1			
2			
3	Technical note: Large offsets between different datasets of sea water		Mis en forme : Police :+Corps (Cambria)
4	isotopic composition:		
5	an illustration of the need to reinforce intercalibration efforts		
6			
7			
8	Gilles Reverdin ¹ , Claire Waelbroeck ¹ , Antje H. L. Voelker ^{2, 3} , Hanno Meyer ⁴		
9			
10			
11			
12 13	¹ <u>Laboratoire LOCEAN/IPSL, Sorbonne Université-CNRS-IRD-MNHN, Paris, 75005.</u> <u>France<mark>LOCEAN, SU/CNRS/IRD/MNHN, Paris, France</mark></u>		
14	² IPMAInstituto Português do Mar e da Atmosfera (IPMA), Algées, Portugal		
15	³ CCMARCenter of Marine Sciences (CCMAR), Universidade do Algarve, Faro, Portugal		
16	⁴ AWI <u>AlfredWegener Institute</u> Potsdam, <u>14473</u> Potsdam, Germany		Mis en forme : Français (France)
17		$\overline{\ }$	Mis en forme : Français (France)
			Mis en forme : Français (France)
18 19	Corresponding author: Gilles Reverdin <u>gilles.reverdin@locean.ipsl.fr</u>	_	Code de champ modifié

_
2
4

20	Abstract	 Mis en forme : Police :+Corps (Cambria)
21	We illustrate offsets in <u>surface</u> seawater isotopic composition between the data sets	
22	presented in two recent studies and the LOCEAN seawater isotopic composition dataset,	
23	as well as other data for the same years and same regions<u>recent</u>, available public data	
24	sets of infrom the Atlantic Ocean and the These comparisons are carried in the surface	
25	waters, for one in the North and South Atlantic, and for the other in the subtropical	
26	South-East Indian Ocean. The observed offsets between data sets <u>-which often</u> exceed	
27	0.10% in $\delta^{18}O$ and 0.50% in $\delta^2H_{\underline{.}}$ They might in part reflect originate from different	 Mis en forme : Police :+Corps (Cambria)
28	<u>sampling of</u> seasonal <u>, interannual</u> or spatial variability. However, , they are rather	
29	systematic, so_ they likely <u>mostly</u> originate_ , at least partially, from different	
30	instrumentations and protocols used to measure the water samples. They need to be	
31	adjustedEstimation of the systematic offsets is required in order to ultimately merge	
32	thebefore merging the different data sets, in order to investigate spatio-temporal	
33	variability of isotopic composition in the world ocean surface waters. This highlights the	
34	need to actively share seawater isotopic composition samples dedicated to specific	
35	intercomparison of data produced in the different laboratories.	

3

38	1. Introduction	_
39	Seawater isotopic composition (180/160 and 2H/1H ratios expressed as δ^{18} 0 and δ^{2} H in	
40	‰ in the VSMOW/SLAP scale) is classified as an Essential Ocean/Climate Variable	
41	(EOV/ECV) in international programs such as GEOTRACES and GO-SHIP. Stable	
42	seawater isotopes (δ^{18} O, δ^{2} H) are used to trace sources of freshwater (precipitation,	
43	evaporation, runoff, melting glaciers, sea ice formation and melting), both at the ocean	
44	surface and in the ocean interior (Schmidt et al., 2007; Hilaire-Marcel et al., 2021).	
45	Except for fractionation during phase changes, the water isotopic composition is nearly	
46	conservative in the ocean.	
47	A major emphasis is on high latitude oceanography <u>. T, where, continental (or iceberg)</u>	
48	glacial melt, formation or melt of sea ice, and high-latitude river inputs (for the Arctic)	
49	leave different imprints on the surface ocean isotopic composition <u>, as well as below the</u>	
50	surface down to 800 m close to ice shelves in the southern ocean , as well as below the	
51	surface down to 800 m close to ice shelves in th southern ocean <u>(Randall-Goodwin et al.</u>,	
52	2015; Biddle et al., 2019, Hennig et al., 2024). In contrast, few studies have been	
53	performed on the isotopic signature in the deep ocean (e.g., Prasanna et al., 2015;	
54	Voelker et al., 2015). Seawater isotopes in the upper ocean at low latitudes are often	
55	vital for paleoclimatic studies, as they are needed to calibrate proxies of past ocean	
56	variability in marine carbonate records such as corals and foraminifera (e.g., PAGES	
57	CoralHydro2k working group; Konecky et al., 2020). Seawater isotopes are also	
58	important tracers in the coastal ocean, with emphasis on upwelling (Conroy et al., 2014,	
59	2017; Kubota et al., 2022; Lao et al., 2022), and river discharges (e.g., Amazon) (Karr and	
60	Showers, 2001). Surface ocean seawater isotopes are also used to characterize	
61	evaporation rates and air-sea interactions (Benetti et al., 2017).	
62	The isotopic signatures of these different processes are evolving in our warming world,	
63	which will imprint on the seawater isotopic composition (Oppo et al., 2007).	
64	Additionally, seawater isotope data provide model boundary conditions and allow the	
65	assessment of model performance in isotope-enabled Earth system models (e.g. Schmidt	
66	et al., 2007; Brady et al., 2019; Cauquoin et al., 2019), thereby improving climate model	

67 projections of the future.

