## pH

## 30 September 2023

### Personnel

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### Station occupied

A total of 38 stations (Leg 1: 24, Leg 2: 14) were occupied for pH. Station location and sampling layers of them are shown in Figures C.8.1 and C.8.2, respectively.

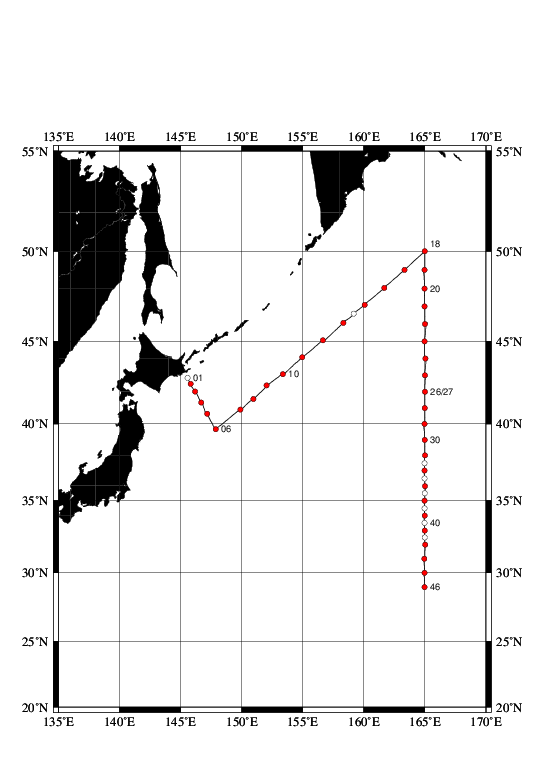


Figure C.8.1. Location of observation stations of pH. Closed and open circles indicate sampling and no-sampling stations, respectively.

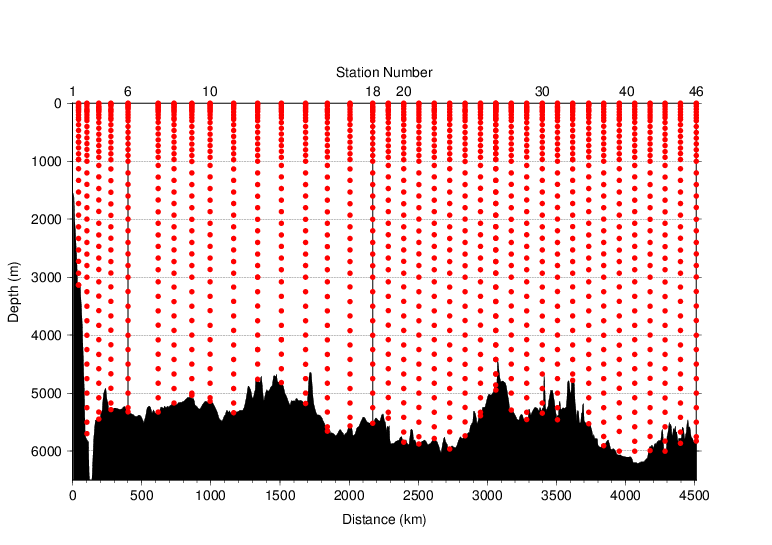


Figure C.8.2. Distance-depth distribution of sampling layers of pH.

### Instrument

The measurement of pH was carried out with a pH analyzer (Nihon ANS Co. Ltd, Japan).

### Sampling and measurement

Methods of seawater sampling, poisoning, spectrophotometric measurements using the indicator dye *m*-cresol purple (hereafter *m*CP) and calculation of pHT (on the total hydrogen ion scale; Appendix A1) were based on Saitoet al. (2008). The pHT is calculated from absorbance ratio (*R*) with the following equations,

(C8.1)

(C8.2)

where p*K*2 is the acid dissociation constant of *m*CP,

(C8.3)

(293 K ≤ *T* ≤ 303 K, 30 ≤ *S* ≤ 37).

and in equation (C8.2) are absorbance of seawater itself and dye plus seawater, respectively, at wavelength ** (nm). The value of p*K*2 in equation (C8.3) is expressed as a function of temperature *T* (in Kelvin) and salinity *S* (in psu). Finally, pHT is reported as the value at temperature of 25 °C. Details are shown in Appendix A1.

