MASIS:

Towards best practices for Measuring and Archiving Stable Isotopes in Seawater

Working Group proposal submitted to SCOR, May 2022

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Summary/abstract

Seawater stable isotopic composition and the carbon isotopic composition of dissolved inorganic carbon are essential ocean tracers that have been widely measured since the 1960s. They are particularly important to measure well in times of wide-spread changes in the hydrological cycle, the bio-geochemical cycles, as well as the anthropogenic carbon penetration and induced acidification of the oceans, because they serve as a fingerprint of these ongoing changes in the ocean. However, substantial issues of data collection, quality control, and compilation exist: common reference materials in seawater are not widely available, analysis methods have strongly diversified, and intercomparison exercises are lacking, to the extent that large differences exist between different data sets. These differences currently prohibit the community from making full use of the potential of stable isotopes to identify climatic changes.

This working group is dedicated to remedy the current issues of data collection, quality control, and compilation of stable isotopes in seawater. First, we will assess the validation stage of the available stable isotopic datasets, as well as corresponding metadata and where and how they are communicated. This effort will lead to a report of best practices from sample collection to measurement and quality control. Second, we will review methods for adjustment of biases in archives and reassess these biases. Third, we will work towards complementing existing databases, with particular effort on missing surface ocean sampling data, either discrete or continuous. In parallel with the aforementioned tasks/efforts, the working group will promote and carry intercomparison exercises, and will actively carry out capacity-building.
1. Scientific background/rationale

Seawater stable isotopic composition (the $^{18}$O/$^{16}$O and $^2$H/$^1$H ratios expressed as δ$^{18}$O and δ$^2$H in ‰ in the VSMOW/SLAP scale), and the carbon isotopic composition (δ$^{13}$C/$^{12}$C expressed as δ$^{13}$C in ‰ versus VPD) of dissolved inorganic carbon (DIC) have been widely measured since the 1960s, thanks to the use of mass spectrometry techniques that could be operated in well-equipped spectrometric laboratories, and required moderate volumes of water (on the order of 1-100 ml). These are the most commonly measured isotopic properties in seawater and its dissolved constituents, and there are important scientific reasons to first tackle those constituents, both classified as EOV/ECVs (Essential ocean/climate variables) by GOOS, CLIVAR, and IODE (UNESCO). Also, the recommendations that will be made on acquisition, quality control, and data assembly for these parameters will likely be relevant for a wider range of isotopic measurements.

Stable seawater isotopes (δ$^{18}$O and δ$^2$H) are used to investigate the water cycle, and 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. Although there is limited global sampling - despite the GEOTRACES campaigns -, 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) differently imprint seawater isotopic composition. In contrast, few studies have been performed on the isotopic signature in the deep ocean (e.g., Prasanna et al., 2015). There is another emphasis on the upper ocean at low latitudes, often associated with coral and paleoclimate studies (for validating climate variability ‘indicators’, see PAGES CoralHydro2K working group; Konecky et al., 2020), as well as in the coastal ocean, with different signatures imprinted by evaporation, rain (Conroy et al., 2014, 2017), or major river inputs (e.g. Amazon) (Karr and Showers, 2001). Additional applications in the surface ocean aim to better characterize the evaporation and air-sea interactions (Benetti et al., 2017). The isotopic signatures of these different sources are evolving in our warming world, which will imprint the seawater isotopic composition.

The isotopic composition of dissolved inorganic carbon (referred to as δ$^{13}$C-DIC) is measured, in particular in the upper oceanic layers, to characterize biological processes associated with fractionation during biomass fixation, as well as remineralisation of organic matter (for those, these data are complementary to DIC, TA, inorganic nutrients). Modern ocean data is also used to ground truth isotopic signals in carbonate shelled organisms (e.g., benthic foraminifera shells; Schmittner et al., 2017). Finally, it is often measured to better estimate the anthropogenic carbon penetration in the ocean, due to the δ$^{13}$C lowering related to anthropogenic carbon emissions (the so-called Suess effect) (Eide et al., 2017). This can thus yield an alternate estimation of the ocean storage of anthropogenic carbon, provided that the data are of sufficient accuracy and spatial coverage and that seasonal variability near the surface is taken into account (Quay et al., 2003, 2017).