Mis en forme : Police :+Corps (Cambria)

68 Stable seawater isotope data have thus been massively produced in the last decades by a variety of methods. For example, most data compiled in the "GISS Global Seawater 69 70 Oxygen-18 Database -V1.21" for stable seawater isotopes (LeGrande and Schmidt, 2006) 71 originate from Isotope-ratio Mass Spectrometry (IRMS). They were mostly measured in 72 earlier decades by dual-inlet technology (highest precision), whereas, more recently, the 73 continuous-flow method (lower precision) became widespread for seawater isotope 74 analysis. In the last decade, cavity ring-down spectroscopy (CRDS) turned into another 75 commonly used method as it allows parallel measurement of δ^{18} O and δ^{2} H, but with 76 often lower precision, at least early on (e.g., Voelker et al., 2015). 77 Reverdin et al. (2022) recently compiled a mix of data produced by IRMS and CRDS at 78 LOCEAN (https://www.seanoe.org/data/00600/71186/). As CRDS and other laser

techniques (Glaubke et al., 2024) have become more prevalent recently, they contribute
a significant part of the new data produced and thus also to the soon to be released

- 81 CoralHydro2k seawater database for δ^{18} O (δ^{2} H) (focus on the tropics (35°N-35°S);
- 82 Atwood et al., 2024).
- 83 There are potential differences between the data produced by the two methods.
- 84 Typically, CO₂-water or H₂-water equilibration was used for the IRMS measurements
- 85 and yields measurements of the activity of water, which decreases with increasing
- 86 salinity. Furthermore, concentration of divalent cations like Mg⁺⁺ are responsible
- 87 for slight changes in fractionation factors. On the other hand, the laser methods such as
- 88 CRDS evaporate the entire sample. If the samples have not been distilled beforehand,
- 89 there is an issue of salt deposition and of resulting absorption or desorption of water
- 90 with fractionation effects. In the LOCEAN database (Reverdin et al., 2022), an attempt
- 91 was made to adjust the data, based on the analysis of Benetti et al (2017b). This was also
- 92 adopted by at least one other group (Haumann et al., 2022), but overall, there is the
- 93 possibility of an offset of these data with respect to the ones of other groups using CRDS.
- 94 IHowever, it should be noted however that On the other hand, there is some
- 95 <u>evidencesome studies have reportinged that unadjusted δ^{18} 0 measurements from CRDS</u>
- 96 and IRMS technique with CO₂-water equilibration provide data that were
- 97 <u>undistinguishable within instrumental precision (Walker et al., 2016; Hennig et al.,</u>
- 98 <u>2024).</u>

Code de champ modifié

99 It is actually quite common when using water isotope data in studies involving more 100 than one data set, to first evaluate whether there are possible offsets. Intercomparison 101 with earlier data or reference materials was a prerequisite for GEOTRACES sampling 102 campaigns, although for the water isotopes this was, unfortunately, seldomly followed 103 (e.g., Voelker et al., 2015). These intercomparisons often outline systematic differences 104 which could result from the issue outlined above, or from other issues, such as 105 uncertainties in reference materials used, analysis protocols, or isotopic changes in the 106 samples during their handling and storage (Benetti et al., 2017a; Akhoudas et al., 2019; 107 Hennig et al., 2024). In other cases, this was not done, either because the data stood by themselves (Bonne et al., 2019, for $\delta^{18}\text{O}$ and $\delta^{2}\text{H}$ data), or there was no comparison data 108 109 available in the same region (Glaubke et al., 2024, for δ^{18} O data). The possible offsets can 110 however become an issue, when these data are placed in a larger context. For example, 111 Glaubke et al. (2024) identify a large difference in the S- δ^{18} O relationship in the 112 subtropical Indian Ocean between their data in the south-eastern part and other data in 113 the south-western Indian Ocean. They also discuss and question differences in the deep 114 water-masses isotopic values between separate data sets, but as these might also be 115 explained by large uncertainties in these data, we will not address them further.

Using these two examples (Bonne et al., 2019; Glaubke et al., 2024), the aim of this note
is to point out the interest when producing a new data set, of exchanging collected
samples to carry a direct comparison, or, if this was not done, to compare the data with
other published data and evaluate potential systematic differences.

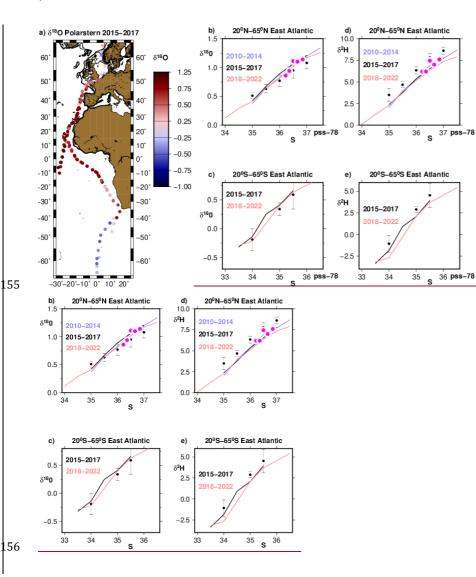
120 2. Comparisons

121 For identifying possible offsets, we consider surface ocean subsets of the LOCEAN data 122 base in specific regions for roughly the same years as the other data collected. The data 123 extracted are from the same regions as in the datasets of the two studies and are 124 gathered in S- δ^{18} O space as well as in S- δ^{2} H space (available only for the Bonne et al 125 (2019) data set), where S is reported as a practical salinity with the practical salinity 126 scale of 1978 (pss). The assumption done here as in many papers is that the S- δ^{18} O 127 relationship holds on fairly large scales in the surface layer (for the eastern subtropical 128 North Atlantic, see for example, the discussion in Voelker et al (2015) and in Benetti et 129 al. (2017a)). Obviously, this has limitations, such as in areas influenced by more than

- 130 one water mass or by multiple freshwater end-members (meteoric, continental run-off, 131 sea ice melt or formation, evaporation). 2.1 Daily surface data collected from R.V. Polarstern 132 133 The surface seawater samples originated from daily collection during two years on 134 board RV Polarstern in 2015-2017 (Bonne et al., 2019). There is no salinity provided 135 with the data, and here we chose to associate them with the simultaneously collected 136 thermosalinograph (TSG) data collected on board the RV Polarstern and available from 137 PANGAEA (for each cruise, an indexed file with title starting by 'Continuous 138 thermosalinograh oceanography along Polarstern' is included in PANGAEA: for example, 139 TSG data for the first cruise (PS90) associated with the isotopic seawater data are found at <u>https://doi.org/10.1594/PANGAEA.858885</u>). The water samples were not collected 140 141 from the same water line and pumping depth as the TSG data, which can result in 142 differences. This is however likely to be small in most circumstances away from large 143 freshwater input at the sea surface, such as from melting sea ice, intense rainfall and 144 river estuaries (Boutin et al., 2016). We also applied an adjustment of +0.25% to the L45 δ^{18} O data of Bonne et al. (2019), based on post-analysis identification of a bias in an internal reference material. 146 147 We then estimate averages of all the data as a function of salinity in two domains 148 extending poleward of the subtropical salinity maximum toward the higher latitudes in 149 the eastern part of the Atlantic Ocean (thus, 20°N to 65°N and the same in the southern 150 hemisphere). This is done by sorting out the data by salinity classes of 0.5. The LOCEAN 151 data until 2016 in the North and tropical Atlantic were presented in Benetti et al 152 (2017a), showing the tightness of the S- δ^{18} O and S- δ^{2} H relationships in vast domains of
- 153 the eastern Atlantic. In the North Atlantic, LOCEAN data have been continuously
- 154 collected since 2011, and south of 10°S in the eastern Atlantic mostly since 2017.