### pH perturbation caused by addition of *m*-cresol purple solution

The *m*CP solution using as indicator dye was prepared in our laboratory (Appendix A2) and was subdivided into some bottles (*m*CP batches) that attached to the apparatus. The injection of *m*CP solution perturbs the sample pHT slightly because the acid-base equilibrium of the seawater is disrupted by the addition of the dye acid-base pair (Dickson et al., 2007).

Before applying *R* to the equation (C8.1), the measured *R* in the sample was corrected to that value expected to be unperturbed by the addition of the dye (Dickson et al., 2007; Clayton and Byrne, 1993). The magnitude of the perturbation (*R*) was calculated empirically from that by the second addition of the dye and absorbance ratio measurement as follows:

*R* = *R*2 − *R*1, (C8.4)

where *R*1 and *R*2 are the absorbance ratio after the initial addition of dye solution in the sample measurement and after the second addition in the experimental measurement, respectively. Because the value of *R* depends on the pHT of sample, we expressed *R* as a quadratic function of *R*1 based on experimental *R* measurement obtained at this cruise as follows:

. (C8.5)

In each measurement for a station, *R* was measured for about 10 samples from various depths to obtain wide range of *R*1 and experimental *R* data. For each *m*CP batch bottle, coefficients (C0, C1 and C2) were calculated by equation (C8.5), and *R* was evaluated for each *R*1. The coefficients for each *m*CP batch are showed in Table C.8.1. The plots and function curves are illustrated in Figure C.8.3.

Table C.8.1. Summary of coefficients; C2, C1 and C0 in .

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Stations | *m*CP batch | C2 | C1 | C0 |
| 2–26 | 1 | −7.12302E−03 | 1.84608E−04 | 7.27697E−03 |
| 27–46 | 2 | 1.40192E−04 | −1.67665E−02 | 1.35675E−02 |

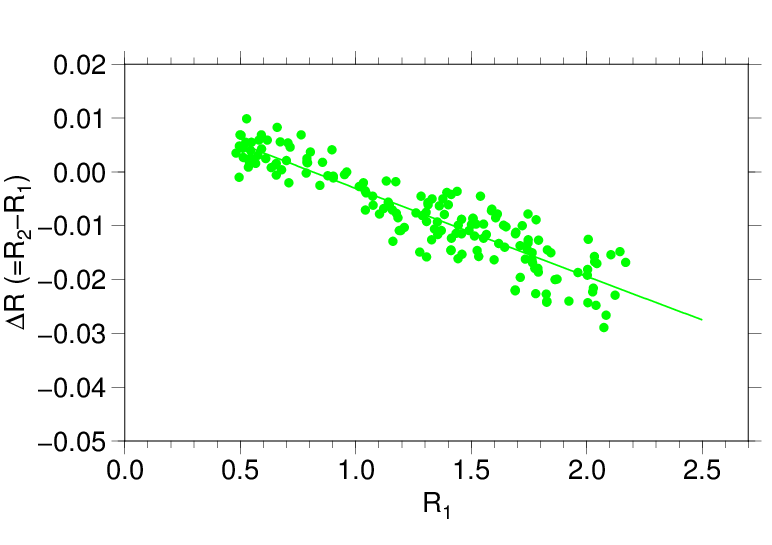
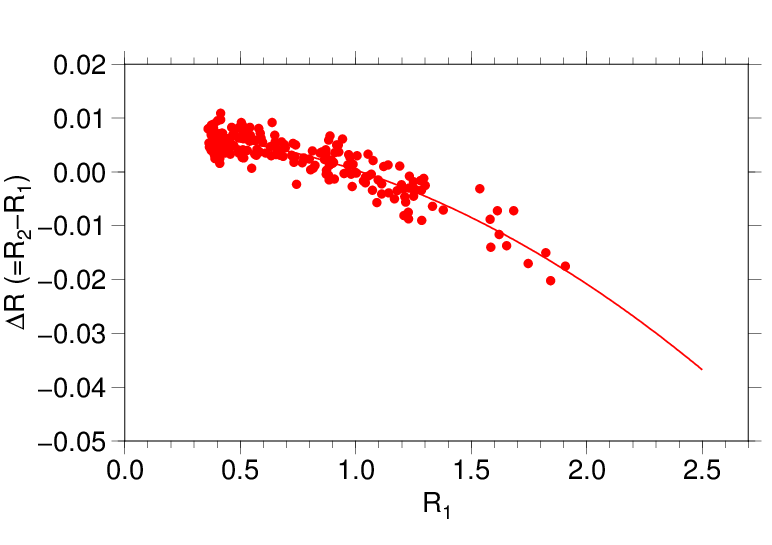


Figure C.8.3. The function curve of the *R* (= *R*2 − *R*1) vs *R*1 for (left) first and (right) second *m*CP batch of solution shown in Table C.8.1.

