Open Access

Earth System

Science

Data

Discussions

The CISE-LOCEAN sea water isotopic database (1998-2021)

Gilles Reverdin[1], Claire Waelbroeck[1], Catherine Pierre[1], Camille Akhoudas[1], Giovanni Aloisi[2], Marion Benetti[1], Bernard Bourlès[3], Magnus Danielsen[4], Jérôme Demange[1], Denis Diverrès[3], Jean-Claude Gascard[1], Marie-Noëlle Houssais[1], Hervé Le Goff[1], Pascale Lherminier[5], Claire Lo Monaco[1], Herlé Mercier[5], Nicolas Metzl[1], Simon Morisset[6], Aïcha Naamar[1], Thierry Reynaud[5], Jean-Baptiste Sallée[1], Virginie Thierry[5], Susan E. Hartman[7], Edward W. Mawji[7], Solveig Olafsdottir[4], Torsten Kanzow[8], Antje Voelker[9,10], Igor Yashayaev[11]

1 Sorbonne University, LOCEAN - IPSL, CNRS–IRD–MNHN, Paris, France

2 Université de Paris, Institut de Physique du Globe de Paris, CNRS, 75005 Paris, France

3 UMS IMAGO, IRD, Plouzané, France

4 Marine and Fresh Water Institute, Iceland

5 University of Brest, LOPS, IUEM, UBO–CNRS–IRD–Ifremer, Plouzané, France

6 Amundsen Science, Québec, Canada

7 National Oceanogaphy Center, Southampton, UK

8 MARUM/Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany

9 Instituto Português do Mar e da Atmosfera, Lisbon, Portugal

10 Centro de Ciencias do Mar, Faro, Portugal

11 Bedford Institute of Oceanogaphy, Dartmouth, Nova Scotia Canada

Corresponding author: Gilles Reverdin, gilles.reverdin@locean.ipsl.fr

1 Abstract
2 The characteristics of the CISE-LOCEAN sea water isotope data set (δ^{18}O, δ^2H, later designed
3 as δD) are presented. This data set covers the time period from 1998 to 2021 and currently
4 includes close to 8000 data entries, all with δ^{18}O, three quarters of them also with δD, associated
5 with a time and space stamp and usually a salinity measurement. Until 2010, samples were
6 analysed by isotopic ratio mass spectrometry, and since then mostly by cavity ring-down
7 spectroscopy (CRDS). Instrumental uncertainty on individual data in this dataset is usually with
8 a standard deviation as low as 0.03 / 0.15‰ for δ^{18}O and δD. An additional uncertainty is related
9 to uncertain isotopic composition of the in-house standards that are used to convert daily data
10 into the VSMOW scale. Different comparisons suggest that since 2010 the latter have remained
11 within at most 0.03/0.20‰ for δ^{18}O and δD. Therefore, combining the two suggests a
12 standard deviation of at most 0.05 / 0.25‰ for δ^{18}O / δD.
13 Finally, for some samples, we find that there has been evaporation during collection and
14 storage, requiring adjustment of the isotopic data produced by CRDS, based on d-excess. This
15 adds an uncertainty on the adjusted data of roughly 0.05 / 0.10‰ on δ^{18}O and δD. This issue of
16 conservation of samples is certainly a strong source of quality loss for parts of the database, and
17 'small' effects may have remained undetected.
18 The internal consistency of the database can be tested for subsets of the dataset, when time
19 series can be obtained (such as in the southern Indian Ocean or North Atlantic subpolar gyre).
20 These comparisons suggest that the overall uncertainty of the spatially (for a cruise) or
21 temporally (over a year) averaged data is on the order of or less than 0.03 / 0.15‰ for δ^{18}O /
22 δD. On the other hand, 17 comparisons with duplicate sea water data analysed in other
23 laboratories or with other data sets in deep regions suggest a larger scatter. When averaging the
24 17 comparisons done for δ^{18}O, we find a difference close to the adjustment applied at LOCEAN
25 to convert salty water data from the activity to the concentration scale. Such a difference is
26 expected, but the scatter found suggests that care is needed when merging datasets from
27 different laboratories. Examples of time series in the surface North Atlantic subpolar gyre
28 illustrate the temporal changes in water isotope composition that can be detected with a
29 carefully validated dataset.
30

1. Introduction

Stable isotope analyses of ocean water (δ^{18}O, δ^2H later designed as δD) were first discussed by Craig and Gordon (1965) as tracers of water masses, and of the different components of the global hydrological cycle, in particular the signals gained through evaporation, precipitation, the interaction with sea ice, and continental water inputs, for example from the ice caps of Greenland and Antarctica, and ice shelves. Sea water stable isotopes have been used to verify ocean model circulation and characterize processes controlling their spatial variability (Xu et al., 2012). Sea water isotopes have also been used to provide information on what controls the oxygen isotopic ratio of calcite plankton shells, in order to reconstruct past ocean salinity and circulation. The GEOSECS program (Östlund et al., 1987) provided the first consistent global dataset of sea water isotopes, but with a limited data coverage. The Global Seawater Oxygen-18 Database at GISS (Schmidt et al, 1999) has assembled most water isotope data collected prior to 1998, with an effort to homogenize the dataset, when possible, by estimating biases based on multiple measurements of deep-water samples (Schmidt, 1999; Bigg and Rohling, 1999). A large part of the early analyses was done by isotope ratio mass spectrometry (IRMS) and more recently using cavity ring-down spectrometry (CRDS). Walker et al. (2016) illustrated that the two measurement techniques can provide equivalent results with no obvious biases.

Since 1998, the CISE-LOCEAN isotopic platform facility has measured sea water isotopic composition of samples collected on a series of oceanographic cruises or ships of opportunity, mostly in the North Atlantic, in the equatorial Atlantic, in the southern Indian Ocean and Southern Ocean. This LOCEAN data set of the oxygen and hydrogen isotopes (δ^{18}O and δD) of marine water covers the period 1998 to 2021, and is ongoing. Most data prior to 2010 (only δ^{18}O) were produced using an Isoprime IRMS coupled with a Multiprep system (dual inlet method), whereas most data since 2010 (and a few earlier data) were obtained by CRDS, usually with a Picarro L2130-i, or less commonly on a Picarro L2120-i. Occasionally, some data were also run on an Isoprime IRMS coupled to a GasBench (dual inlet method) at the university of Iceland (Reykjavik). There are also a few pairs of samples measured on both systems. Most of these LOCEAN data are not currently included in the Global Seawater Oxygen-18 Database at GISS (Schmidt, Bigg and Roehling, 1999), except for the 1998 OISO cruise data (NB: earlier datasets measured by co-author C. Pierre on other mass spectrometers preceding the current IRMS are included in the GISS database). Subsets of the LOCEAN data have been used in publications (Akhoudas et al., 2020, 2021; Benetti et al., 2016; Benetti et al., 2017; Benetti et al., 2015), where the subsets correspond to measurements at LOCEAN over a short period with specific instrumental and analysis protocols. A regional surface Atlantic subset of the data was also presented in Reverdin et al. (2018).

Here, we review the errors and uncertainties in this published dataset (Waterisotopes-CISE-LOCEAN, 2021), and the extent the overall dataset of δ^{18}O, δD, and d-excess (d-excess=δD - 8 δ^{18}O) presented as per mil V-SMOW, is internally consistent. We will also discuss how the CISE-LOCEAN sea water isotopic database compares with other datasets, in particular GISS, and provide some overall statistics on the number of data and their distribution.

2. Uncertainties

We will first review the different sources of uncertainties relevant for this dataset, before discussing the scale used and correction and flagging of data.

