# Physical and chemical oceanographic data during *Umitaka-maru* cruise of the 59th Japanese Antarctic Research Expedition in January 2018

Keishi SHIMADA<sup>1\*</sup>, Shintaro TAKAO<sup>2,3\*\*</sup>, Kunio T. TAKAHASHI<sup>2,3</sup>, Yujiro KITADE<sup>1</sup>,

Jota KANDA<sup>1</sup>, and Tsuneo ODATE<sup>2,3</sup>

<sup>1</sup>Tokyo University of Marine Science and Technology, 4-5-7 Konan, Minato-ku, Tokyo 108-8477.

<sup>2</sup> National Institute of Polar Research, Research Organization of Information and Systems, 10-3 Midori-cho, Tachikawa, Tokyo 190-8518.

<sup>3</sup> Department of Polar Science, School of Multidisciplinary Sciences, SOKENDAI (The Graduate

University for Advanced Studies), 10-3 Midori-cho, Tachikawa, Tokyo 190-8518.

\*Corresponding author: Keishi Shimada (kshima0@kaiyodai.ac.jp)

\*\*Current affiliation: National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba,

Ibaraki 305-8506.

(Received November 2, 2020; Accepted February 10, 2021)

**Abstract:** The Southern Ocean connects all major ocean basins and plays a pivotal role in the meridional overturning circulation of the global oceans. High-quality physical (temperature, salinity, and dissolved oxygen) and chemical (nutrients) oceanographic data from the Southern Ocean are thus critical for an improved understanding of future climates. As part of the 59th Japanese Antarctic Research Expedition, and also as a part of annually conducted monitoring observations, we have obtained high-quality Conductivity-Temperature-Depth (CTD) and water sampling data (salinity, dissolved oxygen, and nutrients) at 6 sites located along a 110°E transect in January 2018. Sea surface temperature and salinity were obtained continuously with a thermosalinograph (TSG) along the cruise track between the ports of Fremantle and Hobart, except within the Australian Exclusive Economic Zone. Data quality was validated by following as far as possible the recommendations for instruments and methods of the Global Ocean Ship-Based Hydrographic Investigation Program. CTD data and water sampling data are provided in the Exchange format employed by the World Ocean Circulation Experiment Hydrographic Program, while TSG data are provided in .csv format.

#### 1. Background & Summary

Connecting all the major ocean basins, the Southern Ocean has a pivotal role in the meridional overturning circulation, and therefore in global climate (e.g., Schmitz, 1996<sup>1</sup>). In particular, Antarctic Bottom Water (AABW) production in the Southern Ocean is an integral component of the overturning circulation, making an important contribution to the transport and storage of heat, carbon, and other properties that influence climate<sup>2</sup>.

Since after 1990s, rapid and widespread freshening, possibly linked to enhanced basal melting of the Antarctic Ice Sheet (e.g., Rignot *et al.*, 2013<sup>3</sup>), was observed in the Sothern Ocean<sup>4, 5</sup>. There also has been clear evidence of warming in AABW, which may reflect a reduction in meridional overturning circulation<sup>6, 7, 8</sup>. Further, both freshening and warming induced remarkable sea level rise<sup>9</sup>. In the latest study, however, reversals in the freshening trend of the AABW, possibly due to a decrease in basal melting of the Antarctic Ice Sheet<sup>10</sup> and/or increase in sea ice formation in the source region of AABW<sup>11</sup> is reported. Considering these non-monotonic signals in the Southern Ocean, high-quality data obtained from sustained annual monitoring observations are undoubtedly critical for an improved understanding of future climates.

Oceanographic observations have been taken en route between Japan and the Japanese Antarctic Station, Syowa (69°00'S, 39°35'E), as part of the annual JARE (Japanese Antarctic Research Expedition) routine observations since JARE 7 in 1965/66, when the JARE research programs were re-opened and re-structured in accordance with a decision of the Japanese Cabinet. Between JARE 7 and JARE 50 in 2008/2009, the Hydrographic Division of the Japan Maritime Safety Agency (now re-named the "Hydrographic and Oceanographic Department, Japan Coast Guard") has been in charge of maintaining and continuing these oceanographic observations, as well as publication of the JARE Data Reports series.

After JARE 51 in 2009/2010, the responsibility for maintaining the routine oceanographic observations was transferred to the Ministry of Education, Culture, Sports, Science and Technology (MEXT) as the lead agency, but an actual program of restructuring and implementing the oceanographic observations was not established. However, through the efforts of the Japanese Antarctic oceanographic community, the oceanographic observations continued within the JARE framework, and observations were carried out during JARE 52 in 2010/2011 as one of the JARE research projects. The training and research vessel *Umitaka-maru*, which belongs to the Tokyo University of Marine Science and Technology (TUMSAT), was used as a platform for in-situ oceanographic observations under an agreement between TUMSAT and the National Institute of Polar Research (NIPR).

The present report summarizes the routine oceanographic observations made on board the *Umitaka-maru* during the UM-17-09 cruise in 2018, as part of the JARE 59 research project.

#### 2. Observation sites

During the UM-17-09 cruise, in-situ oceanographic observations were conducted along a cruise track between the ports of Fremantle and Hobart. Surface monitoring with a thermosalinograph (TSG) and water sampling were carried out along the entirety of the cruise track (Fig. 1). Top-to-bottom Conductivity-Temperature-Depth (CTD) profiler observations were conducted at 6 sites on a meridional transect at  $110^{\circ}$ E (Fig. 1). The geographical settings of the 6 sites, and complementary information on CTD operations, are summarized in Table 1.