Earlier syntheses have been done such as the GISS Global Seawater Oxygen-18 Database for stable seawater isotopes (LeGrande and Schmidt, 2006), and GLODAP (Olsen et al., 2016, 2020) for the biogeochemistry observations collected during selected oceanographic
research cruises. These syntheses have been used for validating modelling studies in which these parameters are explicit diagnostic variables (e.g., Roche and Caley, 2013; Schmittner et al., 2013, Kwon et al., 2022).

An optimal data accuracy on the order of 0.05 ‰ for δ18O (0.25‰ for δ2H) and 0.03‰ for δ13C is required to get the full benefit of these data sets. This accuracy is a demanding task, but not out of reach, as specific data studies suggest (for δ13C-DIC, Humphreys et al., 2016; for water isotopes, Haumann et al., 2019).

However, in practice, this requirement is currently not reached in many cases for three main reasons:

1: For both sets of variables, there are issues with internal standards and reference material (RM) used in the laboratories. For the seawater isotopes, a seawater RM is not widely available. Moreover, biases on the produced data originating from sea salt are likely to happen, which depend on instrumentation, analysis methods. For δ13C-DIC, there is no internationally-recognized liquid seawater RM, although some groups have used reference water material distributed primarily for DIC and total alkalinity. There have been attempts to run intercomparison studies with the same sample shared between different laboratories. For water isotopes, this is regularly organized by IAEA (WICO tests described in Wassenaar et al., 2021, usually for fresh water samples), whereas, for δ13C-DIC, it is not regularly done, but there has been an interesting recent inter-comparison exercise (Cheng et al., 2019). In both instances, the comparisons often reveal large offsets between some laboratories, and a large spread of values between the different participants.

2: For both sets of variables, traditionally measured by mass spectrometry, other analysis techniques have recently spread, in particular using laser spectroscopy, such as cavity ring-down spectroscopy (CRDS) (Walker et al., 2016; Su et al., 2019). These new techniques, previously used for measurements in the atmosphere and in fresh water, are much easier to implement in small laboratories, but present challenges, in particular due to the effect of salt deposits (for seawater isotopes), memory effects, and the stability and accuracy of the standards and reference materials used. These instruments can also be used in a continuous way, for example on surface water during cruises, and there too, the accuracy of the data has not been precisely assessed (Friedrichs et al., 2010; Becker et al., 2012; Munksgaard et al., 2012; Bass et al., 2014). Because such instruments can be easily implemented with limited expertise, required documentation and metadata is not always available, limiting their use for comparisons and data-model integrations.

3: For both sets of variables, constructing earlier syntheses implied checking for biases, and adjusting subsets of data (Schmidt et al., 2012; Becker et al., 2016; Schmittner et al., 2017). However, this has not been done fully, and large biases/errors remain in subsets of the current databases, limiting their potential use. Updates of these databases are lagging behind (since 2000) possibly because the way isotopic data are archived and transmitted has evolved, with thousands of samples analysed each year in an increasing number of laboratories. These data are mostly either internally archived or not archived in a systematic, internationally organized way. For example, one often finds them associated with publications or cruise data sets (e.g. in PANGAEA). However, in some laboratories,
specific databases exist that have been carefully intercalibrated, checked, and assessed (e.g., for seawater isotopes, at LOCEAN (Reverdin et al., 2022), or the ACE archive, (Haumann et al., 2019)). For example, the LOCEAN seawater database covers measurements done over more than two decades. Its validation revealed issues of sample contamination during collection and storage, and the difficulty of properly flagging and quality controlling such data, as well as properly assessing uncertainties resulting from the analysis (Reverdin et al., 2022).