### Quality Control

**(6.1) Replicate and duplicate analyses**

We took replicate (pair of water samples taken from a single Niskin bottle) and duplicate (pair of water samples taken from different Niskin bottles closed at the same depth) samples for pHT determination throughout the cruise. Table C.8.2 summarizes the results of the measurements. Figure C.8.4 shows details of the results. The calculation of the standard deviation from the difference of sets of measurements was based on a procedure (SOP 23) in DOE (1994).

Table C.8.2. Summary of replicate and duplicate measurements of pHT.

|  |  |
| --- | --- |
| **Measurement** | **Average magnitude of difference ± S.D.** |
| Replicate | 0.0020±0.0019 (N=110) |
| Duplicate | 0.0026±0.0021 (N=10) |

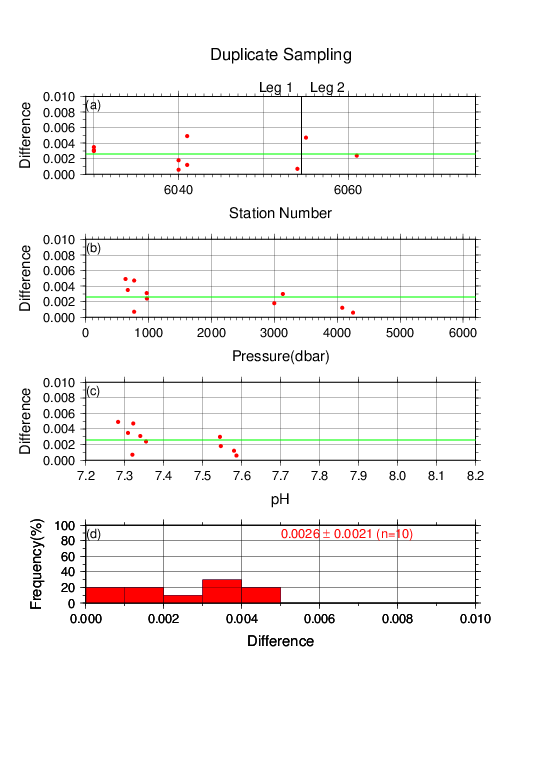
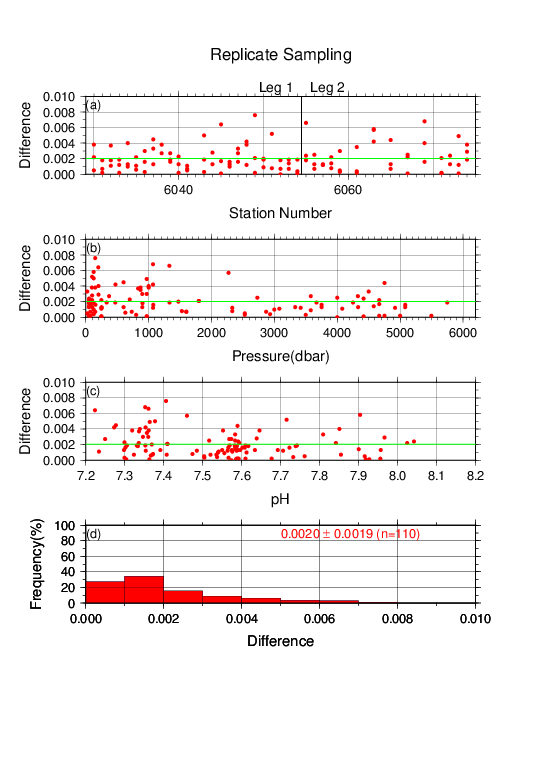


Figure C.8.4. Results of (left) replicate and (right) duplicate measurements during the cruise versus (a) station number, (b) pressure and (c) pHT. The green lines denote the averages of the measurements. The bottom panels (d) show histograms of the measurements.

