The CISE-LOCEAN seawater 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], Anton Velo[9], Antje Voelker[10,11], Igor Yashayaev[12], Alexander Haumann[13], Melanie J. Leng[14], Carol Arrowsmith[14], Michael Meredith[15]

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 UAR 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 Intituto de Investigaciones Marinas de Vigo, CSIC, Vigo, Spain

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

11 Centro de Ciencias do Mar, Faro, Portugal

12 Bedford Institute of Oceanogaphy, Dartmouth, Nova Scotia Canada

13 Dept of Geosciences, Princeton University, Princeton, USA

14 British Geological Survey, Nottingham, UK

15 British Antarctic Survey, Cambridge, UK

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

Abstract

The characteristics of the CISE-LOCEAN seawater isotope data set ($\delta^{18}O$, $\delta^{2}H$, later designated as δD) are presented. This data set covers the time period from 1998 to 2021 and currently includes close to 8000 data entries, all with $\delta^{18}O$, three quarters of them also with δD, associated with a time and space stamp and usually a salinity measurement. Until 2010, samples were analysed by isotopic ratio mass spectrometry, and since then mostly by cavity ring-down spectroscopy (CRDS). Instrumental uncertainty on individual data in this dataset is usually with a standard deviation as low as 0.03 and 0.15‰ for $\delta^{18}O$ and δD, respectively. An additional uncertainty is related to uncertain isotopic composition of the in-house standards that are used to convert daily data into the Vienna Standard Mean Ocean Water (VSMOW) scale. Different comparisons suggest that since 2010 the latter have remained within at most 0.03/0.20‰ for $\delta^{18}O$ and δD. Therefore, combining the two suggests a standard deviation of at most (0.05, 0.25)‰ for ($\delta^{18}O$, δD).

Finally, for some samples, we find that there has been evaporation during collection and storage, requiring adjustment of the isotopic data produced by CRDS, based on d-excess (δD – 8 x $\delta^{18}O$). This adds an uncertainty on the adjusted data of roughly 0.05 and 0.10‰ for $\delta^{18}O$ and δD, respectively. This issue of conservation of samples is certainly a strong source of quality loss for parts of the database, and 'small' effects may have remained undetected.

The internal consistency of the database can be tested for subsets of the dataset, when time series can be obtained (such as in the southern Indian Ocean or North Atlantic subpolar gyre). These comparisons suggest that the overall uncertainty of the spatially (for a cruise) or temporally (over a year) averaged data is on the order of or less than 0.03 and 0.15‰ for $\delta^{18}O$ and δD, respectively. On the other hand, 17 comparisons with duplicate seawater data analysed in other laboratories or with other data sets in deep regions suggest a larger scatter. When averaging the 17 comparisons done for $\delta^{18}O$, we find a difference close to the adjustment applied at LOCEAN to saline water data produced either by CRDS or IRMS. Such a difference is expected, but the scatter found suggests that care is needed when merging datasets from different laboratories. Examples of time series in the surface North Atlantic subpolar gyre illustrate the temporal changes in water isotope composition that can be detected with a carefully validated dataset.

1. Introduction

Stable isotope analyses of ocean water ($\delta^{18}O$, $\delta^{2}H$ later termed 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. Seawater stable isotopes have been used to verify ocean model circulation and characterize processes controlling their spatial variability (Xu et al., 2012). Seawater 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 seawater 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 isotopic platform facility at LOCEAN (later 'CISE-LOCEAN') has measured seawater isotopic composition of samples collected on a series of oceanographic cruises or ships of opportunity, mostly in the North Atlantic, the equatorial Atlantic, the southern Indian Ocean and the Southern Ocean. This data set of the oxygen and hydrogen isotopes ($\delta^{18}O$ and δD) of marine water covers the period 1998 to 2021, and is ongoing. Most data prior to 2010 (only $\delta^{18}O$) 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 samples 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 et al., 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., 2015; Benetti et al., 2017a; Benetti et al., 2017b; Reverdin et al., 2019), 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. (2018b).

Here, we review the errors and uncertainties in this published dataset (Waterisotopes-CISE-LOCEAN, 2021), and the extent to which the overall dataset of $\delta^{18}O$, δD, and d-excess (d-excess=δD - 8 x $\delta^{18}O$) presented as per mil V-SMOW, is internally consistent. We will also discuss how the CISE-LOCEAN seawater 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.

Uncertainties in the data reported originate from:

- the water collection and storage in bottles (Sect. 2.1)
- the uncertainties resulting from the experimental laboratory set-up and analysis protocols (Sect. 2.2)
- the uncertainties on the internal standards which are used in the experimental set-up (Sect. 2.3)

2.1 Collection and storage

At LOCEAN, we have mostly used glass-tinted bottles (volume 20 or 30 ml) with a hard cap including an internal rim to minimize water exchange through the cap (referred to later on as 'common' cap). No independent internal stopper or insert is used, and the bottles are not collected full. For some, but not all, cruises, the cap has been secured with parafilm after sample collection. When arriving in the laboratory, samples are commonly stored in a cold room or in a refrigerator at 4°C, except when the analysis is expected within 3 months after the arrival of the samples. The analysis has commonly been done within 1 year – 18 months after collection, and for some subsets such as for SURATLANT (Reverdin et al., 2018b), the analysis was usually done within 3 months after collection. However, due to various changes at LOCEAN, there has been at times a long backlog, with some samples having been stored in the cold room for 5 years or more. The longest storage time was for OISO-18 data collected in 2010 and analyzed 9 years later in 2019. Storage time was also very long for most samples of cruises OISO-21, OISO-22, OISO-23, OISO-25 and OISO-26 (South Indian Ocean, 2012 to 2016). Before analysis, samples are checked for obvious signs of evaporation, such as low water level or salt crystals around the bottle's neck.

We tested whether the samples in 'common' cap bottles change during storage by aging three reference waters of the same deep equatorial Atlantic origin over two years in a laboratory room which is not air-conditioned and without securing the 'common' caps with parafilm. Water is extracted every three months for isotopic analysis, which so far over 23 months has not revealed any significant drift, certainly not larger than 0.02 and 0.1 ‰ in $\delta^{18}O$ and δD, respectively. We expect that drifts would be even smaller when samples are stored at 4°C or with parafilm, if the caps are properly tightened.

In 2019, new caps were introduced which were not rigid and would often not provide a tight seal, with very large sample evolution over less than a year, sometimes reaching close to 1 ‰ in $\delta^{18}O$. This was the case in particular for the samples collected on M/V Nuka Arctica in April 2019 resulting in 32% of samples with suspected breathing (indicated by unexpected low d-excess and high $\delta^{18}O$; we verified this hypothesis by aging water in bottles with this cap, which also showed large drifts after three months at room temperature).

Even for bottles with the 'common' caps, issues of poor conservation have been suspected in some cases, in particular after long storage (typically, for 5 years or more). There is also the possibility that breathing has happened during transport, in particular when the samples have experienced very high temperatures, for instance for cruises ending in tropical ports and with long-time storage in containers. This was probably the case for samples from the EUREC4A-OA cruise collected in February 2020 (Stevens et al, 2021) with an almost two-months storage in a container placed without sun-shielding in Pointe-à-Pitre (Guadeloupe, France), for which close to 22% of the bottles with no parafilm securing the cap are suspected to have breathed (during analysis, we noticed that the cap was often not tightly closed; their isotopic values also contrasted with the ones from special tightly closed nutrient vials pasteurized at 80°C for 40 minutes after collection that did not present any anomalous d-excess). There are also other subsets with data presenting obvious breathing. The extreme case is for samples collected on

M/V Nuka Arctica in 2018-2019, for which we suspect evaporation for 20% of the water samples. In this case, the water was transferred from salinity bottles during the salinity analysis to be stored in bottles with the 'common' cap, where they stayed for close to 18 months before analysis.

2.2 Laboratory measurements

2.2.1 Method and protocol of analysis

Until 2011, the seawater samples $\delta^{18}O$ were directly measured on an Isoprime IRMS coupled to a Multiprep system (dual inlet method). A typical run lasted more than 24 hours, with a few in-house/internal standards interspersed in the run. Drifts in the values corresponding to the internal standard used at the time ('Eau de Paris', referred to as EDP) were corrected for, assuming that the correction is not dependent on salinity or isotopic value. When checking the records, we found that $\delta^{18}O$ drift between successive EDP samples were often larger than 0.05 ‰. Uncertainty on correcting these drifts probably is on the order of 0.05 ‰.