81 Uncertainties in the data reported originate from:
82 - the water collection and storage in bottles (Sect. 2.1)
83 - the uncertainties resulting from the experimental laboratory set-up and analysis protocols
84 (Sect. 2.2)
85 - the uncertainties on the internal standards which are used in the experimental set-up (Sect.
86 2.3)
87
88 2.1 Collection and storage
89 At LOCEAN, we have mostly used glass-tinted bottles (volume 20 or 30 ml) with a hard cap
90 including an internal rim to minimize water exchange through the cap (referred to later on as
91 'common' cap). No independent internal stopper or insert is used. For some, but not all, cruises,
92 the cap has been secured with parafilm after sample collection. When arriving in the laboratory,
93 samples are commonly stored in a cold room or in a refrigerator at 4°C, except when the
94 analysis is expected within 3 months after the arrival of the samples. The analysis has
95 commonly been done within 1 year – 18 months after collection, and for some subsets such as
96 for SURATLANT (Reverdin et al., 2018b), the analysis was usually done within 3 months after
97 collection. However, due to various changes at LOCEAN, there has been at times a long
98 backlog, with some samples having been stored in the cold room for 5 years or more. The
99 longest storage time was for OISO-18 data collected in 2010 and analyzed 9 years later in 2019.
100 Storage time was also very long for most samples of cruises OISO-21, OISO-22, OISO-23,
101 OISO-25 and OISO-26 (South Indian Ocean, 2012 to 2016).
102
103 We tested whether the samples in 'common' cap bottles change during storage by aging three
104 reference waters of the same deep equatorial Atlantic origin over two years in a laboratory room
105 which is not air-conditioned and without securing the 'common' caps with parafilm. Water is
106 extracted every three months for isotopic analysis, which so far over 23 months has not revealed
107 any significant drift, certainly not larger than 0.02/0.1 ‰ in $\delta^{18}O$ / δD. We expect that drifts
108 would be even smaller when samples are stored at 4°C or with parafilm, if the caps are properly
109 tightened.
110
111 In 2019, new caps were introduced which were not rigid and would often not provide a tight
112 seal, with very large sample evolution over less than a year, sometimes reaching close to 1 ‰
113 in $\delta^{18}O$. This was the case in particular for the samples collected on M/V Nuka Arctica in April
114 2019 resulting in 32% of samples with suspected breathing (indicated by unexpected low d-
115 excess and high $\delta^{18}O$; we verified this hypothesis by aging water in bottles with this cap, which
116 also showed large drifts after three months at room temperature).
117
118 Even for bottles with the 'common' caps, issues of poor conservation have been suspected in
119 some cases, in particular after long storage (typically, for 5 years or more). There is also the
120 possibility that breathing has happened during transport, in particular when the samples have
121 experienced very high temperatures, for instance for cruises ending in tropical ports and with
122 long-time storage in containers. This was probably the case for samples from the EUREC4A-
123 OA cruise collected in February 2020 (Stevens et al, 2021) with an almost two-months storage
124 in a container placed without sun-shielding in Pointe-à-Pitre (Guadeloupe, France), for which
125 close to 22% of the bottles with no parafilm securing the cap are suspected to have breathed
126 (during analysis, we noticed that the cap was often not tightly closed; their isotopic values also
127 contrasted with the ones from special tightly closed nutrient vials pasteurized at 80°C for 40
128 minutes after collection that did not present any anomalous d-excess). There are also other
129 subsets with data presenting obvious breathing. The extreme case is for samples collected on
130 M/V Nuka Arctica in 2018-2019, for which we suspect evaporation for 20% of the water

131 samples. In this case, the water was transferred from salinity bottles during the salinity analysis
132 to be stored in bottles with the 'common' cap, where they stayed for close to 18 months before
133 been analyzed.
134
135
136 2.2 Laboratory measurements
137
138 2.2.1 Method and protocol of analysis
139 Until 2011, the seawater samples $\delta^{18}O$ was directly measured on an Isoprime IRMS coupled to
140 a Multiprep system (dual inlet method). A typical run lasted more than 24 hours, with a few in-
141 house/internal standards interspersed in the run. Drifts in the values corresponding to the
142 internal standard used at the time ('Eau de Paris', referred to as EDP) were corrected for,
143 assuming that the correction is not dependent on salinity or isotopic value. When checking the
144 records, we found that $\delta^{18}O$ drift between successive EDP samples were often larger than 0.05
145 ‰. Uncertainty on correcting these drifts probably is on the order of 0.05 ‰.
146
147 Since 2011, CRDS has been used, which simultaneously measures the samples $\delta^{18}O$ and δD.
148 Each sample is vaporized, then injected in the cavity, a process repeated 6 to 12 times. The
149 average and SD of the sample $\delta^{18}O$ and δD are computed out of the last (2 to 8) injections after
150 stabilization is reached (Skzypek and Ford, 2014). This way, memory effects due to
151 contamination by the previous sample are small, in particular for $\delta^{18}O$ (Lis et al., 2008;
152 Skrzypek and Ford, 2014; Vallet-Coulomb et al., 2021). The SD computed on the 2 to 8 selected
153 injections is taken as an estimate of the instrumental error on the sample $\delta^{18}O$ and δD
154 measurements.
155
156 When a Picarro CRDS was first used at LOCEAN in 2011-2015, samples were distilled, and
157 the measurement was thus done on freshwater (see Benetti et al., 2017a, for the average effect
158 of the distillation on isotopic composition). Since 2016, seawater samples have been most often
159 directly measured using a wire mesh (liner) to limit the spreading of sea salt in the vaporizer
160 (https://www.picarro.com/sites/default/files/Salt%20Liner%20App%20Note_180323_final.pd
161 f).
162 We most commonly used a Picarro L2130-i CRDS, but at times, a Picarro L2120-i CRDS was
163 used, resulting in a larger standard deviation, in particular for δD. On both CRDS analyzers,
164 when repeatability of the different injections of the sample was not sufficient or the daily run
165 presented a too large drift, the samples were analyzed at least a second time. In that case, either
166 the best value or an average of the different values was taken/retained.
167
168 The typical daily run at LOCEAN currently includes one or two reference water samples
169 followed by three freshwater standards at the beginning to establish a slope calibration, as well
170 as regularly interspersed reference water samples afterwards (usually, from KonaDeep mineral
171 water with a value close to 0.8 / 2.0 ‰ in $\delta^{18}O$ / δD). In addition to these freshwater in-house
172 reference materials, a series can contain up to 12 isotopically-uncharacterized water samples,
173 using a little over 1 ml of the sample placed in a cap-closed vial. Until 2015, when samples
174 were distilled, series typically included 12 water samples. Since 2015, when salt water was
175 directly placed in the vials, we have mostly run not more than 9 samples in a run, because the
176 deposit of salt in the liner induces water retention or release, and thus noise in the measurements
177 after roughly 60 injections of salty samples, as well as drifts in the reference water (Fig. 1) and
178 possibly slope calibration. Another source of drift is the appearance of condensation on the top
179 cap of the vials after a few hours, which will result in enriching the residual vial water, although
180 it is by no means the largest source of drift.

181
182 Each sea water sample is injected 6 times, and usually 9 to 12 times for the internal standards
183 at the beginning and end of the run. Whenever possible, samples expected to be in the same
184 range of values are placed together in the run to minimize the memory effect on the CRDS
185 which is largest for δD. We reject the first injection, as well as later injections if they are not
186 stable, retaining between two and eight injections that we average. Two methods were tested,
187 an empirical one, when we look for successive injections of the sample with close values
188 (typically 0.02‰ in $\delta^{18}O$), and the systematic selection of the values within 1 sigma starting
189 with the last three injections. The retained injection values are then averaged. Differences in
190 the estimates produced by the two methods is usually within 0.02 ‰ in $\delta^{18}O$ (0.10 ‰ in δD for
191 the L2103-i). In the current database, the data retained are the ones obtained with the empirical
192 approach.
193
194 If a significant drift in the reference water values is noticed through the run, it is corrected,
195 usually by adjusting it linearly between the successive values of the reference water (Fig. 1).
196 We thus assume that the estimated drift is independent of the $\delta^{18}O$, δD values. In addition, in
197 2017-2019, the response slope of the Picarro CRDS was adjusted by interpolating between the
198 three-point slope estimate (based on 3 internal standards) at the beginning and at the end of the
199 runs, when that was deemed possible. However, this adjustment was discontinued in 2020
200 because the last internal standard samples were often not as reliably measured, with values more
201 sensitive to the number of injections, probably as a result of salt deposits in the liner. Since
202 2020, we only check the instrument's response at the end of the run with one of the freshwater
203 internal standards.
204
205 Accuracy is best when samples are distilled, and for δD it is better on the Picarro CRDS L2130-
206 i than on the Picarro CRDS L2120-i. Usually, the reproducibility of the $\delta^{18}O$ measurements
207 between the different selected injections is within ± 0.05 ‰ and of the δD measurements within
208 ± 0.15 ‰, which should be considered an upper estimate of the random error on a measurement
209 with the Picarro L2130-i CRDS. Samples with a SD larger than 0.06 ‰ in $\delta^{18}O$ were considered
210 too uncertain and were rerun, as well as often (after 2015) the first and last samples of each run.
211
212 In addition to the instrumental error of each sample $\delta^{18}O$ and δD described above, other
213 uncertainties arise from the data processing and conversion of measured $\delta^{18}O$ and δD into the
214 VSMOW scale. These additional sources of uncertainties are detailed in the next sections.
215
216
217 2.2.2 Data processing
218 The second source of uncertainty (for Picarro CRDS) is due to the way we process the data of
219 a daily run with salty water samples. As commented above, we first adjust the values to
220 compensate for the drift in reference water. Usually, this drift is relatively small, not exceeding
221 0.1/0.6 ‰ in $\delta^{18}O$ / δD during the run, but in about 10% of the runs, it exceeded 0.2 ‰ in $\delta^{18}O$
222 over the whole run, or 0.10 ‰ in $\delta^{18}O$ over successive reference water samples (23 out of 214
223 daily runs over which statistics were established from 06/2020 to 04/2021). When these large
224 changes are encountered, the run is estimated noisy and is usually rerun. However, even for the
225 other runs, a drift is usually observed with salty samples, and it often is a positive drift, in
226 particular between the reference water samples before and after the three initial internal
227 standards (Fig. 1). The average (SD) drift in reference water during a run was 0.081 (0.106)
228 ‰ in $\delta^{18}O$, and 0.62 (0.53) ‰ in δD in the 191 (out of 214) daily runs retained. The drift is
229 also found in the internal standard water analysed at the end of the run compared with the one
230 analysed just after the initial reference waters with an average (SD) drift of 0.069 (0.073) ‰ in

231   δ^{18}O, and 0.43 (0.34) ‰ in δD for the same 191 daily runs subset. These values slightly differ
232   from the drifts for the reference water, not significantly at 99% for δ^{18}O, but significantly
233   at 99% for δD. This may be indicative of errors resulting from linearly adjusting the drift, in
234   particular for the initial standard water samples. This suspicion of a slight non-linearity in the
235   initial drift is reinforced by 7 runs in 2020-2021 when the three standards were also measured
236   at the end of the run. However, as this is too uncertain, a correction has not been attempted for
237   that, but in addition to being a source of random error (at least 0.02/0.1 ‰ in δ^{18}O / δD) for
238   individual runs, this might also contribute to absolute errors (i.e. in the VSMOW scale) in the
239   range of 0.01/0.05 in δ^{18}O / δD.

