.g. $\pm 20 \mu\text{mol kg}^{-1}$).
541 Flags 4 (bad or certainly bad) were assigned when clear anomalies were detected for unknown reason (e.g. a

542 sample probably not fixed with HgCl_2). A secondary quality control was performed by the PIs of each project
 543 based on data inspection, duplicates, A_T /Salinity relationship, or the mean observations in deep layers where
 544 large variability in A_T and C_T is unlikely to occur from year to year. An example presents all data from the
 545 MOOSE-GE cruises conducted in 2010-2019 in the Mediterranean Sea (Coppola et al., 2020; Testor et al., 2010)
 546 where clear outliers have been identified (Figure S3). For the 10 MOOSE-GE cruises and a total of 1847 A_T and
 547 C_T analyses, 26 were identified flagged as bad (flag 4), 139 for A_T and 141 for C_T listed as questionable (flag 3)
 548 and 1682 for A_T and 1680 for C_T considered as good data (flag 2, i.e. more than 90%). Similar control was
 549 performed for each project.

550 The synthesis of various cruises in the same region and period also offers verification and secondary
 551 control of the data. For example, several cruises were conducted in the Mediterranean Sea in 2014 (MOOSE-GE,
 552 SOMBA, ANTARES and DYFAMED). The mean values of C_T and A_T in the deep layers ($> 1800\text{m}$) for each
 553 cruise confirmed the coherence of the data (Table 4). This enabled to merge the different datasets for
 554 interpretations of the temporal trends and processes driving the CO_2 cycle (Coppola et al., 2019, 2020; Ulses et
 555 al., 2023) or to train and validate a regional neural network to reconstruct the carbonate system (e.g. CANYON-
 556 MED, Fourier et al., 2020, 2022).

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 558
 559 **Table 4:** Mean observations in the deep layers ($> 1800\text{m}$) of the Western Mediterranean Sea for different cruises
 560 conducted in 2014. Results in deep layers ($> 1800\text{m}$) for the DEWEX cruise in 2013 and the PEACETIME
 561 cruise in 2017 in the same region are also listed. N- A_T and N- C_T are A_T and C_T normalized at salinity = 38. Nb =
 562 number of data (with flag 2). Standard-deviations are in brackets. References for these cruises are listed in
 563 Supplementary Material.

Cruise	Period	Nb	Pot. Temp ($^{\circ}\text{C}$)	Salinity (PSU)	N- A_T ($\mu\text{mol kg}^{-1}$)	N- C_T ($\mu\text{mol kg}^{-1}$)
All cruises	Feb/Dec-2014	76	12.905 (0.007)	38.486 (0.005)	2562.9 (5.3)	2303.7 (4.7)
ANTARES	Feb/Nov-2014	14	12.913 (0.004)	38.488 (0.006)	2564.0 (3.8)	2301.9 (3.5)
DYFAMED	Mar/Dec-2014	9	12.905 (0.0016)	38.487 (0.004)	2560.1 (5.0)	2304.3 (6.8)
MOOSE-GE	Jul-2014	21	12.909 (0.004)	38.487 (0.005)	2565.6 (4.6)	2303.5 (4.1)
SOMBA	Aug/Sep-2014	32	12.899 (0.005)	38.483 (0.005)	2561.5 (5.6)	2304.6 (4.8)
DEWEX	Feb/Apr-2013	44	12.903 (0.010)	38.588 (0.006)	2556.0 (4.3)	2294.0 (5.7)
PEACETIME	May/Jun-2017	7	12.904 (0.002)	38.486 (0.003)	2567.2 (10.6)	2308.1 (8.9)

593 The total number of data for the Global Ocean and the Mediterranean Sea are gathered in Table 5 with
 594 corresponding flags for each property. Overall, the synthesis includes more than 94% of good data for both A_T

595 and C_T . About 5% are questionable and 2% are likely bad. Overall, we believe that all data (with flag 2) in this
 596 synthesis have an accuracy better than $4 \mu\text{mol kg}^{-1}$ for both A_T and C_T , the same as for quality-controlled data in
 597 GLODAP (Olsen et al., 2020; Lauvset et al., 2021). The uncertainty ranges between the “Climate goal” ($2 \mu\text{mol}$
 598 kg^{-1}) and the “Weather Goal” ($10 \mu\text{mol kg}^{-1}$) for ocean acidification studies (Newton et al., 2015; Tilbrook et al.,
 599 2019). This accuracy is also relevant to validate or constraint data-based methods that reconstruct A_T and C_T
 600 fields with an error of around $10\text{-}15 \mu\text{mol kg}^{-1}$ for both properties (Bittig et al., 2018; Broullón et al., 2019, 2020;
 601 Fourrier et al., 2020; Chau et al., 2023).

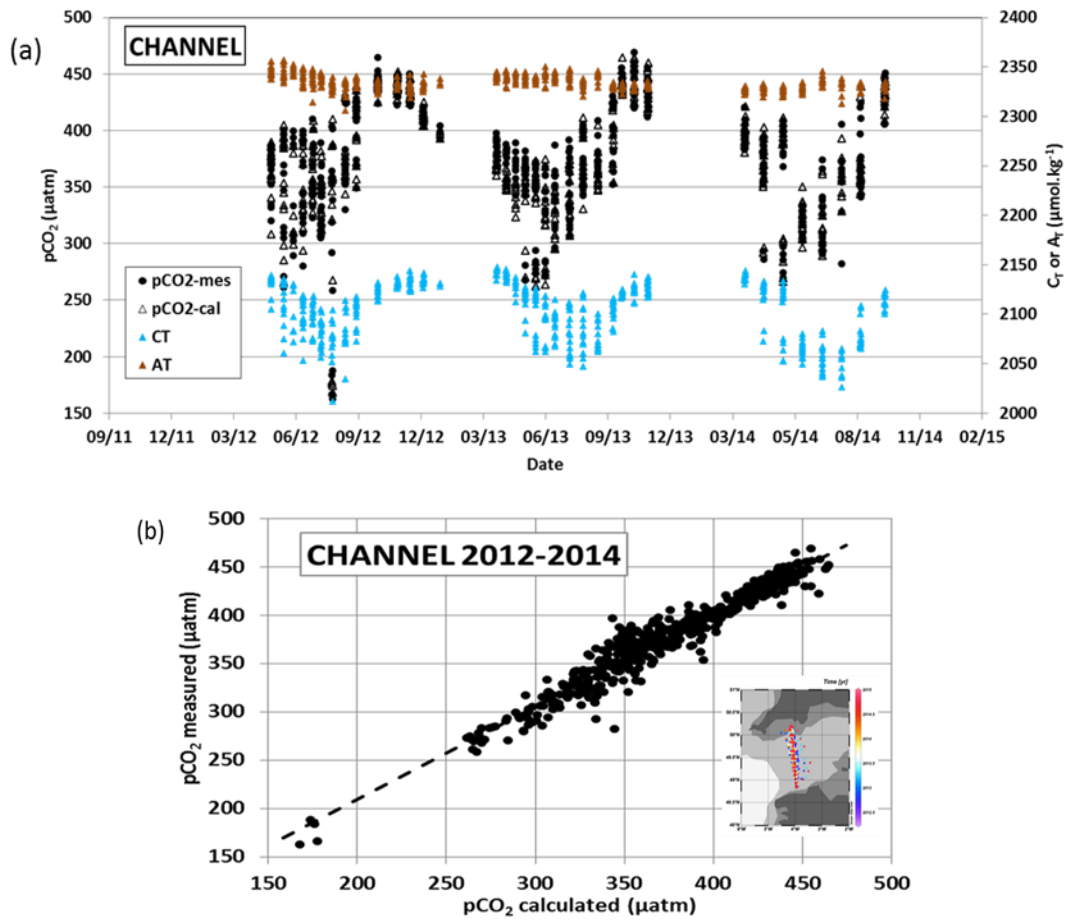
602
 603 **Table 5:** Number of Temperature, Salinity, A_T and C_T data in the synthesis identified for flags 2, 3, 4, 9. The
 604 data are given for the full data-set Global Ocean and for the Mediterranean Sea. Last column is the percentage of
 605 flag 2 (Good).
 606

	Flag 2	Flag 3	Flag 4	Flag 9	% Flag 2
Global Ocean					
Temperature	43538	410	0	478	99.07
Salinity	44033	319	2	71	99.28
A_T	39331	2144	1165	1787	92.24
C_T	39921	2091	1148	1279	92.50
Mediterranean Sea					
Temperature	9843	1	0	65	99.99
Salinity	9879	8	2	20	99.99
A_T	8853	425	411	220	91.37
C_T	8854	451	389	211	91.33

627 3.5 Using A_T and C_T to calculate $f\text{CO}_2$ and pH and compare with $f\text{CO}_2$ and pH measurements