#### 3. Materials, methods, and technical validation

The data obtained from CTD observations were conductivity (S/m), temperature (°C), and pressure (dbar), and those obtained from CTD water sampling were salinity (PSS-78), dissolved oxygen ( $\mu$ mol L<sup>-1</sup>), nitrate ( $\mu$ mol L<sup>-1</sup>), nitrite ( $\mu$ mol L<sup>-1</sup>), phosphate ( $\mu$ mol L<sup>-1</sup>), and silicate ( $\mu$ mol L<sup>-1</sup>). TSG observations provided sea surface conductivity (S/m) and temperature (°C). For both CTD and TSG observations, salinity (PSS-78) was also derived from conductivity, temperature and pressure, using the algorithm for the practical salinity scale 1978<sup>12</sup>. In this section, details of the instruments and methods used to obtain and validate the data are given.

#### 3.1. TSG

A TSG system developed by CT&C Co. Ltd. was used to observe sea surface temperature and conductivity (and hence salinity), along the entirety of the cruise track except for the Australian Exclusive Economic Zone, from 1st to 21st January 2018. The water intake was located approximately 4.3 m below the sea surface. For the conductivity and temperature sensor, an ETSG2 thermosalinograph (S/N: 1424-30JULY05), provided by Falmouth Scientific Inc., was used. The nominal accuracy for temperature and salinity are  $\pm 0.1^{\circ}$ C and  $\pm 0.02$  PSS-78, respectively.

16 water samples were obtained from the TSG intake to calibrate TSG salinity. TSG salinity was corrected using the following equation.

$$S_{cor} = s_0 \times S_{obs} + s_1 \times t + s_2$$

where  $S_{cor}$  is the corrected salinity,  $S_{obs}$  is the observed salinity, and t is the elapsed time since the cruise started. The coefficients  $S_0$ ,  $S_1$ , and  $S_2$  are calibration coefficients, and were estimated by a least squares method so that minimize the sum of the squared difference between corrected salinity and bottle salinity (details for determining bottle salinity are given in Section 3.4.). A comparison between TSG and bottle salinity is summarized in Fig. S1.

# 3.2. CTD

The methods and instruments used to obtain CTD data basically followed those of McTaggart *et al.*  $(2010)^{13}$ , as described below.

#### **3.2.1.** CTD system configuration

We used a CTD system composed of a CTD SBE9plus and a 24-position carousel water sampler provided by Sea-Bird Electronics (hereafter referred to as SBE) Inc. 8-liter Niskin bottles were mounted on the frame and were used for sampling water. The CTD system was equipped with pressure, temperature (primary and secondary), conductivity (primary and secondary), and altitude sensors (details of the sensors are given in <u>Table S1</u>). The nominal accuracy for pressure, temperature and conductivity are  $\pm 0.015\%$  of full scale range (correspond to  $\pm 0.9$  dbar),  $\pm$  $0.001^{\circ}$ C, and  $\pm 0.0003$  S/m (correspond to  $\pm 0.004$  PSS-78), respectively. Please note that the salinity accuracy is derived by applying typically observed range of pressure, temperature, and conductivity in the Southern Ocean to the algorithm for the practical salinity scale 1978<sup>12</sup>. Pre-cruise calibrations were performed for the pressure, temperature and conductivity sensors from August to September 2017 at SBE Inc. The secondary temperature and conductivity sensors were used only to monitor and back up the primary sensors, and an altitude sensor was used to ensure the acquisition of near-bottom data. Therefore, data obtained with these sensors are not provided.

#### **3.2.2.** Data acquisition

The raw CTD data were acquired in real time using Seasave-Win32 (ver.7.23.2) software, provided by SBE Inc., and stored on the hard disk of a personal computer. Water samples were collected during the upcast by sending a fire command. The CTD system was stopped at each sampling depth for 60 seconds before bottle closure, so that water inside and surrounding the bottle to settle to equilibrium.

# 3.2.3. Data processing

The acquired CTD data were processed mainly using the SBE Data Processing-Win32 (ver.7.23.2) software provided by SBE Inc., with some originally developed modules. Details of the processing are given below; the names of the processing modules are enclosed by double quotation marks. The modules were derived from the SBE Data Processing-Win32 (ver.7.23.2) software, unless otherwise specified.

The raw binary data were converted to engineering unit data by "DATCNV", which was also used to extract the CTD data in the vicinity of each Niskin bottle closure depth. The duration and the offset of the data acquisition were set to 3.0 and 0.0 seconds, respectively.

Data were re-aligned from the time sequence to the pressure (depth) sequence using "ALIGNCTD". This procedure ensured that all the calculations (e.g., salinity) were made using

measurements from the same parcel of water.

Extreme outliers were identified by "WILDEDIT". The first pass of "WILDEDIT" is intended to obtain the true standard deviation of the data. For this purpose, data were flagged if they deviated from the mean by more than 10 standard deviations computed over blocks of 1000 scans. The second pass computed a standard deviation over the same 1000 scans, excluding the flagged values. Then, data were marked as bad if they deviated from the mean by more than 20 standard deviations. This process was applied to the pressure, depth, temperature, and conductivity data.

Conductivity cell thermal mass effects were removed from the conductivity data using "CELLTM". The applied values for the thermal anomaly amplitude ( $\alpha$ ) and the time constant (1/ $\beta$ ) were 0.03 and 7.0, respectively.

A low-pass filter with a time constant of 0.15 seconds was applied to the pressure data using "FILTER". To avoid temporal shifts, the filter was first run forward and then backward.

To remove invalid data (e.g., data obtained while the CTD package was above the sea surface, or while the pump was inactive), "SBE\_SECTION" (an original module developed by the author) was applied. The first and last valid scans were defined as the first scan after starting the downcast and the last scan with the CTD package beneath the sea surface, respectively. We applied "LOOPEDIT" to remove data obtained while the descending motion was reversed during downcast, due to the ship roll.

Finally, salinity was calculated with "DERIVE", and 1-dbar pressure bins averages were obtained with "BINAVG".