241   Occasionally, after the correction of the drift, the value of the last internal standard (last sample
242   port of the run) is shifted for no obvious reason, sometimes by more than 0.10‰ in δ^{18}O from
243   what is expected. This might result from a temporary pollution that influences the
244   measurements (organic matter or particles, either left in the cavity of the vaporizer, on the filter
245   or on the salt liner), which can also happen for other sample ports. Often, when this happens,
246   there is also a larger scatter between the different injections, either for this sample or the initial
247   in-house standards. Running the set of samples again or a selection of them, sometimes
248   evidences isotopic shifts that can exceed 0.05/0.2 ‰ in δ^{18}O / δD. Repeating the analysis helps
249   mitigate this source of uncertainty. But, this has not always been done, except for data sets on
250   which there was a specific emphasis.

252   2.3 Internal standard waters

254   The last large source of uncertainty is the value (in the VSMOW scale) attributed to the internal
255   standards used. On the Isoprime IRMS, most internal standards were extracted from different
256   batches of 'Eau de Paris' (EDP) stored in a tank covered with paraffin, whereas since 2012,
257   three internal standards are regularly extracted from metal tanks where they are kept for up to
258   5-6 years with a slight overpressure of dry air (following Gröning, 2018, TEL Technical Note
259   No. 03). The internal standards have been calibrated using VSMOW and GISP (or GRESP),
260   usually more than once, and some were also sent to other laboratories at different times to
261   independently evaluate their characteristics. Comparisons were done in 2013-2014 for three
262   internal LOCEAN standards with 6 laboratories for δ^{18}O and 4 laboratories for δD, which, taken
263   together, did not reveal an average bias larger than 0.01/0.10 ‰. However, there seems to be
264   differences for the individual standards (Table 1), with the one at -3.26/-21.32 ‰ presenting an
265   average positive difference of 0.029/0.19 ‰, whereas the two other ones present a negative
266   difference (i.e. LOCEAN standards seemed too low) smaller or equal to -0.01/-0.19 ‰.

268   After further limited comparisons in 2017-2018, that were not conclusive and mostly internal,
269   the next round of comparisons of the LOCEAN internal standards took place in 2019-2021,
270   with 5 other European laboratories and for two of them, two different setups for δ^{18}O (most of
271   those with IRMS, except for one with a PICARRO L2130 CRDS). Thus, this includes 7
272   comparisons for δ^{18}O and 5 for δD. This set of comparisons (Table 1) was done for the three
273   internal standards used in 2019-2021, and presents a large scatter between the different
274   laboratories, on the order of 0.055/0.7 ‰ in δ^{18}O / δD. As the differences between laboratories
275   are similar for the three internal standards, this suggests some systematic differences between
276   laboratories. However, the large scatter implies that the average differences found are very
277   uncertain. The differences found for the three internal standards used in 2019-2021 range in
278   δ^{18}O / δD between 0.029/0.21 ‰ for the most negative standard to -0.010/0.02 ‰ for the most
279   positive one (Table 1). This might indicate that we have a positive bias for two of our recent
280   internal standards. This could also produce a small difference in the response slopes of the

281 Picarro CRDS adopted since 2020. A set of four calibration runs done in November 2021 at
282 LOCEAN with new VSMOW, GRESP as well as three USGS standards with intermediate
283 values confirmed a positive bias on the most negative internal standard (MIX2). This run
284 however did not confirm the average biases on the other internal standards at LOCEAN
285 suggested by Table 1, nor any major slope error. Therefore, the correction of a systematic bias
286 has only been applied on the MIX2 value for analyses since August 2020. For some internal
287 standards, we witnessed larger differences for measurements done in June 2020 after the
288 L2130-i just returned from a cruise and long shipping and storage for more than 9 months. We
289 assume that this anomaly is instrumental, and did not last for a long time, as the anomaly was
290 not reproduced during later tests in August 2020, nor in November 2021.
291
292 The two storage methods used successively for internal standard waters were designed to
293 minimize water vapor exchange. It is however possible that small isotopic drifts of the internal
294 standards have taken place with time, due to evaporation or possible oxidation of the tanks (rust
295 was found in one nearly empty tank). As mentioned, based on different comparisons over time,
296 sometimes over remnants of the tank waters, we could verify that these drifts have remained
297 smaller than 0.02/0.1 ‰ in $\delta^{18}O$ / δD. Finally, standards for the daily runs are temporarily
298 stored, for up to a month, in glass bottles stored at 4°C, which are briefly opened every day to
299 extract water. Through its storage life, this water will slightly breath, by exchange with the
300 outside air that penetrates when the bottle is briefly opened. Back of the envelope estimates
301 suggest that the effect should be less than 0.01/0.05 ‰ in $\delta^{18}O$ / δD, even after a month.
302
303 2.4 Conversion to the concentration scale
304 Both oxygen and hydrogen isotope compositions are reported in parts per thousand (‰) on the
305 VSMOW scale. One issue is that we analyse saline samples on the activity scalewhile the
306 internal standards are fresh water standards, and the method of analysis has changed over time.
307 We have adjusted LOCEAN data converting them from the activity to the concentration scale
308 based on the study of Benetti et al. (2017a) as well as on complementary tests with the different
309 wire meshes used more recently and between duplicated IRMS/CRDS samples. The values we
310 report are thus internally consistent, but could present differences with datasets processed in
311 other institutions without this adjustment of up to 0.10/0.20 ‰ in $\delta^{18}O$ / δD, as indicated in
312 Benetti et al. (2017a). For example, Walker et al. (2016) find very close $\delta^{18}O$ values in
313 unadjusted measurements of the same saline samples done on different IRMS and CRDS
314 instruments. We thus expect that adjusted LOCEAN CRDS $\delta^{18}O$ data would be higher (more
315 enriched in heavy isotopes) than these other CRDS and more common IRMS data.
316
317 2.5 Correction and flagging of samples having probably breathed
318 In regions where there is enough information in the LOCEAN dataset to establish an average
319 relationship between d-excess and salinity (Benetti et al., 2017), a large evaporation of a sample
320 during storage can be detected using its d-excess value, which is then too low compared to the
321 expected relationship. This was recently checked on a set of 10 water samples originating from
322 salinity bottles collected in the surface North Atlantic in 2021 on MV Tukuma Arctica that did
323 not have the usual plastic insert, and thus had breathed as witnessed by the comparison of their
324 salinity with thermosalinograph records. These samples indeed present, higher practical salinity
325 (S), d-excess lower than expected and $\delta^{18}O$ and δD higher than the expected values, estimated
326 by average linear fits of d-excess versus salinity and $\delta^{18}O$ versus S for this region. The average
327 values of the deviations are $\Delta S=0.29$, $\Delta\delta^{18}O=0.15$‰; $\Delta\delta D=0.33$ ‰, Δd-excess=-0.82 ‰. The
328 deviations from these expected values present a loose relationship of the deviation in $\delta^{18}O$
329 ($\Delta\delta^{18}O$) on the order of -20% of the deviation of d-excess (Δd-excess) (Fig. 2). This relationship
330 is close to the one used by Benetti et al. (2017b) based on other data in the Labrador Sea, where

331 $\Delta\delta^{18}O$=-1/7 Δd-excess, $\Delta\delta D$=2 $\Delta\delta^{18}O$ and Δd-excess = 0.34 ΔS. On the other hand, the
332 correlation between Δd-excess and ΔS is not significantly different from 0, which might be
333 caused by uncertainties on sampling time causing errors in estimating salinity deviation.

