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RESEARCH ARTICLE

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Key Points:

- The CO₂ system is strongly influenced by the dilution effect of the basal melting of the Shirase Glacier Tongue (SGT)
- The decrease of pCO₂ by basal melting caused the water to shift from a CO₂ source to a sink of atmospheric CO₂ in Lützow-Holm Bay
- Surface water was strongly influenced by biological processes near the SGT

Supporting Information:

Supporting Information may be found in the online version of this article.

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The Effect of Basal Melting of the Shirase Glacier Tongue on the CO₂ System in Lützow-Holm Bay, East Antarctica

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Abstract To clarify the effect of basal melting of ice tongues/ice shelf on the CO₂ system in the Antarctic continental margin, seawater samples were collected for analysis of dissolved inorganic carbon (DIC), total alkalinity (TA), nutrients, chlorophyll a (chl.a), and oxygen isotopic ratios at the ice front of the Shirase Glacier Tongue (SGT) in Lützow-Holm Bay (LHB), East Antarctica during the summers of 2017 and 2018. At depths greater than ~20 dbar in LHB, CO₂ system parameters were strongly influenced by the dilution effect of SGT basal melting and the inflow of modified Circumpolar Deep Water (mCDW). The distributions of DIC and TA agreed well with an offshore origin of mCDW that flowed beneath the SGT and mixing of basal meltwater and mCDW beneath the SGT. The fraction of SGT meltwater was highest at the station near the ice front. Dilution by SGT basal meltwater reduced the partial pressure of CO₂ in the mCDW from 431 to 387 μ atm. The water then became a sink rather than source of atmospheric CO₂. In the sea surface, DIC and TA were strongly influenced by biological processes. Salinity-normalized DIC decreased with the increase of salinity-normalized TA in accord with 106:16 C:N molar stoichiometry; the chl.a concentration at the sea surface was as high as 31 μ g L⁻¹.

Plain Language Summary Oceanographic observations were made during the summers of 2017 and 2018 near the ice shelf in an ice-covered bay in East Antarctica. Results revealed that the parameters such as dissolved inorganic carbon (DIC), total alkalinity (TA), and nutrients at subsurface layer (>20 m) was strongly influenced by the dilution effect of the melting of ice sheet and the inflow of warm and high salinity water from outside of the bay. In contrast, within the surface layer, DIC, TA, and nutrients were strongly influenced by phytoplankton activity.

1. Introduction

The ocean absorbs more than 25% of anthropogenic carbon dioxide (CO₂) emitted by human activities (Friedlingstein et al., 2019; Le Quéré et al., 2016). The Southern Ocean accounts for 40% of the anthropogenic CO₂ absorbed by the ocean, and it plays an important role in the global carbon cycle as a sink of anthropogenic CO₂ (Gruber et al., 2019; Sabine et al., 2004; Takahashi et al., 2009). However, the estimation of air–sea CO₂ exchange is limited to the open water area of the Southern Ocean. The air–sea CO₂ flux on the Antarctic continental shelves, which are covered with sea ice seasonally or throughout the year, are uncertain because direct observations have been limited (Lenton et al., 2013).

In the ocean, CO₂ exists in three different inorganic forms: as aqueous CO₂ (CO₂ (aq)), as HCO₃⁻, and as CO₃²⁻. The sum of the three different inorganic forms is called the dissolved inorganic carbon (DIC) (Zeebe & Wolf-Gladrow, 2001). The processes that affect the DIC in the polar oceans include: (1) photosynthesis and respiration by biological activity, (2) mixing of water masses (dilution effect by melting of shelf ice and sea ice), (3) precipitation and dissolution of calcium carbonate (CaCO₃ · 6H₂O), and (4) air–sea CO₂ exchange. In the Antarctic coastal zone, (1) and (2) are considered to be especially important processes (e.g., Arroyo et al., 2019; Legge et al., 2017; Shadwick et al., 2017). In coastal polynyas (open-water areas), phytoplankton primary productivity becomes very high when the melting of sea ice exposes surface seawater to solar radiation in the spring (Arrigo and van Dijken, 2003; Murakami et al., 2020). As a result, the DIC concentration and partial pressure of CO₂ (pCO₂) in surface seawater decrease, and the ocean absorbs CO₂.

from the atmosphere in the spring. Coastal polynyas such as the Mertz Polynya (Shadwick et al., 2017), the Cape Darnley polynya (Murakami et al., 2020), and the polynyas found in Prydz Bay (Roden et al., 2013), the Ross Sea (DeJong & Dunbar, 2017), the Amundsen Sea (Yager et al., 2016), and off the West Antarctic Peninsula (Legge et al., 2017) therefore play an important role as sinks for atmospheric CO₂ in the spring and summer. On the other hand, in the winter, the polynyas would be a source for atmospheric CO₂ due to the active brine convection associated with sea-ice formation and respiration, leading high pCO₂ in seawater (e.g., Murakami et al., 2020).