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 630 For some projects, the A_T and C_T data presented in this synthesis were used to calibrate or validate in
 631 situ $f\text{CO}_2$ sensors (Bozec et al., 2011; Marrec et al., 2014; Merlivat et al., 2018). The A_T and C_T data were also
 632 used to calculate $f\text{CO}_2$ and to derive associated air-sea CO_2 fluxes, especially during periods when no direct $f\text{CO}_2$
 633 measurements were available (e.g. in the North Atlantic, Figure 4, Watson et al., 2009; Mc Kinley et al., 2011).
 634 For example, Marrec et al. (2014) successfully used the calculated $p\text{CO}_2$ (with A_T/C_T pairs) to adjust the drift of
 635 the $p\text{CO}_2$ data recorded with a Contros-HydroC/ CO_2 FT sensor mounted on a FerryBox for regularly sampling
 636 the Western English Channel (CHANNEL project). Here we show the results for the period 2012-2014 (Figure
 637 6). In this region the total alkalinity is relatively constant over time; the average of A_T for 528 samples at
 638 different seasons and years is $2334.4 (\pm 7.2) \mu\text{mol kg}^{-1}$. On the opposite, the C_T concentrations show distinctive
 639 seasonality, with higher concentrations in winter and lower in summer when biological activity is pronounced
 640 (Marrec et al., 2013, 2014; Kitidis et al., 2019). This controls the seasonal $p\text{CO}_2$ distribution revealed each year
 641 in both measured and calculated $p\text{CO}_2$ (Figure 6). For 528 co-located samples the mean difference between
 642 calculated and measured $p\text{CO}_2$ is $-1.9 (\pm 11.9) \mu\text{atm}$ with no distinct differences depending on the season and
 643 year.
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Figure 6: (a): Time-series of A_T (brown triangles, right Y-axis), C_T (blue triangles, right Y-axis), $p\text{CO}_2$ calculated (open triangles, left Y-axis) and $p\text{CO}_2$ measured (filled circles) in the Western English Channel in 2012-2014 (Marrec et al., 2014). (b): Measured $p\text{CO}_2$ versus calculated $p\text{CO}_2$ for the same samples. The mean difference ($p\text{CO}_{2\text{cal}}-p\text{CO}_{2\text{mes}}$) for 528 samples is $-1.9 \mu\text{atm}$ ($\pm 11.9 \mu\text{atm}$). Data from Marrec and Bozec (2016 a,b; 2017). Localization of the samples is shown in the inserted map.

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In the Ligurian Sea, following the first high frequency in situ $f\text{CO}_2$ measurements in 1995-1997 at the DYFAMED time-series station (Hood and Merlivat, 2001), a new CARIOCA $f\text{CO}_2$ sensor was deployed at that location in 2013 (BOUSSOLE project, Merlivat et al., 2018). The CARIOCA sensor was calibrated with regular A_T/C_T analyses performed at LOCEAN. Based on these data, the mean difference between CARIOCA- $f\text{CO}_2$ measurements and calculated- $f\text{CO}_2$ data was estimated to be around $\pm 4.4 \mu\text{atm}$ for 2013-2015, i.e. the same order than the precision of the CARIOCA sensor ($\pm 5 \mu\text{atm}$, Merlivat et al., 2018). Here we extend the results for the period 2013-2018 (Golbol et al., 2020; data also in SOCAT version v2021, Bakker et al., 2016) and compared the CARIOCA $f\text{CO}_2$ time-series with A_T and C_T data from different cruises (BOUSSOLE, DYFAMED and MOOSE-GE) selected in the layer 0-20m at that location (Figure S4). For 67 co-located samples at different seasons and years, the mean difference between calculated and measured $f\text{CO}_2$ ($f\text{CO}_{2\text{cal}}-f\text{CO}_{2\text{mes}}$) was $-3.7 \mu\text{atm}$ ($\pm 10.8 \mu\text{atm}$) where $f\text{CO}_2$ was calculated from A_T/C_T pairs using the constant from Lueker et al (2000). At that location, the alkalinity is relatively constant over 2013-2018 with an average concentration of $2569.8 (\pm 13.2) \mu\text{mol kg}^{-1}$. C_T concentrations show a clear seasonality, decreasing by around $50 \mu\text{mol kg}^{-1}$ from winter to late summer driving the large seasonal cycle of $f\text{CO}_2$ (range $80 \mu\text{atm}$) revealed in both measured and calculated values (here $f\text{CO}_2$ is normalized at 13°C , Figure S4). In addition to calibration purposes, a regional A_T /Salinity relationship was derived from the A_T data measured at that location and successfully used to construct time-

693 series of C_T and pH calculated from the high-frequency CARIOCA fCO_2 data to investigate and interpret the
694 long-term change of fCO_2 and acidification in the Ligurian Sea (Merlivat et al., 2018; Coppola et al., 2020).

695 A CARIOCA sensor was also deployed in 2003 near the SOMLIT-Brest time-series site in the Bay of
696 Brest (Bozec et al., 2011; Salt et al., 2016). As for BOUSSOLE in the Ligurian Sea, samples collected for A_T and
697 C_T were used for validation of the pCO_2 recorded by the CARIOCA sensor and the comparison with calculated
698 pCO_2 showed a good agreement, i.e. $pCO_{2cal} = 0.98 * pCO_{2mes} + 7 \mu atm$ (Bozec et al., 2011). CARIOCA sensors
699 were also deployed on moorings in the Tropical Atlantic (PIRATA project, e.g. Lefèvre et al., 2008, 2016;
700 Parard et al., 2010). With the discrete A_T and C_T data included in this synthesis (EGEE and PIRATA-FR cruises),
701 the fCO_2 data from CARIOCA sensor associated with an adapted A_T /Salinity relationship were used to derive pH
702 (Lefèvre et al., 2016) or C_T time-series to evaluate net community production in the Eastern tropical Atlantic
703 (Parard et al., 2010; Lefèvre and Merlivat 2012).

704 Although this is not a direct instrumental inter-comparison, differences between pCO_2 (or fCO_2)
705 calculated using A_T/C_T pairs with direct pCO_2 measurements give a glimpse of the quality of A_T and C_T data in
706 this synthesis given the uncertainty attached to the pCO_2 or pH calculations (Orr et al., 2015). For example, in
707 the frame of the SURATLANT project in the North Atlantic, calculated fCO_2 data were compared with co-
708 located fCO_2 measurements for different seasons and years (Figure S5). The mean differences ($fCO_{2cal} - fCO_{2mes}$)
709 ranged between $-4.3 \mu atm (\pm 12.9) \mu atm$ (2004-2007, 74 co-located samples) and $-3.0 (\pm 12.1) \mu atm$ (2014-2015,
710 98 co-located samples). The differences are almost the same for different years (and seasons) and are thus
711 attributed to method uncertainties (including sampling time, measurement errors, and data processing). Based on
712 these comparisons and the consistency between data we are confident that the A_T and C_T data presented in this
713 synthesis could be used to calculate fCO_2 (and pH) and interpret temporal changes and drivers of these
714 parameters as well as to estimate air-sea CO_2 fluxes in the North Atlantic (e.g. Corbière et al., 2007; Schuster et
715 al., 2009, 2013; Watson et al., 2009; Metzl et al., 2010; Mc Kinley et al., 2011; Reverdin et al., 2018, Kitidis et
716 al., 2019; Leseurre et al., 2020).

717 The A_T and C_T data in this synthesis have been also successfully used for fCO_2 and air-sea CO_2 fluxes
718 calculations in other regions: the tropical Atlantic (Koffi et al., 2010), the tropical Pacific (Moutin et al., 2018;
719 Wagener et al., 2018), the Solomon sea (Ganachaud et al., 2017) or the Mediterranean sea and coastal zones (De
720 Carlo et al., 2013; Marrec et al., 2015; Kapsenberg et al., 2017; Coppola et al., 2020; Keraghel et al., 2020;
721 Wimart-Rousseau et al., 2020a; Gattuso et al., 2023).

722 In addition, A_T and C_T data in the surface and the water-column are also relevant to calculate pH and
723 evaluate its rate of change for addressing ocean acidification topic in different regions (Kapsenberg et al., 2017;
724 Ganachaud et al., 2017; Wagener et al., 2018; Coppola et al., 2020; Leseurre et al., 2020; Lo Monaco et al.,
725 2021). At the time-series station ECOSCOPIA in the Bay of Brest (Fleury et al., 2023; Petton et al., 2023), pH
726 calculated with A_T/C_T data were compared with direct pH measurements (Figure S6). In 2017-2019, pH (at
727 standard temperature 25°C, pH-25C) was always lower than 8 and presented a large seasonal signal of 0.3 (high
728 pH values in spring, low in winter). The mean difference between calculated and measured pH-25C for 46
729 samples was equal to $+0.013 (\pm 0.010)$ which is in the range of the pH uncertainty evaluated by error
730 propagation when calculated from A_T/C_T pairs (A_T and C_T error of $\pm 3 \mu mol kg^{-1}$ leads to pH error of ± 0.0144).
731 Part of these A_T and C_T data used to calculate pH also helped for interpreting the response of marine species to
732 acidification, e.g. pteropodes or coccolithophores (*Emiliana huxleyi*) in the Mediterranean Sea (Howes et al.,
733 2015, 2017; Meier et al., 2014) or in the Southern Ocean (Beaufort et al., 2011). The A_T and C_T data were also

734 supporting environmental analysis in coral reef ecosystems in the tropical Pacific (TARA Expedition, Douville
735 et al., 2022; Lombard et al., 2023; Canesi et al., 2023).