335 In cases when breathing was not too large (resulting in an increase of less than 0.11‰ in $\delta^{18}O$),
336 we used the deviation from the expected d-excess relationship to S to estimate an adjusted $\delta^{18}O$
337 and δD (Benetti et al., 2017b). When this method is used, $\delta^{18}O$ and δD data are flagged to
338 'probably good' and d-excess to probably bad, as these data are certainly not as accurate as the
339 data with no 'correction', with the adjustment adding an uncertainty on the order of 0.05/0.10
340 ‰ in $\delta^{18}O$ / δD. For larger suspected evaporation, $\delta^{18}O$ and δD data are flagged as 'probably
341 bad'. Altogether, we have flagged 12.3% of the CRDS-measured samples, most of which
342 (11.3%) correspond to unadjusted data with anomalously low d-excess and thus suspected
343 evaporation. There is of course also the possibility that for some samples, too low or too high
344 (for 1% of the cases) d-excess might just result from an occasional large uncertainty in the
345 analysis.

347 We recently tested the effectiveness of applying this adjustment for 32 samples from cruise
348 OVIDE2018 (North Atlantic Ocean in 2018; Lherminer, 2018) which were from pairs of
349 samples analyzed both by CRDS at LOCEAN and by IRMS at Geozentrum Erlangen, and out
350 of which 11 LOCEAN-analyzed samples had been slightly adjusted based on their low d-
351 excess. An average difference is estimated between the 21 non-adjusted samples at LOCEAN
352 and the IRMS data, which we apply to all the IRMS data before comparison. The comparison
353 suggests that the adjustment we applied to some of the LOCEAN data, based on their d-excess,
354 results in diminishing from 0.060 to 0.041 ‰ the standard deviation of the $\delta^{18}O$ differences
355 between the 32 LOCEAN and Geozentrum Erlangen isotopic values. The adjustment of the 11
356 samples also diminished the standard deviation of d-excess from the d-excess versus S
357 relationship derived for the entire LOCEAN dataset from 0.25 to 0.15 ‰. As a comparison,
358 when the set is restricted to the 21 non-adjusted LOCEAN samples, the corresponding standard
359 deviations for the $\delta^{18}O$ differences between LOCEAN and Geozentrum Erlangen values, and
360 d-excess differences to the expected d-excess versus S relationship were 0.043 and 0.14 ‰,
361 respectively. These values are very close to what is found for the set of 32 samples including
362 the 11 adjusted samples, suggesting that we have not over-adjusted the LOCEAN samples.

364 For earlier IRMS analyses at LOCEAN, we base the identification of possible evaporated data
365 on excessive scatter in the $\delta^{18}O$ versus S scatter plots or between successive data compared to
366 what we have previously measured in regions with repeated cruises, and outliers (6%) are
367 flagged as probably bad. The smaller (by half) proportion of flagged IRMS analyses than for
368 the CRDS analyses suggests either that this validation missed some evaporated IRMS samples,
369 or that these earlier data had evaporated less than the more recent ones (some were analyzed
370 sooner after collection), or that the IRMS runs had smaller uncertainties than the latter CRDS
371 runs.

373 3. Validation
374 As discussed in section 2, in addition to random errors or to issues related with evaporation of
375 samples, there is the possibility of shifts between subsets of the data, due to the different internal
376 standard waters, methods of processing or conversion from the activity to the concentration
377 scale. We thus need to compare this database with data analyzed in other laboratories, and
378 evaluate time series when the data have been repeated in time at the same location. In particular,
379 the LOCEAN dataset contains a limited number of samples for different cruises in deep-water
380 masses that are unlikely to have experienced much change in their isotopic composition over

381   the last 50 years, due to their weak ventilation and small salinity variability. Examining data in
382   such deep-waters can thus provide a test of consistency between subsets of the LOCEAN data,
383   or relative to other datasets.

385   Within the LOCEAN dataset, relevant deep waters have been sampled in different years (in the
386   Southern Indian Ocean (OISO cruises), in the equatorial Atlantic (PIRATA cruises) and in the
387   North Atlantic subpolar gyre (mostly OVIDE cruises), with statistics presented in Table 2.
388   These comparisons on a limited set of cruises, but corresponding to analyses done throughout
389   the 22 last years of the spectrometry platform suggest that internally the $\delta^{18}O$ dataset is coherent
390   in time to within 0.03 ‰ (after an adjustment applied on LOCEAN IRMS data which most of
391   the time was +0.09 ‰ to adjust to CRDS data). For δD, the period of comparison is more
392   limited with data from Picarro CRDS only since 2010, and the standard error of yearly δD
393   averages is typically on the order of 0.15 ‰. The comparison also highlights cruises with more
394   noisy data than others. This is for example the case of the 2002 OISO08 IRMS data (without
395   the OISO08 data, the mean (standard error) $\delta^{18}O$ for subset 1 decreases to 0.078 (0.030) ‰).
396   There are also some suggestions of systematic differences between cruises (for example, for
397   subsets 1-2, OISO29 (2019) samples tend to have lower $\delta^{18}O$ and δD values, whereas OISO31
398   (2021) samples tend to have higher values). However, this is within the uncertainties of the
399   means and is not fully understood. Thus, no further correction is warranted.

401   There are $\delta^{18}O$ data from a few cruises sampling deep-waters which can be compared with
402   subsets of the LOCEAN data. These together with duplicates sets of samples between
403   LOCEAN and other facilities form the basis for estimating consistency relative to the other data
404   (details in App. A). The different comparisons yielded very varied results. It is often difficult
405   to understand what is the source of the differences, but one commonly suspects choices of
406   protocols, characteristics of the instrument used or internal standards (see also Aoki et al, 2017;
407   Wassenaar et al., 2021). Altogether, although the limited inter-comparisons listed above have
408   a large scatter (the standard deviation in the set of 17 average differences listed in App. A is
409   0.055 ‰), there is a tendency for LOCEAN $\delta^{18}O$ values reported in the concentration scale to
410   be higher (relatively enriched in heavy isotopes). The average of these 17 different comparisons
411   is 0.093 ‰ with a standard error of 0.013 ‰. This average difference happens to be close to
412   the 0.09 ‰ change to the concentration scale that was applied to recent CRDS salty water
413   samples analysed since 2015 at LOCEAN, an adjustment that is not done on CRDS or IRMS
414   datasets produced in other facilities.

416   In summary, these external comparisons, together with the internal consistency tests on the
417   LOCEAN database in a few regions, suggest that the LOCEAN $\delta^{18}O$ dataset are within +0.035
418   ‰ absolute accuracy, at least when averaged spatially or in time (Table 2). Individual data have
419   larger uncertainties as discussed before, because of the instrumental and internal standards
420   uncertainty (resulting in a total uncertainty of usually less than 0.05 ‰ in $\delta^{18}O$) and possible
421   aging/evaporation during collection and storage. We are not able to provide similar
422   comparisons for δD or d-excess, as the database for comparison is much reduced.

424   4. The data
425   4.1 Data distribution
426   Fig. 3 presents the spatial distribution of the LOCEAN-analyzed data close to the surface, with
427   the largest data collection being in the North Atlantic (in particular, with OVIDE cruises since
428   2002 and the SURATLANT ship of opportunity dataset since 2011), the tropical Atlantic (in
429   particular, the EGEE and PIRATA cruises since 2005), and the South Indian Ocean (OISO
430   cruises since 1998).