## 3.2.4. Post-cruise calibration

Considering pressure sensitivity, the temperature obtained from the primary temperature sensor (03P2863) was corrected according to Uchida *et al.*  $(2007)^{14}$  as follows:

$$T_{cor} = T_{obs} - 3.20069 \times 10^{-7} \times P$$

where  $T_{cor}$  is the corrected temperature,  $T_{obs}$  is the observed temperature, and P is the pressure. The calibration coefficient of -3.20069×10<sup>-7</sup> (°C/dbar), which implies subtraction of 1.44×10<sup>-3</sup> °C at the deepest observation ( $\Box$  4500 dbar), was derived from direct comparison with SBE 35 (Deep Ocean Standards Thermometer) in January 2015. Ambiguity remained about temporal drift. However, based on previous calibration results provided by SBE Inc., and the time elapsed since the pre-cruise calibration, it was expected not to exceed 1×10<sup>-3</sup> °C during the observation period. It is thus likely that the overall accuracy of the temperature was lesser than that of the World Ocean Circulation Experiment (WOCE)<sup>15</sup> and the Global Ocean Ship-Based Hydrographic Investigation Program (GO-SHIP)<sup>16</sup> target (2×10<sup>-3</sup> °C).

Considering the pressure sensitivity and temporal drift during the cruise, conductivity was corrected using the following equation:

$$C_{cor} = c_0 \times C_{obs} + c_1 \times P + c_2 \times C_{obs} \times P + c_3 \times t + c_4$$

where  $C_{cor}$  is the corrected conductivity,  $C_{obs}$  is the observed conductivity, P is the pressure (dbar), and t is the elapsed time since the cruise started. The coefficients  $C_0$ ,  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  are calibration coefficients, and were estimated by the least squares method so that minimize the sum of the squared differences between the corrected conductivity and the conductivity calculated from bottle salinity (details for determining bottle salinity are given in Section 3.4.). The corrected salinity was then derived from  $T_{cor}$ ,  $C_{cor}$ , and pressure. A comparison between CTD and bottle salinity is summarized in Fig. S2.

The pressure offset from the pre-cruise calibration was also assessed by comparing the on-deck pressure with atmospheric pressure. The on-deck pressure was measured for 2 minutes both before and after each CTD cast. The mean offset over the whole period, however, was negligible (-0.15 dbar) and post-cruise calibration was therefore not conducted.

# 3.3. Water sampling

Using 8-liter Niskin bottles mounted on a CTD frame, water samples for the measurement of salinity, dissolved oxygen, and nutrients were obtained from 24 layers (25, 50, 75, 100, 125, 150, 200, and 250 dbar; 100-dbar intervals from 300 to 1000 dbar; 1250 and 1500 dbar; 500-dbar intervals from 2000 to 3500 dbar; the deepest layer; and an arbitrary selected layer) for each cast. Surface layer water samples were complemented using a bucket sampler at each site. Sampling was omitted if the bottom depth was shallower than the sampling layer. Considering the sensitivity of the measurements to contamination from air entering the Niskin bottles, samples were collected in the order of dissolved oxygen, salinity, and nutrients. Also, as mentioned in Section 3.1., 16 salinity samples were also obtained from the TSG intake for calibration purposes.

To assess the repeatability of the sampling and subsequent measurements, replicate samples were obtained for the CTD water sampling. For salinity, replicate samples were obtained from 4 layers: the second, fourth, sixth, and eighth layers from the bottom. For dissolved oxygen, replicate samples were obtained from 5 layers: the first, third, fifth, and seventh layers from the bottom. For nutrients, replicate samples were obtained from 5 layers: the third, fourth, fifth, sixth, eighth, and thirteenth layers from the bottom. In the following subsections, the methods and instruments used for sampling and measurements are described for salinity (Section 3.4.), dissolved oxygen (Section 3.5.), and nutrients (Section 3.6.).

# 3.4. Salinity

The method of salinity measurement followed that of Kawano (2010)<sup>17</sup> as described below.

# 3.4.1. Sampling

We sampled water with 8-liter Niskin bottles, a bucket, and the TSG. A 250-mL clear glass sample bottle with an inner cap was used, and each bottle was rinsed 3 times with sample water before being filled with sample water to the neck. The bottles were stored for more than 24 hours in the laboratory before the measurements. During the cruise, 171 samples from Niskin bottles and buckets (including 23 replicate samples), and 16 samples from TSG water, were measured.

# 3.4.2. Measurement

Sample salinity was determined using a salinometer (Model 8400B "AUTOSAL", Guildline Instruments Ltd., S/N 63904). The measurable salinity range of the instrument was 0.005 to 42 (PSS-78) with an accuracy better than  $\pm 0.002$  (PSS-78) over 24 hours without re-standardization. The maximum resolution of the salinometer was better than  $\pm 0.002$  (PSS-78) at a salinity of 35 (PSS-78).

During the measurements, the temperature of the salinometer bath and the laboratory were monitored with precision digital thermometers (Model 1502A, FLUKE Co.), with an accuracy of 0.006°C, and a thermo-recorder (TR-77Ui, T&D Co.) with an error limit of  $\pm 0.1$ °C. The temperature of the air-conditioned laboratory on board the ship varied in the range of 23 to 24°C. The salinometer bath temperature was stable, and varied by  $\pm 0.002$ °C, with the set temperature being 24°C.

Measurements were conducted with a double conductivity ratio. Each measurement was started 5 s after the sample water had filled the cell, and it took roughly 11 s to determine the stable reading. The cell was rinsed with sample water 5 times before data measurement was performed. If the difference between the first and second measurements was less than 0.00002, the mean value was used to calculate the bottle salinity using the algorithm for the practical salinity scale 1978<sup>12</sup>. Otherwise, the mean value of the second and third measurements was adopted, if their difference was less than 0.00002. If the third measurement did not satisfy this criterion, we added two more and used the median of the five measurements.

#### 3.4.3. Quality control

The measurements were validated using Standard Sea Water (SSW), which is specified as Batch P160: conductivity ratio 0.99983 (double conductivity ratio 1.99966), salinity 34.993, expiration date 20 July 2019.