Basal melting of the ice shelf/glacial tongue along the coast of Antarctica has recently been significant (Rignot et al., 2013), and the resultant supply of meltwater to the ocean surface is thought to have had an important effect on the biogeochemistry of the seawater. For example, the basal melt rate of ice shelves adjacent to coastal polynyas was by far the most important environmental factor controlling local phytoplankton abundance (Arrigo et al., 2015). The effect of basal melting on the CO₂ system and biogeochemistry in ice-covered areas is unclear, especially in regions where there is multi-year, land-fast ice. Land-fast ice is found along the coast of Antarctica, and in some places there is multi-year ice (Frazer et al., 2012) and thick ice (Nomura, Aoki, et al., 2018). Ship-based oceanographic observations are therefore difficult for logistical reasons. The location examined in this study—Lützow-Holm Bay (LHB) off Queen Maud Land, East Antarctica—is a multi-year, land-fast ice region. The Shirase Glacier Tongue (SGT) is found in the southern part of LHB. The basal melt rate of the SGT is higher than that of other ice shelves/glacier tongues in East Antarctica (satellite observation: $7.0 \pm 2.0 \text{ m yr}^{-1}$) (Rignot et al., 2013). The high basal melt rate is attributed to the inflow of warm modified Circumpolar Deep Water (mCDW) from offshore into the region beneath the SGT along a trough in the center of LHB (Hirano et al., 2020).

The surface of LHB is covered by thick, land-fast sea ice all year round (Aoki, 2017; Ushio, 2006). In the austral autumn of 2016, however, large areas of land-fast ice broke up (Aoki, 2017), and the relatively new and thin (1–2 m) land-fast ice that covered the surface of LHB allowed us to access the bay during January–February of 2017 and 2018. Although some observations have been made in the coastal polynyas to assess the effect of basal melting on biogeochemistry (e.g., Arrigo et al., 2015), no observations have been made in the ice-covered part of the ocean (mixture of multi-year land-fast sea ice and icebergs) close to the ice shelves/glacier tongues. That area was generally not accessible for water sampling, and it is difficult to monitor the surface of the ocean around Antarctica via satellites due to the presence of sea ice.

In this study, we examined the factors affecting the CO₂ system in the ice-covered waters of LHB using the biogeochemical characteristics of the seawater. We estimated the fraction of SGT basal meltwater in our samples using the oxygen isotopic ratio ($\delta^{18}\text{O}$) of the water. We calculated the potential decrease of the partial pressure of CO₂ due to basal melting to estimate the dilution effect of the basal meltwater on the transition of LHB from CO₂ source to potential sink of atmospheric CO₂. In addition, we evaluated the effect of primary production on the CO₂ system in LHB using the relationships between DIC and TA for surface water.

2. Materials and Methods

2.1. Sampling

The oceanographic observations were made off the SGT in the ice-covered region of LHB from the Japan Maritime Self-Defense Force icebreaker Shirase during the summer of 2017 (22 January to 15 February) and 2018 (24 January to 15 February) as a part of the 58th and 59th Japanese Antarctic Research Expedition, respectively (Figures 1a–1c). Coordinates of the sampling stations are available in Table S1 of the supporting information.

Vertical profiles of temperature, salinity, and dissolved oxygen (DO) concentrations were measured with a conductivity-temperature-depth (CTD) probe (SBE19, Sea-Bird Electronics) and a DO sensor (SBE43, Sea-Bird Electronics) that was calibrated by the manufacturer before and after the cruise. In addition, seawater samples were taken to calibrate the conductivity sensor. Seawater samples were collected to obtain a vertical profile at subsurface pressures of 20, 50, 100, 200, 300, and 500 dbar and at the bottom pressure minus 27–98 dbar. The samples were collected in rosette-mounted, 4-L Niskin bottles with a water sampling system (SBE55 ECO, Sea-Bird Electronics). In addition, surface seawater was pumped from an inlet at the