431
432 Table 3 reports the number of valid data points by depth range, which indicates that the
433 emphasis in this set has been on near surface data (58% of the $\delta^{18}O$ data above 40m depth, with
434 13% between 40 and 200m depth, and only 12% at 1000m or deeper). There is less valid δD
435 than $\delta^{18}O$ data, the difference corresponding to IRMS-measured data, which correspond to 25%
436 of the total number of water samples in the database. There is even less valid d-excess than δD
437 (by 10%), the difference corresponding to samples for which an adjustment for slight
438 evaporation was done on $\delta^{18}O$ and δD data. The database contains fewer deep samples since
439 the transition to CRDS than before, because of a recent emphasis of sampling the upper ocean.
440
441 4.2 Time series
442 We illustrate the dataset with time series of June (or July) data between 50° and 55°N in the
443 eastern North Atlantic subpolar gyre (NASPG) collected mostly during the OVIDE cruises
444 (Fig. 4). This scatter plot of cruise-averaged S and $\delta^{18}O$ indicates a near alignment of the values.
445 It is striking that the strongest negative (fresher/lighter) anomalies in 2016 fit rather well on the
446 regression line (in red) for water samples in the southwestern NASPG. This regression line is
447 derived from data from the 47–55°N, 30-49°W region, excluding very low salinity data from
448 seasonal sea ice melt or from shelf waters, and is very similar to the distribution in Frew et al.
449 (2000). Thus, this reinforces the hypothesis of Holliday et al. (2019) that the strong freshening
450 present in the eastern subpolar gyre in 2016 originated from the transport of Arctic freshwater
451 from the western boundary current into the eastern basins, and not from local rainfall, which
452 would have likely resulted in higher $\delta^{18}O$ at the same 'low' salinity such as depicted by the
453 black line (Frew et al., 2000; C. Risi, pers. comm., 2021).
454
455 The SURATLANT surveys provided a seasonal sampling of water isotopes between late 2011
456 and 2019 along the western flank of the Reykjanes Ridge in the central part of the gyre (53-
457 56°N/38°-44°W). Annual summaries of these data are provided on Fig. 5a. There is less
458 alignment of the interannual values on the average southwestern NASPG linear regression line
459 than for the OVIDE surveys (Fig. 4). However, there is some aliasing of the seasonal cycle in
460 the annual averages (see Reverdin et al., 2018b), which contributes to the scatter, as well as
461 noise on the data, and natural variability. On this plot the freshest year appears to be 2017, in
462 agreement with an analysis using a much more complete salinity dataset (Reverdin et al.,
463 2018a). 2017 is also one of the lighter $\delta^{18}O$ years. The corresponding d-excess versus S diagram
464 (Fig. 5b) presents yearly anomalies that are fairly aligned with the average regression between
465 southwestern NASPG d-excess and salinity data. Error bars are large, but nevertheless, low
466 salinity waters exhibit high d-excess, as described in Benetti et al. (2016).
467
468 5. Data availability:
469 The dataset described is version V2 at https://doi.org/10.17882/71186 (Waterisotopes-
470 CISE-LOCEAN, 2021).
471
472 6. Conclusions
473 Instrumental uncertainty on individual data in this dataset is as low as 0.03/0.15‰ for most
474 runs, with occasional much larger uncertainties. One needs to add to that the uncertainties on
475 the internal standards that are used to convert measured values into the VSMOW scale.
476 Different comparisons suggest that the internal standard values have almost always remained
477 defined within at most 0.03/0.2‰ for $\delta^{18}O$ / δD since 2012. There was however a short-term
478 larger difference found for the most negative standard (equal to 0.1‰ for $\delta^{18}O$), most likely
479 related to the readjustment of the instrument to laboratory conditions in May 2021. When using
480 the CRDS Picarro L2130-i, we also found periods with quite uncertain analyses, in particular

481 due to salt or particle deposit in the vaporizer or filters. These samples could often be run again
482 afterwards to reach lower resulting uncertainty.
483
484 Finally, there is the issue of possible evaporation during collection and storage. When the
485 analysis is done on a CRDS, we are usually able to detect possible biases larger than 0.05‰ in
486 $\delta^{18}O$, by comparing d-excess with the expected d-excess derived from regional d-excess-S
487 linear relationships. Attempts were made here to correct $\delta^{18}O$ and δD when the resulting
488 uncertainty does not exceed 0.05/0.1‰. In particular this was done for some OISO cruise
489 samples which were analysed many years after collection, or in the case of faulty caps being
490 used, or caps that were not properly closed and with no parafilm. This is certainly a strong
491 source of quality loss for part of the database, and 'small' effects may have remained
492 undetected.
493
494 Possible long-term drifts due to changes in internal standards, storage, instrumentation and
495 protocols are difficult to estimate. This is done here by checking the consistency of different
496 subsets of the database, for instance when time series can be obtained (such as in the southern
497 Indian Ocean or North Atlantic subpolar gyre), or by comparison with duplicate data analysed
498 in other laboratories, or with other datasets in deep regions commonly sampled. These
499 comparisons are encouraging. On one hand, they suggest that the internal consistency in the
500 database is usually within a 0.03/0.15‰ uncertainty for $\delta^{18}O/\delta D$. On the other hand, although
501 other datasets sometimes differ by much more with a large scatter between the 17 comparisons
502 (with a standard deviation of 0.055‰ for $\delta^{18}O$), the average difference (0.093‰) found with
503 them is close to the change that is applied to the LOCEAN data to report them on the
504 concentration scale (0.09‰ for $\delta^{18}O$ analyzed with a salt liner since 2015). Of course, there is
505 still the possibility of errors and biases in subsets that could not be compared in a similar way,
506 such as surface samples collected from ships of opportunity or sailing vessels in the tropics,
507 that could result from different handling of the samples during collection and more uncertain
508 storage conditions. There are also small errors originating from memory effects in the Picarro
509 CRDS runs that could be better corrected and taken into account (Vallet-Coulomb et al., 2021).
510
511 We also illustrated the possibility of using this dataset to investigate ocean variability. Of
512 course, the interest of a data archive is to merge different institutes datasets such as this one,
513 while retaining a similar accuracy. This was attempted in the Global Seawater Oxygen-18
514 Database at GISS (Schmidt et al., 1999), although biases between subsets of this mostly $\delta^{18}O$
515 dataset remain at a level that makes the overall analysis of variability difficult to carry. The few
516 comparisons we could do suggest that differences with other datasets are at times large. The
517 effort to correctly adjust for these differences and produce a larger coherent archive is required
518 to get full use of the data collected. There is still a need of more and better calibrated sea water
519 isotope data to reconstruct tropical hydroclimate variability, such as formulated for the tropical
520 coral archives by PAGES CoralHydro2k Project, or for high latitude studies of the various
521 sources of freshwater in the ocean, including continental runoff, sea ice, iceberg melt and air-
522 sea exchanges.
523
524 Appendix A: Comparisons of LOCEAN data with other isotopic data
525 This includes on one hand comparisons with data of other cruises, in areas where we expect
526 variability to have been weak, such as in the deep ocean, and on the other hand, considering
527 duplicate sets of samples analysed in different institution.
528
529 Akhoudas et al. (2021) used the first approach in the deep Weddell Sea, comparing the
530 LOCEAN 2017 Wapiti cruise data with data from other cruises over a fairly large range of

531 neutral density surfaces. They identified a cruise whose δ¹⁸O values were lower by 0.13‰ than
532 at LOCEAN, as well as datasets that fit the Wapiti cruise values to within the data uncertainties
533 (for example, from ANT-X12 cruise on RV Polarstern in 1995). Another water mass which can
534 be used for comparison is the near - bottom waters in Fram Strait (below 2000m), which are
535 either originating from the Arctic Ocean, or recirculating from the Greenland Sea. This water
536 mass is regularly sampled, and has not been strongly ventilated recently. In 1998-2015 during
537 German-led cruises, these waters presented an average δ¹⁸O value close to 0.28‰ (after
538 removing suspiciously high data of a cruise in 2011 and large positive outliers in 2012; Paul
539 Dodd, personal communication). The LOCEAN database contains seven δ¹⁸O samples close to
540 the bottom across Fram Strait from MSM76 cruise on RV Maria S Merian in 2018, with average
541 (SD) value close to 0.395 (0.035) ‰, thus averaging higher by 0.115‰.
542
543 We extracted individual profiles from the GISS Global Seawater Oxygen-18 Database
544 (Schmidt et al., 1999) that can be compared with the LOCEAN station data, in deep and old
545 water masses. In the southern Indian Ocean, for example numerous profiles collected during
546 1993-1994 cruises (CIVA1 (Archambeau et al., 1998), ADOX1, SWINDEX, ADOX2)
547 suggest that LOCEAN δ¹⁸O in the deep layers are higher by 0.10 to 0.17 ‰ depending on the
548 cruise. There is also one GEOSECS 1978 station with a single deep value within 0.01 ‰ of
549 close-by OISO stations, as well as some 1984 (INDIVAT1) and 1996 (CIVA2) station data
550 with larger uncertainties that indicate higher LOCEAN δ¹⁸O values by 0.15 to 0.22 ‰,
551 depending on how outliers are identified and removed.
552
553 In the North Atlantic, there are data from three cruises that can be directly compared with
554 LOCEAN data, focusing on deep waters with T-S properties close to the ones of the
555 LOCEAN dataset. Comparison with one GEOSECS 1972 station south of Greenland suggests
556 higher δ¹⁸O LOCEAN values by ~ 0.060 ‰ (there is a small salinity shift between the two
557 profiles which required to adjust the LOCEAN δ¹⁸O value to the same salinity based on the
558 average δ¹⁸O-S relationship). Data of 4 stations of the CONVEX1991 cruise (Frew et al.,
559 2000) indicate higher δ¹⁸O in LOCEAN dataset by ~ 0.090 ‰ (after adjustment done to
560 consider small salinity differences). On the other hand, data close to the North East Atlantic
561 deep-water layer from stations collected in 6/1995 in the southern Labrador Sea (Khatiwala et
562 al., 1999) do not show a significant difference with LOCEAN stations closer to south
563 Greenland (southern Irminger Sea) at a similar salinity. In the equatorial Atlantic there are
564 deep data of two GEOSECS stations collected in 10/1972 and 2/1973 that can be compared
565 with the LOCEAN data (mostly near 1000-2000m depth). These limited comparisons (often
566 at large distance, but at a similar salinity) suggest that LOCEAN values are larger than the
567 GEOSECS δ¹⁸O by 0.055 ‰.
568
569 Finally, there are a few instances of sea water samples that have been duplicated and shared
570 with other laboratories. Some of these in 2013-2014 have been used to validate how to convert
571 IRMS or CRDS measurements into the concentration scale, with or without distillation (Benetti
572 et al, 2017), that we will not include here, and that suggested a scatter in the comparisons with
573 different IRMS laboratories for natural or artificial sea water samples often on the order of 0.10
574 ‰. More recently, 18 samples of the WAPITI2017 cruise were duplicated with analyses both
575 at LOCEAN and at the British Geological Survey stable isotope facility (BGS), which indicated
576 lower LOCEAN δ¹⁸O averaging -0.09 ‰ (SD = 0.035 ‰) (Akhoudas et al., 2021). In the same
577 region, a small set of 11 samples was duplicated in 2020 with Hokkaido University, which
578 suggests that LOCEAN δ¹⁸O values are higher by 0.139 ‰ with a SD of 0.019 ‰ (Shigeru
579 Aoki, pers. comm., 2021).
580

