GEOTRACES Intercalibration Report

Cruise ID*: **PANDORA**
Submitting investigator*: **Patrick Rafter - University of California, Irvine- prafter@uci.edu**
Parameters to be intercalibrated*:

- NITRATE_15_14_D_DELTA_BOTTLE::qs0dim per mil
-NITRATE_18_16_D_DELTA_BOTTLE:: zhttuq per mil

*Once generated, these headings must not be changed or altered.

1. **Did your lab participate in an intercalibration exercise (**http://www.geotraces.org/sic/intercalibrate-data/intercalibration-exercices**)? If so, please provide a relevant figure or table, describe the results of the intercalibration, identifying your laboratory, and provide a reference for the intercalibration exercise, if published.**

No.

2. Did your sampling method at sea follow the GEOTRACES cookbook (available at: http://www.geotraces.org/cookbook**)? Please give a brief description of your sampling methodology (e.g., what bottles were used, what type and size of filters were used, how the samples were treated at sea, etc.).**

For the most part, yes. The sampling and storage procedures followed the GEOTRACES cookbook: (1) seawater samples were collected from Niskin bottles into pre-rinsed square 60 mL high-density polyethylene (HDPE) bottles, (2) Each sample was filled to approximately ¾ the bottle height to prevent sample overflow during ice expansion, (3) Samples were stored immediately in upright position at -20°C. The one difference between the sampling for the PANDORA cruise and the GEOTRACES cookbook is that these samples were not filtered before freezing. As per the GEOTRACES cookbook, filtration is recommended, but prior tests showed no difference between filtered and non-filtered samples for nitrate isotope measurements (at least within 18 months of sampling).

3. **Briefly outline the analytical methodology used in your laboratory, and provide associated metadata and references, as appropriate.**

Samples were analyzed by the Denitrifier Method (Casciotti et al., 2002; Sigman et al., 2001), with technical updates described by (Weigand et al., 2016). Specific protocols for these samples are described in (Marconi et al., 2015) and in detail along with extensive analysis of reference solution results in (Weigand et al., 2016). All isotope analyses were performed on a MAT253 Thermo IRMS equipped with a

custom-sample preparation system, described by Weigand et al. (2016). Nitrite was not removed from these samples, so they should be considered as possibly "Nitrate + Nitrite" measurements.

Raw data were calibrated to nitrate reference materials IAEA-NO3 and UGSS34, dissolved in low-nitrate seawater collected from the mixed layer at BATS. Samples were bracketed in nitrate concentration by the reference nitrate solutions. When nitrate reference solutions indicated a concentration trend in nitrate d18O, a correction was applied based on those results. These and other aspects of the data processing are described in detail by Weigand et al. (2016).

4. Report your blank values and detection limits, and explain how these were defined and evaluated.
Standard sample analysis uses 20 nanomoles of nitrate for samples >5 µmoles L-1 and 10 nanomoles of nitrate for <5 µmoles L-1. (These sample volumes are controlled by sample injection volume.) Methodological blanks—presumably via continued bacterial conversion of nitrate to N2O—are identified by analyzing nitrate-free seawater. As such, all blanks were below detection limit. See Weigand et al. (2016) for more information.

5. Report how you monitored the internal consistency of your data (e.g., through replicate analyses of samples).
With our system, the analytical precision (at the time the PANDORA samples were measured) was based on replicate measurements of our 38 uM "Deep Pacific Reference" (DPR) in-house standard (included in every batch of analyses). (For lower nitrate concentrations, I diluted the DPR standard with nitrate-free water to create a 2 uM in-house standard, but that is not applicable for the >10 uM samples that were measured here.) The variability of this in-house standard at the time the PANDORA samples were measured was ±0.04 per mil for nitrate d15N and ±0.09 per mil for nitrate d18O. These values are reported as the "standard deviation" for nitrate d15N and nitrate d18O where only one measurement was made. For samples measured more than once, we report the observed standard deviation.