Since 2011, CRDS has been used, which simultaneously measures the samples $\delta^{18}O$ and δD. Each sample is vaporized, then injected in the cavity, a process repeated 6 to 12 times. The average and SD of the sample $\delta^{18}O$ and δD are computed out of the last (2 to 8) injections after stabilization is reached (Skzypek and Ford, 2014). This technique is applied to minimize the contamination from the previous sample, even though such memory effects should be small, in particular for $\delta^{18}O$ (Lis et al., 2008; Skrzypek and Ford, 2014; Vallet-Coulomb et al., 2021). The SD computed on the 2 to 8 selected injections is taken as an estimate of the instrumental error on the sample $\delta^{18}O$ and δD measurements.

When a Picarro CRDS was first used at LOCEAN in 2011-2015, samples were distilled, and the measurement was thus done on freshwater (see Benetti et al., 2017c, for the average effect of the distillation on isotopic composition). Since 2016, seawater samples have been most often directly measured using a wire mesh (liner) to limit the spreading of sea salt in the vaporizer (https://www.picarro.com/sites/default/files/Salt%20Liner%20App%20Note_180323_final.pdf).
We most commonly used a Picarro L2130-i CRDS, but at times, a Picarro L2120-i CRDS was used, resulting in a larger standard deviation, in particular for δD. On both CRDS analyzers, when repeatability of the different injections of the sample was not sufficient or the daily run presented an unacceptably drift, the samples were analyzed at least a second time. In that case, either the best value or an average of the different values was taken/retained.

The typical daily run at LOCEAN currently includes one or two reference water samples followed by three freshwater standards at the beginning to establish a slope calibration, as well as regularly interspersed reference water samples afterwards (usually, from KonaDeep mineral water with a value close to 0.8 and 2.0 ‰ in $\delta^{18}O$ and δD, respectively). In addition to these freshwater in-house reference materials, a series can contain up to 12 isotopically-uncharacterized water samples, using a little over 1 ml of the sample placed in a cap-closed vial. Until 2015, when samples were distilled, series typically included 12 water samples. Since 2015, when salt water was directly placed in the vials, we have mostly run not more than 9 samples in a run, because the deposit of salt in the liner induces water retention or release, and thus noise in the measurements after roughly 60 injections of salty samples, as well as drifts in the reference water (Fig. 1a, b) and possibly slope calibration. Another source of drift is the

appearance of condensation on the top cap of the vials after a few hours, which will result in enriching the residual vial water, although it is very likely a small source of drift.

Each seawater sample is injected 6 times, and usually 9 to 12 times for the internal standards at the beginning and end of the run. Whenever possible, samples expected to be in the same range of values are placed together in the run to minimize the memory effect on the CRDS which is largest for δD. We reject the first injection, as well as later injections if they are not stable, retaining between two and eight injections that we average. Two methods were tested, an empirical one, when we look for successive injections of the sample with close values (typically 0.02‰ in $\delta^{18}O$), and the systematic selection of the values within 1 σ starting with the last three injections. The retained injection values are then averaged. Differences in the estimates produced by the two methods is usually within 0.02 ‰ in $\delta^{18}O$ (0.10 ‰ in δD for the L2103-i). In the current database, the data retained are the ones obtained with the empirical approach.

If a significant drift in the reference water values is noticed through the run, it is corrected, usually by adjusting it linearly between the successive values of the reference water (Fig. 1c, d). We thus assume that the estimated drift is independent of the $\delta^{18}O$, δD values. In addition, in 2017-2019, the response slope of the Picarro CRDS was adjusted by interpolating between the three-point slope estimate (based on 3 internal standards) at the beginning and at the end of the runs, when that was deemed possible. However, this adjustment was discontinued in 2020 because the last internal standard samples were often not as reliably measured, with values more sensitive to the number of injections, probably as a result of salt deposits in the liner. Since 2020, we only check the instrument's response at the end of the run with one of the freshwater internal standards.

Accuracy is best when samples are distilled, and for δD it is better on the Picarro CRDS L2130-i than on the Picarro CRDS L2120-i. Usually, the reproducibility of the $\delta^{18}O$ measurements between the different selected injections is within ± 0.05 ‰ and of the δD measurements within ± 0.15 ‰, which should be considered an upper estimate of the random error on a measurement with the Picarro L2130-i CRDS. Samples with a SD larger than 0.06 ‰ in $\delta^{18}O$ were considered too uncertain and were rerun, as well as often (after 2015) the first and last samples of each run.

In addition to the instrumental error of each sample $\delta^{18}O$ and δD described above, other uncertainties arise from the data processing and conversion of measured $\delta^{18}O$ and δD into the Vienna Standard Mean Ocean Water (VSMOW) scale. These additional sources of uncertainties are detailed in the next sections.

2.2.2 Data processing

The second source of uncertainty (for Picarro CRDS) is due to the way we process the data of a daily run with salty water samples. As mentioned above, we first adjust the values to compensate for the drift in reference water. Usually, this drift during the run is relatively small, not exceeding 0.10 and 0.6 ‰ in $\delta^{18}O$ and δD, respectively, but in about 10% of the runs, it exceeded 0.20 ‰ in $\delta^{18}O$ over the whole run, or 0.10 ‰ in $\delta^{18}O$ over successive reference water samples (23 out of 214 daily runs over which statistics were established from 06/2020 to 04/2021). When these large changes are encountered, the run is estimated noisy and is usually rerun. However, even for the other runs, a drift is usually observed with salty samples, and it often is a positive drift, in particular between the reference water samples before and after the three initial internal standards (Fig. 1a, b). The average (SD) drift in reference water during a run was +0.081 (0.106) ‰ in $\delta^{18}O$, and +0.62 (0.53) ‰ in δD in the 191 (out of 214) daily

runs retained. The drift is also found in the internal standard water analysed at the end of the run compared with the one analysed just after the initial reference waters with an average (SD) drift of +0.069 (0.073) ‰ in $\delta^{18}O$, and +0.43 (0.34) ‰ in δD for the same 191 daily runs subset. These values slightly differ from the drifts for the reference water, which at 99% confidence level is not significant for $\delta^{18}O$, but significant for δD. This may be indicative of errors resulting from linearly adjusting the drift, in particular for the initial standard water samples. This suspicion of a slight non-linearity in the initial drift is reinforced by 7 runs in 2020-2021 when the three standards were also measured at the end of the run. However, as this is too uncertain, a correction has not been attempted for that, but in addition to being a source of random error (at least 0.02 and 0.1 ‰ in $\delta^{18}O$ and δD, respectively) for individual runs, this might also contribute to absolute errors (i.e. in the VSMOW scale) in the range of 0.01 and 0.05 in $\delta^{18}O$ and δD, respectively.

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

2.3 Internal standard waters

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

After further limited comparisons in 2017-2018 that were not conclusive and mostly internal, the next round of comparisons of the LOCEAN internal standards took place in 2019-2021, with 5 other European laboratories and for two of them, two different setups for $\delta^{18}O$ (most of those with IRMS, except for one with a PICARRO L2130-i CRDS). Thus, this includes 7 comparisons for $\delta^{18}O$ and 5 for δD. This set of comparisons (Table 1) was done for the three internal standards used in 2019-2021, and presents a large scatter between the different laboratories, with standard deviation on the order of 0.055 and 0.7 ‰ in $\delta^{18}O$ and δD, respectively. As the differences between laboratories are similar for the three internal standards, this suggests some systematic differences between laboratories. However, the large

scatter implies that the average differences found are very uncertain. The differences in $\delta^{18}O$ and δD found for the three internal standards used in 2019-2021 range between +0.029 and +0.21 ‰ for the most negative standard to -0.010 and 0.02 ‰ for the most positive one, respectively (Table 1). This might indicate that we have a positive bias for two of our recent internal standards. This could also produce a small difference in the response slopes of the Picarro CRDS adopted since 2020. A set of four calibration runs done in November 2021 at LOCEAN with new VSMOW, GRESP as well as three USGS standards with intermediate values confirmed a positive bias on the most negative internal standard (MIX2). This run however did not confirm the average biases on the other internal standards at LOCEAN suggested by Table 1, nor any major slope error. Therefore, the correction of a systematic bias has only been applied on the MIX2 value for analyses since August 2020. For some internal standards, we witnessed larger differences for measurements done in June 2020 after the L2130-i just returned from a cruise and long shipping and storage for more than 9 months. We assume that this anomaly is instrumental, and did not last for a long time, as the anomaly was not reproduced during later tests in August 2020, nor in November 2021.