**(6.2) Measurements of CRM and working reference materials**

The precision of the measurements was monitored by using the CRMs and working reference materials bottled in our laboratory (Appendix A2 in C.6). Although the pHT value of the CRM was not assigned, it could be calculated from certified parameters of DIC and TA (https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/oceans/Dickson\_CRM/batches.html) based on the chemical equilibrium of the carbonate system (Lueker et al., 2000). The pHT of the CRM (batch 157) was calculated to be 7.8405. Working reference material measurements were carried out first at every station. If the results of the measurements were confirmed to be good, measurements on seawater samples were begun. CRM (batch 157) measurements were done at every few (about 3) stations. The measurement for seawater sample and working reference material was made once for a single bottle, and that for CRM was made twice. Table C.8.3 summarizes the means of difference of pHT between two measurements and pHT values for a CRM bottle and the means of the pHT value for a working reference material for each *m*CP batch. Figures C.8.5–C.8.7 show detailed results.

Table C.8.3. Summary of difference and means of the pHT values for two measurements for a CRM bottle, and mean of pHT for a working reference material, which was calculated with data with good measurements.

|  |  |  |  |
| --- | --- | --- | --- |
|  | **CRM** |  | **Working reference material** |
| ***m*CP Batches** | **Magnitude of difference**  **Ave. ± S.D.** | **Mean**  **Ave. ± S.D.** | **Mean**  **Ave. ± S.D.** |
| 1 | 0.0012±0.0011 (N=12) | 7.8373±0.0017 (N=12) | 7.8985±0.0014 (N=25) |
| 2 | 0.0010±0.0008 (N=7) | 7.8418±0.0011 (N=7) | 7.9033±0.0023 (N=18) |

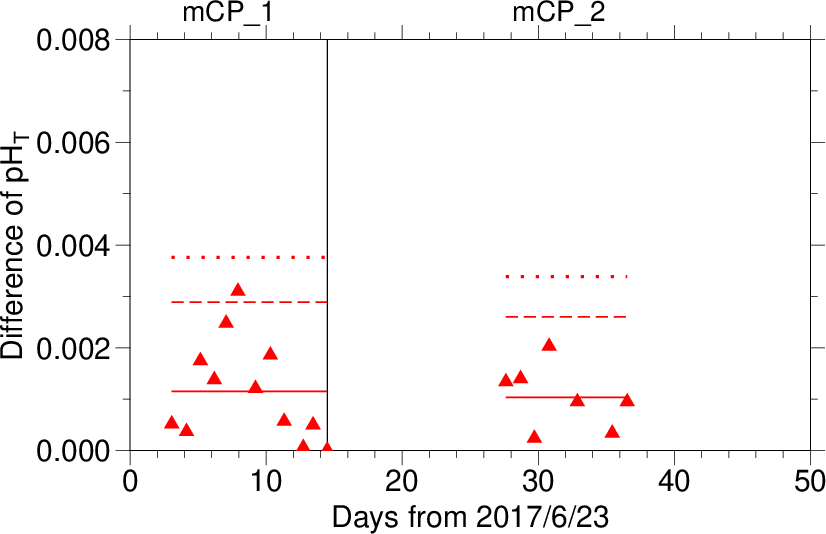


Figure C.8.5. The absolute difference (*R*) of pHT between two measurements of a CRM bottle. The *m*CP batch names are shown above the graph, and vertical lines denote the day *m*CP batches were changed. The solid, dashed and dotted lines denote the average range (), upper warning limit (2.512) and upper control limit (3.267) for each *m*CP batch bottle, respectively (see Dickson et al., 2007).