Two sets of measurements were conducted during the cruise, and the standardization control of the salinometer was changed from 856 for the first set to 692 for the second set. The values of STANBY and ZERO were changed from  $5292\pm0001$  and -0.00025 (first set) to  $5879\pm0001$  and 0.00019 (second set), respectively. In total, 6 bottles of SSW (P160) were measured.

The temporal drift in the salinometer readings was not remarkable during the cruise (Fig. S3). The linear trend was estimated by the least squares' method, and the measured double conductivity ratios of the SSW and samples were corrected to compensate for this. The corrected time series of the SSW (P160) double conductivity ratios is shown by orange dots and line; the mean of the double conductivity ratio was 1.99965, with a standard deviation of 0.00000 (equivalent to 0.0003 in salinity).

To detect sudden drift in the salinometer between the SSW measurements, the salinity of sub-standard seawater was measured for every 6 samples. Sub-standard seawater was made from filtered sea water and stored in a 20-liter polyethylene container, and was stirred for at least 24 hours in the laboratory before measurement.

The accuracy of the salinity measurements was estimated from the standard deviation of the measured salinity of SSW after correction. The accuracy was 0.0003 PSS-78. Precision was then assessed using 23 pairs of replicate samples taken from the same Niskin bottle. The root-mean-square of the absolute difference among the 23 pairs was 0.0005 PSS-78 (Fig. S4). Therefore, both the accuracy and precision of the determined salinity satisfied the requirements of both WOCE<sup>15</sup> (0.002 PSS-78 for accuracy and 0.001 PSS-78 for precision) and GO-SHIP<sup>16</sup> (0.001 PSS-78 for accuracy and precision).

# 3.5. Dissolved oxygen

Dissolved oxygen was measured by the Winkler titration method, according to the methods described by Dickson  $(1996)^{18}$  and Langdon  $(2010)^{19}$  as follows.

### 3.5.1. Sampling

We sampled water with 8-liter Niskin bottles and buckets. A volume-calibrated flask (approximately 100 mL) was used for sampling. The temperature was measured with a digital thermometer, while three times the volume of seawater was overflowed from the flask. Two reagent solutions (Winkler reagents I and II; 1.0 mL each) were then added immediately, and the stopper was inserted carefully into the flask. The flask was then shaken vigorously to thoroughly mix the contents. After the precipitate had settled at least halfway down the flask, the flask was again shaken vigorously to redisperse the precipitate. The flasks containing the samples were stored in a laboratory until they were titrated. During the cruise, 178 samples from Niskin bottles and buckets (including 30 replicate samples) were measured.

#### 3.5.2. Measurement

At least two hours after the re-shaking, the samples were measured on board. 1 mL sulfuric acid solution and a magnetic stir bar were added to the sample flask, and stirring began. Samples were titrated with a sodium thiosulfate solution, whose molarity was determined as described in the

next subsection. The temperature of the sodium thiosulfate during titration was recorded using a thermometer. The dissolved oxygen concentration ( $\mu$ mol L<sup>-1</sup>) was calculated based on the sample temperature obtained during sampling, the flask volume, and the titrated volume of sodium thiosulfate solution. Details of the instruments and reagents are summarized in <u>Table S2</u>.

## 3.5.3. Quality control

The concentration of the sodium thiosulfate titrant was determined with potassium iodate solution. Pure potassium iodate was dried in an oven at 130°C. Accurately weighted out 1.7835 g of potassium iodate was dissolved in deionized water and diluted to a final volume of 5 L in a volume-calibrated flask. The resulting molarity was 0.001667 mol L<sup>-1</sup>. 10 mL of the standard potassium iodate solution was added to a flask using a volume-calibrated dispenser. Then, 90 mL of deionized water, 1.0 mL of sulfuric acid solution, and 1.0 mL each of Winkler reagents II and I were added to the flask in that order. The molarity of the sodium thiosulfate titrant was calculated from the volume titrated. This volume was usually the average of 5 measurements.

The oxygen contents of the Winkler reagents I (1.0 mL) and II (1.0 mL) were assumed to be  $7.6 \times 10^{-8} \text{ mol}^{20}$ . The blank due to anything other than oxygen was determined as follows. 1 and 2 mL of the standard potassium iodate solution were added to two flasks, respectively, using a calibrated dispenser. Then, 100 mL of deionized water, 1 mL of sulfuric acid solution, and 1.0 mL of Winkler reagent solutions II and I were added to the flask in that order. The blank was determined from the difference between the first (1 mL of KIO<sub>3</sub>) titrated volume of sodium thiosulfate and the second (2 mL of KIO<sub>3</sub>). The results of triplicate blank determinations were averaged (Table S3).

The overall precision of this procedure was assessed using 30 pairs of replicate samples obtained from the same Niskin bottle. The standard deviation of the replicate measurement, estimated following Dickson *et al.*  $(2007)^{21}$ , was 0.11 µmol L<sup>-1</sup>. The precisions stipulated by the WOCE<sup>15</sup> and GO-SHIP<sup>16</sup> requirements are less than 0.1 % and 0.08 % of the highest concentration found in the ocean, respectively. By using the maximum dissolved oxygen concentration determined during the cruise (400 µmol L<sup>-1</sup>) as a reference for the highest concentration found in the ocean, the criteria became 0.40 µmol L<sup>-1</sup> and 0.32 µmol L<sup>-1</sup>, respectively. Therefore, our precision satisfied both WOCE<sup>15</sup> and GO-SHIP<sup>16</sup> requirements.

# 3.6. Nutrients

The nutrient (nitrate, nitrite, silicate and phosphate) concentration measurements followed the methods of Hydes *et al.*  $(2010)^{22}$  as described below.

#### 3.6.1. Sampling

We sampled water with 8-liter Niskin bottles and a bucket. Unused 10-mL polyacrylate vials were used for sampling. The vials were rinsed 3 times with sample water and immediately capped

after filling. To stabilize the sample temperature, the vials were stored in an air-conditioned laboratory (room temperature 23 to 24 °C) before the measurements, which were taken within 24 hours of collection. During the cruise, 184 samples from Niskin bottles and buckets (including 36 replicate samples) were measured.