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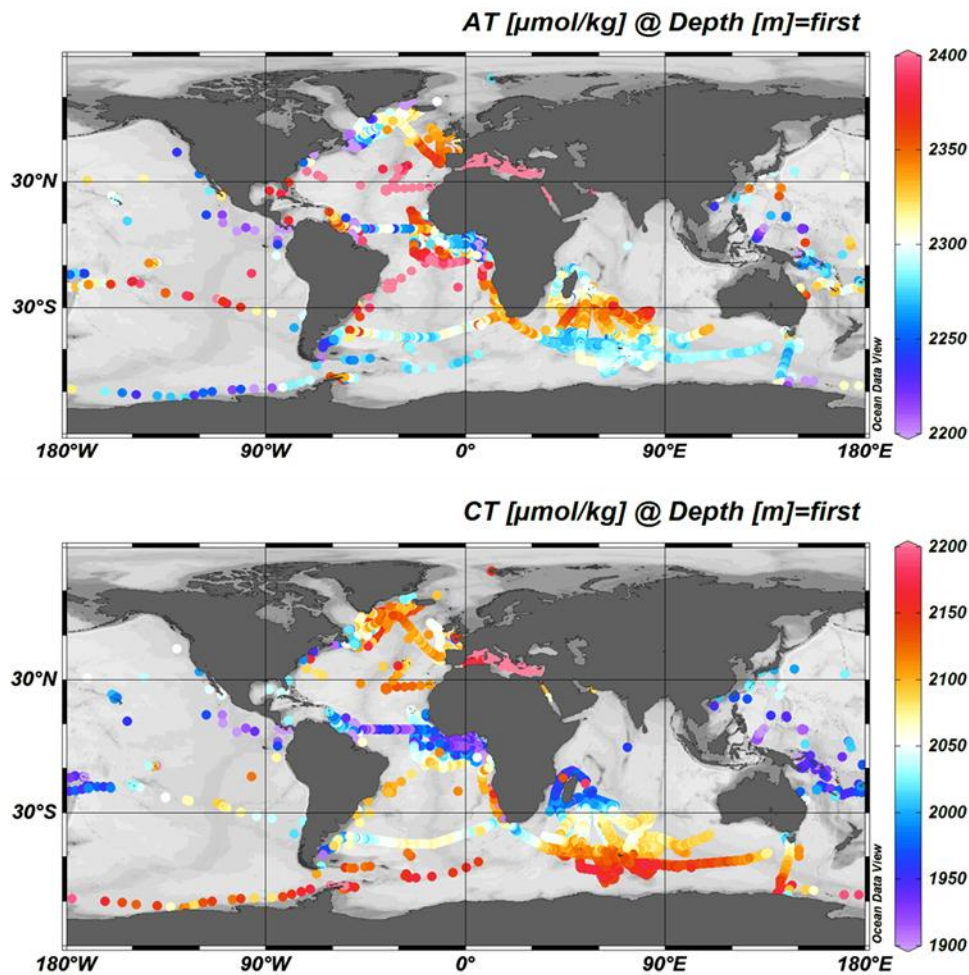
737 4 Global distribution and relationships from A_T and C_T based on the SNAPO-CO2 dataset

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739 The surface distribution in the global ocean based on the SNAPO-CO2 dataset is presented in Figure 7
740 for A_T and C_T . In the open ocean, high A_T concentrations are identified in the subtropics in all basins (Jiang et al.,
741 2014; Takahashi et al., 2014) with highest concentrations up to $2484 \mu\text{mol kg}^{-1}$ in the central North Atlantic
742 (STRASSE cruise in August 2012, $26^\circ\text{N}/36^\circ\text{W}$). In surface and at depth, the A_T /Salinity and A_T/C_T relationships
743 are clearly identified and structured at regional scale (Figure 8).

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Figure 7: Distribution of A_T (top) and C_T (bottom) concentrations ($\mu\text{mol.kg}^{-1}$) in surface waters (0-10m). Only data with flag 2 are presented in these figures. Figures produced with ODV (Schlitzer, 2018).

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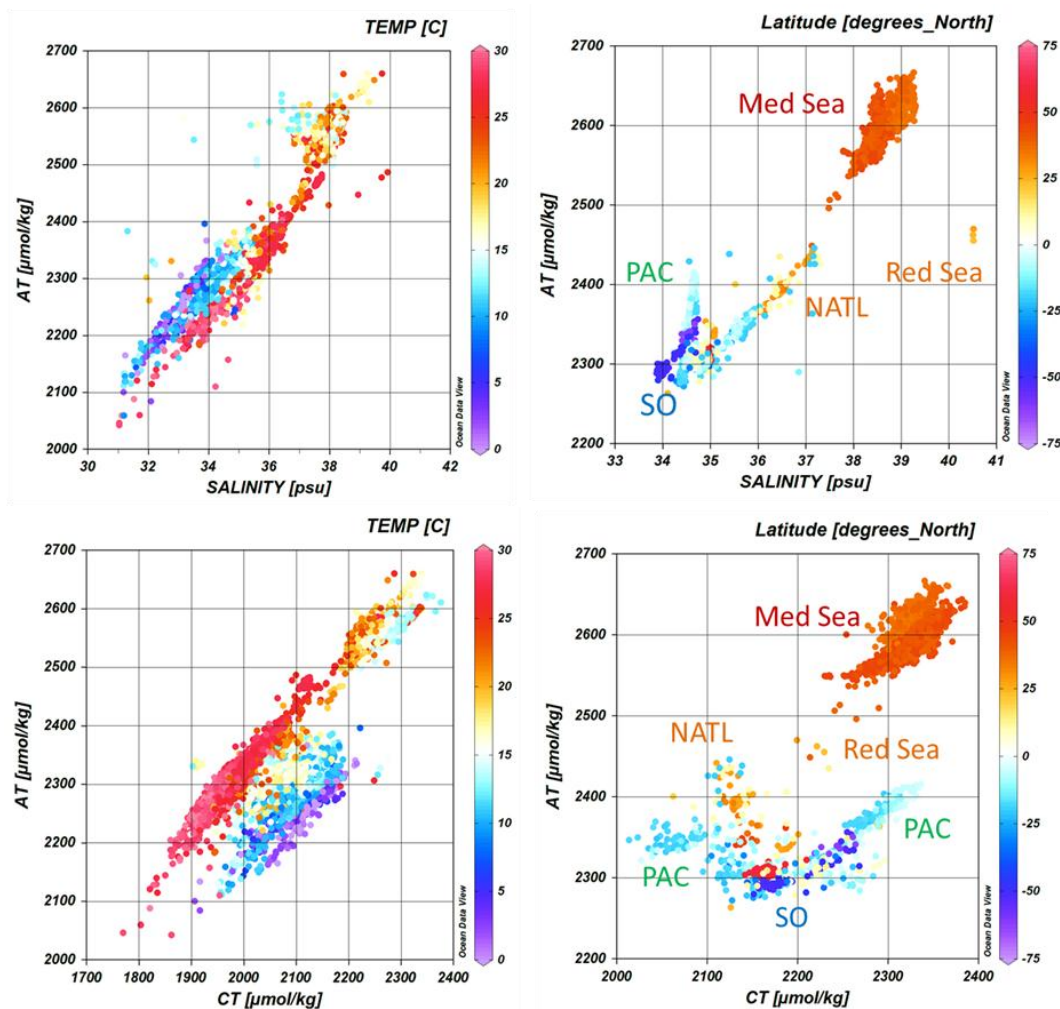