Code de champ modifié

Mis en forme : Police :+Corps (Cambria)



159	Figure 1: Comparison to Bonne et al. (2019). (a) map of RV Polarstern original data set		Mis en forme : Police :+Corps (Cambria)
160	points in eastern Atlantic Ocean east of 30°W. Water isotopes-S scatter diagrams		Mis en forme : Police :+Corps (Cambria)
161	averaged as a function of salinity in 0.5 pss-practical salinity bins (left for δ^{18} 0, and right	_	Mis en forme : Police :+Corps (Cambria)

.63 of 30°W and outside of [20°N, 20°S]. The colored curves represent average relationships of water isotopes in the LOCEAN data base as a function of <u>practical</u> salinity for three .64 .65 different period ranges, whereas the black dots with error bars are the binned averages .66 of the Bonne et al. (2019) RV Polarstern data in 2015-2017 (after adjustment of .67 +0.25‰ to δ_1^{18} O), with the root mean square of the variance reported as error bars. Five individual surface points from Voelker et al (2023) are also plotted (magenta dots). 168 169 The average relationships found in the LOCEAN data set for three periods overlay well 170 in particular in the northern hemisphere. Uncertainties on individual curves (not 171 shown) are estimated based on the scatter of individual data in each salinity bin. They 172 are typically on the order of 0.01-0.02 (0.05-0.10) % for δ^{18} O (δ^{2} H) respectively in the 173 northern hemisphere (top panel), and a little larger for the less sampled southern hemisphere curves in 2015-2017. Sampling is usually also insufficient at the low end of 174 175 the salinity range, to reliably estimate an uncertainty. Thus, these different curves nearly 176 overlay within the sampling uncertainty. Five surface samples that were collected in the 177 Northeast Atlantic during the same years within the same salinity range (Voelker et al., 178 2023), also fit well on the North Atlantic curves. The adjusted δ^{18} O data from Bonne et 179 al. (2019) are slightly shifted downward with respect to the curves (Fig. 1b, c), with the 180 plotted standard deviation of individual data around the average not overlapping the 181 LOCEAN data average curves in most cases for the same years 2015-2017. The situation 182 is opposite for the 35 pss salinity bin in the northern hemisphere, with the adjusted δ^{18} O 183 data from Bonne et al. (2019) being above the three LOCEAN average curves, which 184 might be due to samples collected uniquely in the English Channel and North Sea by RV 185 Polarstern in this salinity range, whereas sampling is more geographically-spread in the 186 LOCEAN data base.

for δ^2 H), top for the northern hemisphere and bottom for the southern hemisphere, east

- AlltogetherAltogether, the average δ¹⁸O offset is small, with the -{LOCEAN data
 above being higher by 0.02 ± 20.01 ‰ than the δ¹⁸O from Bonne et al. (2019)}, which is
 not significantly different from 0 based on the interannual differences witnessed in the
 LOCEAN curves and the scatter/uncertainty in the Polarstern data. A systematic
 difference is, also however, found for δ²H, with LOCEAN data been lower than δ²H from
- Bonne et al. (2019) by 0.99 ± with 0.07% estimated error (Fig. 1d, e).

Mis en forme : Police :+Corps (Cambria)

Mis en forme : Police :+Corps (Cambria)

Mis en forme : Police :+Corps (Cambria) Mis en forme : Police :+Corps (Cambria)

8



195 Glaubke et al. (2024) describe a synthesis of water isotope data in the southern Indian 196 Ocean combining their new dataset in the southeastern Indian Ocean (CROCCA-2S) with 197 earlier data in the south-western Indian Ocean, in particular from LOCEAN, as well as data from the south Australian shelf collected mostly in 2010 (Richardson et al., 2019), 198 199 and in the equatorial Indian Ocean (Kim et al., 2021). In the most recent version of the LOCEAN data set, in addition to data included in Glaubke et al. (2024) for comparison 200 201 and collected mostly west of 80°E, there are two transects with surface data through the 202 southeastern Indian Ocean, one collected in February 2017, and the other in March 203 2024, thus in mid to late austral summer. These transects cross the region covered by 204 the CROCCA-2S data set, albeit not close to west Australia, as well as the area of the 205 Richardson et al. (2019) data set, south of Australia. The LOCEAN data set also contains 206 surface data south of Tasmania (in 2017, as well as in 2020 to 2024). All these data correspond to samples analyzed on a CRDS Picarro L2130 at LOCEAN, and with the 207 208 protocols discussed in Reverdin et al. (2022). The bottles in which the samples were 209 stored were the same for all the samples, and time between collection and analysis 210 varied, but was mostly on the order of 6 months or less. Thus, this is a rather 211 homogeneously produced set of data in for the years 2016-2024, which spatially and 212 temporally overlaps with the data used in Glaubke et al. (2024) collected south of 213 Australia and in the southeastern Indian Ocean (Fig. 2).

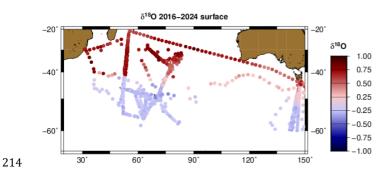


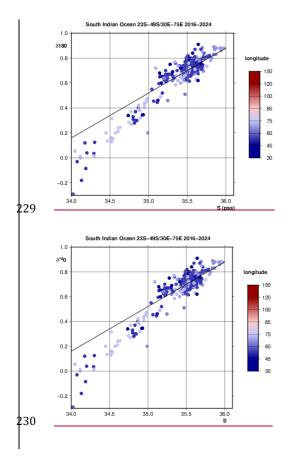
Figure 2: Map of δ^{18} O surface data in the LOCEAN archive for 2016-24, north of 60°S. All these data are associated with S and δ^{2} H data.