## 3.6.2. Measurement

Nutrient concentrations were measured with a QuAAtro 2-HR system (provided by BL Tec K.K.). To measure all the samples within 24 hours of collection, we made QuAAtro runs immediately after leaving every station (6 runs in total).

The analytical methods used for the determination of nutrient (nitrate, nitrite, silicate and phosphate) concentrations were as follows.

For the nitrate + nitrite and nitrite analyses, a modification of Grasshoff's (1976)<sup>23</sup> method was applied. The nitrate in the sample was reduced to nitrite in a cadmium tube, the inside of which was coated with copper. The sample stream with its equivalent nitrite was treated with an acidic sulfanilamide reagent; the nitrite forms nitrous acid, which reacts with the sulfanilamide to produce diazonium ions. N-1-Naphthylethylene-diamine was added to the sample stream and then coupled with the diazonium ion to produce a red azo dye. In cases where nitrate is reduced to nitrite, both nitrate and nitrite react, and both are measured. In the absence of reduction, only nitrite reacts. No reduction was therefore performed for the nitrite analysis, and an alkaline buffer was not required. Finally, the nitrate content was computed by the difference.

The method used for silicate analysis is analogous to that for phosphate, as described in the next paragraph. The method essentially followed that of Grasshoff *et al.* (1999)<sup>24</sup>, wherein silicomolybdic acid is first formed from the silicate in the sample, and molybdic acid then added; the silicomolybdic acid is reduced to silicomolybdous acid, or "molybdenum blue", using ascorbic acid as the reductant.

The analytical method for phosphate was a modification of the procedure described by Murphy and Riley  $(1962)^{25}$ . The seawater sample was added to molybdic acid to form phosphomolybdic acid, which was then reduced to phosphomolybdous acid using L-ascorbic acid as the reductant. The flow diagrams and reagents used for each component are given in Fig. S5.

# 3.6.3. Data processing

The QuAAtro 2-HR raw data were processed as follows. After the baseline shift check, the shape and position of each peak was checked, and the position was shifted if necessary. Carry-over correction and baseline drift correction were applied to each peak height and then, sensitivity correction was applied each peak. In the baseline and sensitivity corrections, linear regression was used. Nutrient concentrations were calculated using seawater density derived from CTD pressure, bottle salinity, and laboratory temperature. Finally, nutrient concentrations were corrected using

calibration curves which is obtained by quadratic regression.

#### 3.6.4. Quality control

For the nitrate standard, we used "potassium nitrate 99.995 suprapur®", provided by Merck (Lot B0993065, CAS No. 7757-79-1). For the nitrite standard, we used "nitrous acid iron standard solution (NO<sub>2</sub><sup>-</sup> 1000, Lot TWN2722, Code No. 140-06451)", provided by Wako (since after 2018, the corporation is re-named as FUJIFILM Wako pure Chemical Co.). This standard solution was certified by Wako using the ion chromatograph method. The calibration result was 1002 mg/L at 20°C. The expanded uncertainty of the calibration (k = 2) was 0.7 %. For the silicate standard, we used "Silicon standard solution SiO<sub>2</sub> in NaOH 0.5 mol/l CertiPUR®", provided by Merck (Lot HC68513536, CAS No. 170236). The silicate concentration was certified by NIST-SRM3150, with an uncertainty of 0.7 %. The HC68513536 silicate standard was certified as 1000 mg L<sup>-1</sup>. For the phosphate standard, we used "potassium dihydrogen phosphate anhydrous 99.995 suprapur®", provided by Merck (Lot B1144508, CAS No. 7778-77-0).

To maintain inter-comparability of the measurements, Certified Reference Materials (hereafter referred to as CRM) were prepared. The prepared CRM (CK, CD, CJ, CC, CB and BZ; details are given in <u>Table S4</u>) covered the full range of nutrient concentrations in the Southern Ocean. Lot CB was measured at every run to detect any temporal drift. The calibration curves for the respective nutrient components were obtained for every run using 6 reference points, which were derived from the CRM and in-house standards, as summarized in <u>Table S5</u>.

The repeatability of all the above methods was assessed based on measurements of the in-house standard, which were made every 6 to 9 samples. Coefficients of variation (CV) were then estimated from the means and standard deviations of the in-house standard measurements (<u>Table S6</u>). These were less than 0.08, 0.16, 0.07 and 0.10% for nitrate, nitrite, silicate and phosphate, respectively.

#### 4. Data Records

Vertical CTD profiles (temperature and salinity) and CTD water sampling data (salinity, dissolved oxygen, and nutrient concentrations) are shown in Figs. S6 and S7, respectively. The sea surface temperature and salinity obtained by TSG are shown in Fig. S8. The CTD data and water sampling data are provided in the WHP-Exchange Format<sup>26</sup>. The TSG data are provided in the simple .csv format. The data columns in the TSG file are as follows: Nav Date/Time – date/time derived from the GPS mounted on the ship (UTC); Latitude/Longitude – latitude/longitude derived from the GPS mounted on the ship; C-T Temp – temperature derived from the ETSG2 thermosalinograph; Salinity – salinity derived from the ETSG2 thermosalinograph.

# 5. Competing interests

The authors declare no competing financial interests.

# 6. Figure



Fig. 1. Cruise track and locations of observation sites during the UM-17-09 cruise. Black circles indicate locations where CTD observations were conducted. Gray triangles show positions where salinity samples were obtained from TSG. The broken line indicates the cruise track. The diamond and inverted triangle indicate the locations of the ports of Fremantle and Hobart, respectively. The bottom-right inlet map provides the locations of the observation region (solid line) and cruise track (broken line) in the Southern Ocean.