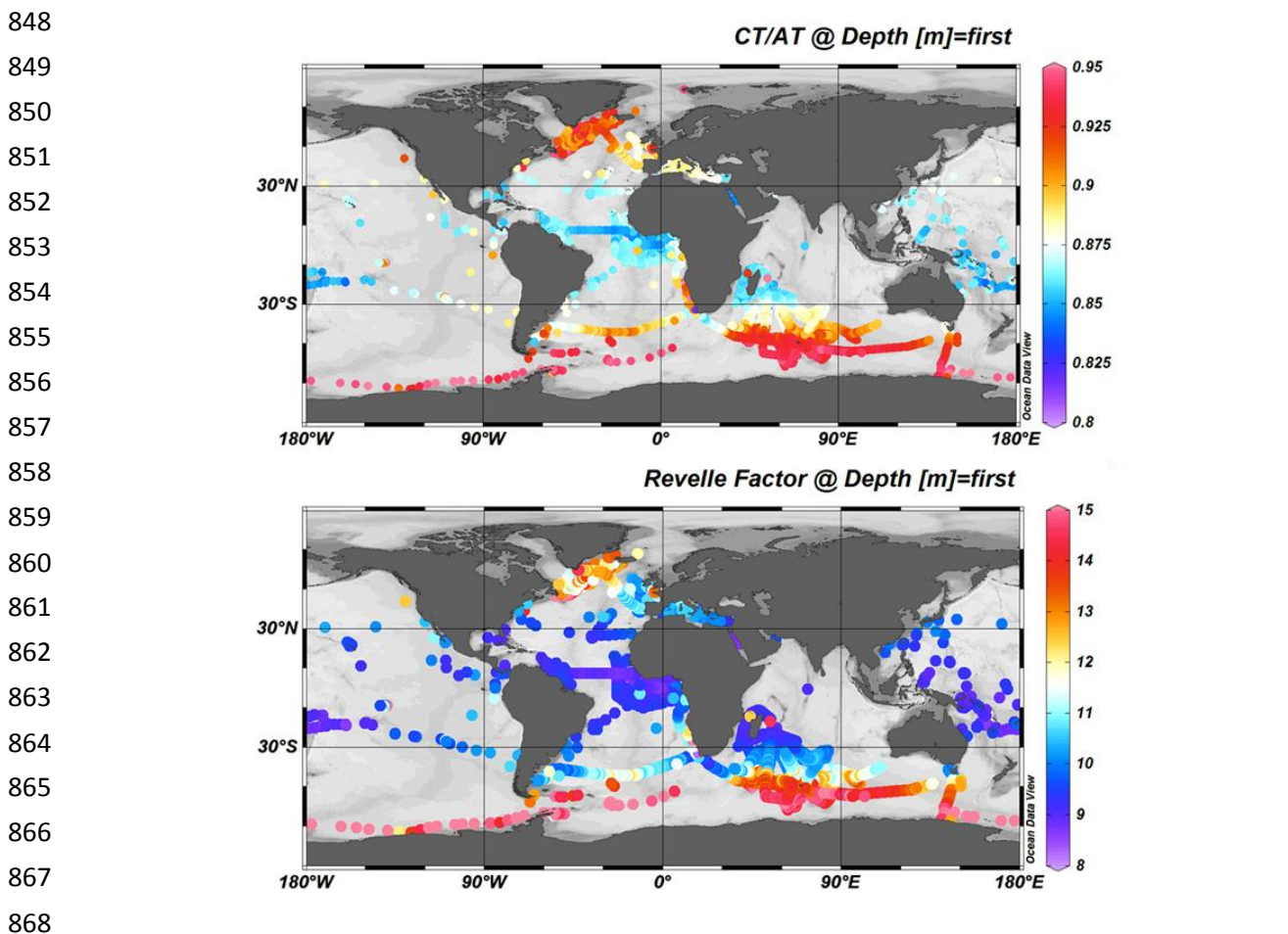
Figure 8: Relationships between A_T and Salinity (upper panel) and A_T versus C_T (lower panel) for samples in surface waters (0-10m and SSS > 31) (left) and in the water column below 100m (right). Only data with flag 2 are presented. The color scales correspond to the temperature (left) or the latitude (right). Some location of data are identified: Mediterranean Sea (Med Sea), Red Sea, Tropical Pacific (PAC), North Atlantic (NATL) and Southern Ocean (SO). Figures produced with ODV (Schlitzer, 2018).

In the Eastern tropical Atlantic (ETA) where the Congo River impacts the salinity field (Vangriesheim et al., 2009), A_T concentrations range between 2100 and 2400 $\mu\text{mol kg}^{-1}$. The regional A_T /Salinity relationship in the ETA based on data from the EGEE cruises in 2005-2007 (Koffi et al., 2010) is robust and validated with more recent measurements from PIRATA-FR cruises in 2010-2019 (Lefevre et al., 2021). The strong A_T /Salinity relationship in the ETA was also recognized using data from the TARA-MICROBIOME cruise in May-July 2022 (Figure S7). Low salinity (< 30) and low A_T (1700-2200 $\mu\text{mol kg}^{-1}$) are also observed in the Western tropical Atlantic near the Amazon River plume. The A_T /Salinity relationships in both river plume regions are very similar (Figure S7).

For C_T , the lowest concentrations were observed in the coastal regions of the Tropical Atlantic, on the eastern side in the Gulf of Guinea (BIOZAIRE cruise in 2003, 6°S/11°E, $C_T=1390 \mu\text{mol kg}^{-1}$, Vangriesheim et al., 2009) and on the Western side in coastal zone off French Guyana (PLUMAND cruise in 2007, 5°N/51°W, $C_T=1512 \mu\text{mol kg}^{-1}$, Lefèvre et al., 2010). Such low C_T concentrations were also observed around 5°N/51°W in the Amazon River plume during the recent EUREC4A-OA cruise in 2020 and the TARA-MICROBIOME cruise in 2021 ($C_T=1451 \mu\text{mol kg}^{-1}$) leading to low oceanic $f\text{CO}_2$ (< 350 μatm) and a CO_2 sink in this region (Olivier et al., 2022).

832 The high C_T concentrations were mainly observed in the Southern Ocean (OISO and ACE cruises)
 833 south of the Polar Front around 50°S linked to the upwelling of C_T -rich deep water (Figure 7, Metzl et al., 2006;
 834 Wu et al., 2019; Chen et al., 2022). This leads to a high C_T/A_T ratio and a high Revelle factor in the Southern
 835 Ocean (Figure 9, Fassbender et al., 2017). The high C_T content and low temperature in the Southern Ocean also
 836 lead to low calcite and aragonite saturation state (Ω) (Takahashi et al., 2014; Jiang et al., 2015). We calculate Ω
 837 from A_T and C_T data at insitu temperature, salinity and pressure. At present the surface ocean is not under-
 838 saturated with regard to aragonite (Figure 10); however, under-saturation levels ($\Omega-Ar < 1$) were found around
 839 500 m in the Southern Ocean (ACE cruise in 2017, MODYDICK cruise in 2018), 1000 m in the Tropical Pacific
 840 (PANDORA 2012 and OUTPACE 2015 cruises) and 2200 m in the North Atlantic (OVIDE 2012 and 2014
 841 cruises, see also Turk et al., 2017) (Figure 10). Samples at 400 m from the TARA-Oceans cruise in 2009-2012
 842 also indicated aragonite under-saturation in the Equatorial Atlantic, Equatorial Pacific, as well as off South
 843 America (73°W-34°S, Chile) associated to equatorial or eastern boundary upwelling systems (Feely et al., 2012;
 844 Lauvset et al., 2020).

845 In surface, $\Omega-Ar > 3$ is found in the latitudinal band 45°S-54°N and $\Omega-Ar < 3$, below the critical
 846 threshold of $\Omega-Ar = 3.25$ that represents a limit for distribution of tropical coral reefs (Hoegh-Guldberg et al.,
 847 2007) is observed at very few locations in the tropics.



869 **Figure 9:** Distribution of the C_T/A_T ratio (top) and the Revelle factor (bottom) in surface waters (0-10m). Only
 870 data with flag 2 were used. Figures produced with ODV (Schlitzer, 2018).

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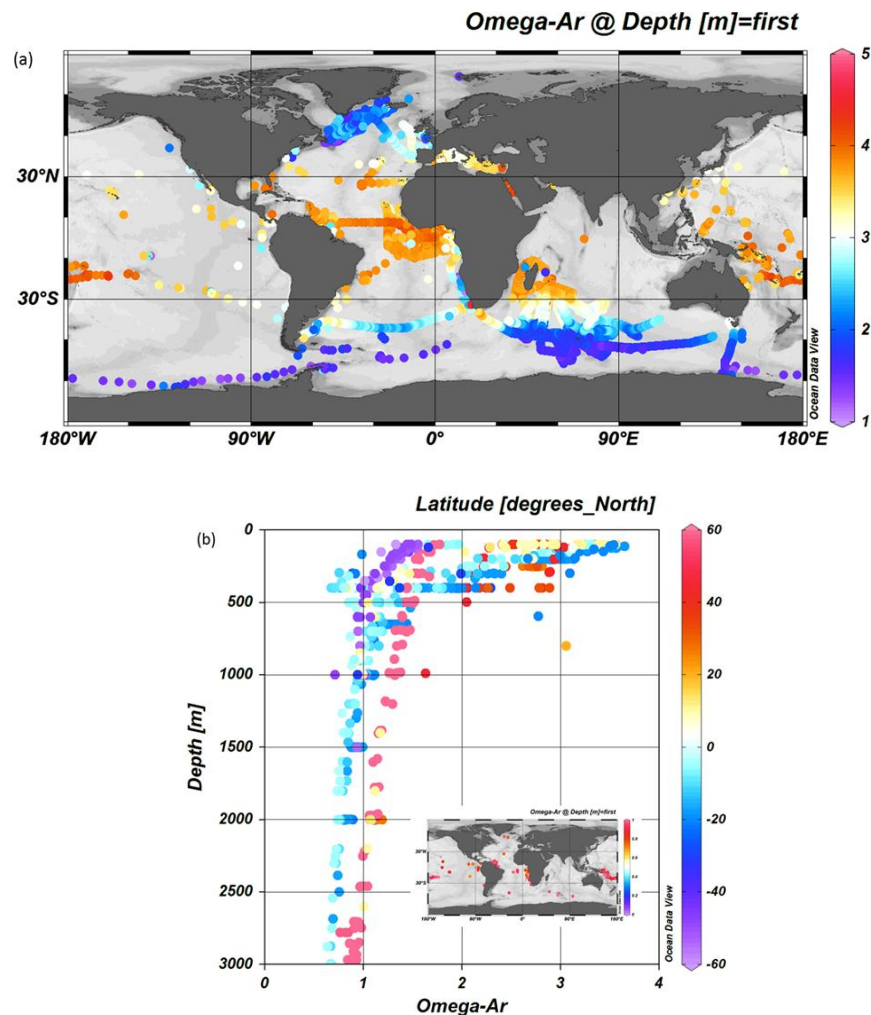
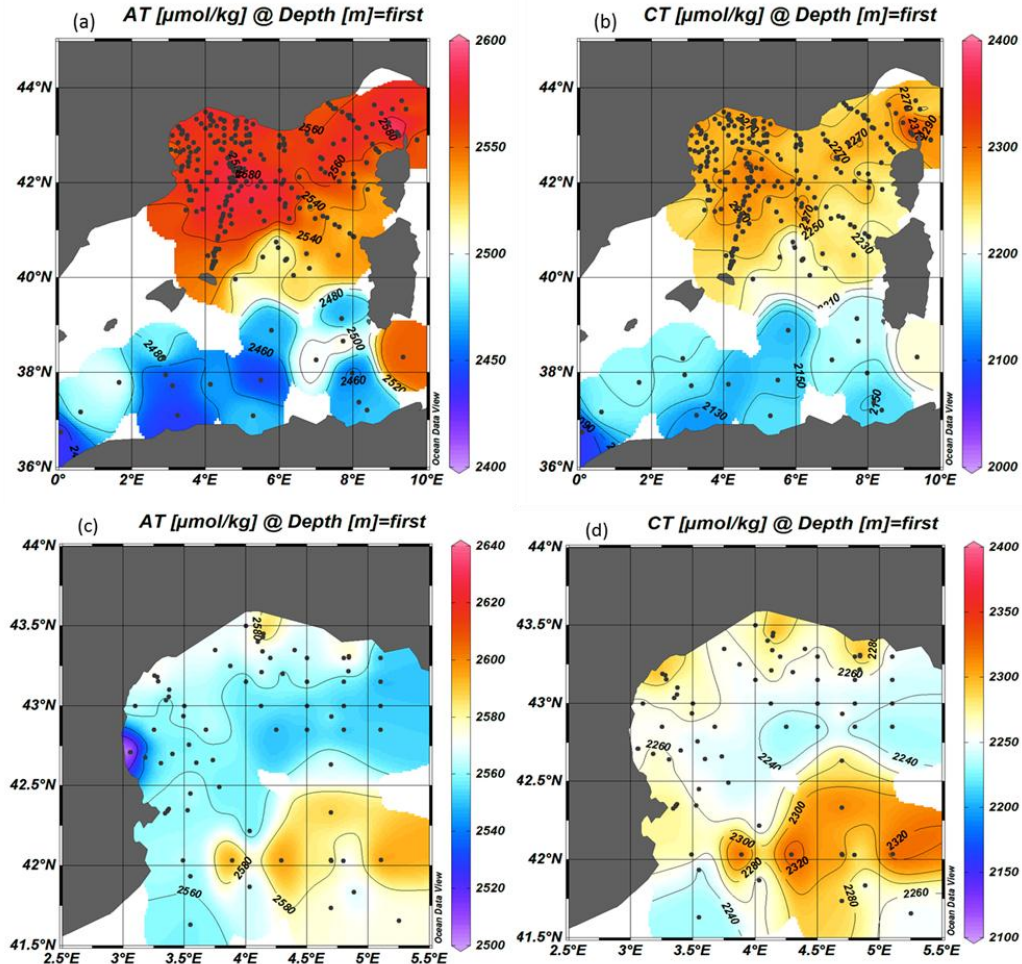