Figure 1. (a) CTD stations (red symbols: 2017; blue symbols: 2018) in Lützow-Holm Bay, East Antarctica. The oceanographic observations were made off the Shirase Glacier Tongue (SGT) with the Japan Maritime Self-Defense Force icebreaker *Shirase* during the summer of 2017 (22 January to 15 February) and 2018 (24 January to 15 February) during the 58th and 59th Japanese Antarctic Research Expedition, respectively. The area between SGT and SGT Ice front was occupied by the ice bergs from the SGT. North of SGT Ice front was occupied mainly by the multi-year land-fast sea ice and the small amount of the ice bergs. The stations marked by circle and square indicate longitudinal and latitudinal lines, respectively. Line E was the stations along deep trough in Lützow-Holm Bay. (b and c) MODIS-Terra satellite images from 10 February 2017 and 19 January 2018, respectively.

bottom of the ship (a subsurface pressure of ~ 9 dbar). Sea surface temperature (SST) was measured using a temperature probe (SBE 38, Sea-Bird Electronics) at an inlet on the bottom of the ship. Sea surface salinity (SSS) was measured at the same inlet with a salinity probe (SBE45, Sea-Bird Electronics).

Seawater was subsampled into (1) a 200-mL amber glass vial (Maruemu Co., Ltd.) for measurement of DIC and total alkalinity (TA), (2) a 15-mL glass screw-cap vial (Nichiden-Rika Glass Co. Ltd.) for measurement of $\delta^{18}\text{O}$, (3) a 10-mL polyethylene screw-cap vial (Eiken Chemical Co. Ltd.) for measurement of inorganic nutrient concentrations (NO_3^- , PO_4^{3-} , and $\text{Si}(\text{OH})_4$), and (4) a 500-mL Nalgene polycarbonate bottle (Thermo Fisher Scientific Inc.) for measurement of the chlorophyll a (chl.a) concentration. Teflon tube was used to transfer DIC and TA sample from the Niskin bottle to a 200 mL bottle. In order to avoid the bubble formation during transfer, seawater was filled smoothly from the bottom of the bottle using a Teflon tube and overflowed by a 200 mL.

Immediately after subsampling for DIC and TA, a 6.0% (wt.) mercuric chloride (HgCl_2) solution (200 μL) was added to the samples for DIC and TA in a 200-mL amber glass vial to stop biological activity. Samples for DIC, TA, and $\delta^{18}\text{O}$ were stored in a refrigerator ($+4^\circ\text{C}$). Samples for nutrient analyses were stored in a freezer (-30°C). Samples for chl.a measurements were immediately filtered through 25-mm-diameter Whatman GF/F filters. Chlorophyll pigments on the filters were then extracted with dimethylformamide (Suzuki & Ishimaru, 1990) for 24 h and stored at -80°C .

2.2. Sample Analysis

The DIC of seawater was determined by coulometry (Johnson et al., 1985, 1992) using a hand-made CO₂ extraction system (Ono et al., 1998) and a coulometer (CM5012, UIC Inc.). The TA of seawater was determined by titration (Dickson et al., 2007) using a TA analyzer (ATT-05, Kimoto electric Co, Ltd.). Both DIC and TA measurements were calibrated with reference seawater materials (Batch AK and AQ; KANSO Technos Co., Ltd.) traceable to the Certified Reference Material distributed by Prof. A. G. Dickson (Scripps Institution of Oceanography). The standard deviations of the DIC and TA measurements, calculated from 10 subsamples taken from reference water with a DIC value of 2037.0 $\mu\text{mol kg}^{-1}$ and a TA value of 2296.7 $\mu\text{mol kg}^{-1}$, were less than 2.0 $\mu\text{mol kg}^{-1}$ and 2.0 $\mu\text{mol kg}^{-1}$, respectively. Surface-water pCO₂ was computed from DIC and TA using the program CO2SYS, version 02.05 (Orr et al., 2018). We used the carbonic acid dissociation constants (K_1 and K_2) of Mehrbach et al. (1973) as revised by Dickson and Millero (1987) and the K_{HSO_4} determined by Dickson (1990).

The $\delta^{18}\text{O}$ of seawater was determined with a mass spectrometer (DELTA plus; Finnigan MAT) via the equilibration method. The $\delta^{18}\text{O}$ in per mil (‰) was calculated using the $^{18}\text{O}:^{16}\text{O}$ ratio of standard mean ocean water as the standard. The standard deviation of the $\delta^{18}\text{O}$, calculated from 10 subsamples taken from the reference water with a $\delta^{18}\text{O}$ value of 0.241‰, was 0.026‰.