There are also issues due to long storage, and poor conservation of samples or internal water standards prior to analyses. Recommendations exist in that respect, although they might not be widely followed (i.e., Terzer-Wassmuth and Wassenaar, 2021; McNichol et al., 2020). However, proper metadata need to be collected to be able to assess these issues.
2. Terms of reference (ToR)

- 1. Assess the existing best practices and standard measurement procedures, including new techniques such as CRDS, and identify reference materials (liaise with IAEA and the OCB working group on carbon isotopes in the ocean).

- 2. Assess, at the institute, national and international levels, which data and metadata on stable isotopes in seawater are stored, what is their status of validation/qualification, and how can they be recovered and accessed. Establish a unified standard of data distribution (metadata and data) that allows an effective quality control to be shared between producers and scientific users.

- 3. Organize a cruise-based intercomparison effort at large scale, engaging new sample collectors and data producers, and encouraging data collection and sharing.

- 4. Assess methods to evaluate the accuracy of the available data, such as intercomparing different data subsets in the same region, using derived properties such as d-excess, or the δ¹³C-DIC relationship (Quality Control/Quality Assessment).

- 5. Implement methods to check the internal consistency of the new or updated global databases.

- 6. Present the results/outcome/perspectives at large international conferences and in publications.
3. Working plan.

During year 1 (2023), we will organize four online meetings to design a detailed action plan with a schedule and timeline for activities and deliverables, assign tasks and responsibilities to WG members, and prepare workshops and venues to communicate with a wider community. For this and for the other tasks, we will establish four different sub-groups: (i) one on data production/acquisition, reference materials used, and which will identify data sets and their metadata (ToR 1-2), (ii) one on the intercomparison exercises (ToR 3), (iii) one on methods of qualification/validation of the data (ToR 4), and (iv) one on data validation, error assessments, and data distribution and archiving (ToR 5). At the start of the WG, we will set up an online communication forum to facilitate actively interacting and sharing of data and validation tools. The sub-groups will remain active to year 3.

A wide-ranging workshop could be run in parallel to an AGU fall meeting (2023) or OS (2024) in a hybrid mode (on site + remote) to ease the access to a wide user community and to the US OCB-sponsored working group on ‘Carbon isotopes in the ocean’ (McNichol et al., 2021), and to the US efforts to update the database of seawater stable isotopes (mostly in the tropics, linked with PAGES CoralHydro2k, DeLong et al., 2022). A similar workshop could be run in parallel to the EGU meeting (2024, Vienna), with a link to IAEA. We will also organize two regional workshops (venues to be decided) in years 2 (2024) and 3 (2025), probably one in India (Bangalore) with focus on the South-Asian communities, and one in Brazil, to better interact with scientists in South America and South Africa, by potentially liaising with the All-Atlantic Alliance (AANChOR) which fosters collaboration between states neighbouring the North and South Atlantic. The regional workshops are key for capacity building, and could also be ways to practically share some of the water samples of the intercomparison exercises.

In addition to organizing meetings and fostering shared activities with the wider research community, the working group will carry out the following tasks, with required interactions between the different sub-working groups that will be managed by on-line meetings.

**ToR 1, year 1**: Review the existing best practices and standard operating procedures, and liaise with IAEA and OCB working group on carbon isotopes in the ocean

**ToR 1, years 2-3**: Work on an updated white paper and companion publication on data production, validation/qualification, and data distribution (list best practises and Standard Operating Procedures). We will adopt the Ocean Best Practices platform (OBP, https://www.oceanbestpractices.org/; cf also https://exchange-format.readthedocs.io/en/latest/) as the repository for these.