The two storage methods used successively for internal standard waters were designed to minimize water vapor exchange. It is however possible that small isotopic drifts of the internal standards have taken place with time, due to evaporation or possible oxidation of the tanks (rust was found in one nearly empty tank). As mentioned, based on different comparisons over time, sometimes over remnants of the tank waters, we could verify that these drifts have remained smaller than 0.02 and 0.1 ‰ in $\delta^{18}O$ and δD, respectively. Finally, standards for the daily runs are temporarily stored, for up to a month, in glass bottles stored at 4°C, which are briefly opened every day to extract water. Through its storage life, this water will slightly breath, by exchange with the outside air that penetrates when the bottle is briefly opened. Back of the envelope estimates suggest that the effect should be less than 0.01 and 0.05 ‰ in $\delta^{18}O$ and δD, respectively, even after a month.

2.4 Concentration scale

Both oxygen and hydrogen isotope compositions are reported in parts per thousand (‰) on the VSMOW scale. One issue is that we analyse saline samples, while the internal standards are fresh water standards, and the method of analysis has changed over time. There is still a large uncertainty on the correction to be applied to account for the effect of salt on IRMS and CRDS seawater analyses. Here we have applied the corrections provided by Benetti et al. (2017c). Note that in some instances IRMS and CRDS analyses of the same seawater samples may yield similar values. For example, Walker et al. (2016) found very close $\delta^{18}O$ values in unadjusted measurements of seawater samples from the same water mass done on different IRMS and CRDS instruments. We have adjusted LOCEAN CRDS and IRMS data on the concentration scale based on the study of Benetti et al. (2017c) as well as on complementary tests with the different wire meshes used more recently and between duplicated IRMS/CRDS samples. The values we report are thus internally consistent, but could present differences with datasets processed in other institutions without this proposed adjustment or with other changes of scale of up to (0.10, 0.20) ‰ in ($\delta^{18}O$, δD), as indicated in Benetti et al. (2017c). We thus expect that adjusted LOCEAN CRDS $\delta^{18}O$ data would be higher (more enriched in heavy isotopes) than these other CRDS and more common IRMS data.

2.5 Correction and flagging of samples having probably breathed

In regions where there is enough information in the LOCEAN dataset to establish an average relationship between d-excess and salinity (Benetti et al., 2017a), a large breathing of a sample during storage can be detected using its d-excess value, which is then too low compared to the

expected relationship. This was recently checked on a set of 10 water samples originating from salinity bottles collected in the surface North Atlantic in 2021 on MV Tukuma Arctica that did not have the usual plastic insert, and thus had evaporated as witnessed by the comparison of their salinity with thermosalinograph records. These samples indeed present, higher practical salinity (S), d-excess lower than expected and $\delta^{18}O$ and δD higher than the expected values, estimated by average linear fits of d-excess versus salinity and $\delta^{18}O$ versus S for this region. The average values of the deviations are ΔS=+0.29, $\Delta\delta^{18}O$=+0.15‰; $\Delta\delta D$=+0.33 ‰, Δd-excess=-0.82 ‰. The deviations from these expected values present a loose relationship with the deviation in $\delta^{18}O$ ($\Delta\delta^{18}O$) on the order of -20% of the deviation of d-excess (Δd-excess) (Fig. 2). This relationship is close to the one used by Benetti et al. (2017a) based on other data in the Labrador Sea, where $\Delta\delta^{18}O$=-1/7 Δd-excess, $\Delta\delta D$=+2 $\Delta\delta^{18}O$ and Δd-excess = +0.34 ΔS. On the other hand, the correlation between Δd-excess and ΔS is not significantly different from 0, which might be caused by uncertainties on sampling time causing errors in estimating salinity deviation.

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

We recently tested the effectiveness of applying this adjustment for 32 pair of samples collected during cruise OVIDE2018 (North Atlantic Ocean in 2018; Lherminer, 2018) which were stored in different bottles. One set was analyzed by CRDS at LOCEAN and the other by IRMS at Geozentrum Erlangen. Among the LOCEAN samples, 11 show indications of breathing and have been slightly adjusted based on their low d-excess. An average difference is estimated between the 21 non-adjusted samples at LOCEAN and the IRMS data, which we apply to all the IRMS data before comparison. The comparison suggests that the adjustment we applied to some of the LOCEAN data, based on their d-excess, results in diminishing from 0.060 to 0.041 ‰ the standard deviation of the $\delta^{18}O$ differences between the 32 LOCEAN and Geozentrum Erlangen isotopic values. The adjustment of the 11 samples also diminished from 0.25 to 0.15 ‰ the standard deviation in the differences between d-excess and d-excess estimated from the d-excess versus S relationship derived for the entire LOCEAN dataset. As a comparison, when the set is restricted to the 21 non-adjusted LOCEAN samples, the corresponding standard deviations for the $\delta^{18}O$ differences between LOCEAN and Geozentrum Erlangen values, and d-excess differences to the expected d-excess versus S relationship were 0.043 and 0.14 ‰, respectively. These values are very close to what is found for the set of 32 samples including the 11 adjusted samples, suggesting that we have not over-adjusted the LOCEAN samples.

For earlier IRMS analyses at LOCEAN, we base the identification of possible evaporated data on excessive scatter in the $\delta^{18}O$ versus S scatter plots or between successive data compared to what we have previously measured in regions with repeated cruises, and outliers (6%) are flagged as probably bad. The smaller (by half) proportion of flagged IRMS analyses than for the CRDS analyses suggests either that this validation missed some evaporated IRMS samples,

or that these earlier data had evaporated less than the more recent ones (some were analyzed sooner after collection), or that the IRMS runs had smaller uncertainties than the latter CRDS runs.

3. Validation

As discussed in section 2, in addition to random errors or to issues related with evaporation of samples, there is the possibility of shifts between subsets of the data, due to the different internal standard waters, methods of processing, adjustment (for CRDS) or conversion from the activity to the concentration scale (for IRMS). We thus need to compare this database with data analyzed in other laboratories, and evaluate time series when the data have been repeated in time at the same location. In particular, the LOCEAN dataset contains a limited number of samples for different cruises in deep-water masses that are unlikely to have experienced much change in their isotopic composition over the last 50 years, due to their weak ventilation and small salinity variability. Examining data in such deep-waters can thus provide a test of consistency between subsets of the LOCEAN data, or relative to other datasets.

Within the LOCEAN dataset, relevant deep waters have been sampled in different years (in the Southern Indian Ocean (OISO cruises), in the equatorial Atlantic (PIRATA cruises) and in the North Atlantic subpolar gyre (mostly OVIDE cruises), with statistics presented in Table 2. These comparisons on a limited set of cruises, but corresponding to analyses done throughout the 22 last years of the spectrometry platform suggest that internally the $\delta^{18}O$ dataset is coherent in time to within 0.035 ‰ (after an adjustment applied on LOCEAN IRMS data which most of the time was +0.09 ‰ to adjust to CRDS data). For δD, the period of comparison is more limited with data from Picarro CRDS only since 2010, and the standard error of yearly δD averages is typically on the order of 0.15 ‰. The comparison also highlights cruises with more noisy data than others. This is for example the case of the 2002 OISO08 IRMS data (without the OISO08 data, the mean (standard error) $\delta^{18}O$ for subset 1 decreases to +0.078 (0.030) ‰). There are also some suggestions of systematic differences between cruises (for example, for subsets 1-2, OISO29 (2019) samples tend to have lower $\delta^{18}O$ and δD values, whereas OISO31 (2021) samples tend to have higher values). However, this is within the uncertainties of the means and is not fully understood. Thus, no further correction is warranted.