The concentrations of NO_3^- , PO_4^{3-} , and $\text{Si}(\text{OH})_4$ in the seawater were determined in accord with the Joint Global Ocean Flux Study (JGOFS) spectrophotometric method (JGOFS, 1994) using auto-analyzer systems: a QuAAtro 2-HR system (BL-tec) and a Seal Analytical system. The analyzers were calibrated with reference materials for nutrient analysis (Lots AW and BG; KANSO Technos Co., Ltd.). The standard deviations of the nutrient concentrations, calculated from 20 subsamples taken from reference water samples (KANSO Technos Co., Ltd.) with NO_3^- , PO_4^{3-} , and $\text{Si}(\text{OH})_4$ concentrations of 9.8, 2.1, and 117.5 $\mu\text{mol L}^{-1}$, were 0.3, 0.1, and 1.1 $\mu\text{mol L}^{-1}$, respectively.

The concentrations of chl.a were determined with a fluorometer (Model 10AU, Turner Designs, Inc.) in accord with the method described by Parsons et al. (1984). Standards (0.28–282.30 $\mu\text{g L}^{-1}$ chl.a) prepared from a liquid chl.a standard (Wako Pure Chemical Industries Ltd.) by stepwise dilution with N,N-dimethylformamide were used to calibrate the fluorometer before chl.a measurements.

3. Results

3.1. Vertical Profiles

3.1.1. Hydrographic Properties

Figure 2 shows vertical sections and Figure 3 shows profiles of temperature, salinity, and DO concentrations. Low temperature, low salinity, and high DO concentrations characterized Winter Water (WW: $T < -1.5^\circ\text{C}$) (Ohshima et al., 1996) from the sea surface to the subsurface (350–400 dbar) (Figure 2). Below the subsurface, we found mCDW that was characterized by higher temperature, higher salinity, and lower DO concentrations ($T = +0.5^\circ\text{C}$, $S = 34.6$, and $\text{DO} = 4.8 \text{ ml L}^{-1}$, St. G2–2017, 500 dbar) than WW ($T = -1.7^\circ\text{C}$, $S = 33.9$, and $\text{DO} = 7.0 \text{ ml L}^{-1}$, St. G2–2017, 100 dbar). The temperature and salinity above the subsurface (e.g., <400 dbar) were higher and the DO was lower near the SGT ice front station (St. A3) than at other stations (Figure 3).

3.1.2. CO₂ System and Biogeochemical Properties

Vertical profiles (>20 dbar) of DIC and TA revealed a pattern characteristic of summer: DIC and TA were low in the surface layer and increased toward the deep layer (Figures 2d, 2e, 4a, and 4b). The DIC concentrations in the surface layer (20 dbar) were lowest off LHB (St. G2) (2151 $\mu\text{mol kg}^{-1}$) and highest near the SGT ice front (St. A3) (2196 $\mu\text{mol kg}^{-1}$) (Figure 4a). The DIC concentration in the subsurface layer (300 dbar) was highest at St. A3 (2217 $\mu\text{mol kg}^{-1}$). The DIC concentration in the mCDW below the subsurface was high at St. G2 (2243 $\mu\text{mol kg}^{-1}$) and low at St. A3 (2238 $\mu\text{mol kg}^{-1}$) and St. E2 (2224 $\mu\text{mol kg}^{-1}$) (Figure 4a). The TA followed a pattern similar to that of the DIC (Figures 2e and 4b). The TA in the surface layer (20 dbar) was high at St. A3 (2302 $\mu\text{mol kg}^{-1}$) (Figure 4b).

Figure 2. Vertical sections of (a) temperature ($^{\circ}\text{C}$), (b) salinity, (c) DO (ml L^{-1}), (d) DIC ($\mu\text{mol kg}^{-1}$), (e) TA ($\mu\text{mol kg}^{-1}$), (f) NO_3^- ($\mu\text{mol L}^{-1}$), (g) PO_4^{3-} ($\mu\text{mol L}^{-1}$), and (h) Si(OH)_4 ($\mu\text{mol L}^{-1}$) along deep trough in Lützow-Holm Bay (i). The mCDW and MW indicate modified Circumpolar Deep Water and meltwater, respectively. Data for 2017 and 2018 was combined, except for TA and PO_4^{3-} (only 2018).