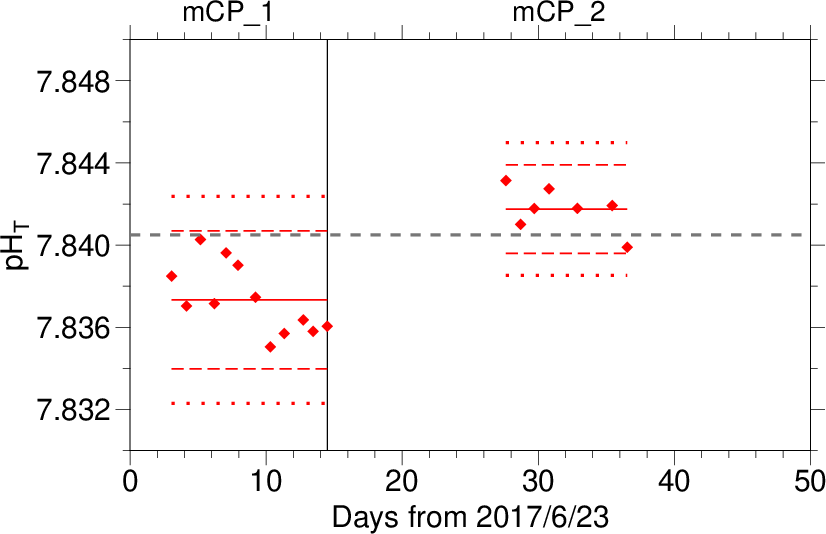


Figure C.8.6. The mean of pHT values between two measurements of a CRM bottle. The *m*CP batch names are shown above the graph, and vertical lines denote the day when the *m*CP batch was changed. The solid, dashed, and dotted lines denote the mean of measurements, upper/lower warning limit (mean ± 2S.D.), and upper/lower control limit (mean ± 3S.D.) for each *m*CP batch bottle, respectively (see Dickson et al., 2007). The gray dashed line denotes pHT of CRM calculated from certified parameters.

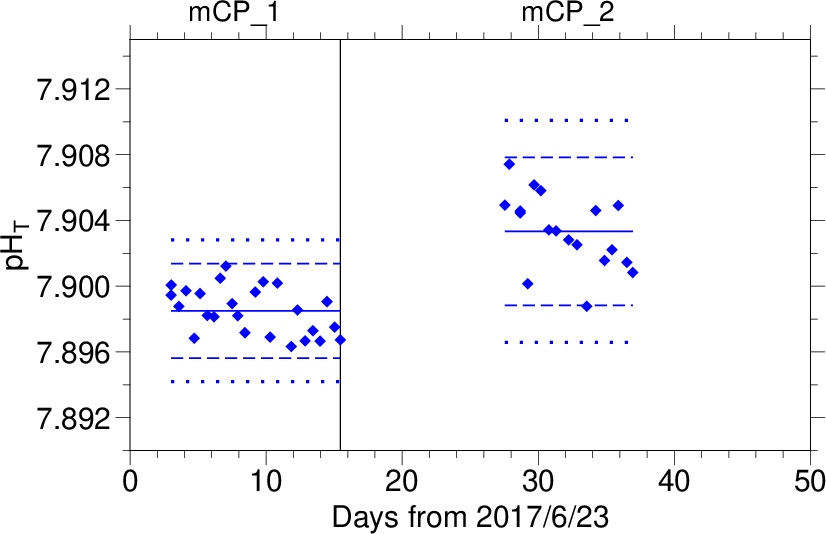


Figure C.8.7. Same as C.8.6, but for working reference material.

**(6.3) Quality control flag assignment**

A quality control flag value was assigned to the pH measurements (Table C.8.4) using the code defined in the IOCCP Report No.14 (Swift, 2010).

Table C.8.4. Summary of assigned quality control flags.

|  |  |  |
| --- | --- | --- |
| Flag | Definition | Number of samples |
| 2 | Good | 1280 |
| 3 | Questionable | 4 |
| 4 | Bad (Faulty) | 5 |
| 5 | Not reported | 2 |
| 6 | Replicate measurements | 110 |
| Total number of samples | | 1401 |

**(6.4) Comparison at cross-stations during the cruise**

There was a cross-station during the cruise located at 42˚N/165˚E. At stations of Stn.26 and Stn.27, hydrocast sampling for pHT was conducted two times at interval of 13 days. These profiles are shown in Figure C.8.8.