581 There have also been duplicates of LOCEAN samples during OVIDE cruises in 2010, 2016 and
582 2018 analysed in different facilities (Antje Voelker, pers. comm., 2021), which suggested
583 different average differences for the different years. In particular for 2016 samples close to
584 2500m, LOCEAN values average higher by 0.035 ‰, whereas in 2018, the average difference
585 is closer to 0.07‰, but with a few stations at the north-western end of the section in Irminger
586 sea with differences on the order of 0.02 ‰.

587
588 Author contribution:
589 Gilles Reverdin and Claire Waelbroeck have measured parts of the isotopic data,
590 contributed to their validation and written the paper. Catherine Pierre, Camille
591 Akhoudas, Giovanni Aloisi, Marion Benetti, have measured parts of the isotopic data and
592 contributed to their validation. Jérôme Demange has maintained the CISE-LOCEAN IRMS
593 and CRDS and Aïcha Naamar has measured parts of the isotopic data. Denis Diverrès,
594 Magnus Danielsen and Thierry Reynaud have contributed water samples from ships of
595 opportunity with associated salinity measurements. Bernard Bourlès, Jean-Claude
596 Gascard, Hervé Le Goff, Marie-Noëlle Houssais, Pascale Lherminier, Claire Lo Monaco,
597 Herlé Mercier, Nicolas Metzl, Simon Morisset, Jean-Baptiste Sallée, Virginie Thierry, Susan
598 Hartman, Ed Mawji, Solveig Olafsdottir, Torsten Kanzow, Antje Voelker, and Igor
599 Yashayaev have contributed to the sample collection, and in some cases provided
600 duplicate samples from other institutions.

601
602 Competing interests:
603 The authors declare that they have no conflict of interest.

604

631   Minster at LSCE, Penny Holliday at NOC in Southampton, Paul Dodd at the Norwegian Polar
632   Institute in Tromsoe, and Shigeru Aoki at Hokkaido University.
633
634
635

636 References:
637 Akhoudas, C., Sallée, J.-B., Reverdin, G., Aloisi, G., Benetti, M., Vignes, L., and Gelado. M.:
638 Ice-shelf basal melt and influence on dense water outflow in the southern Weddell Sea, J.
639 Geophys. Res.: Oceans, 125, e2019JC015710, doi:10.1029/2019JC015710, 2020.
640 Akhoudas, C. H., Sallée, J.B., Reverdin, G., Meredith, M. P., Naveira Garabato, A., Haumann,
641 F. A., Jullion, L., Aloisi, G., Benetti, M., Leng, M. L., Arrowsmith, C. : Ventilation of the abyss
642 in the Atlantic sector of the Southern Ocean, Nature Sci Repc 11, 16733 (2021),
643 https://doi.org/10.1038/s41598-021-95949-w, 2021.
644 Aoki, S., Kobayashi, R. , Rintoul, S. R., Tamura, T., and Kusahara, K.: Changes in water
645 properties and flow regime on the continental shelf off the Adélie/George V Land coast,
646 East Antarctica, after glacier tongue calving, J. Geophys. Res.: Oceans, 122 (8), 6277 –
647 6294, 2017.
648 Archambeau A.S., Pierre C., Poisson A., Schauer, B.: Distribution of CFC-12, Oxygen and
649 carbon stable isotopes in the Water masses of the Southern Ocean at 30°E from Africa to
650 Antarctica, J. Mar. Sys., 17, 25-38, 1998.

651 Benetti, M., Reverdin, G., Pierre, C., Khatiwala, S., Tournadre, B., Olafsdottir, S., and
652 Naamar, A.: Variability of sea ice melt and meteoric water input in the surface Labrador
653 Current off Newfoundland., J. Geophys. Res. Oceans, 121, 2841–2855,
654 doi:10.1002/2015JC011302, 2015.

655 Benetti, M., Reverdin, G., Yashayaev, I., Holliday, N.P., Tynuan, E., Torres-Valdes, S.,
656 Lherminier, P., Tréguer, P., Sarthou, G., and Lique, C.: Composition of freshwater in the
657 spring of 2014 on the southern Labrador shelf and slope. J. Geophys. Res.: Oceans, 122,
658 1102-1121, doi: 10.1002/2016JC012244, 2016.

659 Benetti, M., Sveinbjörnsdottir, A.E., Leng, M.J., Arrowsmith, C., Debondt, K., Fripiat, F., and
660 Aloisi, G.: Inter-comparison of salt effect correction for δ ^{18}O and δ ^{2}H measurements in
661 seawater by CRDS and IRMS using the gas-H_2O equilibration method, Mar. Chem., 194,
662 114–123, Doi :10.1016/j.marchem.2017.05.010, 2017a.

663 Benetti, M., Reverdin, G., Aloisi, G., and Sveinbjörnsdóttir, A.: Stable isotopes in surface
664 waters of the Atlantic Ocean: indicators of ocean-atmosphere water fluxes and oceanic mixing
665 processes, J. Geophys. Res. Oceans, doi:10.1002/2017JC012712, 2017b.
666 Benetti, M., Reverdin, G., Clarke, J. S.,Tynan, E., Holliday, N. P., Torres-Valdes, S.,
667 Lherminier, P., Yashayaev, I.: Sources and distribution of fresh water around Cape Farewell in
668 2014, J. Geophys. Res., doi:10.1029/2019JC015080, 2019.
669 Bigg, G.R., and Rohling, E.J.: An oxygen isotope dataset for marine water, J. Geophys. Res.
670 Atmos., 105, 8527-8536, doi:10.1029/2000JC900005, 1999.
671 Craig, H., and Gordon, L.I. : Deuterium and oxygen18 variations in the ocean and marine
672 atmosphere, In:Tongiogi,E.(Ed.),Proc. Stable Isotopes in Oceanographic Studies and
673 Paleotemperatures, pp.9–130 (V.Lishie e F., Pisa), 1965.
674 Frew, R., Dennis, P.F., Heywood, K., Meredith, M.P., and Boswell, S.M.: The oxygen isotope
675 composition of water masses in the Northern North Atlantic, Deep-Sea Res. I, 47, 2265-2286,
676 doi:10.1016/S0967-0637(00)00023-6, 2000.
677 Gröning, M.: Stable Isotope Internal Laboratory Water Standards: Preparation, Calibration
678 and Storage., TEL Technical Note No. 03, (revised from IHL Technical Procedure Note
679 No.43, Tanweer et al., as of May 2009), 2018.
680 Holliday et al., 2019.
681 Khatiwala, S. P., Fairbanks, R. G., and Houghton, R. W.:Freshwater sources to the coastal
682 ocean off northeastern North America: Evidence from $H_2^{18}O/H_2^{16}O$, J. Geophys.Res. 104:
683 18241–18255, doi:10.1029/1999JC900155, 1999.

684   Lherminier, P.: OVIDE 2018 cruise, RV Thalassa, https://doi.org/10.17600/18000510.

685   Lis, G., Wassenaar, L., and Hendry, M.: High-precision laser spectroscopy D/H and 18O/16O
686   measurements of microliter natural water samples, Analytical chemistry 80(1), 287-293,
687   2008.

688   Östlund, H.G., Craig, H., Broecker, W. S., and Spenser, D.: GEOSECS Atlantic, Pacific and
689   Indian Ocean Expeditions: Shore based Data and Graphics,Technical Report, National
690   Science Foundation, Washington, DC, p.220, 1987.

691   Reverdin G, Alory, G., Diverres, D., Bringas, F., Goni, G., Heilmann, L., Chafik, L., Szekely,
692   T., and Friedman, A.R.: North Atlantic subpolar gyre along predetermined ship tracks since
693   1993: a monthly data set of surface temperature, salinity, and density, Earth Syst. Sci. Data
694   10: 1403-1415, doi:10.5194/essd-10-1403-2018, 2018a.