There are $\delta^{18}O$ data from a few cruises sampling deep-waters which can be compared with subsets of the LOCEAN data. These together with duplicates sets of samples between LOCEAN and other facilities form the basis for estimating consistency relative to the other data (details in App. A). The different comparisons yielded very varied results. It is often difficult to understand what is the source of the differences, but one commonly suspects choices of protocols, characteristics of the instrument used or internal standards (see also Aoki et al, 2017; Wassenaar et al., 2021). Altogether, although the limited inter-comparisons listed above have a large scatter (the standard deviation in the set of 18 average differences listed in App. A is 0.055 ‰), there is a tendency for LOCEAN $\delta^{18}O$ values reported in the concentration scale to be higher (relatively enriched in heavy isotopes). The average of these 18 different comparisons is +0.082 ‰ with a standard error of 0.016 ‰ (assuming that the 18 comparisons have the same uncertainty). This average difference happens to be close to the +0.09 ‰ adjustment that was applied to recent CRDS salty water samples analysed since 2015 at LOCEAN based on Benetti (2017c), an adjustment that was not done on CRDS or IRMS datasets produced in other facilities.

In summary, these external comparisons, together with the internal consistency tests on the LOCEAN database in a few regions, suggest that the LOCEAN $\delta^{18}O$ dataset are within +0.035

‰ absolute accuracy, at least when averaged spatially or in time (Table 2). Individual data have larger uncertainties as discussed before, because of the instrumental and internal standards uncertainty (resulting in a total uncertainty of usually less than 0.05 ‰ in $\delta^{18}O$) and possible aging/evaporation during collection and storage. We are not able to provide similar comparisons for δD or d-excess, as the database for comparison is much reduced.

4. The data

4.1 Data distribution

Fig. 3 presents the spatial distribution of the LOCEAN-analyzed data close to the surface, with the largest data collection being in the North Atlantic (Fig. 3a) (in particular, with OVIDE cruises since 2002 and the SURATLANT ship of opportunity dataset since 2011), the tropical Atlantic (in particular, the EGEE and PIRATA cruises since 2005), and the South Indian Ocean (Fig. 3b) (OISO cruises since 1998).

Table 3 reports the number of valid data points by depth range, which indicates that the emphasis in this set has been on near surface data (58% of the $\delta^{18}O$ data above 40m depth, with 13% between 40 and 200m depth, and only 12% at 1000m or deeper). There is less valid δD than $\delta^{18}O$ data, the difference corresponding to IRMS-measured data, which correspond to 25% of the total number of water samples in the database. There is even less valid d-excess than δD (by 10%), the difference corresponding to samples for which an adjustment for slight evaporation was done on $\delta^{18}O$ and δD data. The database contains fewer deep samples since the transition to CRDS than before, because of a recent emphasis of sampling the upper ocean.

4.2 Time series

We illustrate the dataset with time series of June (or July) data between 50° and 55°N in the eastern North Atlantic subpolar gyre (NASPG) collected mostly during the OVIDE cruises (Fig. 4). This scatter plot of cruise-averaged S and $\delta^{18}O$ indicates a near alignment of the values. It is striking that the strongest negative (fresher/lighter) anomalies in 2016 fit rather well on the regression line (in red) for water samples in the southwestern NASPG. This regression line is derived from data from the 47–55°N, 30-49°W region, excluding very low salinity data from seasonal sea ice melt or from shelf waters, and is very similar to the distribution in Frew et al. (2000). Thus, this reinforces the hypothesis of Holliday et al. (2020) that the strong freshening present in the eastern subpolar gyre in 2016 originated from the transport of Arctic freshwater from the western boundary current into the eastern basins, and not from local rainfall, which would have likely resulted in higher $\delta^{18}O$ at the same 'low' salinity such as depicted by the black line (Frew et al., 2000; C. Risi, pers. comm., 2021).

The SURATLANT surveys provided a seasonal sampling of water isotopes between late 2011 and 2019 along the western flank of the Reykjanes Ridge in the central part of the gyre (53-56°N/38°-44°W). Annual summaries of these data are provided on Fig. 5a. There is less alignment of the interannual values on the average southwestern NASPG linear regression line than for the OVIDE surveys (Fig. 4). However, there is some aliasing of the seasonal cycle in the annual averages (see Reverdin et al., 2018b), which contributes to the scatter, as well as noise on the data, and natural variability. On this plot the freshest year appears to be 2017, in agreement with an analysis using a much more complete salinity dataset (Reverdin et al., 2018a). 2017 is also one of the lighter $\delta^{18}O$ years. The corresponding d-excess versus S diagram (Fig. 5b) presents yearly anomalies that are fairly aligned with the average regression between southwestern NASPG d-excess and salinity data. Error bars are large, but nevertheless, low salinity waters exhibit high d-excess, as described in Benetti et al. (2017a, b).

5. Data availability:

The dataset described is version V2 at https://doi.org/10.17882/71186 (Waterisotopes-CISE-LOCEAN, 2021).

6. Conclusions

Instrumental uncertainty on individual data in this dataset is as low as 0.03, 0.15‰, in $\delta^{18}O$ /, δD, respectively, for most runs, with occasional much larger uncertainties. One needs to add to that the uncertainties on the internal standards that are used to convert measured values into the VSMOW scale. Different comparisons suggest that the internal standard values have almost always remained defined within at most 0.03 and 0.2‰ for $\delta^{18}O$ and δD, respectively, since 2012. There was however a short-term larger difference found for the most negative standard (equal to 0.1‰ for $\delta^{18}O$), most likely related to the readjustment of the instrument to laboratory conditions in May 2021. When using the CRDS Picarro L2130-i, we also found periods with quite uncertain analyses, in particular due to salt or particle deposit in the vaporizer or filters. These samples could often be run again afterwards to reach lower resulting uncertainty.

Finally, there is the issue of possible evaporation during collection and storage. When the analysis is done on a CRDS, we are usually able to detect possible biases larger than 0.05‰ in $\delta^{18}O$, by comparing d-excess with the expected d-excess derived from regional d-excess-S linear relationships. Attempts were made here to correct $\delta^{18}O$ and δD when the resulting uncertainty does not exceed 0.05 and 0.1‰, respectively. In particular this was done for some OISO cruise samples which were analysed many years after collection, or in the case of faulty caps being used, or caps that were not properly closed and wrapped with parafilm. This is certainly a strong source of quality loss for part of the database, and 'small' effects may have remained undetected.

Possible long-term drifts due to changes in internal standards, storage, instrumentation and protocols are difficult to estimate. This is done here by checking the consistency of different subsets of the database, for instance when time series can be obtained (such as in the southern Indian Ocean or North Atlantic subpolar gyre), or by comparison with duplicate data analysed in other laboratories, or with other datasets in deep regions commonly sampled. These comparisons are encouraging. On one hand, they suggest that the internal consistency in the database is usually within a 0.03 and 0.15‰ uncertainty for $\delta^{18}O$ and δD, respectively. On the other hand, although other datasets sometimes differ by much more with a large scatter between the 17 comparisons (with a standard deviation of 0.055‰ for $\delta^{18}O$), the average difference (+0.093‰) found with them is close to the adjustment that is applied to the LOCEAN data to report them on the concentration scale (+0.09‰ for $\delta^{18}O$ analyzed with a salt liner since 2015). Of course, there is still the possibility of errors and biases in subsets that could not be compared in a similar way, such as surface samples collected from ships of opportunity or sailing vessels in the tropics, that could result from different handling of the samples during collection and more uncertain storage conditions. There are also small errors originating from memory effects in the Picarro CRDS runs that could be better corrected and taken into account (Vallet-Coulomb et al., 2021).

We also illustrated the possibility of using this dataset to investigate ocean variability. Of course, the interest of a data archive is to merge different institutes datasets such as this one, while retaining a similar accuracy. This was attempted in the Global Seawater Oxygen-18 Database at GISS (Schmidt et al., 1999), although biases between subsets of this mostly $\delta^{18}O$ dataset remain at a level that makes the overall analysis of variability difficult to carry. The few comparisons we could do suggest that differences with other datasets are at times large. The

effort to correctly adjust for these differences and produce a larger coherent archive is required to get full use of the data collected. There is still a need of more and better calibrated seawater isotope data to reconstruct tropical hydroclimate variability, such as formulated for the tropical coral archives by PAGES CoralHydro2k Project, or for high latitude studies of the various sources of freshwater in the ocean, including continental runoff, sea ice, iceberg melt and air-sea exchanges.