Figure 10: (a): Distribution of the aragonite saturation state (Ω -Ar) in surface waters (0-10m). Only data with flag 2 were used. (b): Depth profiles (100-3000m) of Ω -Ar at few locations in the Tropical Pacific, Atlantic and Southern Oceans. Stations where under-saturation is detected (Ω -Ar<1) at depth are identified in the inserted map. Figures produced with ODV (Schlitzer, 2018).

Compared to the open ocean, A_T concentrations are much higher in the Mediterranean Sea (Copin-Montégut, 1993; Schneider et al., 2007; Álvarez et al., 2023) with values up to $2600 \mu\text{mol kg}^{-1}$ (Figure 8). The A_T and C_T data obtained in 1998-2019 show on average a clear contrast between the northern and southern regions of the Western Mediterranean sea (Figure 11 a, b) with higher concentration in the Ligurian Sea and the Gulf of Lion (Gemayel et al., 2015). However, the basin scale average distribution view smoothed the meso-scale signals recognized in the Mediterranean Sea (e.g. Bosse et al., 2017; Petrenko et al., 2017). In the Gulf of Lion the synthesis of 11 cruises conducted from May 2010 to June 2011 (CARBORHONE, CASCADE, LATEX, MOLA, MOOSE-GE) highlights the contrasting distributions of A_T and C_T in the coastal zones and off shore (Figure 11 c, d). The averaging of all data in 1998-2019 also smoothed the seasonal signal and the inter-annual variability described below.

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943 **Figure 11:** Distribution of A_T (a) and C_T (b) in $\mu\text{mol kg}^{-1}$ in surface waters of the Western Mediterranean Sea (0-
 944 10m) from all data for 1998-2019. Detailed distribution of A_T (c) and C_T (d) in $\mu\text{mol kg}^{-1}$ in surface waters of the
 945 Gulf of Lion for the period 2010-2011 only (cruises CARBORHONE, CASCADE, LATEX, MOLA, MOOSE-
 946 GE). Figures produced with ODV (Schlitzer, 2018).
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948 **5 Temporal variations of A_T and C_T : examples from the SNAPO-CO2 dataset**

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950 Time-series stations such as BATS, ESTOC, HOT in the subtropics and stations in the Irminger Sea or
 951 in the Iceland Sea are the only way to detect the long-term change in the ocean carbonate system in the surface
 952 and the water column (Bates et al., 2014). These important time-series help to understand driving processes (e.g.
 953 Hagens and Middelburg, 2016) and are often used to validate the $p\text{CO}_2$, A_T , C_T , or pH reconstructed fields (e.g.
 954 Rödenbeck et al., 2013; Broullón et al., 2019, 2020; Keppler et al., 2020; Gregor and Gruber, 2021; Chau et al.,
 955 2023; Ma et al., 2023).

956 Here we show examples of the temporal surface variations at locations where data were obtained for
 957 more than 10 years (Figure 12). We thus selected the following contrasting regions: the North Atlantic subpolar
 958 gyre (NASPG around $60^\circ\text{N}/30^\circ\text{W}$, period 1993-2018), the Equatorial Atlantic (at $2^\circ\text{N}-2^\circ\text{S}/12^\circ\text{W}-8^\circ\text{W}$, period
 959 2005-2017), the Indian Ocean subtropical sector ($26-35^\circ\text{S}/50-56^\circ\text{E}$, period 1998-2018), the Indian Ocean high
 960 latitude ($54-60^\circ\text{S}/60-70^\circ\text{E}$, period 1998-2018), the Ligurian Sea (around DYFAMED station, $43.5-42.5^\circ\text{N}/5.5-
 961 9^\circ\text{E}$, period 1998-2019) and times-series stations in the coastal zones off Brittany (period 2008-2019).
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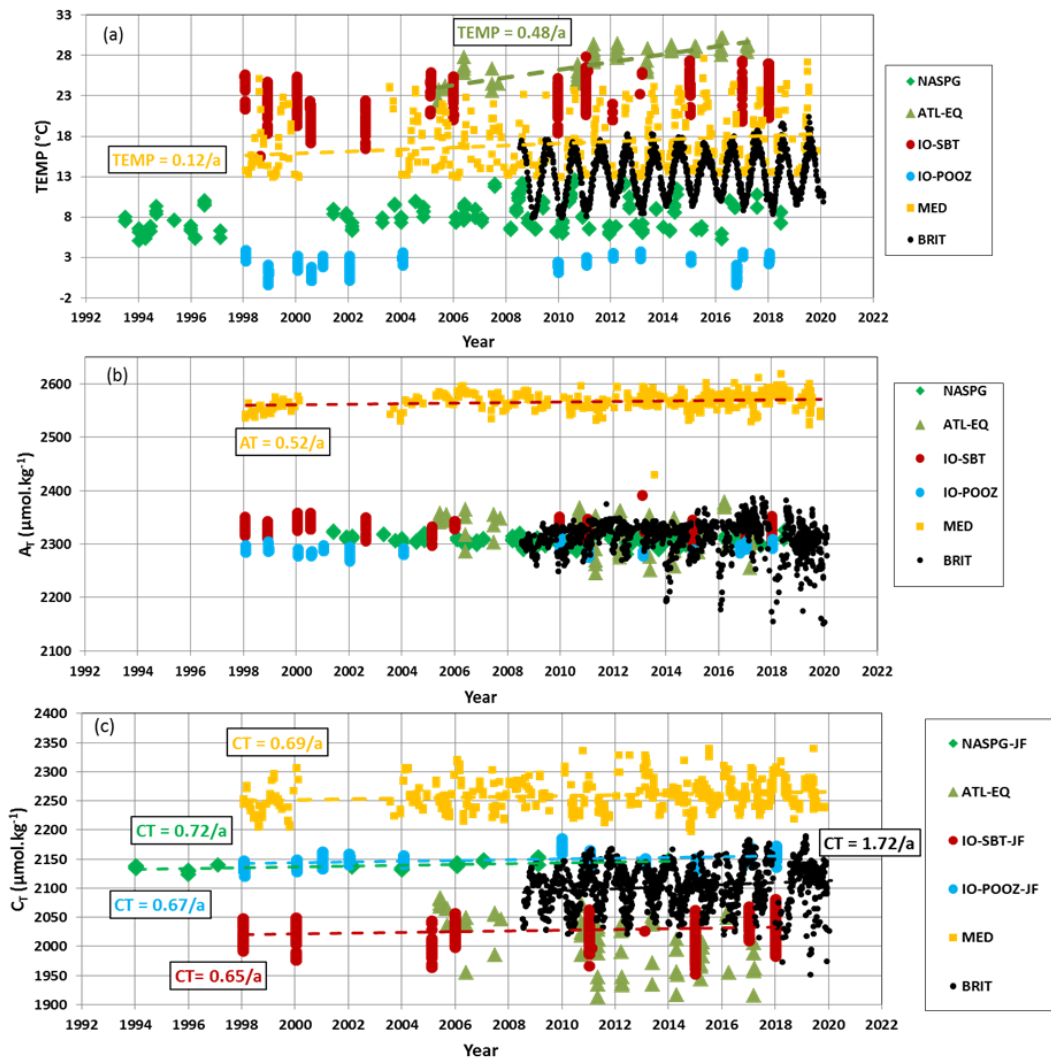