Based on calculations using DIC and TA and CO2SYS, version 02.05 (Orr et al., 2018), the pCO_2 of $431 \pm 12 \mu\text{atm}$ for the mCDW that flowed into LHB was calculated using DIC and TA (I line, >500 dbar). In addition, the pCO_2 of $421 \pm 12 \mu\text{atm}$ for the bottom near the SGT ice front was calculated using DIC and TA (A line, >600 dbar). Furthermore, the pCO_2 of $373 \pm 22 \mu\text{atm}$ for the ice-pumped mixture of mCDW and basal meltwater near the SGT was calculated using DIC and TA (A line, 20 dbar).

To correct for the effect of dilution on DIC and TA due to the melting of sea ice during the winter-to-summer transition, we normalized the DIC and TA values to a salinity of 34.25 (average salinity at the depth where the DIC and TA samples were collected) with the following equations:

$$\text{nDIC} = \text{DIC}_{\text{obs}} \cdot 34.25 / S_{\text{obs}} \quad (1)$$

$$\text{nTA} = \text{TA}_{\text{obs}} \cdot 34.25 / S_{\text{obs}} \quad (2)$$

Figure 3. Vertical profiles (>20 dbar) of (a) temperature (°C), (b) salinity, and (c) DO (ml L⁻¹) in Lützow-Holm Bay. The vertical profiles of the stations along the deep trough are shown in bright colors. Profiles at other stations are shown in gray.

where nDIC, nTA, and S represent salinity-normalized DIC and TA, and salinity, respectively. The subscript, “obs” refer to the observed sample values.

Figures 4d and 4e show vertical profiles of nDIC and nTA. The nDIC were low in the surface layer and slightly increased toward the deep layer. The nTA were constant from the surface layer to the deep layer ($2317 \pm 2 \mu\text{mol kg}^{-1}$). The chl.a concentration was $<1.0 \mu\text{g L}^{-1}$ at most stations throughout the water column, but at stations near the ice front (Sts. A5 and A7), the chl.a concentrations were high: $3.6\text{--}4.6 \mu\text{g L}^{-1}$ (Figure 4c). Nutrient concentrations (NO_3^- , PO_4^{3-} , and $\text{Si}(\text{OH})_4$) were relatively high from the sea surface to the subsurface at the ice front station (St. A3) compared to other stations. The $\delta^{18}\text{O}$ value increased toward the north and was -0.48‰ at the surface of St. G2 (20 dbar). The $\delta^{18}\text{O}$ value was lowest at the sea surface of St. A3 near the SGT ice front (-0.78‰) (Figure 4f).

3.2. SGT Basal Meltwater Fraction

We used salinity and $\delta^{18}\text{O}$ to calculate the fractions (%) of SGT basal meltwater (F_{mw}) and sea ice meltwater (F_{si}) from the surface to the subsurface (e.g., Meredith et al., 2008) with the following equations:

$$F_{\text{mcdw}} + F_{\text{mw}} + F_{\text{si}} = 1 \quad (3)$$

$$F_{\text{mcdw}} \cdot S_{\text{mcdw}} + F_{\text{mw}} \cdot S_{\text{mw}} + F_{\text{si}} \cdot S_{\text{si}} = S_{\text{obs}} \quad (4)$$

$$F_{\text{mcdw}} \cdot \delta_{\text{mcdw}} + F_{\text{mw}} \cdot \delta_{\text{mw}} + F_{\text{si}} \cdot \delta_{\text{si}} = \delta_{\text{obs}} \quad (5)$$

Figure 4. Vertical profiles (>20 dbar) of (a) DIC ($\mu\text{mol kg}^{-1}$), (b) TA ($\mu\text{mol kg}^{-1}$), (c) chl.a ($\mu\text{g L}^{-1}$), (d) nDIC ($\mu\text{mol kg}^{-1}$), (e) nTA ($\mu\text{mol kg}^{-1}$), (f) $\delta^{18}\text{O}$ (‰), (g) NO_3^- ($\mu\text{mol L}^{-1}$), (h) PO_4^{3-} ($\mu\text{mol L}^{-1}$), and (i) Si(OH)_4 ($\mu\text{mol L}^{-1}$). Colors have the same meaning as in Figure 3.