1	Mis en forme : Police :+Corps (Cambria)
	Mis en forme : Police :+Corps (Cambria)
-	Mis en forme : Police :+Corps (Cambria)

9

217 The LOCEAN data distribution indicates some scatter in the S- δ^{18} O distribution in the 218 southwestern Indian Ocean (Fig. 3a) for S larger than 35-pss. Data above the regression 219 line on Fig. 3a, established for all data with S between 35 and 36-pss, are present only for 220 S larger than 35.0-pss, and are found north of 28°S and in the far south-western Indian 221 Ocean, but with some remnants found all the way to the core of the subtropical gyre 222 near 75°E/35°S (Fig. 3b). Data below the regression line contain most of the data south 223 of 28°S and east of 60°E and connect the salinity maximum region with the lower 224 salinity south of the <u>S</u>subtropical <u>F</u>front and down to the region south of the <u>P</u>polar 225 **<u>F</u>**front (Fig. 3c). These subtropical lower values in S- δ^{18} O space, which appear in the 226 repeated French OISO cruises (in 1998-2024) at 50°E, albeit not all the time, dominate 227 east of 60°E.

228 a)



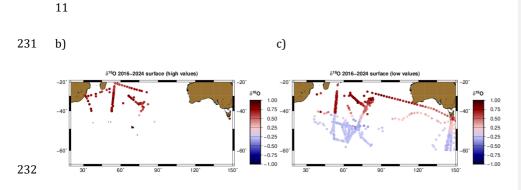


Figure 3: (a) scatter diagram of (S, δ^{18} O) <u>0-30m</u> LOCEAN data within the southwestern region (30-75°E/23-49°S) coloured as a function of longitude, with the regression line of

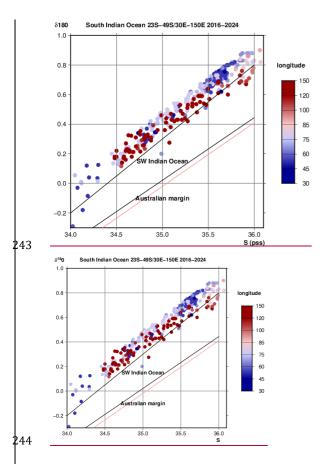
the data having a <u>practical</u> alinity between 35 and 36 pss (black line) overlaid. The

 $\mathbf{2}$ spatial distributions of the LOCEAN data with higher and lower $\delta_{\mathbf{1}}^{18}$ relative to that

- regression line in the whole Indian Ocean north of 60°S are shown on panels (b) and (c),respectively.
- 239 When focusing on the lower part of the distribution in S- δ^{18} O space (Fig. 3c), one
- 240 observes a gradual lowering of δ^{18} O from west to east for salinities above 35 (Fig. 4) all
- 241 the way to 150°E. This lowering is on the order of 0.15 at most, even for the higher
- 242 salinities (35.5 or more) for which it is strongest (Fig. 4).

233

Mis en forme : Police :+Corps (Cambria)	
Mis en forme : Police :+Corps (Cambria)	
Mis en forme : Police :+Corps (Cambria)	
Mis en forme : Police :+Corps (Cambria)	



245	Figure 4: The <u>0-30m</u> LOCEAN data below the regression line of Fig. 3a (the ones mapped
246	in Fig. 3c) in S- δ_{18}^{18} O space, color-coded as a function of longitude. The two linear
247	relationships for the 0-100m layer recommended in this region between 23°S and 49°S
248	by Glaubke et al. (2024) for the south-west Indian Ocean and for the Australian margin
249	(south of Australia) (we use the original <u>relation</u> δ_1^{18} 0 = 0.4231 * S - 14.7876, instead of
250	the rounded-up relation reported in the paper; R. H. Glaubke, pers. <u>c</u> omm., 2024) are
251	also plotted (black lines), as well as the earlier linear relationship for the 0-600m layer
252	along the Australian margin by Richardson et al. (2018) (in pink).
253	Thus, besides some gradual and smaller changes, we do not observe in the LOCEAN
254	surface dataset a large sudden change in the (S, δ^{18} O) distribution near 75°E or 85°E

 $255 \qquad between the southeastern and southwestern Indian Ocean, nor a further strong change$

Mis en forme : Police :+Corps (Cambria) Mis en forme : Police :+Corps (Cambria)

Mis en forme : Police :+Corps (Cambria)

256	closer to the Australian coastal margin, as suggested by figures 6 and 7 of Glaubke et al.
257	(2024). Most of the LOCEAN (S, $\delta^{18}\text{O}$) data south of 28°S correspond to the mixing of a
258	low salinity end-member characteristic of the fresh waters of the Southern Ocean (at S <
259	34- pss) with waters which are imprinted by air-sea exchange of water in a wider range
260	of values at S > 36-pss, as discussed in Glaubke et al (2024). These LOCEAN (S, δ^{18} O)
261	values are significantly above the linear relationships proposed by Glaubke et al. (2024).
262	This positive excess offset seems to be by about 0.15‰ in the southwestern Indian
263	Ocean, but close to 0.50‰, in particular for the Australian coastal margins, although but
264	for which we could not access the individual data for that latter region. This ese offsets
265	are is certainly much larger than the scatter present in the LOCEAN data, which is of the
266	order of $1000000000000000000000000000000000000$
267	secondary low salinity end member at S < 35 $\frac{1}{1000}$ with heavier isotopic composition,
268	contributing to the water mass properties in the far southwestern Indian Ocean as well
269	as for the area sampled between 20°S and 28°S north of the subtropical salinity
270	maximum. This could be a contribution of the Indonesian Through Flow and tropical
271	western Indian Ocean surface waters, as discussed by Kim et al. (2021) and Glaubke et
272	al. (2024). We could not carry out a comparable comparison for $\delta^2 H$ which is not
273	presented in Glaubke et al. (2024), and with which exhibits a too large scatter in the δ^2 H
274	data of the CROCCA-2S data set to reach a firm conclusionude.