Appendix A: Comparisons of LOCEAN data with other isotopic data

This includes on one hand comparisons with data of other cruises, in areas where we expect variability to have been weak, such as in the deep ocean, and on the other hand, considering duplicate sets of samples analysed in different institution.

Akhoudas et al. (2021) used the first approach in the deep Weddell Sea, comparing the LOCEAN 2017 Wapiti cruise data with data from other cruises over a fairly large range of neutral density surfaces. They identified a cruise whose $\delta^{18}O$ values were lower by 0.13‰ than at LOCEAN, as well as datasets that fit the Wapiti cruise values to within the data uncertainties (for example, from ANT-X12 cruise on RV Polarstern in 1995). Another water mass which can be used for comparison is the near - bottom waters in Fram Strait (below 2000m), which are either originating from the Arctic Ocean, or recirculating from the Greenland Sea. This water mass is regularly sampled, and has not been strongly ventilated recently. In 1998-2015 during German-led cruises, these waters presented an average $\delta^{18}O$ value close to +0.28‰ (after removing suspiciously high data of a cruise in 2011 and large positive outliers in 2012; Paul Dodd, personal communication). The LOCEAN database contains seven $\delta^{18}O$ samples close to the bottom across Fram Strait from MSM76 cruise on RV Maria S Merian in 2018, with average (SD) value close to +0.395 (0.035) ‰, thus averaging higher by 0.115‰ than the other set in 1998-2015.

We extracted individual profiles from the GISS Global Seawater Oxygen-18 Database (Schmidt et al., 1999) that can be compared with the LOCEAN station data, in deep and old water masses. In the southern Indian Ocean, for example numerous profiles collected during 1993-1994 cruises (CIVA1 (Archambeau et al., 1998), ADOX1, SWINDEX, ADOX2) suggest that LOCEAN $\delta^{18}O$ in the deep layers are higher by 0.10 to 0.17 ‰ depending on the cruise. There is also one GEOSECS 1978 station with a single deep value within 0.01 ‰ of close-by OISO stations, as well as some 1984 (INDIVAT1) and 1996 (CIVA2) station data with larger uncertainties that indicate higher LOCEAN $\delta^{18}O$ values by 0.15 to 0.22 ‰, depending on how outliers are identified and removed.

In the North Atlantic, there are data from three cruises that can be directly compared with LOCEAN data, focusing on deep waters with T-S properties close to the ones of the LOCEAN dataset. Comparison with one GEOSECS 1972 station south of Greenland suggests higher $\delta^{18}O$ LOCEAN values by ~ 0.060 ‰ (there is a small salinity shift between the two profiles which required to adjust the LOCEAN $\delta^{18}O$ value to the same salinity based on the average $\delta^{18}O$-S relationship). Data of 4 stations of the CONVEX1991 cruise (Frew et al., 2000) indicate higher $\delta^{18}O$ in LOCEAN dataset by ~ 0.090 ‰ (after adjustment done to consider small salinity differences). On the other hand, data close to the North East Atlantic deep-water layer from stations collected in 6/1995 in the southern Labrador Sea (Khatiwala et al., 1999) do not show a significant difference with LOCEAN stations closer to south Greenland (southern Irminger Sea) at a similar salinity. In the equatorial Atlantic there are deep data of two GEOSECS stations collected in 10/1972 and 2/1973 that can be compared with the LOCEAN data (mostly near 1000-2000m depth). These limited comparisons (often at large distance, but at a similar salinity) suggest that LOCEAN values are larger than the GEOSECS $\delta^{18}O$ by 0.055 ‰.

Finally, there are a few instances of seawater samples that have been duplicated and shared with other laboratories. Some of these in 2013-2014 have been used to validate how to convert IRMS or CRDS measurements into the concentration scale, with or without distillation (Benetti et al, 2017c), that we will not include here, and that suggested a scatter in the comparisons with different IRMS laboratories for natural or artificial seawater samples often on the order of 0.10 ‰. More recently, 18 samples of the WAPITI2017 cruise were duplicated with analyses both at LOCEAN and at the British Geological Survey stable isotope facility (BGS), which indicated lower LOCEAN $\delta^{18}O$ averaging -0.09 ‰ (SD = 0.035 ‰) (Akhoudas et al., 2021). In the same region, a small set of 11 samples was duplicated in 2020 with Hokkaido University, which suggests that LOCEAN $\delta^{18}O$ values are higher by +0.139 ‰ with a SD of 0.019 ‰ (Shigeru Aoki, pers. comm., 2021). Another set of 137 samples was duplicated in 2017 in the Southern Ocean from the Antarctic Circumnavigation Experiment cruise with samples analyzed at BGS (Haumann et al., 2019), which yielded an average difference of +0.004 (SD = 0.055 ‰).

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

Author contribution:
Gilles Reverdin and Claire Waelbroeck have measured parts of the isotopic data, contributed to their validation and written the paper. Catherine Pierre, Camille Akhoudas, Giovanni Aloisi,

Marion Benetti, have measured parts of the isotopic data and contributed to their validation. Jérôme Demange has maintained the CISE-LOCEAN IRMS and CRDS and Aïcha Naamar has measured parts of the isotopic data. Denis Diverrès, Magnus Danielsen and Thierry Reynaud have contributed water samples from ships of opportunity with associated salinity measurements. Bernard Bourlès, Jean-Claude Gascard, Hervé Le Goff, Marie-Noëlle Houssais, Pascale Lherminier, Claire Lo Monaco, Herlé Mercier, Nicolas Metzl, Simon Morisset, Jean-Baptiste Sallée, Virginie Thierry, Susan Hartman, Ed Mawji, Solveig Olafsdottir, Torsten Kanzow, Antje Voelker, Igor Yashayaev, Anton Velo, Alexander Haumann have contributed to the sample collection, and in some cases provided duplicate samples from other institutions. Melanie Leng and Carol Arrowsmith analyzed water samples, and contributed to the qualification of some of the reference materials. Michael Meredith contributed to the planning and sampling strategy of the ACE fieldwork, with the ACE and ORCHESTRA projects.

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

Acknowledgments: Data were measured at the CISE-LOCEAN facility housed by the LOCEAN laboratory and part of the OSU ECCE Terra analytical services. Support by OSU ECCE Terra, by LOCEAN, and by various French national institutes and programs is gratefully acknowledged (including INSU/CNRS, IFREMER, IPSL, IRD, IPEV, LEFE program, ANR GEOVIDE), as well as support by different French 'Services nationaux d'Observation', such as PIRATA, SSS and OISO/CARAUS. Many of the data originate from research cruises on French Research vessels: R.V. Suroit, Thalassa, Atalante, Marion Dufresne 2, Tara. Some data were collected during research cruises on non-French vessels, such as MIDAS in 2013 as well as BOCATS1 in 2016 and BOCATS2 in 2021 on the Spanish R.V. Sarmiento de Gamboa, HUD2014007 on the Canadian R.V. Hudson, 2014 JR302 in 2014 and 2017 JR16004 cruises on the U.K. HMS James Clarke Ross, the Arctic cruises in 2006-2008, 2013, and the 2020-2021 Microbiome cruise on French S.V. Tara, the Nordic seas MIZEX cruises in 2002-2004 on Swedish R.V. Oden, the 2017 SPURS2 cruise on R.V. Revelle, and the 2018 east Greenland cruise MSM76 on German R.V. Maria S. Merian. The SURATLANT data were collected on merchant vessels with support from Iceland-based EIMSKIP and Marine and Fisheries Research Institute in Iceland and the Nuka Arctica/Tukuma Arctica dataset was collected on the merchant vessels Nuka Arctica and Tukuma Arctica from Greenland-based company RAL. Data were also collected from different Merchant Vessels recruited by SNO SSS for the Atlantic Ocean monitoring. Finally, data were collected from sailing vessels, including the Rara Avis (AJD), the Boogaloo and Ragnar (OceanoScientific), the Northabout (UnoMundo) and the UltimIII (SODEBO). In all instances, we are thankful for the contribution of the crew, and numerous scientists and technicians who contributed to the sampling. We also acknowledge the contribution of the scientists and technicians of the Vigo CO2 group who participated in the CATARINA, BOCATS1 and BOCATS2 (PID2019-104279GB-C21/AEI/10.13039/501100011033) campaigns funded by the Spanish Research Agency, as well as in other OVIDE cruises. The WAPITI project received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement 637770). The Antarctic Circumnavigation Expedition was made possible by funding from the Swiss Polar Institute and Ferring Pharmaceuticals, and F.A. Haumann was supported by the SNSF grant numbers P2EZP2_175162 and P400P2_186681. Intercomparisons of samples were done with various other institutions to which we are very grateful. In particular, we acknowledge the contributions by Robert van Geldern at Geozentrum Nordbayern, Melanie Leng at the British Geological Survey, Arne E Sveinbjörnsdóttir and Rosa Ólafsdóttir at the University of Reykjavik, Pal Morkved at the University of Bergen, Bénédicte