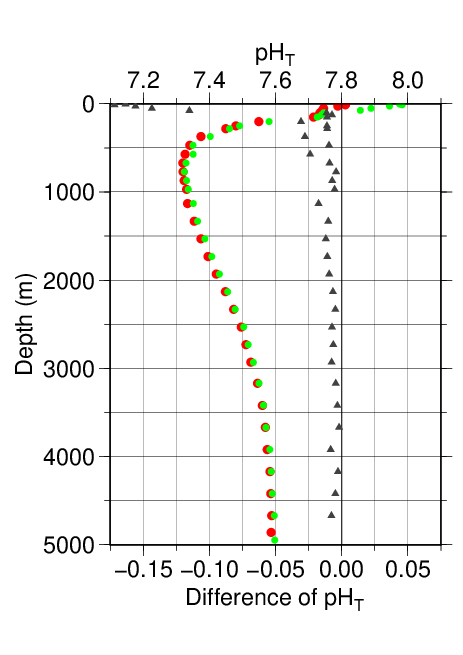
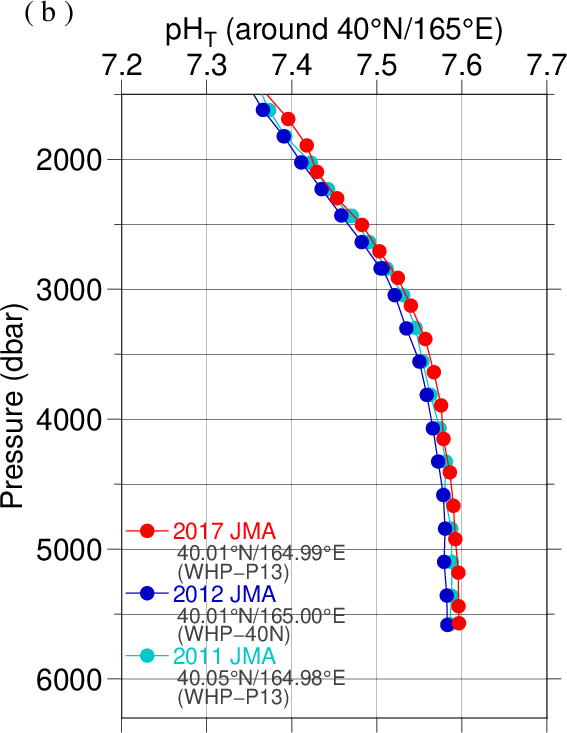
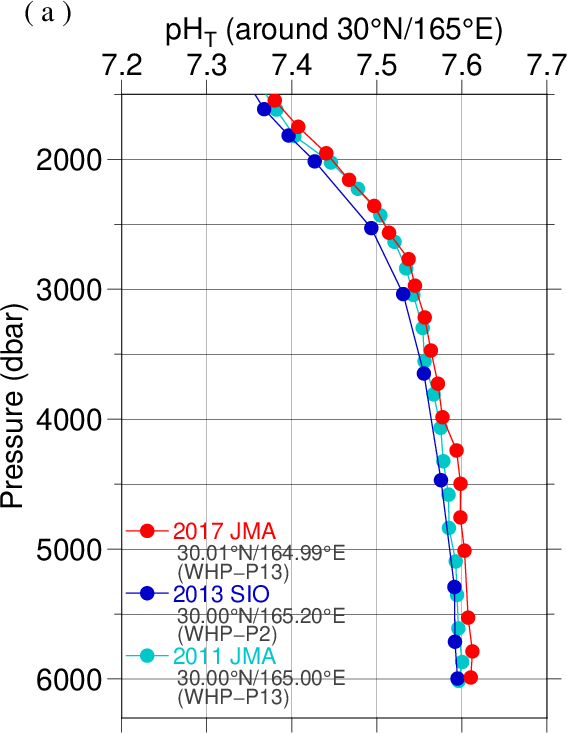


Figure C.8.8. Comparison of pHT observed at same location in different legs of this cruise: 42˚N/165˚E (stations 26 and 27). The red and green circles denote station 26 and station 27, respectively. Triangles denote the difference in pHT measured at same depth in different legs.

**(6.5) Comparison at cross-stations of WHP cruises**

We compared pHT data of this cruise and other WHP cruises by JMA, Japan Agency for Marine-Earth Science and Technology (JAMSTEC) and Scripps Institution of Oceanography (SIO) at cross points. Summary of the comparisons are shown in Figure C.8.9(a) for cross point with WHP-P2 line (around 30˚N/165˚E), Figure C.8.9(b) for cross point with WHP-40N line (around 40˚N/165˚E), and Figure C.8.9(c) for cross point with WHP-P1 line (around 47˚N/160˚E). Data of other cruises are downloaded from the CCHDO web site (https://cchdo.ucsd.edu).