695   Reverdin, G., Metzl, N., Olafsdottir, S., Racapé, V., Takahashi, T., Benetti, M.,
696   Valdimarsson, H., Benoit-Cattin, A., Danielsen, M., Fin, J., Naamar, A., Pierrot, D., Sullivan,
697   K., Bringas, F., and Goni, G. : SURATLANT: a 1993–2017 surface sampling in the central
698   part of the North Atlantic subpolar gyre, Earth Syst. Sci. Data, 10, 1901-1924,
699   doi:10.5194/essd-10-1901-2018, 2018b.

700   Reverdin, G., Metzl, N.., Reynaud, T., Poli, P., Griboval, Y. : L'Exploreur OceanoScientific
701   "Boogaloo" - Une campagne péri-Antarctique, 26/01/2017 - 04/04/2017, La Météorologie,
702   April 2020, doi :10.1002/2016JC012244, 2019.

703   Schmidt, G.A.: Error analysis of paleosalinity calculations, Paleoceanography , 14, 422-
704   429, doi:10.1029/1999PA900008, 1999.

705   Schmidt, G.A., Bigg, G.R., and Rohling E.J.: Global Seawater Oxygen-18 Database – Data,
706   GISS, http://www.giss.nasa.gov/data/o18data/, 1999.

707   Skrzypek, G., and Ford, D.: Stable isotope analysis of saline water samples on a cavity
708   ringdown spectroscopy instrument, Environ. Sci. Technol., 48, 2827-2834,
709   doi:10.1021/es4049412, 2014.

710   Stevens et al : EUREC^{4}A , Earth Sys. Sci. Data, 13, 4067–4119, https://doi.org/10.5194/essd-13-
711   4067-2021, 2021.

712   Vallet-Coulomb C., Couapel M., and Sonzogni C.: Improving memory effect correction to
713   achieve high-precision analysis of delta O-17, delta O-18, delta H-2, O-17-excess and d-
714   excess in water using cavity ring-down laser spectroscopy, Rapid Comm. In Mass Spectr.,
715   35 (14), p. e9108 [16 p.] ISSN 0951-4198, 2021.

716   Voelker, A.H., Colman, A. , Olack, G., and Waniek, J.: Oxygen and hydrogen isotope
717   signatures of northeast Atlantic water masses, Deep Sea Res. II, 116,
718   doi:10.1016/j.dsr2.2014.11.006, 2015.

719   Walker, S.A., Azetsu-Scott, K., Normandeau, C., Kelley, D.E., Friedrich, R., Newton, R.,
720   Schlosser, V, McKay, J.L., Abdi, W., Kerrigan, E., Craig, S.E., and Wallace, D.W.R.: A
721   comparison of cavity ring-down spectroscopy (CRDS) and isotope ratio mass spectrometry
722   (IRMS), Limnology and Oceanogr.: Meth., doi: 10.1002/lom3.10067, 2016.

723   Wassenaar, L.I., Terzer-Wassmuth, S., and Douence, C.: Progress and challenges in dual- and
724   triple-isotope (δ^{18}O, δ^2H, Δ^{17}O) analyses of environmental waters: an international assessment
725   of laboratory performance, Rap. Comm. In Mass Spectrom., in Press, doi:10.1002/rcm.9193,
726   2021.

727   Waterisotopes-CISE-LOCEAN, Water isotopes of sea water analyzed since 1998 at
728   LOCEAN, SEANOE. https://doi.org/10.17882/71186, 2021.

729   Xu, X., Werner, M., Butzin, M., and Lohmann, G.: Water isotope variations in the global
730   ocean model MPI-OM, Geosci. Model Dev., 5,809-818, doi:10.5194/gmd-5-809-2012, 2012.

731

732

733   Table 1

734   Comparison of standards measured at LOCEAN and in other laboratories (in ‰).

Date	Internal Standard	LOCEAN $\delta^{18}O$ ‰	LOCEAN δD ‰	$\delta^{18}O$ deviation ‰	Nber of $\delta^{18}O$ lab settings	δD deviation ‰	Nber of δD lab settings
2013-2014	EDP	-6.610	-44.30	-0.010	6	-0.19	4
2013-2014	MIX	-3.260	-21.32	0.029	6	0.19	4
2013-2014	KONA	-0.050	0.46	-0.007	6	-0.18	4
2019-2021	MIX2	-2.610	-17.93	0.029	7	0.21	5
2019-2021	BERING	-0.805	-4.56	0.028	7	0.19	5
2019-2021	KONA3	1.220	3.40	-0.010	7	0.02	5

735

736   Table 2:

737   Comparison of LOCEAN annually-averaged data in a few selected deep-water masses which
738   exhibit little variability in their salinity, and have likely not been recently ventilated:
739   1: OISO cruises (1998 to 2021) near 1000-1500m in South Indian Ocean Antarctic sector of
740   the Southern Ocean (50°S-58°S) (1998*, 2002*, and most years since 2010)
741   2: OISO cruises (1998 to 2021) near 2000m in the western South Indian Ocean subtropical gyre
742   (1998*, 2002*, and most years since 2010)
743   3: PIRATA and EGEE cruises (2005-2021) near 1000m in eastern equatorial Atlantic (2005*,
744   2006*, 2007*, 2015, 2020, 2021)
745   4: OVIDE and RREX2017 data between 2000m and 3500m in eastern North Atlantic subpolar
746   gyre (data in 2002*, 2016, 2017, 2018, 2021)
747   Reported S, $\delta^{18}O$, δD and d-excess values are average values for all samples and all years
748   (standard error). The number of years (N years) refers to the $\delta^{18}O$ data. The standard error is
749   computed as the standard error of the different annual averages, i.e. the standard deviation of
750   the different annual averages divided by $\sqrt{N}$.

751

Cruise set	1	2	3	4
N years	13	9	6	5
S	34.710 (0.005)	34.695 (0.002)	34.615 (0.005)	34.936 (0.005)
$\delta^{18}O$ (‰)	0.095 (0.035)	0.085 (0.025)	0.150 (0.009)	0.287 (0.025)
δD (‰)	-0.25 (0.13)	-0.29 (0.09)	0.24 (0.14)**	1.18 (0.18)
d-excess (‰)	-0.80 (0.15)	-1.03 (0.18)	-0.81 (0.0)**	-1.05 (0.09)

752   * IRMS estimates for $\delta^{18}O$ only.
753   ** only two years

754

755   Table 3: number of valid sea water isotopic data by depth range in Waterisotopes-CISE-
756   LOCEAN (2021, version V2) (a total of 7595 valid data for $\delta^{18}O$ out of 7703 data entries)

757

Depth range (m)	$\delta^{18}O$ (‰)	δD (‰)	d-excess (‰)
0-40	4517	3416	3180
40-199	1029	716	625
200-999	1245	1029	919
> 999	804	539	465
total	7595	5700	5189

758
759

760
761 Figure captions
762 Figure 1: A typical run (on 2/08 2021) of 19 samples using three internal standards and
763 KonaDeep-water samples (left for δ^{18}O and right for δD). Top panels: the deviations of isotopic
764 values (‰) of internal standards (in blue) and of the KonaDeep-water samples (in red) relative
765 to their expected values. Error bars are the standard deviation of the different injections, and
766 the vertical scale is arbitrary set so that 0 corresponds to KonaDeep sample 6 (after the three
767 internal standards). The lower panels present the values obtained after adjusting for the drifts
768 identified with the KonaDeep-water samples through the run.

769
770 Figure 2: Scatter diagram of the deviation of δ^{18}O (‰) versus the deviation of d-excess (‰) for
771 a set of samples extracted from salinity bottles with no plastic inserts that had evaporated (2021,
772 mostly from MV Tukuma in the North Atlantic). The deviations are estimated by subtracting
773 from the isotopic data the isotopic value estimated as a function of practical salinity, based on
774 the other regional data. The error bars on each sample are the standard deviation between the
775 different injections and assuming that the standard deviation of δ^{18}O and δD are independent
776 when estimating d-excess. The red line is the regression used in Benetti et al. (2016).

777
778 Figure 3: Six maps which include most of the near-surface δ^{18}O data in the LOCEAN archive
779 (color scale in ‰).

780
781 Figure 4: Scatter plot of cruise averages of near surface (upper 100-m) δ^{18}O (‰) versus
782 practical salinity in the Iceland Basin, close to the NAC fronts. The bars indicate the standard
783 deviation between the individual data that are averaged. Notice the fresher and isotopically
784 lighter data from the BOCATS (OVIDE transect) cruise in 2016. The red line corresponds to
785 the average linear relationship in the south-western NA SPG (SURATLANT dataset within 47–
786 55°N and 30-49°W, with practical salinity between 33.1 and 35.5), whereas the black line
787 reports the slope expected from mixing with local rainfall end-member.

788
789 Figure 5: Scatter plots in the southern Irminger Sea/NASPG of annually averaged
790 SURATLANT surveys data. The left panel presents δ^{18}O (‰) versus practical salinity, whereas
791 the right panel presents d-excess (‰) versus practical salinity. The bars indicate the standard
792 deviation between the individual data that are averaged. The red lines correspond to the average
793 linear relationships in the SURATLANT dataset within 47–55°N and 30-49°W, with salinity
794 between 33.1 and 35.5 (see Reverdin et al., 2018b), the red line on the left panel, being the same
795 as on Fig. 4.