**ToR 2, years 1-3**: Investigate potential datasets that would update the current databases, both for water stable isotopes and δ13C-DIC. The largest effort will be for the period since 2000, and for continuously acquired measurements. A special effort will be devoted to measurements from surface monitoring projects, noting for example that for δ13C-DIC, they are currently not included in GLODAP. We will thus establish an inventory of what is available, where, and whether the metadata are complete or can be complemented. We will also define quality flags to be attributed to the different datasets or different versions of the same data set (we will for example investigate whether GEOTRACES flag choices can be
adopted; also see https://exchange-format.readthedocs.io/en/latest/). The inventory will be shared with groups producing the data bases.

**ToR 3, year 2:** Intercomparison effort. Collect larger volume of seawater samples from different cruises to be subdivided into several subsamples analyzed in different laboratories using the different methods (e.g. dividing each water sample into up to 50 subsamples). Those samples will be from the ‘deep’ ocean, but also from the surface ocean to provide a range of values. This intercomparison could be done regionally, to lessen logistical issues, but also with a few core institutions that will participate to all regional intercomparisons. Sample distribution would happen during meetings and/or shipped directly to participants.

**ToR 3, year 3:** Report analyses of the intercalibration experiments (including all the metadata) and the statistical summary of these.

**ToR 4, years 1-2:** Review and test existing statistical techniques to identify biases or errors, and estimate required adjustments in the databases.

**ToR 5, years 1-2:** Prepare the databases for the application of the methods developed in ToR 4. This will require to be able to link validation and quality flagging of data sets already archived in data centres, such as PANGAEA, or as part of data products such as GLODAPv2 (Olsen et al., 2020) with the original data/metadata. The assessment and application of the methods will likely involve other measured (auxiliary) parameters, which implies that the stable isotopic data have to be correctly cross-referenced with the other relevant data set/database; this will thus require to liaise with efforts done for the UN Ocean Decade, e.g. the World Ocean Database Programme (WODP) and in particular IODE (cf https://catalogue.odis.org), GEOTRACES, and potentially with the European Marine Observation and Data Network (EMODnet), NCEI and other regional/national centers for Chemistry and/or Physics. An outcome of this effort might be to propose a unified standard of data distribution (metadata and data) (ToR 5).

**ToR 5, years 2-3:** Implementation of the methods to check internal consistency of updated or newly produced data sets.

**ToR 6, year 4:** In the last year (year 4), we will present the results/outcome/perspectives at large international conferences. We will finalize reports and publications from the different ToRs (see deliverables).
4. Deliverables

- **1.** A report of best practices, from sample collection to analysis and data qualification/validation, to be summarized in a publication (ToR 1).

- **2.** A doi-referenced report identifying orphan stable isotopic datasets, corresponding metadata and dissemination requirements (ToR 2). Also, we will issue recommendations on how ‘orphan’ isotopic data can be distributed (for example, surface $\delta^{13}$C-DIC data sets).

- **3.** A publication with the results of at least two intercomparison exercises of seawater samples (stable water isotopes and $\delta^{13}$C-DIC) (ToR 3).

- **4.** A methodological paper with recommendations on error and bias detection as well as on the adjustments that could be proposed to databases (ToR 4).

- **5.** An assessment report of new data products, examining sources of data errors and proposed adjustments to be applied (ToR 5). The data products will not be produced by the working group, but the proposed adjustments will be communicated to the managers of the data products, as well as through proper identification to the originators of the data to update the associated metadata in repositories.

- **6.** Any data collected and validated within the working group, together with metadata/quality flags will be made public following the FAIR principles.
5. Capacity building

It will be key to integrate stakeholders who will outlast the working group, and to promote the transfer of analytical techniques/expertise to other teams and countries than the traditional data providers (until 2000, largely in Europe/North America/Japan/Australia). In addition to the important role that the members of the working group will play in their own countries, we have also established informal contacts in Chile, and will seek contacts with countries outside the ‘member countries’, in particular during the regional meetings.