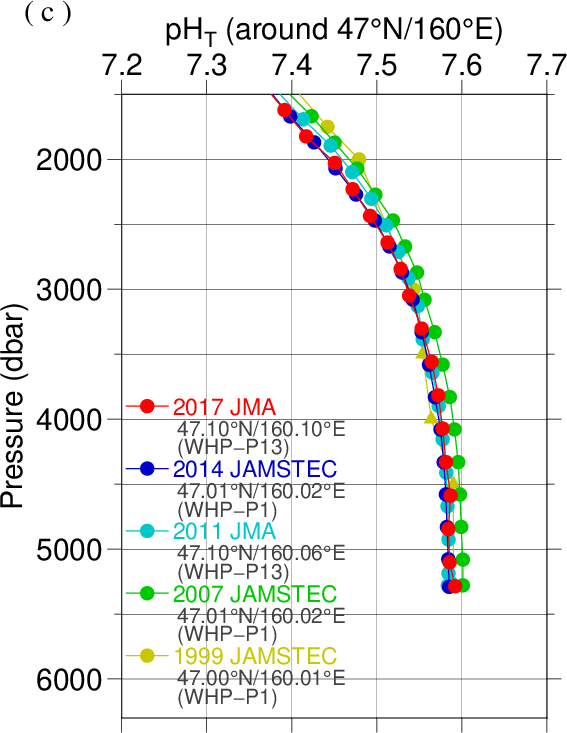


Figure C.8.9. Comparison of pHT profiles at (a) 30˚N/165˚E (cross point with WHP-P2 line), (b) 40˚N/165˚E (cross point with WHP-40N line), and (c) 47˚N/160˚E (cross point with WHP-P1 line). Circles and triangles denote good and questionable values, respectively. The red ones show this cruise.

### Appendix

**A1. Methods**

**(A1.1) Seawater sampling**

Seawater samples were collected from 10-liters Niskin bottles mounted on CTD-system and a stainless steel bucket for the surface. Samples for pH were transferred to Schott Duran® glass bottles using sample drawing tubes. Bottles were filled smoothly from the bottom after overflowing double a volume while taking care of not entraining any bubbles, and lid temporarily with ground glass stoppers.

After all sampling finished, 2 mL of sample is removed from each bottle to make a headspace to allow thermal expansion. Although the procedure is differed from Standard Operating Procedure (SOP) described in PICES Special Publication 3, SOP-2 (Dickson, 2007), poisoned with 0.2 mL of saturated HgCl2 solution to prevent change in pHT caused by biological activity. Finally, samples were sealed with ground glass stoppers lubricated with Apiezon® grease (L).

**(A1.2) Measurement**

Custom-made pH analyzer (2009 model; Nihon ANS) was prepared and operated in the cruise. The analyzer comprised of a sample dispensing unit, a pre-treatment unit combined with an automated syringe, and two (sample and reference) spectrophotometers combined with a high power xenon light source. Spectrophotometric cell was made of quartz tube that has figure of “U”. This cell was covered with stainless bellows tube to keep the external surface dry and for total light to reflect in the tube. The temperature of the cell was regulated to 25.0 ± 0.1 °C by means of immersing the cell into the thermostat bath, where the both ends of bellows tube located above the water surface of the bath. Spectrophotometer, cell and light source were connected with optical fiber.

The analysis procedure was as follows:

a) Seawater was ejected from a sample loop.

b) A portion of sample was introduced into a sample loop including spectrophotometric cell. The spectrophotometric cell was flushed two times with sample in order to remove air bubbles.

c) An absorption spectrum of seawater in the visible light range was measured. Absorbance at wavelengths of 434 nm, 488 nm, 578 nm and 730 nm as well as cell temperature were recorded. To eject air bubbles from the cell, the sample was moved four times and the absorbance was recorded at each stop.

d) 10 l of indicator *m*CP was injected to the loop.

e) Circulating 2 minutes 40 seconds through the loop tube, seawater sample and indicator dye was mixed together.

f) Absorbance of *m*CP plus seawater was measured in the same way described above (c).

