

Technical note: Large offsets between different datasets of sea water isotopic composition: an illustration of the need to reinforce intercalibration efforts

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Abstract

1. Introduction

- 33 Seawater isotopic composition $(^{18}O/^{16}O$ and $^2H/^{1}H$ ratios expressed as $\delta^{18}O$ and $\delta^{2}H$ in ‰ in the VSMOW/SLAP scale) is classified as an Essential Ocean/Climate Variable (EOV/ECV) in international programs such as GEOTRACES and GO-SHIP. Stable 36 seawater isotopes (δ^{18} O, δ^{2} H) are used to trace sources of freshwater (precipitation, evaporation, runoff, melting glaciers, sea ice formation and melting), both at the ocean surface and in the ocean interior (Schmidt et al., 2007; Hilaire-Marcel et al., 2021). Except for fractionation during phase changes, the water isotopic composition is nearly conservative in the ocean. A major emphasis is on high latitude oceanography, where continental (or iceberg) glacial melt, formation or melt of sea ice, and high-latitude river inputs (for the Arctic) leave different imprints on the surface ocean isotopic composition. In contrast, few studies have been performed on the isotopic signature in the deep ocean (e.g., Prasanna et al., 2015; Voelker et al., 2015). Seawater isotopes in the upper ocean at low latitudes are often vital for paleoclimatic studies, as they are needed to calibrate proxies of past ocean variability in marine carbonate records such as corals and foraminifera (e.g., PAGES CoralHydro2k working group; Konecky et al., 2020). Seawater isotopes are also important tracers in the coastal ocean, with emphasis on upwelling (Conroy et al., 2014, 2017; Kubota et al., 2022; Lao et al., 2022), and river discharges (e.g., Amazon) (Karr and Showers, 2001). Surface ocean seawater isotopes are also used to characterize evaporation rates and air-sea interactions (Benetti et al., 2017). The isotopic signatures of these different processes are evolving in our warming world, which will imprint on the seawater isotopic composition (Oppo et al., 2007). Additionally, seawater isotope data provide model boundary conditions and allow the assessment of model performance in isotope-enabled Earth system models (e.g. Schmidt et al., 2007; Brady et al., 2019; Cauquoin et al., 2019), thereby improving climate model projections of the future.
- Stable seawater isotope data have thus been massively produced in the last decades by a variety of methods. For example, most data compiled in the "GISS Global Seawater Oxygen-18 Database -V1.21" for stable seawater isotopes (LeGrande and Schmidt, 2006) originate from Isotope-ratio Mass Spectrometry (IRMS). They were mostly measured in

(e.g., Voelker et al., 2015). These intercomparisons often outline systematic differences

which could result from the issue outlined above, or from other issues, such as

uncertainties in reference materials used, analysis protocols, or isotopic changes in the

samples during their handling and storage (Benetti et al., 2017a; Akhoudas et al., 2019;

Hennig et al., 2024). In other cases, this was not done, either because the data stood by

93 themselves (Bonne et al., 2019, for δ^{18} O and δ^{2} H data), or there was no comparison data

samples to carry a direct comparison, or, if this was not done, to compare the data with

other published data and evaluate potential systematic differences.

2. Comparisons

 For identifying possible offsets, we consider surface ocean subsets of the LOCEAN data base in specific regions for roughly the same years as the other data collected. The data extracted are from the same regions as in the datasets of the two studies and are 109 gathered in S- δ^{18} O space as well as in S- δ^{2} H space (available only for the Bonne et al (2019) data set), where S is reported as a practical salinity with the practical salinity 111 scale of 1978 (pss). The assumption done here as in many papers is that the $S-¹⁸O$ relationship holds on fairly large scales in the surface layer (for the eastern subtropical North Atlantic, see for example, the discussion in Voelker et al (2015) and in Benetti et al. (2017a)). Obviously, this has limitations, such as in areas influenced by more than one water mass or by multiple freshwater end-members (meteoric, continental run-off, sea ice melt or formation, evaporation).

2.1 Daily surface data collected from R.V. Polarstern

The surface seawater samples originated from daily collection during two years on

board RV Polarstern in 2015-2017 (Bonne et al., 2019). There is no salinity provided

with the data, and here we chose to associate them with the simultaneously collected

thermosalinograph (TSG) data collected on board the RV Polarstern and available from

PANGAEA (for each cruise, an indexed file with title starting by 'Continuous

thermosalinograh oceanography along Polarstern' is included in PANGAEA: for example,

- the eastern Atlantic. In the North Atlantic, LOCEAN data have been continuously
- collected since 2011, and south of 10°S in the eastern Atlantic mostly since 2017.

2.2 Southern subtropical Indian Ocean

193 Figure 2: Map of $\delta^{18}O$ surface data in the LOCEAN archive for 2016-24, north of 60°S. All 194 these data are associated with S and δ^2 H data.