Organizing meeting sessions associated to, or shouldering large international meetings, is a way to enhance the outreach of the working group. We also plan to conduct at least one dedicated workshop in South America, possibly in Brazil, with the hope to better liaise regionally with the different stakeholders. Other workshop opportunities, such as in southern or eastern Asia are also being considered.

Concurrent with the regional workshops lectures to the wider scientific community will be given by 1-2 working group members to disseminate the aims of SCOR and the working group itself. When possible, we will associate the regional workshops or one of the large meetings with a training course on sampling techniques and isotope analysis.

Although meetings are expected to structure the activity and provide a good mean to reach the main goals of the capacity building, it is hoped that other means can help too, such as a discussion forum, interactive websites.

Connections will be established with users of different communities a) the paleoclimate community (such as the PAGES CoralHydro2K working group; those working on the hydrological cycle using speleothems, or stable isotopes in biomarkers) and b) the modeling community (especially groups working on the carbon cycle/biogeochemistry and the hydrological cycle). Both Arctic and Antarctic ocean researchers often include stable isotopes in seawater as tools, in a very inter-disciplinary context, with observations both in the ocean, the sea ice or on the continents. We will also seek connections with these communities. For this task, and for more general advise and help in promoting the working group, we have also established a list of other experts in the field, that will be contacted.
6. Working Group composition

The proposed working group is composed of 10 full members and 10 associate members with a good gender balance (9F; 11 M). It also includes two early career scientists. The geographical composition is a little imbalanced with current under-representation of South America, Africa and Oceania (7 Europe; 6 Asia; 4 North America; 2 South America; 1 Africa). We plan to partially respond to this imbalance by proposing a regional workshop in Brazil with an emphasis on capacity building, and also through contacts in Chile. We feel that the group includes all required competences corresponding to the 6 TORs and the associated work package. It includes experts of data collection, measurements and intercomparison exercises, data bases qualification and validation, data analysis, and modelling of the measured quantities.

Full members

- **(co-Chair) Gilles Reverdin, (LOCEAN, Paris, France)** (Gilles.reverdin@locean.ipsl.fr). Physical oceanographer, interested in recent climate variability, the hydrological cycle, upper ocean, air-sea exchanges, oceanic carbon. Long-time involvement in the observation of the ocean, with experience in stable isotopes research (both water stable isotopes and δ13C-DIC).

- **(co-Chair) Antje Voelker (IPMA, Lisbon, Portugal)** (antje.voelker@ipma.pt). Paleo-climatologist with interest in proxies of past and recent climate variability. Study of stable isotopes in sea water to trace water masses and circulation changes, and to calibrate proxies used in paleoceanography. Contributing to GEOTRACES and PAGES, and liaising with the data related working group of the All Atlantic Alliance (AANChOR).

- **Alexander Haumann (Princeton U., Princeton, USA)** (alexander.haumann@gmail.com). Air-sea-ice interactions, in particular in the Southern Ocean, and their impact on ocean circulation and water mass changes. Experience in qualification/validation stable sea water isotopes (ACE expedition). Ongoing and planned activities in building a unified database for the Southern Ocean. (early career scientist)

- **Andre Luiz Belem (UFF, Rio de Janeiro, Brazil)** (andrebelem@id.uff.br). Coastal oceanography, with analysis of exchanges between the coastal regions with the deep ocean. Use of stable isotopes as tracers of water masses and ocean processes.

- **Doug Wallace (Dalhousie Univ, Nova Scotia, Canada)** (douglas.wallace@dal.ca). Ocean chemistry and geochemistry, with particular North Atlantic and transient tracers focuses. Extensive experience with CRDS measurements and inter-comparison exercises both for stable water isotopes and δ13C-DIC.

- **Eun Young Kwon (Pusan Univ., Pusan, South Korea)** (ekwon957@pusan.ac.kr). Ocean variability at interannual to interdecadal time scales. Water masses, penetration of ocean carbon, data assimilation and modeling. Interest in stable isotopes in seawater.