Figure 12: Time-series of (a) sea surface temperature ($^{\circ}\text{C}$), (b) A_T ($\mu\text{mol kg}^{-1}$) and (c) C_T ($\mu\text{mol kg}^{-1}$) in 6 regions: the North Atlantic subpolar gyre (NASPG 1993-2018, green diamond), the Equatorial Atlantic (ATL-EQ, 2005-2017, green triangle), the Indian subtropical sector (IO-SBT, red circle) and high latitude (IO-POOZ, blue circle) (1998-2018), the Ligurian Sea (MED, 1998-2019, orange square) and times-series stations in the coastal zones off Brittany (BRIT, period 2008-2019, black dots). Trends (dashed lines and values) are shown when relevant for the discussion (C_T trends listed in Table 6).

Table 6: Trend of C_T ($\mu\text{mol kg}^{-1} \text{ yr}^{-1}$) and corresponding standard error in 5 selected regions where data were available for more than 10 years (data are shown in Figure 12). The projects/cruises for selection of the data in each domain are indicated.

Region (acronym)	Period	C_T trend ($\mu\text{mol kg}^{-1} \text{ yr}^{-1}$)	Season	Projects/Cruises
North Atlantic (NASPG)	1994-2014	+0.72 (0.17)	Jan-Feb	SURATLANT
Indian Subtropic (IO-SBT)	1998-2018	+0.65 (0.12)	Jan-Feb	OISO
Indian South. (IO-POOZ)	1998-2018	+0.67 (0.04)	Jan-Feb	OISO
Ligurian Sea (MED)	1998-2019	+0.68 (0.18)	All seasons	DYFAMED, BOUSSOLE, MOOSE-GE
Coast Brittany (BRIT)	2008-2019	+1.72 (0.28)	All seasons	Brest, Roscoff, ECOSCOPIA, PENZE

1012 In the 6 regions, there was a progressive warming most clearly detected in the Mediterranean Sea (e.g.
1013 Nykjaer, 2009). From 1998 to 2019 the warming in the Ligurian Sea was $+0.1208^{\circ}\text{C yr}^{-1}$ (± 0.0227) (Figure 12).
1014 In the equatorial Atlantic, the apparent rapid increase of temperature of $+0.48^{\circ}\text{C}\cdot\text{yr}^{-1}$ (± 0.04) in 2005-2017 from
1015 the selected data indicated a change in water masses and circulation. The colder sea surface in 2005 was
1016 associated with the so-called Atlantic Cold Tongue (ACT) which was one of the most intense ATC since 1982
1017 (Caniaux et al., 2011). The ACT also leads to significant changes in oceanic $f\text{CO}_2$ and air-sea CO_2 fluxes (Parard
1018 et al., 2010; Koseki et al., 2023) and explained the high C_T concentrations observed in 2005 in this region
1019 (Figure 12, Koffi et al., 2010).

1020 Total alkalinity presents rather homogenous concentrations in the NASGP and the south Indian Ocean.
1021 Inter-annual variability of A_T is pronounced in the equatorial Atlantic ranging between 2245 and 2378 $\mu\text{mol kg}^{-1}$.
1022 This is mainly related to salinity as normalized A_T values ($N-A_T$, for salinity= 35) do not show such inter-annual
1023 variability (Mean $N-A_T = 2295.7 \pm 4.6 \mu\text{mol kg}^{-1}$, $n= 67$ for 2005-2017, not shown). In the coastal zones off
1024 Brittany, the A_T is also highly variable (Salt et al., 2016; Gac et al., 2021) ranging between 2150 and 2386 μmol
1025 kg^{-1} (Figure 12).

1026 An interesting signal is the progressive increase of A_T in the Mediterranean Sea. The positive A_T trend
1027 of $+0.53$ (± 0.11) $\mu\text{mol kg}^{-1} \text{yr}^{-1}$ ($n=538$) in 1998-2019 in the region offshore was also observed at the coastal
1028 station SOMLIT-Point-B in 2007-2015 but with a faster increase of $+2.08$ (± 0.19) $\mu\text{mol kg}^{-1} \text{yr}^{-1}$ (Kapsenberg et
1029 al., 2017). Close to the DYFAMED site, at station SOMLIT-Point-B, the A_T trend was not linked to salinity
1030 temporal changes as a positive $N-A_T$ trend was also reported, $+0.52$ (± 0.07) $\mu\text{mol kg}^{-1} \text{yr}^{-1}$ (not shown). Based
1031 on data from the PERLE cruises in 2018-2021 a significant increase in A_T was also identified in the Eastern
1032 Mediterranean Sea (Wimart-Rousseau et al., 2021). Along with the increase of C_T and the warming, the A_T
1033 increase would impact on the $f\text{CO}_2$, air-sea CO_2 fluxes and pH temporal changes (Merlivat et al., 2018).
1034 Processes explaining the A_T increase in the Mediterranean Sea are still unexplained and deserve further
1035 investigations (Coppola et al., 2019).

1036 As expected, because of the anthropogenic CO_2 uptake the C_T concentrations increased in most regions
1037 (Figure 12, Table 6). This is identified in the Indian Ocean (in the subtropics and the high latitude), in the
1038 Mediterranean Sea, and in coastal waters off Brittany. However, the signal is more complex in the NASPG. As
1039 previously shown the C_T trend in the NASPG depends on seasons and decades (Metzl et al., 2010; Reverdin et
1040 al., 2018; Fröb et al., 2019; Leseurre et al., 2020). Here we selected only the data in January-February from the
1041 SURATLANT cruises leading a C_T trend of $+0.72$ (± 0.17) $\mu\text{mol kg}^{-1} \text{yr}^{-1}$. Compared to the regions further north
1042 the C_T trend in the NASPG is about half the C_T trends of $+1.44$ (± 0.23) $\mu\text{mol kg}^{-1} \text{yr}^{-1}$ observed in the Iceland
1043 Sea (Olafsson et al., 2009) or $+1.48$ (± 0.22) $\mu\text{mol kg}^{-1} \text{yr}^{-1}$ at station M in the Norwegian Sea (Skjelvan et al.,
1044 2022).

1045 In the coastal zones off Brittany, although there are large seasonal and inter-annual variabilities (Gac et
1046 al., 2021), an annual C_T trend of $+1.72$ (± 0.28) $\mu\text{mol kg}^{-1} \text{yr}^{-1}$ is detected over 10 years (2009 to 2019). The same
1047 is observed in the Mediterranean Sea where the C_T offshore trend of $+0.69$ (± 0.18) $\mu\text{mol kg}^{-1} \text{yr}^{-1}$ is low
1048 compared to what was observed in the coastal zone (SOMLIT-Point-B, $+2.97$ (± 0.20) $\mu\text{mol kg}^{-1} \text{yr}^{-1}$, Kapsenberg
1049 et al., 2017).

1050 In the southern Indian Ocean, C_T concentrations also increased in both subtropical and high latitudes,
1051 two regions where the primary productivity is relatively low (oligotrophic regime in the subtropics and High
1052 Nutrient Low Chlorophyll regime, HNLC, south of the Polar Front). With the data selected for austral summer

1053 (January-February) the C_T trends appeared almost similar in these two regions, around $+0.65 \mu\text{mol kg}^{-1} \text{yr}^{-1}$
1054 (Table 6).

1055 Finally, in the Equatorial Atlantic the selected data around 0° - 10°W highlighted the large variability
1056 linked to the oceanic circulation. Detecting a C_T trend as well as a possible link with anthropogenic carbon
1057 uptake, at least with the data available in 2005-2017, appears to be intricate as it has been previously discussed
1058 for the period 2006-2013 (Lefèvre et al., 2016). However, the signal of the C_T increase is better identified north
1059 or south of the Equator in the Eastern tropical Atlantic sector (Lefèvre et al., 2021).

1060 In the water column A_T and C_T data from dedicated cruises were used to evaluate the anthropogenic CO_2
1061 (C_{ant}) distribution and pH change since pre-industrial era (e.g. PANDORA cruise, Ganachaud et al., 2017;
1062 OUTPACE cruise, Wagener et al., 2018; SOMBA cruise, Keraghel et al., 2020). Time-series at DYFAMED
1063 station also enabled to investigate the temporal variability of C_T , A_T and C_{ant} in the water column (Touratier and
1064 Goyet, 2009; Coppola et al., 2020; Fourier et al., 2022). As an example of the observed temporal variations at
1065 depth we selected the data in the layer 950-1050m in the Ligurian Sea from different cruises (Figure 13). At that
1066 depth both A_T and C_T present some large anomalies especially noticed in 2013 (lower A_T and C_T in February
1067 2013, DEWEX cruise) and in 2018 (higher A_T and C_T in May 2018, MOOSE-GE cruise) the later probably
1068 linked to episodic convective process that occurred in winter 2018 (Fourier et al., 2022; Coppola et al, 2023).
1069 During the strong convection event in 2013 the positive anomalies of A_T and C_T were mostly identified in the
1070 upper layers (Figure 12c, Ulses et al, 2023).