275 3. Discussion

- 276 In the two cases, we find significantIn the two comparisons of surface data presented in
- 277 this note, we find significant differences. Do theyse differences originate from
- 278 graphispatio-temporal variability or from systematic offsets?

279 -differences between the data sets compared. In the case of the RV Polarstern dataset 280 (Bonne et al., 2019), an error in a specified reference material value was found after the 281 <u>publication</u>, and the adjusted data present only <u>a</u> small<u>, non-significant δ^{18} O negative</u> 282 offsets with respect to LOCEAN data, that are slightly negative but a significant positive 283 <u>δ²H offset for δ¹⁸O and slightly positive for δ²H with respect to LOCEAN data</u>. Differences 284 might arise from spatial differences. For example, in the northern hemisphere, values at 285 salinity close to 35 pss mostly originate from the North Sea and English Channel in the 286 Polarstern dataset, thus with more mid-latitude continental influence than for most of

Mis en forme : Police :(Par défaut) Symbol Mis en forme : Exposant

Commenté [MOU1]: Not sure this is the correct word here. Geophysical would be related to seismic, magnetic etc. changes. Do you may be mean geographical? the LOCEAN data in the same salinity range which have a contribution of more depleted
subpolar and polar freshwater. One expects a larger scatter in the South Atlantic for
salinities less than 35-pss, due to intermittent presence of sea ice or iceberg melt, and at
higher salinities due to the presence of different water masses originating from the

South Atlantic and southeastern Indian Ocean. However, the current data set is notsufficient to estimate it.

293 Furthermore, different seasons were sampled in the two datasets. In the northeastern 294 Atlantic sector, Bonne et al. (2019) surface data east of 30°W were collected in in April 295 and November north of 10°S and in November south of 10°S in the southeastern 296 Atlantic. These data do not suggest large seasonal differences in the Northeast Atlantic, 297 concurring with the LOCEAN (S, δ^{18} O) data in the tropics to mid-latitudes (20 to 50°N), 298 which are tightly distributed along a mean S- δ^{18} O relationship, and thus with low 299 seasonal variability (Benetti et al., 2017a; Voelker et al., 2015). The LOCEAN data are 300 not numerous enough in the South-East Atlantic to further evaluate whether the offset is 301 constant throughout the data set, or presents there a component related to geophysical 302 geographical temporal or spatial variability.

When considering <u>ForTo investigateing</u> the South Indian Ocean <u>sea water isotopic</u>
composition, Glaubke et al. (2024) combined data sets that were processed in different
institutes_{r-and pP}otential offsets between those could <u>thus</u> cause <u>the differences</u>
inapparent spatial variability. In particular, Glaubke et al. (2024) outline large spatial
contrasts in the S-δ¹⁸O relationship across the surface subtropical Indian Ocean and
southern Australia that are <u>not observedat least a factor two smaller</u> in the recent
version of the LOCEAN database.

310 Seasonal or interannual variability might also contribute to the differences shown on 311 Fig. 3, as the data in the southeastern Indian Ocean from Glaubke et al. (2024) were 312 collected in November-December, whereas the data in the LOCEAN database in this 313 region are mostly from February-March. However, at least south of Tasmania, where the 314 LOCEAN data base also contains December data, it does not seem that the seasonal cycle 315 would cause differences larger than 0.05 ‰ at the same salinity. A difference due 316 to seasonality is would be thus be barely identifiable therein that case, noting the 317 possible presence of interannual variability and that 0.05 % is the long-term accuracy

Commenté [UMO2]: "much smaller" is a bit vague. If the spatial contrast found in the LOCEAN database is not significant, it's worth saying so.

318 in the analyses in some centers, such as AWI Potsdam and LOCEAN, is 0.05 %. 319 Richardson et al. (2018) also commented that south of Australia there was little 320 difference between a southern winter cruise and late summer (March) data south of 321 Australia. Further west, near 55-70°E, earlier surface data in the OISO surveys, as well as 322 the vertical upper profiles of OISO station data also suggest a rather modest seasonal 323 variability on the order of 0.10‰. Changes could also arise from interannual variability, 324 but the range of interannual variability in the LOCEAN data base is smaller than the 325 difference between the Glaubke et al (2024) curves for the southeastern Indian Ocean 326 and south of Australia and the corresponding LOCEAN data. Thus, a likely contribution \$27 forcause of the large differences between the South Indian Ocean/Australia margin data 328 combined in the Glaubke et al. (2024) study would be the existence of is the existence of 329 systematic offsets between the South Indian Ocean/Australia margin data produced in 330 three-different institutes that were combined in the Glaubke et al. (2024) study. 331 4. Conclusions 332 What these two comparisons suggest is that offsets are present between different recent 333 data sets published, which exceed 0.10% in δ^{18} O and 0.50% in δ^{2} H, thus larger than the 334 target long-term accuracy of analyses in individual isotopic laboratories. Moreover, 335 errors in reference material values are always possible and require some post-analysis 336 intercomparisons, such as the one that led to the correction of the RV Polarstern Bonne 337 et al. (2019) data set. Furthermore, one contribution to a systematic difference between 338 the LOCEAN data set and data from other institutes is that the LOCEAN data are 339 reported in <u>'freshwater'</u> concentration scale (Benetti et al., 2017b), thus equivalent to 340 'freshwater']. The use of thise concentration scale corrects possible effects of salt in the 341 water activity measured by IRMS with CO2-equilibration and the effect of salt 342 accumulation during evaporation in laser spectroscopy, which both can lead to 343 fractionation, possibly of similar magnitude (Walker et al., 2016). Different comparisons

- 344 based on duplicates collected during cruises suggest that this is a main cause of
- 345 difference between LOCEAN data and other data sets (LOCEAN δ^{18} O data been more
- 346 positive). Poor conservation of the samples during storage, analytical protocols, or
- 347 uncertainties in the specified values of reference material are other sources of
- 348 differences between data produced in different institutes.