6. Report the external consistency of your data (e.g., results from analyses of certified reference materials and/or consensus materials).
Samples were standardized to seawater-based reference material USGS-34 and IAEA-N3 with known $\delta^{15}N$ (vs. air) and $\delta^{18}O$ (vs. VSMOW) of -1.8‰ and -27.9‰ and 4.7‰ and 25.6‰, respectively (Bohlke et al., 2003; Gonfiantini, 1984). Standard were evenly spread throughout the sample runs, bracketing the nitrate concentrations of the samples.

7. If you occupied a crossover station, include a plot and a table that show relevant data and their level of agreement, and explain any significant discrepancies (e.g., where discrepancies may reflect differences in the depth of isopycnal surfaces between occupations). If possible please also include a profile of Temperature & Salinity. Not applicable to our study sites.

8. If you did not occupy a crossover station, report replicate analyses from a different laboratory, or if there were no replicate analyses (e.g., due to large volumes or short half-lives), explain how your data compare to historical data including results from nearby stations, even though they may not be true crossover stations.

Here I am showing a comparison with nearby nitrate d15N (Fig. 1) and nitrate d18O (Fig. 2), based on the compilation of Rafter et al. (2019) in Biogeosciences.

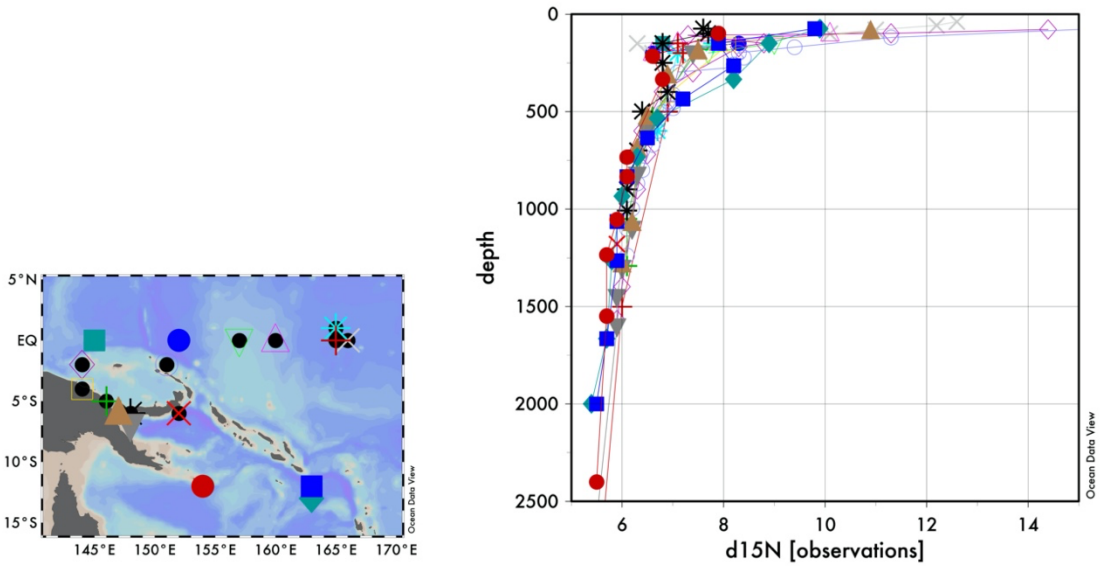

FIGURE 1: A comparison of the PANDORA cruise nitrate d15N (red circles, blue squares, and teal diamonds) compared with historical observations in the western tropical Pacific (from various sources; see the compilation of Rafter et al. 2019 for references). See map inset for the location of each station.