- **Fajin Chen (Guangdong Ocean University, Zhanjiang, China)** (fjchen@gdou.edu.cn). Coastal oceanography. River inputs to the coastal ocean. Measurements of δ13C-DIC and water stable isotopes.

- **Shigeru Aoki (Hokudai Univ, Sapporo, Japan)** (shigeru@lowtem.hokudai.ac.jp). Recent ocean variability in particular in the Southern Ocean. Air-sea-ice interaction and water mass changes. Experience in IRMS and CRDS measurements of stable water isotopes.
Supriya Karapurkar (NIO, Goa, India) (supriya@nio.org). Strong experience in IRMS measurements of sea water samples.

Ulysses Ninnemann (UiB, Bjerkness Center, Bergen, Norway) (Ulysses.ninnemann@uib.no). Interest in climate variability past and present, including investigation of water isotopes in sea water for example. Work with mass spectrometers and IRSM spectrometers.

Associate Members

Anita Flohr (NOC, Southampton, United Kingdom) (anita.flohr@noc.ac.uk). Biogeochemist with interest in ocean carbon and ocean δ¹³C-DIC. Experience with CRDS measurements.

Jessica Conroy (Univ Illinois, USA) (jconro@illinois.edu). Specialized in recent variability in the surface ocean and the hydrological cycle, in particular in the equatorial Pacific, also with interest in coral proxies and their validation. Involved in Pages and CLIVAR water isotopes group.

Leonard I. Wassenaar (Danube University Krems, Austria) (len.wassenaar@wcl.ac.at). Large experience at IAEA in inter-comparison exercises, IRMS, CRDS measurements of water isotopes, and influence of sea water composition on the measurements.

Liping Zhou (Beijing University, China) (lpzhou@pku.edu.cn). Specialist on past and present climate variability. Use of water isotopes in the present climate for calibration of proxies and to trace water masses. PAGES, GEOTRACES.


Meike Becker (University of Bergen and Bjerknes Center for Climate Research, Bergen, Norway) (meike.becker@uib.no). Recent variability of anthropogenic carbon and δ¹³C-DIC changes. Continuous measurements of δ¹³C-DIC in sea water and CRDS measurements. Involved in monitoring programs, and experience with database qualification. (early career scientist)

Prosenjit Ghosh (IISC, Bangalore, India) (pghosh@iisc.ac.in). Geochemist with ocean, atmosphere and land experience. Oceanic focus on Bay of Bengal and Southern Ocean (carbon cycling and relationship with the hydrological cycle). Link with ‘Future earth’ program.

Roberta Hansman (NOSAMS, WHOI, USA) (rhansman@whoi.edu). Mass spectrometry. Biogeochemist, with interest in tracing carbon in the ocean (both using radio-isotopes and stable isotopes).

Sarah Fawcett (Univ Cape Town, South Africa) (sarah.fawcett@uct.ac.za). Biogeochemical oceanographer. Interest in stable isotopes in the ocean, particularly in nitrogen, and recently also including water stable isotopes. Liaise with the Southern Ocean Observing System (SOOS) committee.

Toste Tanhua (GEOMAR, Kiel, Germany) (ttanhua@geomar.de). Chemical oceanographer, with interest in transient tracers, carbon parameters and anthropogenic carbon, including δ¹³C-DIC. Will liaise with GLODAP, GO-SHIP and GOOSE.
7. Selected relevant publications of members

**Gilles Reverdin, co-chair**


**Antje Voelker, co-chair**


Shigeru Aoki


Meike Becker


Andre Belem


Fajin Chen


Jessica Conroy


Luisa Espinosa


Sarah Fawcett


Anita Flohr


Prosenjit Ghosh


Roberta Hansman


Alexander Haumann


Supriya Gauresh Karapurkar


Eun Young Kwon


Toste Tanhua


Douglas Wallace


Leonard Wassenaar


Liping Zhou

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8. References


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