# 7. Table

Table 1. Summary of CTD observations during the UM-17-09 cruise. Station name, latitude/longitude (decimal degrees), start date and time, bottom depth estimated from the ship-mounted depth recorder, maximum depth observed, pressure at maximum depth, and minimum distance above bottom are summarized.

Station	Latitude	Longitude		Date, Tir	ne (UTC)		Bottom depth	Max. depth	Max. pressure	Min. distance above bottom
name	(-5)	(-E)	Voor	Month	Dev	Stort time	(m)	(m)	(ddar)	(m)
			rear	Wohu	Day	Start time				
KC1	40.0002	110.0003	2018	1	1	21:06	4629	4621	4708	9
KC2	45.0078	110.0005	2018	1	3	5:04	3919	3909	3978	10
KC3	49.9998	110.0003	2018	1	5	0:25	3223	3208	3261	15
KC4	54.9998	109.9995	2018	1	6	6:50	3875	3866	3938	9
KC5	60.0015	110.0047	2018	1	7	20:10	4361	4352	4440	9
KC6	64.6732	109.7905	2018	1	11	8:15	3052	3042	3095	10

#### **Author contributions**

K. Shimada performed the sample analysis and wrote the manuscript. S. Takao, T. Kunio and Y. Kitade conducted the field sampling on board the T/V *Umitaka-maru*. T. Odate and J. Kanda directed the monitoring program. All authors commented on and contributed to the final version of the paper.

#### Acknowledgments

We express our heartfelt appreciation to all members of JARE 59 for their support. We also thank the captain, officers and crews of the *Umitaka-maru*. This work was supported by MEXT for physical and chemical oceanographic observations as a part of the Japanese Antarctic Research Expedition (Program Grant Number JPMXD120000000). We thank Dr. H. Uchida of the Japan Agency for Marine-Earth Science and Technology (JAMSTEC), who provided the SBE 35 (Deep Ocean Standards Thermometer) in January 2015 and enabled us to assess the pressure sensitivity of our primary temperature sensor (03P2863).

#### References

- 1. Schmitz, W. J., Jr. The Pacific and Indian Oceans: A global update Vol. 2, On the world ocean circulation, WHOI Tech. Rep. 1996, WHOI-96-08, 241 p. https://doi.org/10.1575/1912/356.
- Broecker, W. S. Thermohaline circulation, the Achilles heel of our climate system: Will man-made CO<sub>2</sub> upset the current balance? Science. 1997, 278, p. 1582–1588. https://doi.org/10.1126/science.278.5343.1582.
- Rignot, E., Jacobs, S., Mouginot, J. and Scheuchl, B. Ice-shelf melting around Antarctica. Science. 2013, 341, p. 266–270. https://doi.org/10.1126/science.1235798.
- 4. Schmidtko, S., Heywood, K. J., Thompson, A. F. and Aoki, S. Multidecadal warming of Antarctic waters. Science. 2014, 346, p. 1227–1231. https://doi.org/10.1126/science.1256117.
- Aoki, S. *et al.* Widespread freshening in the seasonal ice zone near 140°E off the Adélie Land Coast, Antarctica, from 1994 to 2012. J. Geophys. Res. Oceans. 2013, 118, p. 6046–6063. https://doi.org/10.1002/2013JC009009.
- Purkey, S. G. and Johnson, G.C. Global contraction of Antarctic Bottom Water between the 1980s and 2000s. J. Climate. 2012, 25, p. 5830–5844. https://doi.org/10.1175/JCLI-D-11-00612.1.
- Shimada, K., Aoki, S., Ohshima, K. I., and Rintoul, S. R. Influence of Ross Sea Bottom Water changes on the warming and freshening of the Antarctic Bottom Water in the Australian-Antarctic Basin. Ocean Sci. 2012, 8, p. 419–432. https://doi.org/10.5194/os-8-419-2012.
- Katsumata, K., Nakano, H. and Kumamoto, Y. Dissolved oxygen change and freshening of Antarctic Bottom water along 62°S in the Australian-Antarctic Basin between 1995/1996 and 2012/2013. Deep-Sea Res. II. 2015, 114, p. 27–38. https://doi.org/10.1016/j.dsr2.2014.05.016.
- Rye, C. D. *et al.* Rapid sea-level rise along the Antarctic margins in response to increased glacial discharge. Nat. Geosci. 2014, 7, p. 732–735. https://doi.org/10.1038/ngeo2230.
- Aoki, S., Yamazaki, K., Hirano, D., Katsumata, K., Shimada, K., Kitade, Y., Sasaki, H. and Murase, H. Reversal of freshening trend of Antarctic Bottom Water in the Australian-Antarctic Basin during 2010s. Sci. Rep. 2020, 10, 14415. https://doi.org/10.1038/s41598-020-71290-6.
- Silvano, A. *et al.* Recent recovery of Antarctic Bottom Water formation in the Ross Sea driven by climate anomalies. Nat. Geosci. 2020, 13, p. 780–786. https://doi.org/10.1038/s41561-020-00655-3.
- UNESCO. Background papers and supporting data on the Practical Salinity Scale 1978. UNESCO Technical Papers in Marine Science. 1981, No. 37, 144 p.
- McTaggart, K. E., Johnson, G. C., Johnson, M. C., Delahoyde, F. M. and Swift, J. H. Notes on CTD/O<sub>2</sub> data acquisition and processing using Sea-Bird hardware and software (as available). The GO-SHIP repeat hydrography manual: A collection of expert reports and guidelines. 2010, IOCCP Report Number 14, ICPO Publication Series Number 134, edited by Hood, E. M., Sabine, C. L. and Sloyan, B. M. UNESCO-IOC, Paris, France. https://www.go-ship.org/HydroMan.html.
- Uchida, H., Ohyama, K., Ozawa, S. and Fukasawa, M. In Situ Calibration of the SeaBird 9*plus* CTD Thermometer. J. Atmos. Oceanic Technol. 2007, 24, p. 1961–1967.

https://doi.org/10.1175/JTECH2093.1.