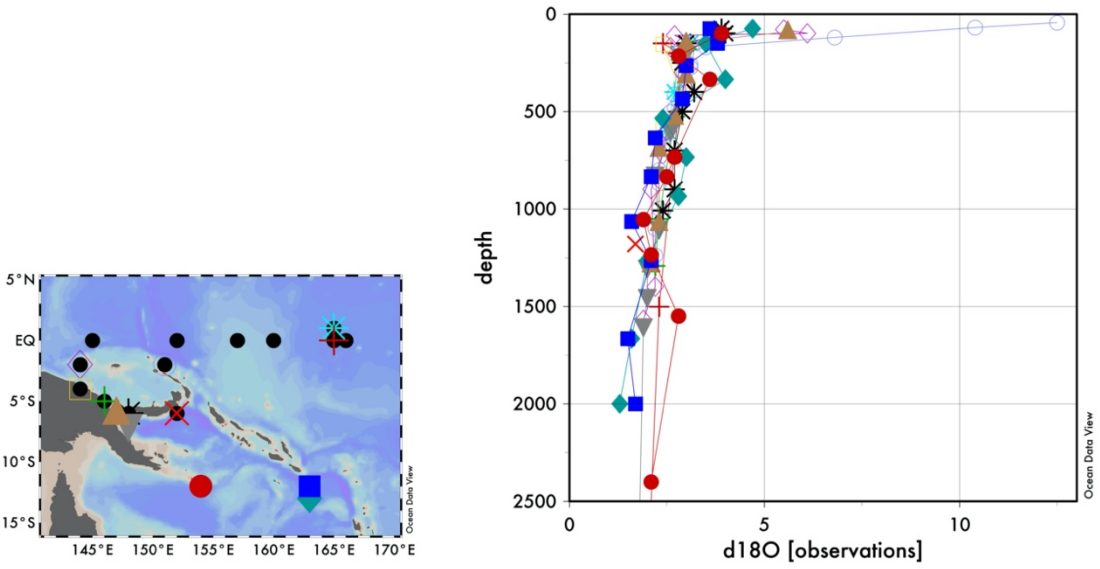

FIGURE 2: A comparison of the PANDORA cruise nitrate d18O (red circles, blue squares, and teal diamonds) compared with historical observations in the western tropical Pacific (from various sources; see the compilation of Rafter et al. 2019 for references). See map inset for the location of each station. Note that all of the historical did not have nitrate d18O measurements available and were not plotted.

9. If not already included in your responses to the questions above, please provide a representative vertical profile or report the range of values, for the parameter(s) that are addressed in this intercalibration report.

Once completed, please upload the report here:
https://geotraces-portal.sedoo.fr/pi/

Bohlke, J. K., Mroczkowski, S. J., & Coplen, T. B. (2003). Oxygen isotopes in nitrate: new reference materials for O-18 : O-17 : O-16 measurements and observations on nitrate-water equilibration. *Rapid Communications in Mass Spectrometry*, *17*(16), 1835–1846. https://doi.org/10.1002/rcm.1123

Casciotti, K. L., Sigman, D. M., Hastings, M. G., Bohlke, J. K., & Hilkert, A. (2002). Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. *Analytical Chemistry*, *74*(19), 4905–

4912. https://doi.org/10.1021/ac020113w

Gonfiantini, R. (1984). I.A.E.A. ADVISORY GROUP MEETING ON STABLE ISOTOPE REFERENCESAMPLES FOR GEOCHEMICAL AND HYDROLOGICAL INVESTIGATIONS (Vol. 2, p. 85). Presented at the Advisory Group Meeting on Stable Isotope ReferenceSamplesfor Geochemicaland Hydrological Investigation, Vienna, Austria: Isotope Geoscience.

Marconi, D., Alexandra Weigand, M., Rafter, P. A., McIlvin, M. R., Forbes, M., Casciotti, K. L., & Sigman, D. M. (2015). Nitrate isotope distributions on the US GEOTRACES North Atlantic cross-basin section: Signals of polar nitrate sources and low latitude nitrogen cycling. *Marine Chemistry*, *177*, 143–156. https://doi.org/10.1016/j.marchem.2015.06.007

Sigman, D. M., Casciotti, K. L., Andreani, M., Barford, C., Galanter, M., & Bohlke, J. K. (2001). A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. *Analytical Chemistry*, *73*(17), 4145–4153. https://doi.org/10.1021/ac010088e

Weigand, M. A., Foriel, J., Barnett, B., Oleynik, S., & Sigman, D. M. (2016). **Updates to instrumentation and protocols for isotopic analysis of nitrate by the denitrifier method**: Denitrifier method protocols and instrumentation updates. *Rapid Communications in Mass Spectrometry*, *30*(12), 1365–1383. https://doi.org/10.1002/rcm.7570