796
797
798
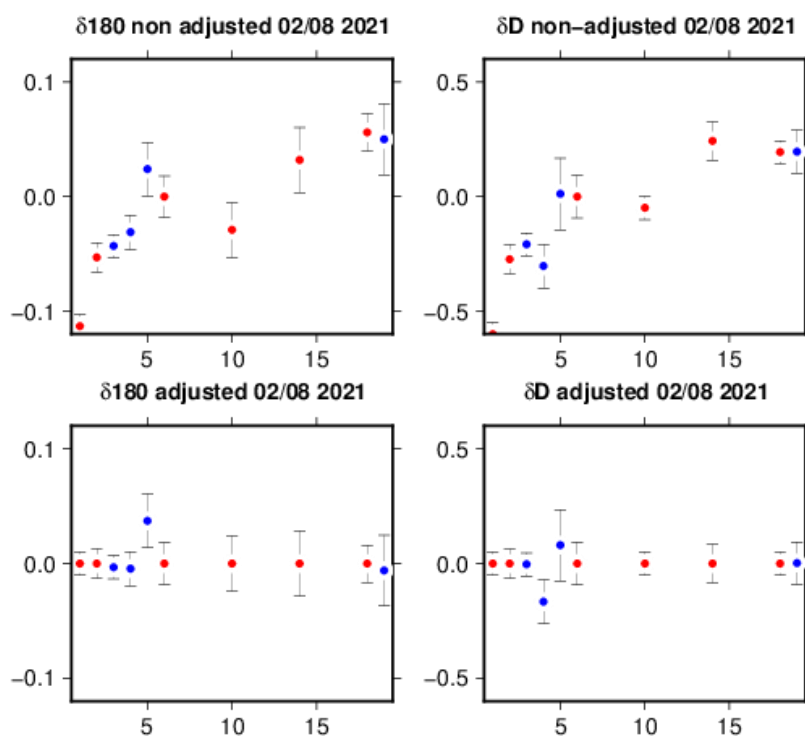
799
Figure 1: A typical run (on 2/08 2021) of 19 samples using three internal standards and
KonaDeep-water samples (left for $\delta^{18}O$ and right for δD). Top panels: the deviations of
isotopic values (‰) of internal standards (in blue) and of the KonaDeep-water samples (in
red) relative to their expected values. Error bars are the standard deviation of the different
injections, and the vertical scale is arbitrary set so that 0 corresponds to KonaDeep sample 6
(after the three internal standards). The lower panels present the values obtained after
adjusting for the drifts identified with the KonaDeep-water samples through the run.
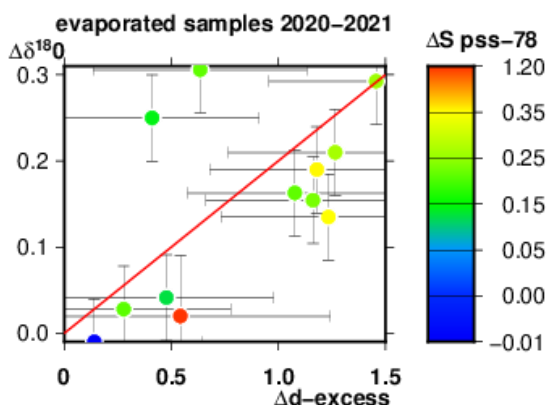
807
808 Figure 2: Scatter diagram of the deviation of δ¹⁸O (‰) versus the deviation of d-excess (‰) for
809 a set of samples extracted from salinity bottles with no plastic inserts that had evaporated (2021,
810 mostly from MV Tukuma Arctica in the North Atlantic). The deviations are estimated by
811 subtracting from the isotopic data the isotopic value estimated as a function of practical salinity,
812 based on the other regional data. The error bars on each sample are the standard deviation
813 between the different injections and assuming that the standard deviation of δ¹⁸O and δD are
814 independent when estimating d-excess. The red line is the regression used in Benetti et al.
815 (2016).
816
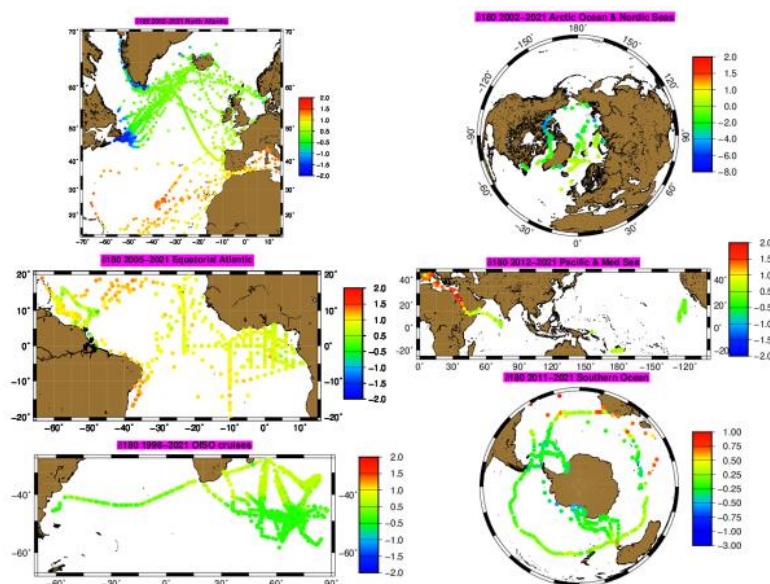
817
818 Figure 3: Six maps which include most of the near-surface δ^{18}O data in the LOCEAN archive
819 (color scale in ‰).
820
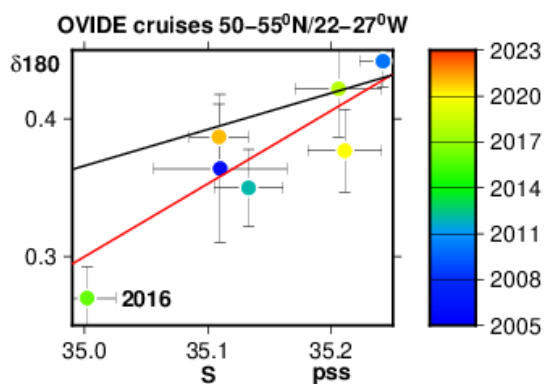
821
822 Figure 4: Scatter plot of cruise averages of near surface (upper 100-m) $\delta^{18}O$ (‰) versus
823 practical salinity in the Iceland Basin, close to the NAC fronts. The bars indicate the standard
824 deviation between the individual data that are averaged. Notice the fresher and isotopically
825 lighter data from the BOCATS (OVIDE transect) cruise in 2016. The red line corresponds to
826 the average linear relationship in the south-western NA SPG (SURATLANT dataset within
827 47–55°N and 30-49°W, with practical salinity between 33.1 and 35.5), whereas the black line
828 reports the slope expected from mixing with local rainfall end-member.
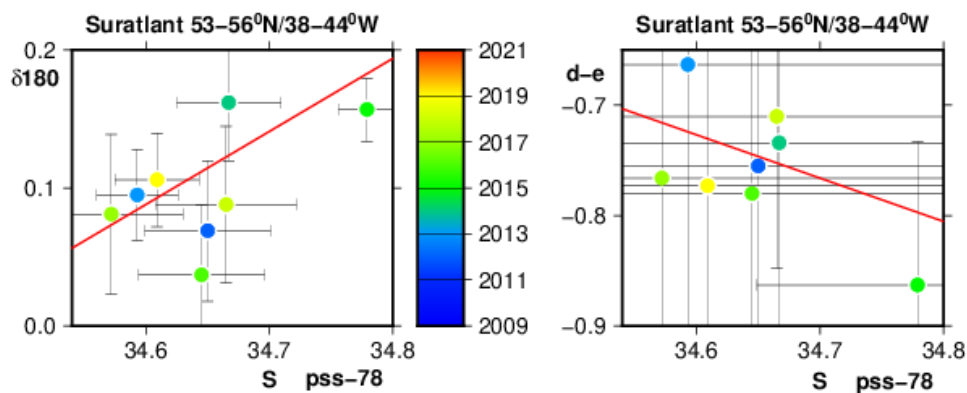
23

Figure 5: Scatter plots in the southern Irminger Sea/NASPG of annually averaged SURATLANT surveys data. The left panel presents $\delta^{18}O$ (‰) versus practical salinity, whereas the right panel presents d-excess (‰) versus practical salinity. The bars indicate the standard deviation between the individual data that are averaged. The red lines correspond to the average linear relationships in the SURATLANT dataset within 47–55°N and 30-49°W, with salinity between 33.1 and 35.5 (see Reverdin et al., 2018b), the red line on the left panel, being the same as on Fig. 4.