Mis en forme : Indice

349	The methods to carry the<u>for</u>-intercompari<u>sonng</u>s and detect <u>ing</u> systematic differences		
350	offsets between different data sets are not numerous. On one hand, one could compare		
351	values obtained in specific water masses, for which we expect little variability of the		
352	water isotopic composition. This is often used, but such data are not always available,		
353	and the resulting uncertainties are difficult to assess <u>, although data sets with deep data</u>		
354	in the Southern Ocean might be used to test use the is approach. One could also develop a		
355	method based on the systematic comparison of nearby data, as is suggested in Fig. 1		
356	when comparing the S-water isotopes surface distribution in the North and South		
357	Atlantic in the LOCEAN and the RV Polarstern (Bonne et al., 2019) data sets. This could		
358	be further improved, but requires that there are enough overlapping data within regions		
359	of relatively homogeneous signals.		
360			
361	As the data density is not always sufficient, these approaches may fail. Thus, an		
362	important alternative-complementary approach is to actively share well-preserved		
363	water samples, distributed quickly, and dedicated to specific intercomparison of data		
364	produced in the different laboratories, building on previous efforts for $\delta^{13}\mbox{C-DIC}$ (Cheng		
365	et al., 2019). This, together with establishing well-accepted systematic guidelines for		
366	data production and quality control, and enhancing scientific exchange between the		
367	different institutes needs to be actively pursued, in order to reduce the errors when		
368	merging different datasets and increase the potential use of the water isotope data as		
369	EOV/ECCVs. This approach is recommended by the recently established working group		
370	MASIS (Towards best practices for Measuring and Archiving Stable Isotopes in Seawater) of	\sim	Mis
371	the Scientific Committee of Oeceanic Research (SCOR). Without this effortsuch direct		Mis (Rom
372	intercomparison of samples, the usefulness of the isotopic data for different		Mis
373	oceanographic and climate studies is strongly reduced, for example resulting in large		
374	uncertainties when establishing different S- $\delta^{18}O$ (or S- $\delta^{2}H$) relationships to validate		
375	studies of proxies to support paleo-climate reconstructions.		
376			
377	Data availability		

- 378 The LOCEAN data are available at <u>https://www.seanoe.org/data/00600/71186/.</u>
- The isotopic data of the Bonne et al. (2019) are available as inidicated in the paper, with
- here S added from the PANGAEA archive, as described in the text-from the PANGAEA
- archive. The Glaubke et al. (2024) data are available as described in the paper. However,

Mis en forme : Police :(Par défaut) Times New Roman Mis en forme : Police :(Par défaut) Times New Roman, 12 pt

lis en forme : Police :(Par défaut) Times New Roman

Code de champ modifié

382	among the data used in this paper, we could not access the data from the Richardson et	
383	al. (2019) paper.	
384		
385	Author contribution: GR initiated the study and prepared the manuscript with	
386	contributions from all coauthors. AV initiated the intercomparison effort, and AV, CW,	
387	and HM contributed to editing the paper. HM was also responsible from producing the	
388	data in the Bonne et <u>a</u> l. (2019) paper.	
389		
390	Competing interests: The authors declare that they have no conflict of interest.	
391		
392	Acknowledgments	
393	The LOCEAN isotopic laboratory is supported by OSU Ecce Terra of Sorbonne Université.	
394	We are thankful to Catherine Pierre and Jérôme Demange who have set and help run the	
395	facility, such as, and for Aïcha Naamar, Marion Benetti and Camille Akhoudas to have	
396	measured some of the water samples. We are grateful for support by INSU. Nicolas Metzl	
397	and Claire Lo Monaco for samples during the OISO cruises on RV MD2 , and, by IPEV	
398	during the SOCISSE program on RV Astrolabe, with on board support by Patrice Bretel	
399	and Rémi Foletto, and by IPSL for supporting the LOCEAN data base and	
400	<u>intercomparisons</u> . A <u>ntje-</u> Voelker thanks J <u>oanna</u> - Waniek (IOW, Germany) for collecting	
401	the NE Atlantic water samples and R <u>obert</u> - van Geldern (GeoZentrum Nordbayern,	
402	Germany) for analyzing them. She, also, acknowledges financial support by Fundação	
403	para a Ciência e a Tecnologia (FCT) through projects Centro de Ciências do Mar do	
404	Algarve (CCMAR) basic funding UIDB/04326/2020	
405	(<u>https://doi.org/10.54499/UIDB/04326/2020</u>) and programmatic funding	Code de champ modifié
406	UIDP/04326/2020 (https://doi.org/10.54499/UIDP/04326/2020) and the CIMAR	
407	associated laboratory funding LA/P/0101/2020	
408	(<u>https://doi.org/10.54499/LA/P/0101/2020</u>). The RV Polarstern data set was funded	Code de champ modifié
409	by the AWI Strategy Fund Project ISOARC. Comments by Alexander Haumann were very	
410	helpful.	
411		

412 References

Mis en forme : Police :+Corps (Cambria)