- Joyce, T. M. Introduction to the collection of expert reports compiled for the WHP programme, in: WHP Operations and Methods, WOCE Operations Manual. 1994, WHP Office Report, WHPO 91-1, WOCE Report No. 68/91, WHP Office, Woods Hole Oceanographic Institution, Woods Hole, Mass., 4 p.
- Hood, E. M., Introduction to the Collection of Expert Reports and Guidelines. 2010, IOCCP Report Number 14, ICPO Publication Series Number 134, edited by Hood, E. M., Sabine, C. L. and Sloyan, B. M. UNESCO-IOC, Paris, France. https://www.go-ship.org/HydroMan.html.
- 17. Kawano, T. Method for Salinity (Conductivity Ratio) Measurement. GO-SHIP repeat hydrography manual: A collection of expert reports and guidelines. 2010, IOCCP Report Number 14, ICPO Publication Series Number 134, edited by Hood, E. M., Sabine, C. L. and Sloyan, B. M. UNESCO-IOC, Paris, France. https://www.go-ship.org/HydroMan.html.
- Dickson, A. G. Determination of dissolved oxygen in sea water by Winkler titration. 1996. https://geo.h2o.ucsd.edu/documentation/manuals/pdf/91\_1/dickson2.pdf (accessed 2018-12-03).
- Langdon, C. Determination of Dissolved Oxygen in Seawater by Winkler Titration Using The Amperometric Technique. GO-SHIP repeat hydrography manual: A collection of expert reports and guidelines. 2010, IOCCP Report Number 14, ICPO Publication Series Number 134, edited by Hood, E. M., Sabine, C. L. and Sloyan, B. M. UNESCO-IOC, Paris, France. https://www.go-ship.org/HydroMan.html.
- Murray, C. N., Riley, J. P. and Wilson, T. R. S. The solubility of oxygen in Winkler reagents used for the determination of dissolved oxygen. Deep-Sea Research. 1968, 15. p. 237–238. https://doi.org/10.1016/0011-7471(68)90046-6.
- Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) Guide to best practices for ocean CO<sub>2</sub> measurements. PICES Special Publication 3. 2007, 191 p.
- 22. Hydes, D. J. *et al.* Determination of Dissolved Nutrients (N, P, Si) in Seawater with High Precision and Inter-Comparability Using Gas-Segmented Continuous Flow Analysers. The GO-SHIP repeat hydrography manual: A collection of expert reports and guidelines. 2010, IOCCP Report Number 14, ICPO Publication Series Number 134, edited by Hood, E. M., Sabine, C. L. and Sloyan, B. M. UNESCO-IOC, Paris, France. https://www.go-ship.org/HydroMan.html.
- Grasshoff, K. Automated chemical analysis (Chapter 13) in Methods of Seawater Analysis. 1976.
  With contribution by Almgreen T., Dawson R., Ehrhardt M., Fonselius S. H., Josefsson B., Koroleff F. and Kremling K. Weinheim, New York: Verlag Chemie.
- Grasshoff, K., Kremling K. and Ehrhardt, M. Methods of Seawater Analysis. Third, Completely Revised and Extended Edition. 1999. WILEY-VCH Verlag GmbH, D-69469 Weinheim (Federal Republic of Germany).
- Murphy, J. and Riley, J. P. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta. 1962, 27, p. 31–36. https://doi.org/10.1016/S0003-2670(00)88444-5.
- 26. Swift, J. H. and Diggs, S. C. Description of WHP-Exchange Format for CTD/Hydrographic Data.

2008, CLIVAR and Carbon Hydrographic Data Office, UCSD Scripps Institution of Oceanography, 19 p.

# **Data Citation**

Shimada, K., Takao, S., Takahashi, K., Kitade, Y., Kanda, J. and Odate, T. Physical and chemical oceanographic data during Umitaka-maru cruise of the 59th Japanese Antarctic Research Expedition in January 2018. 1.00, Japan, Arctic Data archive System (ADS), 2021. https://doi.org/10.17592/001.2020101301.



**Supplemental figures** 

# Fig. S1. Salinity difference between TSG and bottle salinity.

The upper panel shows the time series of differences between TSG and bottle salinity before (blue) and after (red) post-cruise calibration. The lower panel is a histogram of the differences after the calibration. N, and Mean/ $\sigma$  in the lower panel indicate the number of bottle salinities and average/standard deviation of the difference between CTD and bottle salinity, respectively.



# Fig. S2. Difference between CTD salinity (primary) and bottle salinity.

The upper two panels are the time series and vertical profile of the differences between CTD and bottle salinity before (blue) and after (red) post-cruise calibration, respectively. The lower two panels are histograms of the differences after the calibration and are divided according to observed pressure. Here, 950 dbar is chosen as the separation depth because background vertical salinity gradient, which may influence the salinity difference between CTD and bottle through vertical distance between CTD sensors and Niskin bottles (e.g., ~1 m), increases/decreases above/below this depth. N, Ave/Std, and |Max| in the panels indicate the number of bottle salinity, and the maximum value for the absolute difference between CTD and bottle salinity, respectively.



Fig. S3. Time series of the double conductivity ratio for Standard Sea Water (SSW) P160. Measured double conductivity ratios of SSW are shown by blue line with dots. Double conductivity ratios were corrected by removing linear trend during the measurement and corrected double conductivity ratios are shown by orange line with dots. The dotted black line indicates the regression line estimated for the conductivity ratio after correction.



Fig. S4. Histogram of the absolute differences between replicate samples.

## K. Shimada et al.



Fig. S5. The flow diagrams and reagents for channels 1 to 4.



Fig. S6. Vertical profiles of CTD and water sampling data.

The left, middle and right panels show vertical profiles of KC1, KC2 and KC3, respectively. The upper, middle, and lower panels are vertical profiles of CTD data (temperature and salinity), water sampling data (salinity and dissolved oxygen), and water sampling data (nutrients). The broken line in each panel indicates the pressure at the sea floor.