Minster at LSCE, Penny Holliday at NOC in Southampton, Paul Dodd at the Norwegian Polar Institute in Tromsoe, and Shigeru Aoki at Hokkaido University. We thank the two reviewers for their helpful comments.

References:

Akhoudas, C., Sallée, J.-B., Reverdin, G., Aloisi, G., Benetti, M., Vignes, L., and Gelado. M.: Ice-shelf basal melt and influence on dense water outflow in the southern Weddell Sea, J. Geophys. Res.: Oceans, 125, e2019JC015710, doi:10.1029/2019JC015710, 2020.

Akhoudas, C. H., Sallée, J.B., Reverdin, G., Meredith, M. P., Naveira Garabato, A., Haumann, F. A., Jullion, L., Aloisi, G., Benetti, M., Leng, M. L., Arrowsmith, C. : Ventilation of the abyss in the Atlantic sector of the Southern Ocean, Nature Sci Repc 11, 16733 (2021), https://doi.org/10.1038/s41598-021-95949-w, 2021.

Aoki, S., Kobayashi, R. , Rintoul, S. R., Tamura, T., and Kusahara, K.: Changes in water properties and flow regime on the continental shelf off the Adélie/George V Land coast, East Antarctica, after glacier tongue calving, J. Geophys. Res.: Oceans, 122 (8), 6277 – 6294, 2017.

Archambeau A.S., Pierre C., Poisson A., Schauer, B.: Distribution of CFC-12, Oxygen and carbon stable isotopes in the Water masses of the Southern Ocean at 30°E from Africa to Antarctica, J. Mar. Sys., 17, 25-38, 1998.

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

Benetti, M., Reverdin, G., Yashayaev, I., Holliday, N.P., Tynuan, E., Torres-Valdes, S., Lherminier, P., Tréguer, P., Sarthou, G., and Lique, C.: Composition of freshwater in the spring of 2014 on the southern Labrador shelf and slope. J. Geophys. Res.: Oceans, 122, 1102-1121, doi: 10.1002/2016JC012244, 2017a.

Benetti, M., Reverdin, G., Aloisi, G., and Sveinbjörnsdóttir, A.: Stable isotopes in surface waters of the Atlantic Ocean: indicators of ocean-atmosphere water fluxes and oceanic mixing processes, J. Geophys. Res. Oceans, doi:10.1002/2017JC012712, 2017b.

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

Benetti, M., Reverdin, G., Clarke, J. S.,Tynan, E., Holliday, N. P., Torres-Valdes, S., Lherminier, P., Yashayaev, I.: Sources and distribution of fresh water around Cape Farewell in 2014, J. Geophys. Res., doi:10.1029/2019JC015080, 2019.

Bigg, G.R., and Rohling, E.J.: An oxygen isotope dataset for marine water, J. Geophys. Res. Atmos., 105, 8527-8536, doi:10.1029/2000JC900005, 1999.

Craig, H., and Gordon, L.I.: Deuterium and oxygen18 variations in the ocean and marine atmosphere, In:Tongiogi,E.(Ed.),Proc. Stable Isotopes in Oceanographic Studies and Paleotemperatures, pp.9–130 (V.Lishie e F., Pisa), 1965.

Frew, R., Dennis, P.F., Heywood, K., Meredith, M.P., and Boswell, S.M.: The oxygen isotope composition of water masses in the Northern North Atlantic, Deep-Sea Res. I, 47, 2265-2286, doi:10.1016/S0967-0637(00)00023-6, 2000.

Gröning, M.: Stable Isotope Internal Laboratory Water Standards: Preparation, Calibration and Storage., TEL Technical Note No. 03, (revised from IHL Technical Procedure Note No.43, Tanweer et al., as of May 2009), 2018.

Haumann, F. A., K. Leonard, M. P. Meredith, C. Arrowsmith, I. V. Gorodetskaya, J. Hutchings, M. Lehning, M. J. Leng, S. Stammerjohn, M. Tsukernik, Y. Weber, 2019. Seawater stable isotope sample measurements from the Antarctic Circumnavigation Expedition (ACE) (Version 1.0) [Data set]. *Zenodo*. doi:10.5281/zenodo.1494915.

Holliday, N.P., M. Bersch, B. Berx, L. Chafik, S. Cunningham, C. Florindo-López, H. Hátún, W. Johns, S.A. Josey, K. M. H. Larsen, S. Mulet, M. Oltmanns, G. Reverdin, T. Rossby, V. Thierry, H.Valdimarsson, I. Yashayaev, 2020. Ocean circulation changes cause the largest freshening event for 20 years in the eastern subpolar North Atlantic. Nature Communications, 11, DOI: 10.1038/s41467-020-14474-yKhatiwala, S. P., Fairbanks, R. G., and Houghton, R. W.:Freshwater sources to the coastal ocean off northeastern North America: Evidence from $H_2{}^{18}O/H_2{}^{16}O$, J. Geophys.Res. 104: 18241–18255, doi:10.1029/1999JC900155, 1999.
Lherminier, P., 2018: OVIDE 2018 cruise, RV Thalassa, https://doi.org/10.17600/18000510.
Lis, G., Wassenaar, L., and Hendry, M.: High-precision laser spectroscopy D/H and 18O/16O measurements of microliter natural water samples, Analytical chemistry 80(1), 287-293, 2008.
Östlund, H.G., Craig, H., Broecker, W. S., and Spenser, D.: GEOSECS Atlantic, Pacific and Indian Ocean Expeditions: Shore based Data and Graphics,Technical Report, National Science Foundation, Washington, DC, p.220, 1987.
Reverdin G, Alory, G., Diverres, D., Bringas, F., Goni, G., Heilmann, L., Chafik, L., Szekely, T., and Friedman, A.R.: North Atlantic subpolar gyre along predetermined ship tracks since 1993: a monthly data set of surface temperature, salinity, and density, Earth Syst. Sci. Data 10: 1403-1415, doi:10.5194/essd-10-1403-2018, 2018a.
Reverdin, G., Metzl, N., Olafsdottir, S., Racapé, V., Takahashi, T., Benetti, M., Valdimarsson, H., Benoit-Cattin, A., Danielsen, M., Fin, J., Naamar, A., Pierrot, D., Sullivan, K., Bringas, F., and Goni, G. : SURATLANT: a 1993–2017 surface sampling in the central part of the North Atlantic subpolar gyre, Earth Syst. Sci. Data, 10, 1901-1924, doi:10.5194/essd-10-1901-2018, 2018b.
Reverdin, G., Metzl, N.., Reynaud, T., Poli, P., Griboval, Y. : L'Exploreur OceanoScientific "Boogaloo" - Une campagne péri-Antarctique, 26/01/2017 - 04/04/2017, La Météorologie, April 2020, doi :10.1002/2016JC012244, 2019.
Schmidt, G.A.: Error analysis of paleosalinity calculations, Paleoceanography , 14, 422-429, doi:10.1029/1999PA900008, 1999.
Schmidt, G.A., Bigg, G.R., and Rohling E.J.: Global Seawater Oxygen-18 Database – Data, GISS, http://www.giss.nasa.gov/data/o18data/, 1999.
Skrzypek, G., and Ford, D.: Stable isotope analysis of saline water samples on a cavity ringdown spectroscopy instrument, Environ. Sci. Technol., 48, 2827-2834, doi:10.1021/es4049412, 2014.
Stevens et al : EUREC^{4}A , Earth Sys. Sci. Data, 13, 4067–4119, https://doi.org/10.5194/essd-13-4067-2021, 2021.
Vallet-Coulomb C., Couapel M., and Sonzogni C.: Improving memory effect correction to achieve high-precision analysis of delta O-17, delta O-18, delta H-2, O-17-excess and d-excess in water using cavity ring-down laser spectroscopy, Rapid Comm. In Mass Spectr., 35 (14), p. e9108 [16 p.] ISSN 0951-4198, 2021.
Voelker, A.H., Colman, A. , Olack, G., and Waniek, J.: Oxygen and hydrogen isotope signatures of northeast Atlantic water masses, Deep Sea Res. II, 116, doi:10.1016/j.dsr2.2014.11.006, 2015.
Walker, S.A., Azetsu-Scott, K., Normandeau, C., Kelley, D.E., Friedrich, R., Newton, R., Schlosser, V, McKay, J.L., Abdi, W., Kerrigan, E., Craig, S.E., and Wallace, D.W.R.: A comparison of cavity ring-down spectroscopy (CRDS) and isotope ratio mass spectrometry (IRMS), Limnology and Oceanogr.: Meth., doi: 10.1002/lom3.10067, 2016.
Wassenaar, L.I., Terzer-Wassmuth, S., and Douence, C.: Progress and challenges in dual- and triple-isotope ($\delta^{18}O$, $\delta^{2}H$, $\Delta^{17}O$) analyses of environmental waters: an international