13	Aoki, S., Kobayashi, R., Rintoul, SR., et al. : Changes in water properties and flow regime			
14	on the continental shelf off the Adélie/George V Land coast, East Antarctica, after glacier			
15	tongue calving, J. Geophys. Res.: Oceans, 122, 6277-6294, 2017.			
16	Akhoudas, C. H., Sallée, JB., Haumann, FA., Meredith, MP., Garabato, AN., Reverdin,			
17	G.,. Jullion, L., Aloisi, G., Benetti, M., Leng, M.J., and Arrowsmith, C.: Ventilation of the			
18	abyss in the Atlantic sector of the Southern Ocean, Nature scientific reports, 11 , 16733,			
ł19	https://doi.org/10.1038/s41598-021-95949-w, 2020, 2021.			
120	Atwood, A. R., Moore, A.L., Long, S., Pauly, R., DeLong, K., Wagner, A., and Hargreaves, J.A.:		Mis en forme	
121				
122	10.22498/pages.32.1.59, 2024.	$\langle \rangle$	Code de char Mis en forme	
123	Benetti, M., Reverdin, G., Aloisi, G., <u>and Sveinbjörnsdóttir, A.: Stable isotopes in surface</u>	$\langle \rangle$	Mis en forme	
124	waters of the Atlantic Ocean: indicators of ocean-atmosphere water fluxes and oceanic		Mis en forme	
125	mixing processes. J. Geophys. Res. Oceans, doi:10.1002/2017JC012712, 2017a.			
126	Benetti, M., Sveinbjörnsdóttir, A. E., Ólafsdóttir, R., Leng, M. <u>.</u> J., Arrowsmith, C., Debondt,			
127	K., Fripiat, F., and Aloisi, G.:- Inter-comparison of salt effect correction for δ_1^{18} O and δ_2^2 H	_	Mis en forme	
128	measurements in seawater by CRDS and IRMS using the gas-H2O equilibration method,		Mis en forme	
129				
130	Biddle, L. C., Loose, B., and Heywood, K. J.: Upper ocean distribution of glacial meltwater	_	Mis en forme	
131	in the Amundsen Sea, Antarctica. J. Geophys. Res. Oceans, 10.1029/2019JC015133. et al.,	$\overline{\ }$	Mis en forme (États-Unis)	
132			Mis en forme	
133	Bonne, JL., Behrens, M. Meyer, H., Kipfstuhl, S., Rabe, B., Schönicke, L., Steen-Larsen, H.		L	
134	C., Werner, M.: Resolving the controls of water vapour isotopes in the Atlantic sector.			
135	Nature Communications-Comm. 10, 1632, doi: 10.1038/s41467-019-09242-6, 2017.		Code de char	
136	Boutin, J., Chao, Y., Asher, W. E., Delcroix, T., Drucker, D., et al.: Satellite and In Situ	\square	Mis en forme	
137	Salinity: Understanding Near-Surface Stratification and Subfootprint Variability. Bull. of	$\langle \rangle$	Mis en forme	
138	the Amer. Meteor. Soc., 97 (8), pp.1391-1407. 10.1175/BAMS-D-15-00032.1, 2016.	$\left\ \right\ $	Mis en forme	
139	Brady, E, Stevenson, S., Bailey, D., Liu, Z., Noone, D., Nusbaumer, J., Otto-Bliesner, BL.,		Mis en forme Mis en forme	
		/		

- Tabor, C., Thomas, R., Wong, T., Zhang, J., Zhu, J.:The connected isotopic water cycle in
- the Community Earth System Model Version 1, J. Adv. Model. Earth Syst., 11, 8,
- 442 https://doi.org/10.1029/2019MS001663, 2019.
- 43 Cauquoin, A., Werner, M., Lohmann, G.: Water isotopes climate relationships for the
- 44 mid-holocene and preindustrial period simulated with an isotope-enabled version of
- 445 MPI-ESM, Clim. Past 15, 1913-1937, https://doi.org/10.5194/cp-15-1913-2019, 2019.

Mis en forme : Police :+Corps (Cambria)		
Mis en forme : Police :+Corps (Cambria)		
Mis en forme : Police :+Corps (Cambria)		
Code de champ modifié		
Mis en forme : Police :+Corps (Cambria)		
Mis en forme : Police :+Corps (Cambria)		
Mis en forme : Police :+Corps (Cambria)		

Mis en forme : Police :+Corps (Cambria)
Mis en forme : Police :+Corps (Cambria)
Mis en forme : Police :+Corps (Cambria)
Mis en forme : Police :+Corps (Cambria)
Mis en forme : Police :+Corps (Cambria), Anglais (États-Unis)
Mis en forme : Police :+Corps (Cambria)

Co	de de champ modifié
Mis	s en forme : Police :+Corps (Cambria)
Mis	s en forme : Police :+Corps (Cambria)
Mis	s en forme : Police :+Corps (Cambria)
Mis	s en forme : Anglais (États-Unis)
Mis	s en forme : Anglais (États-Unis)
Mis	s en forme : Anglais (États-Unis)
Mis	s en forme : Police :+Corps (Cambria)

446 Cheng, L., Normandeau, C., Bowden, R., Doucett, R., Gallagher, B., Gillikin, D.-P., 47 Kumamoto, Y., McKay, J.-L., Middlestead, P., Ninnemann, U., Nothaft, D., Dubinina, E.-O., 48 Quay, P., Reverdin, G., Shirai, K., Mørkved, P. T., Theiling, B.P., van Geldern, R., and 449 Wallace, D. W. R.: An international intercomparison of stable carbon isotope composition measurements of dissolved inorganic carbon in seawater, Limnology and 450 Oceanography: Methods 17, 200-209, https://doi.org/10.1002/lom3.10300, 2019. 451 452 Glaubke, R. H., Wagner, A., and Sikes, E. L.: Characterizing the stable oxygen isotopic 453 composition of the southeast Indian Ocean, Marine Chemistry, 262, 454 https://doi.org/10.1016/j.marchem.2024.104397, 2024. 455 Haumann, F. A. et al. : [Data set], Zenodo, doi:10.5281/zenodo.1494915, 2019. 456 Hennig, A., Mucciarone, D.-A., Jacobs, S.-S., Mortlock, R.-A., and Dunbar, R.-B.:Meteoric 457 water and glacial meltwater in the southeastern Amundsen Sea: a time series from 1994 458 to 2020, The cryosphere, 18, 791-818, https://doi.org/10.519/tc-18-791-2024, 2024. 459 Hilaire-Marcel, C., Kim, S.T., Landais, A., Ghosh, P., Assonov, S., Lécuyer, C., Blanchard, M., 160 Meijer, H.-A., and Steen-Larsen, H.-C.: A stable isotope toolbox for water and inorganic 461 carbon cycle studies, Nature Reviews Earth & Environment 2 (10), 699-719, 2021. 162 Kim, Y., Rho, T., and Kang, D.-J.: Oxygen isotope composition of seawater and salinity in 463 the western Indian Ocean: Implications for water mass mixing, Mar. Chem. 237, 104035, 164 https://doi.org/10.1016/j.marchem.2021.104035, 2021. Konecky, B._L. et al.: The Iso2k database: a global compilation of paleo- δ^{18} O and δ^{2} H 465 466 records to aid understanding of Common Era climate, Earth Syst. Sci. Data, 12, 2261-2288, https://doi.org/10.5194/essd-12-2261-2020, 2020. 467 468 Kumar, P._K., Singh, A., and Ramesh, R.: Convective mixing and transport of the Bay of 469 Bengal water stir the δ_{18}^{18} O-salinity relation in the Arabian Sea., J. Mar. Sys. 238, 103842, 470 https://doi.org/10.1016/j.jmarsys.2022.103842, 2023. 471 LeGrande, A._N. and Schmidt, G._A.: Global gridded data set of the oxygen isotopic 472 composition in seawater, Geophys. Res. Lett. 33, 473 https://doi.org/10.1029/2006gl026011, 2006. Oppo, D._W., Schmidt, G._A., and LeGrande, A._N.: Seawater isotope constraints on tropical 474 475 hydrology during the Holocene, Geophys. Res. Lett. 34, L13701, https://doi.org/10.1029/2007GL030017, 2007. 476