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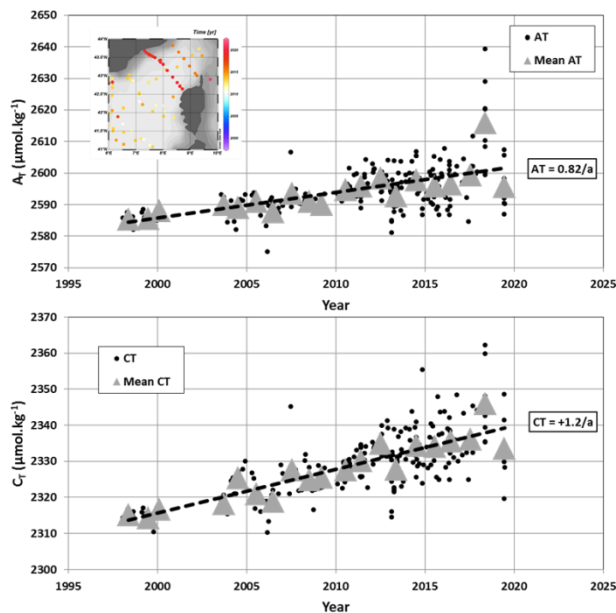
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Figure 13: Time-series of A_T ($\mu\text{mol kg}^{-1}$) and C_T ($\mu\text{mol kg}^{-1}$) in the Ligurian Sea (1998-2019) in the layer 950-1050m. Annual mean (grey triangles) was calculated from all data each year (black dots). The trends (dashed line) based on annual mean are $+0.82 (\pm 0.15) \mu\text{mol kg}^{-1} \text{yr}^{-1}$ for A_T and $+1.20 (\pm 0.12) \mu\text{mol kg}^{-1} \text{yr}^{-1}$ for C_T . In this layer data selected are from cruises ANTARES, CASCADE, DEWEX, DYFAMED, MOOSE-GE and PEACETIME (location of stations shown in the inserted map).

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In this region the long-term increase of A_T indicates that in addition to the anthropogenic CO_2 signal other processes are at play to explain the rapid C_T trend of $+1.20 (\pm 0.12) \mu\text{mol kg}^{-1} \text{yr}^{-1}$ at depth compared to that observed in surface (Figure 12). The signal at depth is probably linked to the variations of the deep convection and mixing with Levantine intermediate water (LIW, Margirier et al., 2020) with higher A_T and C_T

1100 concentrations. The long-term increase of A_T and C_T at depth (here at 1000m, Figure 13) was also observed
1101 below 2000m (Coppola et al., 2020) a signal that has to be investigated in dedicated analysis using other
1102 properties (O_2 , nutrients, following Fourrier et al. (2022) for the period 2012-2020) and a larger dataset in the
1103 Mediterranean Sea (e.g. GLODAP).

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1105 **6 Using A_T and C_T data to validate observations from autonomous instruments**

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1107 The dataset presented in this synthesis would also offer interesting observations to validate properties
1108 (A_T and C_T) derived from BGC-Argo floats equipped with pH sensors (e.g. Bushinsky et al., 2019; Mazloff et al.,
1109 2023; Mignot et al., 2023). The water column in situ A_T and C_T data obtained during the Antarctic Circumpolar
1110 Expedition (ACE) in 2016-2017 were collected at location where SOCCOM floats were launched (Walton and
1111 Thomas, 2018). A SOCCOM float (WMO ID 5905069) was launched on January 11th 2017 at 55°S-96°E south
1112 of the Polar Front in the southern Indian Ocean. The pH, temperature and salinity data from the float were then
1113 used to derive A_T and C_T profiles (here using a multiple linear regression (MLR) algorithm, Williams et al.,
1114 2016, 2017). In the top layers the discrete ACE data (Figure 14) present large variability of A_T and C_T
1115 concentrations not captured in the records derived from the float (MLR method somehow smooth the profiles).
1116 However, given the uncertainty in reconstructed A_T from float data ($5.6 \mu\text{mol kg}^{-1}$) the average values in the first
1117 100m were almost identical ($A_{T-ACE} = 2285.1 (\pm 4.4) \mu\text{mol kg}^{-1}$ and $A_{T-float} = 2278.3 (\pm 0.7) \mu\text{mol kg}^{-1}$; $C_{T-ACE} =$
1118 $2139.7 (\pm 9.2) \mu\text{mol kg}^{-1}$ and $C_{T-float} = 2141.1 (\pm 3.2) \mu\text{mol kg}^{-1}$). Moreover below 200m, profiles from the float
1119 are coherent compared to the A_T and C_T measurements (Figure 14). This is encouraging for using float data to
1120 explore the seasonal variability of A_T and C_T in the Southern Ocean (e.g. Williams et al., 2018; Johnson et al.,
1121 2022) and the estimation of anthropogenic CO_2 in the water column in this sector (Figure 14). Here the C_{ant}
1122 concentrations were calculated below 200m (corresponding to the temperature minimum of the winter winter in
1123 the SO and using the TrOCA method, Touratier et al., 2007). The float data suggest that C_{ant} concentrations are
1124 positive down to about 1000m, with maximum values in subsurface. In 2017 the mean C_{ant} concentration at
1125 200m was $49.1 (\pm 9.0) \mu\text{mol kg}^{-1}$. Below that depth, C_{ant} decreased and reduced to $+29.8 (\pm 8.5) \mu\text{mol kg}^{-1}$ in the
1126 layer 300-400m. To complement the C_{ant} inventories based on GLODAP data product (e.g. Gruber et al., 2019)
1127 C_{ant} estimates derived from BGC-Argo floats as evaluated here in the Southern Ocean could be applied in other
1128 locations as was previously tested in the North Pacific (Li et al., 2019).

1129 In surface water as the A_T derived from the float data are deduced using MLR or LIAR methods
1130 (Williams et al., 2017; Carter et al., 2016), the A_T data in the SNAPO-CO2 synthesis could also be used to
1131 identify A_T anomalies not always captured from floats. This is particularly relevant in coccolithophores blooms
1132 areas when low A_T concentrations and high pCO_2 are observed (e.g. Balch et al., 2016 in the Southern Ocean;
1133 Robertson et al., 1994 in the North Atlantic).

1134

1135 **7 Summary and suggestions**

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1137 The ocean data synthesized in this product are based on measurements of A_T and C_T performed between
1138 the period 1993 and 2022 with an accuracy of $\pm 4 \mu\text{mol kg}^{-1}$. It offers a large data set of A_T and C_T for the global
1139 ocean and regional biogeochemical studies. It includes more than 44 400 surface and water column observations
1140 in all oceanic basins, in the Mediterranean Sea, in the coastal zones, near coral reefs, and in rivers. For the open
1141 ocean this complements the SOCAT and GLODAP data products (Bakker et al., 2016; Lauvset et al., 2022). For

1142 the coastal sites this also complements the synthesis of coastal time-series only done around North America
 1143 (Fassbender et al., 2018; Jiang et al., 2021; OCADS, 2023).

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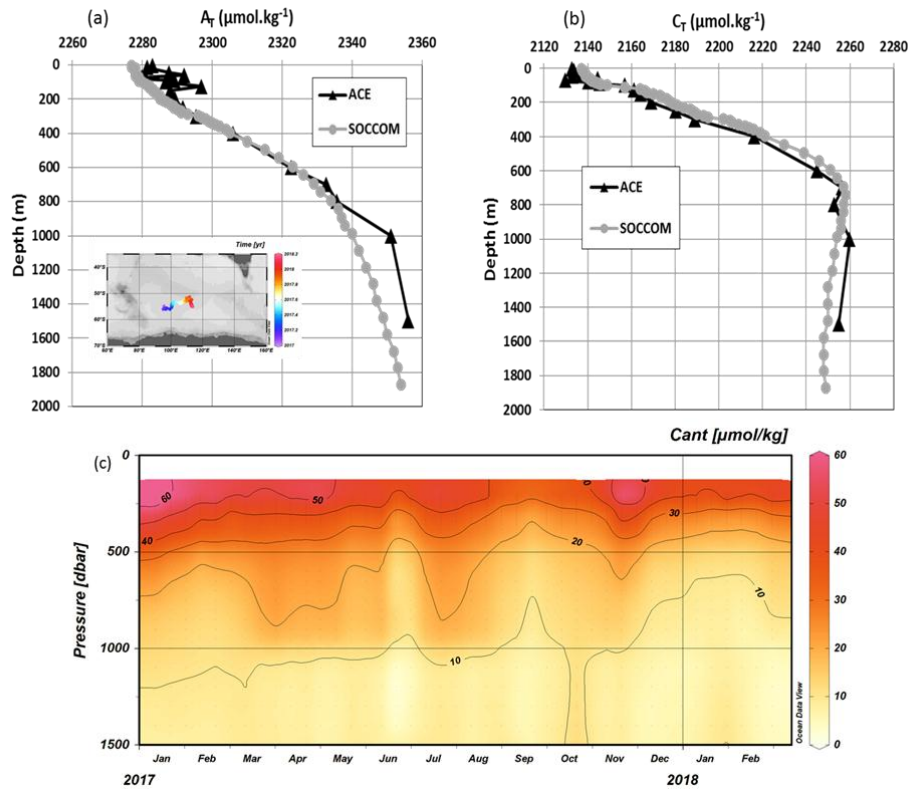
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1164 **Figure 14:** Profiles of (a) A_T ($\mu\text{mol kg}^{-1}$) and (b) C_T ($\mu\text{mol kg}^{-1}$) observed at station ACE-20 (55°S-95°E,
 1165 11/1/17, black triangles) compared with the profiles deduced from the SOCCOM float (WMO code 5905069)
 1166 launched at that location (first data on January 12th 2017, grey circles). The location/drift of the float in 2017-
 1167 2018 is shown on the inserted map. (c) Hovmoller section (Pressure/time) of anthropogenic CO₂ concentrations
 1168 (C_{ant} in $\mu\text{mol kg}^{-1}$) estimated from the float data (A_T , C_T , O_2 , T) below 200m (period January 2017-February
 1169 2018). Section produced with ODV (Schlitzer, 2018).
 1170