195 The LOCEAN data distribution indicates some scatter in the $S-³⁸O$ distribution in the

southwestern Indian Ocean (Fig. 3a) for S larger than 35 pss. Data above the regression

206 a)

a salinity between 35 and 36 pss (black line) overlaid. The spatial distributions of the

- 213 LOCEAN data with higher and lower $\delta^{18}O$ relative to that regression line in the whole Indian
- 214 Ocean north of 60°S are shown on panels (b) and (c), respectively.
- 215 When focusing on the lower part of the distribution in $S- \delta^{18}O$ space (Fig. 3c), one
- 216 observes a gradual lowering of δ^{18} O from west to east for salinities above 35 (Fig. 4) all
- 217 the way to 150°E. This lowering is on the order of 0.15 at most, even for the higher
- 218 salinities (35.5 or more) for which it is strongest (Fig. 4).

219

 Figure 4: The LOCEAN data below the regression line of Fig. 3a (the ones mapped in Fig. 3c) 221 in $S-¹⁸O$ space, color-coded as a function of longitude. The two linear relationships recommended in this region between 23°S and 49°S by Glaubke et al. (2024) for the south- west Indian Ocean and for the Australian margin (south of Australia) (we use the original $124 \delta^{18}O = 0.4231 * S - 14.7876$, instead of the rounded-up relation reported in the paper; R. H. Glaubke, pers. Comm., 2024) are also plotted (black lines), as well as the earlier linear relationship for the 0-600m layer along the Australian margin by Richardson et al. (2018) (in 227 pink).

228 Thus, besides some gradual and smaller changes, we do not observe in the LOCEAN

229 surface dataset a large sudden change in the (S, $\delta^{18}O$) distribution near 75°E or 85°E

230 between the southeastern and southwestern Indian Ocean, nor a further strong change

- 231 closer to the Australian coastal margin, as suggested by figures 6 and 7 of Glaubke et al.
- 232 (2024). Most of the LOCEAN (S, δ^{18} O) data south of 28°S correspond to the mixing of a

3. Discussion

 In the two cases, we find significant differences between the data sets compared. In the case of the RV Polarstern dataset (Bonne et al., 2019), an error in a specified reference material value was found, and the adjusted data present only small offsets with respect 248 to LOCEAN data, that are slightly negative for δ^{18} O and slightly positive for δ^2 H. Differences might arise from spatial differences. For example, in the northern hemisphere, values at salinity close to 35 pss mostly originate from the North Sea and English Channel in the Polarstern dataset, thus with more mid-latitude continental influence than for most of the LOCEAN data in the same salinity range which have a contribution of more depleted subpolar and polar freshwater. One expects a larger scatter in the South Atlantic for salinities less than 35 pss, due to intermittent presence of sea ice or iceberg melt, and at higher salinities due to the presence of different water masses originating from the South Atlantic and southeastern Indian Ocean. However, the current data set is not sufficient to estimate it. Furthermore, different seasons were sampled in the two datasets. In the northeastern

Atlantic sector, Bonne et al. (2019) surface data east of 30°W were collected in in April

and November north of 10°S and in November south of 10°S in the southeastern

Atlantic. These data do not suggest large seasonal differences in the Northeast Atlantic,

262 concurring with the LOCEAN $(S, \delta^{18}O)$ data in the tropics to mid-latitudes (20 to 50°N),

263 which are tightly distributed along a mean $S-³⁸O$ relationship, and thus with low

 seasonal variability (Benetti et al., 2017a; Voelker et al., 2015). The LOCEAN data are not numerous enough in the South-East Atlantic to further evaluate whether the offset is constant throughout the data set, or presents a component related to geophysical temporal or spatial variability.

 When considering the South Indian Ocean, Glaubke et al. (2024) combined data sets that were processed in different institutes, and potential offsets between those could cause the differences in spatial variability. In particular, Glaubke et al. (2024) outline large 271 spatial contrasts in the $S-S^{18}O$ relationship across the surface subtropical Indian Ocean and southern Australia that are not observed in the recent version of the LOCEAN database. Seasonal or interannual variability might also contribute to the differences shown on Fig. 3, as the data in the southeastern Indian Ocean from Glaubke et al. (2024 were collected in November-December, whereas the data in the LOCEAN database in this region are mostly from February-March. However, at least south of Tasmania, where the LOCEAN data base also contains December data, it does not seem that the seasonal cycle would cause differences larger than 0.05 ‰ at the same salinity. A difference due to seasonality is thus barely identifiable, noting the possible presence of interannual variability and that 0.05 ‰ is the long-term accuracy in the analyses in some centers, such as AWI Potsdam and LOCEAN. Richardson et al. (2018) also commented that there was little difference between a southern winter cruise and March data south of Australia. Further west, near 55-70°E, earlier surface data in the OISO surveys, as well as the vertical upper profiles of OISO station data also suggest a rather modest seasonal variability on the order of 0.10‰. Changes could also arise from interannual variability, but the range of interannual variability in the LOCEAN data base is smaller than the difference between the Glaubke et al (2024) curves for the southeastern Indian Ocean and south of Australia and the corresponding LOCEAN data. Thus, a likely contribution for the large differences would be the existence of systematic offsets between the South Indian Ocean/Australia margin data produced in three different institutes that were combined in the Glaubke et al. (2024) study.

4. Conclusions

 What these two comparisons suggest is that offsets are present between different recent 294 data sets published, which exceed 0.10‰ in δ^{18} O and 0.50‰ in δ^{2} H, thus larger than the

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