Fig. S7. As Fig. S6, but for stations KC4 to KC6.



Fig. S8. Time series of temperature and salinity obtained by TSG.

# Supplemental tables

# Table S1. Specifications of the CTD system used during the UM-17-09 cruise.

Type of instruments, product names, manufacturers, serial numbers, and calibration dates are given.

Type of instrument	Product name	Manufacturer	Serial number	Calibration date
Underwater unit	SBE9plus	Sea-Bird Electronics, Inc.	09P22763-0590	September 26, 2017
Pressure sensor	Digiquartz pressure sensor	Sea-Bird Electronics, Inc.	77509	September 26, 2017
Temperature sensor (primary)	SBE03plus	Sea-Bird Electronics, Inc.	03P2863	August 26, 2017
Temperature sensor (secondary)	SBE03plus	Sea-Bird Electronics, Inc.	03P5679	August 26, 2017
Conductivity sensor (primary)	SBE04C	Sea-Bird Electronics, Inc.	44376	September 08, 2017
Conductivity sensor (secondary)	SBE04C	Sea-Bird Electronics, Inc.	42415	September 01, 2017
Altimeter	PSA-916T	Teledyne Benthos, Inc.	59546	
Carousel water sampler	SBE32	Sea-Bird Electronics, Inc.	3273491-0949	
Submersible Pump (primary)	SBE5T	Sea-Bird Electronics, Inc.	052786	
Submersible Pump (secondary)	SBE5T	Sea-Bird Electronics, Inc.	057891	
Bottom contact switch	Bottom contact switch	Sea-Bird Electronics, Inc.		
Deck unit	SBE11plus	Sea-Bird Electronics, Inc.	11P90698-0969	

Table S2. Details of instruments and reagents used during the UM-17-09 cruise.

Instruments/reagents	Details
Burette used for sodium thiosulfate	808 Titrando (Metrohm Japan Ltd.)
Burette used for potassium iodate	789 MPT Titrino (Metrohm Japan Ltd.)
Winkler Reagent I	Manganese chloride solution (3 mol dm <sup>-3</sup> )
Winkler Reagent II	Sodium hydroxide (8 mol dm $^{\text{-3}})$ / sodium iodide solution (4 mol dm $^{\text{-3}})$
Sulfuric acid solution	$5 \text{ mol dm}^{-3}$
Sodium thiosulfate	$0.025 \text{ mol dm}^{-3}$
Potassium iodide	0.001667 mol dm <sup>-3</sup>

Table S3. Results of the standardization and blank determination during the UM-17-09 cruise. Date, KIO<sub>3</sub> ID, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> ID, end-point reading of titration, estimated blank, and applied station are listed.

Date	KIO <sub>3</sub> ID	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ID	End point	Blank	Station
1/1/2018	K1704H01	T1704N-1	3.977	-0.001	KC1, KC2
1/5/2018	K1704H02	T1704N-1	3.982	0.000	KC3, KC4
1/7/2018	K1704H03	T1704N-1	3.985	-0.001	-
1/7/2018	K1704H03	T1704N-3	3.978	0.001	KC5
1/11/2018	K1704H04	T1704N-3	3.976	0.000	KC6
1/15/2018	K1704H05	T1704N-3	3.976	0.000	-

Table S4. Certified concentrations and uncertainties of CRMs.

Certified concentrations with uncertainties (coverage factor k = 2) of nitrate, nitrite, silicate and phosphate are given for CRMs CK, CD, CJ, CC, CB and BZ. All the CRMs were provided by KANSO Co. Ltd. All concentrations are expressed in units of  $\mu$ mol kg<sup>-1</sup>. The values given for nitrite are references. Details are also available at the website of the manufacturer (http://www.kanso.co.jp/eng/production/available\_lots.html).

Lot	Nitrate	Nitrite*	Silicate	Phosphate
СК	$0.02\pm0.03$	$0.01\pm0.01$	$0.73\pm0.08$	$0.048 \pm 0.012$
CD	5.50 ±0.05	$0.02 \pm 0.00$	$13.93\pm0.10$	$0.446\pm0.008$
CJ	$16.20\pm0.20$	$0.03\pm0.01$	$38.50\pm0.40$	$1.190\pm0.020$
CC	$30.88 \pm 0.24$	$0.12\pm0.01$	$86.16\pm0.48$	$2.080\pm0.019$
CB	$35.79\pm0.27$	$0.12\pm0.01$	$109.2\pm0.62$	$2.520\pm0.022$
BZ	$43.35\pm0.33$	$0.22\pm0.01$	$161.0\pm0.93$	$3.056\pm0.033$

Table S5. CRMs and nominal nutrient concentrations for the in-house standard used for the calibration curves. CRM lots and nominal nutrient concentrations for the in-house standard (expressed in units of µmol L<sup>-1</sup>) are given for the nutrient components. The in-house standard is adopted for C-5, and CRMs are adopted for C-1, C-2, C-3, C-4 and C-6.

	C-1	C-2	C-3	C-4	C-5	C-6
NO <sub>3</sub>	СК	CD	CJ	CC	36	BZ
NO <sub>2</sub>	СК	CD	CJ	CC	1.0	BZ
SiO <sub>2</sub>	СК	CD	CJ	CC	113	BZ
PO <sub>4</sub>	СК	CD	CJ	CC	2.4	BZ

Table S6. Descriptive statistics for CV (%) based on the replicate analyses.Statistics (median, mean, maximum and minimum) based on 6 CV estimates are listed for nitrate, nitrite, silicate and phosphate.

	Nitrate	Nitrite	Silicate	Phosphate
Median	0.08	0.16	0.07	0.10
Mean	0.08	0.17	0.07	0.10
Maximum	0.09	0.26	0.07	0.14
Minimum	0.05	0.09	0.05	0.06
Number of CV estimate	6	6	6	6