assessment of laboratory performance, Rap. Comm. In Mass Spectrom., in Press, doi:10.1002/rcm.9193, 2021.
Waterisotopes-CISE-LOCEAN, Water isotopes of seawater analyzed since 1998 at LOCEAN, SEANOE. https://doi.org/10.17882/71186, 2021.
Xu, X., Werner, M., Butzin, M., and Lohmann, G.: Water isotope variations in the global ocean model MPI-OM, Geosci. Model Dev., 5,809-818, doi:10.5194/gmd-5-809-2012, 2012.

Table 1

Comparison of standards measured at LOCEAN and in other laboratories (in ‰). The laboratories in the 2013-2014 comparisons took place at LSCE (France), LDEO (Columbia University, USA), NIOZ (Netherlands), VRIJE (Brussels, Belgium), Dalhousie Univ (Dahlousie, Canada), BGS (Nottingham, UK), U. Ottawa (Ottawa, Canada), and in 2018-2019, at GeoZentrum NordBayern (Erlangen, Germany), AWI (Bremerhaven, Germany), U. Kiel (Kiel, Germany), LSCE (France), U. Bergen (Bergen, Norway).

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

Table 2:

Comparison of LOCEAN annually-averaged data in a few selected deep-water masses which exhibit little variability in their salinity, and have likely not been recently ventilated. S, $\delta^{18}O$, δD and d-excess values are first averaged for each year. The values reported are the mean and standard deviations of these yearly averages. The number of years (N years) refers to the $\delta^{18}O$ data.

1: OISO cruises (1998 to 2021) near 1000-1500m in South Indian Ocean Antarctic sector of the Southern Ocean (50°S-58°S) (1998*, 2002*, and most years since 2010)

2: OISO cruises (1998 to 2021) near 2000m in the western South Indian Ocean subtropical gyre (1998*, 2002*, and most years since 2010)

3: PIRATA and EGEE cruises (2005-2021) near 1000m in eastern equatorial Atlantic (2005*, 2006*, 2007*, 2015, 2020, 2021)

4: OVIDE and RREX2017 data between 2000m and 3500m in eastern North Atlantic subpolar gyre (data in 2002*, 2016, 2017, 2018, 2021)

Cruise set	1	2	3	4
N years	13	9	6	5
S	34.710 (0.013)	34.695 (0.005)	34.615 (0.010)	34.936 (0.010)
$\delta^{18}O$ (‰)	+0.095 (0.035)	+0.085 (0.035)	+0.150 (0.020)	+0.287 (0.030)
δD (‰)	-0.25 (0.13)	-0.29 (0.10)	+0.24 (0.15)**	+1.18 (0.20)
d-excess (‰)	-0.80 (0.15)	-1.03 (0.19)	-0.81 (0.0)**	-1.05 (0.10)

* IRMS estimates for $\delta^{18}O$ only.

** only two years

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

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

Figure captions

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 (a, b): the deviations of isotopic values (‰) of internal standards (in blue) and of the KonaDeep-water samples (in red) relative to their expected values (horizontal axis is sample number). 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 (c, d) present the values obtained after adjusting for the drifts identified with the KonaDeep-water samples through the run.

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

Figure 3: Maps which include most of the near-surface $\delta^{18}O$ data in the LOCEAN archive (color scale $\delta^{18}O$ in ‰). (3a) Arctic and Atlantic oceans; (3b) other oceanic regions.

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

Figure 5: Scatter plots in the southern Irminger Sea/NASPG of annually averaged SURATLANT surveys data. (a) presents $\delta^{18}O$ (‰) versus practical salinity, whereas (b) 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.

839
840

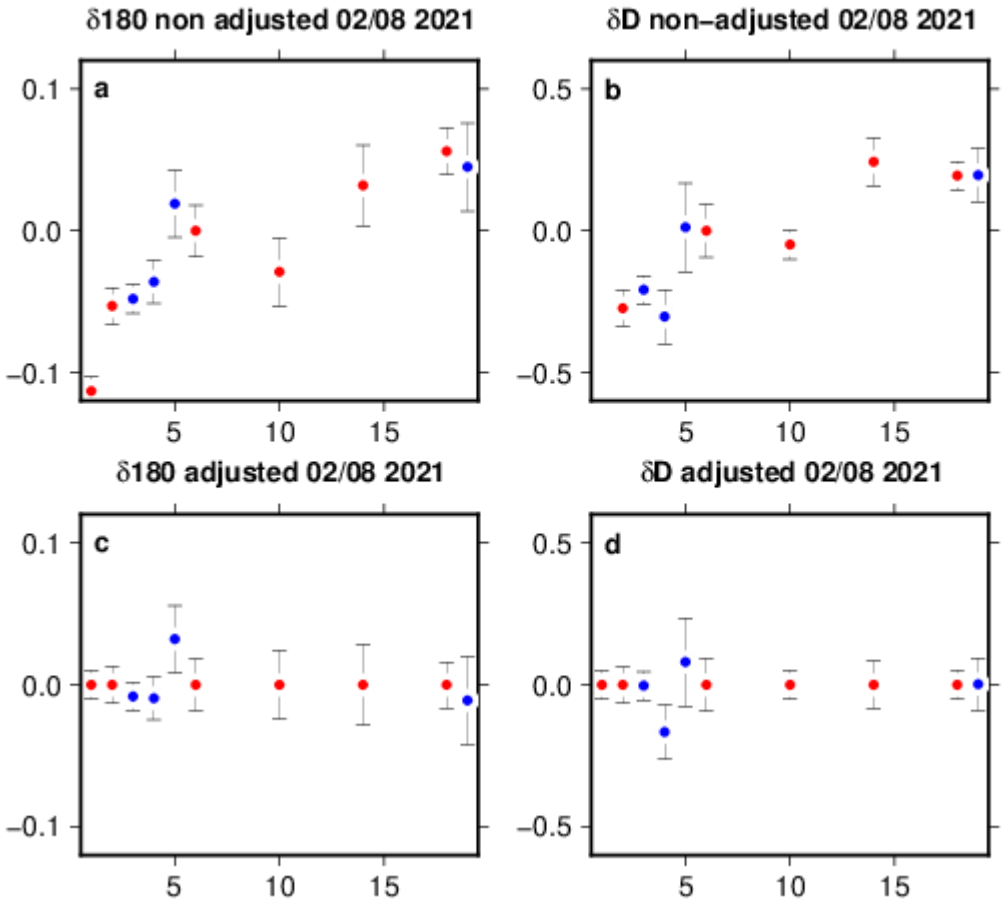

Figure 1: A typical run (on 2/08 2021) of 19 samples using three internal standards and KonaDeep-water samples (left for $\delta^{18}O$ and right for δD). Top panels (a, b): the deviations of isotopic values (‰) of internal standards (in blue) and of the KonaDeep-water samples (in red) relative to their expected values (horizontal axis is sample number). 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 (c, d) present the values obtained after adjusting for the drifts identified with the KonaDeep-water samples through the run.