1171 The SNAPO-CO₂ dataset enables to investigate seasonal variations to decadal trends of A_T and C_T in
 1172 various oceanic provinces. In regions where data are available for more than 2 decades in surface water (North
 1173 Atlantic, Ligurian Sea, Southern Indian Ocean, and coastal regions), all time-series show an increase in C_T .
 1174 Excepted in the Mediterranean Sea, A_T appears relatively constant over time, although the A_T content present
 1175 significant inter-annual variability such as in the NASPG or in the coastal zones including near the Congo and
 1176 Amazon Rivers plumes.

1177 This dataset represents independent data for validation of reconstructed A_T or C_T fields using various
 1178 methods (e.g. Rödenbeck et al., 2013, 2015; Sauzède et al., 2017; Turk et al., 2017; Bittig et al., 2018; Broullón
 1179 et al., 2019, 2020; Land et al., 2019; Keppler et al., 2020; Fourier et al., 2020; Gregor and Gruber, 2021; Sims et
 1180 al., 2023; Chau et al., 2023). It is also useful to validate Earth System Models (ESM) that currently present bias
 1181 to reproduce the seasonal cycle of C_T and A_T due to inadequate representation of biogeochemical cycles,
 1182 including the coupling of biological and physical processes (e.g. Pilcher et al., 2015; Mongwe et al., 2018;
 1183 Lerner et al., 2021). This should be resolved for confident in future projections of the productivity, ocean
 1184 acidification, and the responses of the marine ecosystems (e.g. Kwiatkowski et al., 2020). Recall that OBGGM or
 1185 ESM models calculate $p\text{CO}_2$ from A_T/C_T pairs and the simulated annual CO₂ flux might be correct when

1186 compared to observations but for wrong reasons (e.g. Goris et al., 2018, Lerner et al., 2021). For example, it has
1187 been shown that biases in A_T in ESM models led to an overestimation of the oceanic fCO_2 trend and thus
1188 uncertainty when predicting the oceanic anthropogenic CO_2 uptake (Lebehot et al., 2019). The simulated
1189 seasonal cycle of fCO_2 is also uncertain in ESM models especially in high latitudes (e.g. Joos et al., 2023). It is
1190 thus important to attempt validating ESM models with A_T and C_T data such as presented in this synthesis.

1191 This dataset would also serve for validating autonomous platforms capable of measuring pH and fCO_2
1192 variables and, along with SOCAT and GLODAP datasets, provides an additional reference dataset for the
1193 development and validation of regional biogeochemical models for simulating air-sea CO_2 fluxes. It is also
1194 essential for training and validating neural networks capable of predicting variables in the carbonate system,
1195 thereby enhancing observations of marine CO_2 at different spatial and temporal scales.

1196 The data presented here are available online on the Seanoë server (Metzl et al., 2023,
1197 <https://doi.org/10.17882/95414>) and is divided in two files: one for the Global Ocean, and one for the
1198 Mediterranean Sea. The sources of the original datasets (doi) with the associated references are listed in the
1199 Supplementary Material (Table S3, S4). We invite the users to comment on any anomaly that would have not
1200 been detected or to suggest potential misqualification of data in the present product (e.g. data probably good
1201 although assigned with flag 3, probably wrong). The SNAPO-CO2 dataset will be regularly updated on Seanoë
1202 data server with new observations controlled and archived.

1203 **8 Data availability**

1205 Data presented in this study are available at Seanoë: <https://www.seanoë.org>, <https://doi.org/10.17882/95414>
1206 (Metzl et al., 2023).

1207
1208 *Author contributions.* NM prepared the data synthesis, the figures and wrote the draft of the manuscript with
1209 contributions from all authors. JF measured the discrete samples since 2014, with the help from CM and CLM,
1210 and prepared the individual reports for each project. NM and JF pre-qualified the discrete A_T/C_T data. CLM and
1211 NM are co-Is of the ongoing OISO project and qualified the underway A_T/C_T data from OISO and CLIM-
1212 EPARSEES cruises. All authors have contributed either to organizing cruises, sample collection and/or data
1213 qualification, and reviewed the manuscript.

1214
1215 *Competing interest.* The authors declare that they have no conflict of interest.

1216
1217 *Acknowledgments.* The A_T and C_T data presented in this study were measured at the SNAPO-CO2 facility
1218 (Service National d'Analyse des Paramètres Océaniques du CO_2) housed by the LOCEAN laboratory and part of
1219 the OSU ECCE Terra at Sorbonne University and INSU/CNRS analytical services. Support by INSU/CNRS, by
1220 OSU ECCE Terra and by LOCEAN, is gratefully acknowledged as well as support by different French "Services
1221 nationaux d'Observations", such as OISO/CARAUS, SOMLIT, PIRATA, SSS and MOOSE. We thank the
1222 research infrastructure ICOS (Integrated Carbon Observation System) France for funding a large part of the
1223 analyses. We thank the French oceanographic fleet ("Flotte océanographique française") for financial and
1224 logistic support for most cruises listed in this synthesis and for the OISO program
1225 (<https://campagnes.flotteoceanographique.fr/series/228/>). We acknowledge the MOOSE program (Mediterranean
1226 Ocean Observing System for the Environment, <https://campagnes.flotteoceanographique.fr/series/235/fr/>)
1227 coordinated by CNRS-INSU and the Research Infrastructure ILICO (CNRS-IFREMER). AWIPEV-CO2 was

1228 supported by the Coastal Observing System for Northern and Arctic Seas (COSYNA), the two Helmholtz large-
1229 scale infrastructure projects ACROSS and MOSES, the French Polar Institute (IPEV) as well as the European
1230 Union's Horizon 2020 research and innovation projects Jericho-Next (No 871153 and 951799), INTAROS (No
1231 727890) and FACE-IT (No 869154). The BOUSSOLE time series project was funded by the Centre National
1232 d'Etudes Spatiales (CNES) and the European Space Agency (ESA ESRIN contract 4000119096/17/I-BG), and
1233 the first three years of the CO₂ time series at that site were funded by the French Agence Nationale de la
1234 Recherche (ANR). The EURECA4-OA cruise was also supported by the EUREC4A-OA JPI Ocean and Climate
1235 program. We thank Tara Ocean Foundation and many institutes and funding agencies for supporting TARA
1236 cruises since 2009. The OISO program was supported by the French institutes INSU (Institut National des
1237 Sciences de l'Univers) and IPEV (Institut Polaire Paul-Emile Victor), OSU Ecce-Terra (at Sorbonne Université),
1238 and the French program SOERE/Great-Gases. The CLIM-EPARSEES cruise was supported by TAAF (Terres
1239 Australes et ANtariques Françaises), Fondation du Prince Albert II de Monaco, IRD, OSU Ecce-Terra, CNRS,
1240 MNHN, LOCEAN and LSCE laboratory. Data from the float launched during the ACE cruise were made freely
1241 available by the Southern Ocean Carbon and Climate Observations and Modeling (SOCCOM) Project funded by
1242 the National Science Foundation, Division of Polar Programs (NSF PLR -1425989), supplemented by NASA,
1243 and by the International Argo Program and the NOAA programs that contribute to it. The Argo Program is part
1244 of the Global Ocean Observing System (<http://doi.org/10.17882/42182>, <http://argo.jcompos.org>). We thank
1245 Frédéric Merceur (IFREMER) for preparing the page and data availability on Seanoe. We thank Patrick
1246 Raimbault (retired, former at MIO, Marseille) for managing the MOOSE project until 2019. We thank all
1247 colleagues and students who participated to the cruises and have carefully collected the precious seawater
1248 samples. We warmly acknowledge our colleague Christian Brunet (retired) for his supportive help for the
1249 analysis since the start of the Service facility SNAPO-CO₂. We would like to pay tribute to our late colleague
1250 Frédéric Diaz who contributed to the LATEX cruise in 2010. We thank the associated editor Xingchen Wang to
1251 manage this manuscript, Marta Álvarez and a (more or less) anonymous reviewer for their suggestions that
1252 helped to improve this article.

1253

1254 **References**

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