**(A1.3) Calculation**

In order to state clearly the scale of pH, we mention “pHT” that is defined by equation (C8.A1.3.1),

(C8.A1.3.1)

where [H+]T denotes the concentration of hydrogen ion expressed in the total hydrogen ion scale. , where [H+]F is the concentration of free hydrogen ion, [SO4]T is the total concentration of sulphate ion and is acid dissociation constant of hydrogen sulphate ion (Dickson, 1990). *C*0 is the standard value of concentration (1 mole per kilogram of seawater, mol kg−1). The pHT was reported as the value at temperature of 25 °C in “total hydrogen ion scale”.

pHT was calculated from the measured absorbance (*A*) based on the following equations (C8.A1.3.2) and (C8.A1.3.3), which are the same as (C8.1) and (C8.2), respectively.

(C8.A1.3.2)

(C8.A1.3.3)

where p*K*2 is the acid dissociation constant of *m*CP. [I2−] / [HI−] is the ratio of *m*CP base form (I2−) concentration over acid form (HI−) concentration which is calculated from the corrected absorbance ratio (*R*) shown in the section 8(5) and the ratios of extinction coefficients (Clayton and Byrne, 1993). and in equation (C8.A1.3.3) are absorbance of seawater itself and dye plus seawater, respectively, at wavelength ** (nm). The value of p*K*2 (, k0 = 1 mol kg−1) had also been expressed as a function of temperature *T* (in Kelvin) and salinity *S* (in psu) by Clayton and Byrne (1993), but the calculated value has been subsequently corrected by 0.0047 on the basis of a reported pHT value accounting for “tris” buffer (DelValls and Dickson, 1998):

. (C8.A1.3.4)

(293 K ≤ *T* ≤ 303 K, 30 ≤ *S* ≤ 37)

Finally, pHT determined at a temperature *t* (pHT(*t*), with *t* in °C) was corrected to the pHT at 25.00 °C (pHT(25)) with the following equation (Saito et al., 2008).

.

(C8.A1.3.5)

**A2. pH indicator**

Indicator *m*-cresol purple (*m*CP) solution

Add 0.67 g *m*CP to 500 mL deionized water (DW) in a borosilicate glass flask. Pour DW slowly into flask to weight of 1 kg (*m*CP + DW), and mix well to dissolve *m*CP. Regulate the pH (free hydrogen ion scale) of indicator solution to 7.9±0.1 by small amount of diluted NaOH solution (approx. 0.25 mol L−1) if the pH was out of the range. The pH of indicator solution was monitored using glass electrode pH meter. The reagent had not been refining.

***References***

Clayton T.D. and R.H. Byrne 1993. Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. *Deep-Sea Res. I*, **40**, 2115–2129.

DelValls, T. A and A. G. Dickson, 1998. The pH of buffers based on 2-amino-2-hydroxymethyl-1,3-propanediol (‘tris’) in synthetic sea water. *Deep-Sea Res. I*, **45**, 1541-1554.

Dickson, A.G. 1990. Standard potential of the reaction: AgCl(s) + 1/2 H2(g) = Ag(s) + HCl(aq), and the standard acidity constant of the ion HSO4− in synthetic sea water from 273.15 to 318.15 K. *J. Chem. Thermodynamics*, **22**, 113–127.

Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. Guide to best practices for ocean CO2 measurements. *PICES Special Publication* 3, 191 pp.

Lueker, T.J, A.G. Dickson and C.D. Keeling, 2000. Ocean *p*CO2 calculated from dissolved inorganic carbon, alkalinity, and equations for *K*1 and *K*2: validation based on laboratory measurements of CO2 in gas and seawater at equilibrium. *Marine Chem.*, **70**, 105-119.

Saito, S., M. Ishii, T. Midorikawa and H.Y. Inoue 2008. Precise Spectrophotometric Measurement of Seawater pHT with an Automated Apparatus using a Flow Cell in a Closed Circuit. *Technical Reports of Meteorological Research Institute*, **57**, 1–28.

Swift, J. H. (2010): Reference-quality water sample data, Notes on acquisition, record keeping, and evaluation. *IOCCP Report No.****14****, ICPO Pub. 134, 2010 ver.1*