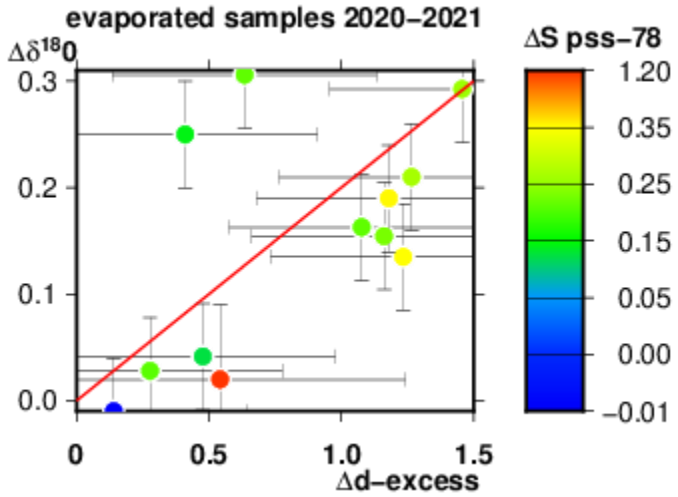

Figure 2: Scatter diagram of the deviation of $\delta^{18}O$ (‰) versus the deviation of d-excess (‰) for a set of samples extracted from salinity bottles with no plastic inserts that had evaporated (2021, mostly from MV Tukuma Arctica in the North Atlantic). The deviations are estimated by subtracting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

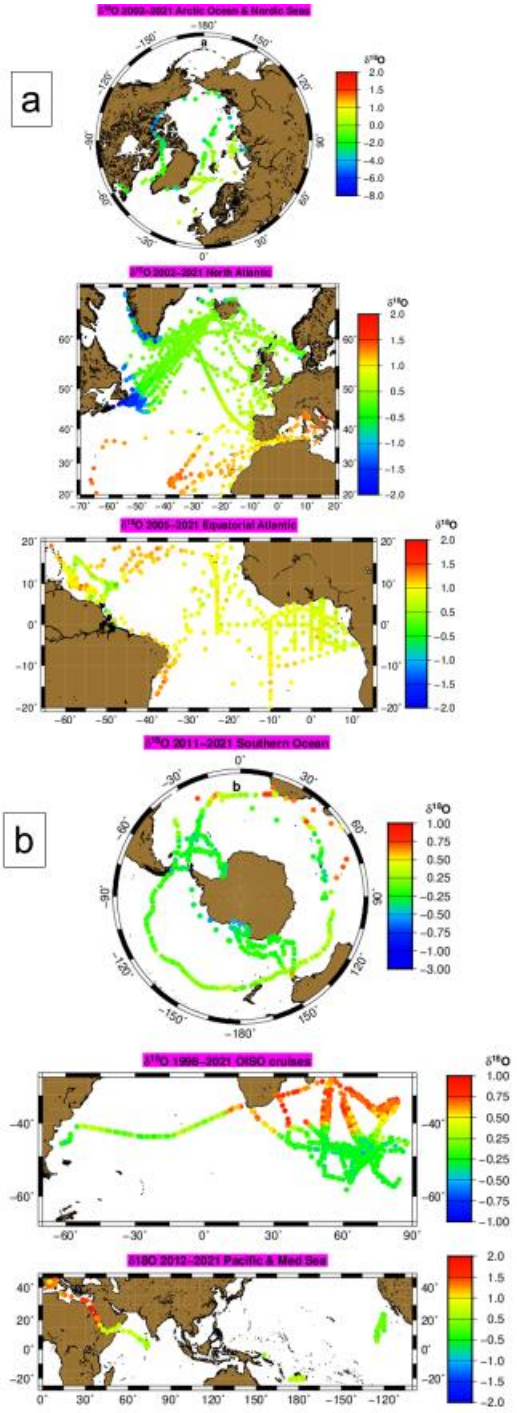

Figure 3: Maps which include most of the near-surface $\delta^{18}O$ data in the LOCEAN archive (color scale $\delta^{18}O$ in ‰). (3a) Arctic and Atlantic oceans; (3b) other oceanic regions.

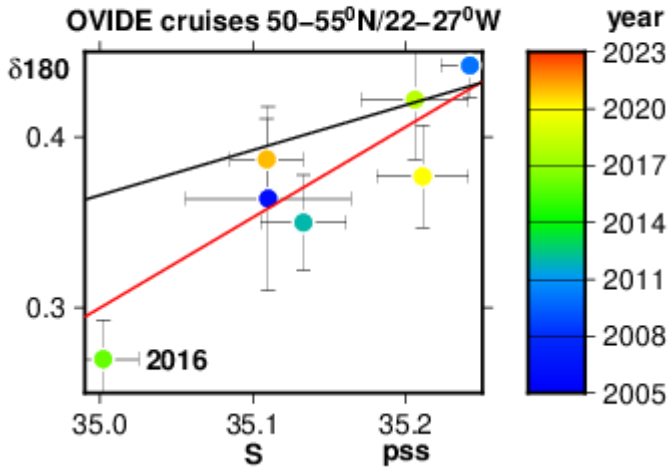

Figure 4: Scatter plot of cruise averages of near surface (upper 100-m) $\delta^{18}O$ (‰) versus practical salinity in the Iceland Basin, close to the NAC fronts. The bars indicate the standard deviation between the individual data that are averaged. Notice the fresher and isotopically lighter data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

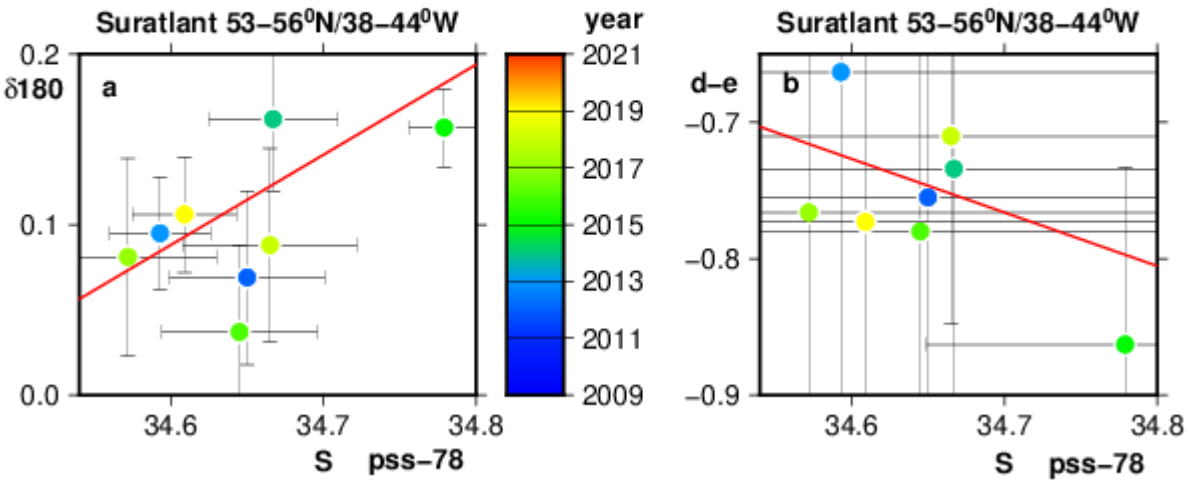

Figure 5: Scatter plots in the southern Irminger Sea/NASPG of annually averaged SURATLANT surveys data. (a) presents $\delta^{18}O$ (‰) versus practical salinity, whereas (b) presents d-excess (‰) versus practical salinity. The bars indicate the standard deviation between the individual data that are 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.