Mis en forme : Police :+Corps (Cambria) Mis en forme : Police :+Corps (Cambria)

-	Mis en forme : Police :+Corps (Cambria)						
-	Mis en forme : Police :+Corps (Cambria)						
	Mis en forme : Police :+Corps (Cambria), Anglais (États-Unis)						

Code de champ modifié

Mis en forme : Police :+Corps (Cambria), Anglais (États-Unis) Mis en forme : Police :+Corps (Cambria) Mis en forme : Police :+Corps (Cambria), Anglais (États-Unis)

Mis en forme : Police :+Corps (Cambria)

Code de champ modifié				
Mis en forme : Police :+Corps (Cambria)				
Mis en forme : Police :+Corps (Cambria)				
Mis en forme : Police :+Corps (Cambria)				
Mis en forme : Police :+Corps (Cambria)				
Mis en forme : Police :+Corps (Cambria)				
Mis en forme : Police :+Corps (Cambria)				
Code de champ modifié				
Mis en forme : Police :+Corps (Cambria)				
Mis en forme : Police :+Corps (Cambria)				
Mis en forme : Police :+Corps (Cambria)				
Code de champ modifié				
Mis en forme : Police :+Corps (Cambria)				
Mis en forme : Police :+Corps (Cambria)				
Mis en forme : Police :+Corps (Cambria)				

477	Randall-Goodwin, E., Meredith, M. P., Jenkins, A., Yager, P. L., Sherrell, R. M., Abrahamsen, 🗲	(Mis en forme : Interligne : 1,5 ligne
478	<u>E. P., Guerrero, R., Yuan, X., Mortlock, R. A., Gavahan, K., Alderkamp, AC., Ducklow, H.,</u>		
479	Robertson, R., and Stammerjohn, S. E.: Freshwater distributions and water mass		
480	structure in the Amundsen Sea polynya region, Antarctica. Elementa: Science of the		Mis en forme : Police :Non Italique, Anglais
481	Anthropocene, 3: 000065, https://doi.org/10.12952/journal.elementa.000065, 2015,		(États-Unis) Mis en forme : Anglais (États-Unis)
482			Code de champ modifié
483	Reverdin, G., et al.: The CISE-LOCEAN sea water isotopic database (1998-2021), Earth		Mis en forme : Anglais (États-Unis)
			Mis en forme : Anglais (États-Unis)
484	sci. sys. data, https://doi.org/10.5194/essd-2022-34, 2022.		Mis en forme : Police :+Corps (Cambria)
485	Richardson, LE., Middleton, JF., Kyser, TK., James, NP., and Opdyke, BN.: Shallow		Code de champ modifié
486	water masses and their connectivity along the southern Australian continental margin,		Mis en forme : Police :+Corps (Cambria)
487	Deep Sea Res. I, Oceanogr. Res. Pap. 152, 103083,)/	Mis en forme : Police :+Corps (Cambria)
488	http://doi.0rg/10.1016/j.dsr.2019.103083, 2019.) (Mis en forme : Police :+Corps (Cambria)
			Code de champ modifié
489	Schmidt, GA., LeGrande, AN., and Hoffmann, G.: Water isotope expressions of intrinsic		Mis en forme : Police :+Corps (Cambria)
490	and forced variability in a coupled ocean-atmosphere model, J. Geophys. Res. 112,		Mis en forme : Police :+Corps (Cambria)
491	D10103, https://doi.org/10.1029/2006jd007781, 2007.	\mathbb{N}	Mis en forme : Police :+Corps (Cambria)
492	Voelker, A., Colman, A., Olack, G., Waniek, J.J., and Hodell, D.: Oxygen and hydrogen		Mis en forme : Police :+Corps (Cambria), Anglais (États-Unis)
493	isotope signatures of Northeast Atlantic water masses, Deep-Sea Res. II, 116, 89-106.	Ý	Mis en forme : Police :+Corps (Cambria)
494	https://doi.org/10.1016/j.dsr2.2014.11.006, 2015.		Code de champ modifié
495	Voelker, AH.: Seawater oxygen and hydrogen stable isotope data from the upper water	\square	Mis en forme : Police :+Corps (Cambria), Non souligné, Couleur de police : Automatique
496	column in the North Atlantic Ocean (unpublished data). Interdisciplinary Earth Data		Mis en forme : Police :+Corps (Cambria), Non
497	Alliance (IEDA), https://doi.org/10.26022/IEDA/112743, 2023,		souligné, Couleur de police : Automatique
498	Walker, S. A., Azetsu-Scott, K., Normandeau, C., Kelly, D. E., Friedrich, R., Newton, R.,		Mis en forme : Police :+Corps (Cambria)
			Code de champ modifié
499	Schlosser, P., McKay, JL. Abdi, W., Kerrigan, E., Craig, SE., and Wallace, DWR.: Oxygen	- // (Mis en forme : Police :+Corps (Cambria)
500	isotope measurement of seawater ($H_2^{18}O/H_2^{16}O$). A comparison of cavity ring-down)(Mis en forme : Police :+Corps (Cambria)
501	spectroscopy (CRDS) and isotope ratio mass spectrometry (IRMS), Limnol. and	(Mis en forme : Police :+Corps (Cambria)
502	Oceanography: Methods, 14, 31-38, https://doi.org/10.1002/lom3.10067, 2016.		