where F , S , and δ represent fraction, salinity, and $\delta^{18}\text{O}$, respectively. The subscripts, “mcdw,” “mw,” “si,” and “obs” refer to the mCDW, meltwater, sea ice, and observed sample values, respectively. The end-member values of the salinity and $\delta^{18}\text{O}$ for each source used in this study were 34.65 ± 0.03 and $-0.1 \pm 0.05\text{‰}$ for mCDW (observed at St. G2), 0.0 and -30‰ for mw (Silvano et al., 2018), and 2.0 and 2.0‰ for sea ice (Kawamura et al., 1997). It is said that the δ_{mw} is the most uncertain end-member ranging from -40‰ to -20‰ (Silvano et al., 2018). In our study, we chose an intermediate value of -30‰ for δ_{mw} . In order to evaluate the differences to use end-member within this range, we calculated the fraction changing between -40‰ and -20‰ and compared the difference with the fraction at -30‰ of δ_{mw} . The calculated differences for each fraction were less than 1.1%. We also calculated the fraction changing within the standard deviation of the $\delta^{18}\text{O}$ measurement and the end-member of “mcdw.” The calculated differences for each fraction were less than 0.1% for $\delta^{18}\text{O}$ measurement and 0.3% end-member of “mcdw.”

Figures 5a and 5c and Figures 5b and 5d show vertical profiles of F_{mw} and F_{si} , respectively. Near the sea surface (subsurface pressure <20 dbar), F_{mw} was highest at the SGT ice-front station (St. A3) ($2.3 \pm 0.3\%$)

Figure 5. Vertical profiles (>20 dbar) of the fractions of SGT basal meltwater (F_{mw}) and sea ice meltwater (F_{si}) along the deep trough (a, b) and along the line A (c, d).

and lowest off LHB (St. G2) ($1.2 \pm 0.2\%$) (Figure 5a) (Standard deviation was calculated based on the standard deviation of the $\delta^{18}\text{O}$ measurement and the end-member of “mcdw” and the range of the end-member of “mw”). In addition, the F_{mw} values at the stations toward the west (Sts. A2 and A3) ($2.2 \pm 0.3\%$ and $2.3 \pm 0.3\%$, respectively), tended to be higher than at St. A6 near the center of the SGT ice front ($1.7 \pm 0.2\%$) (Figure 5c). In contrast, F_{si} was highest at the northern St. G2 at the sea surface ($1.8 \pm 0.2\%$) and low (near 0%) at the other stations (Figures 5b and 5d).

3.3. Surface Water Distribution

Figure 6 shows the spatial distribution of sea surface temperature (SST), SSS, DIC, TA, pCO_2 , chl.a, and nutrient concentrations (NO_3^- , PO_4^{3-} , and Si(OH)_4) in surface water. The values ranged from -1.85 to -0.44°C for SST, 32.71 to 33.96 for SSS, 1966 to 2204 $\mu\text{mol kg}^{-1}$ for DIC, 2229 to 2301 $\mu\text{mol kg}^{-1}$ for TA, 135 to 430 μatm for pCO_2 , 0.1 to 32.0 $\mu\text{g L}^{-1}$ for chl.a, 7.4 to 33.4 $\mu\text{mol L}^{-1}$ for NO_3^- , 1.1 to 2.2 $\mu\text{mol L}^{-1}$ for PO_4^{3-} , and 50.9 to 80.1 $\mu\text{mol L}^{-1}$ for Si(OH)_4 (Figures 6a–6k).

The DIC concentrations, TA, salinity, pCO_2 , and nutrient concentrations were relatively high in the southern part of LHB near the SGT ice front compared to other areas of LHB (Figure 6). In contrast, the salinity, DIC, TA, pCO_2 , and nutrient concentrations in the northern part of LHB were relatively low compared to the southern area. In the open-water area on the east of LHB (Figures 1b and 1c), the SST (-0.44°C) and chl.a concentrations ($32.0 \mu\text{g L}^{-1}$) were high, and the salinity (32.71), DIC concentrations ($1966 \mu\text{mol kg}^{-1}$), pCO_2 (135 μatm), and nutrient concentrations ($7.4 \mu\text{mol L}^{-1}$ for NO_3^- , $1.1 \mu\text{mol L}^{-1}$ for PO_4^{3-} , and $50.9 \mu\text{mol L}^{-1}$ for Si(OH)_4) were relatively low.

Figure 6. Spatial distribution of (a) SST (°C), (b) SSS, (c, d) DIC, nDIC ($\mu\text{mol kg}^{-1}$), (e, f) TA, nTA ($\mu\text{mol kg}^{-1}$), (g) pCO_2 (μatm), (h) chl.a ($\mu\text{g L}^{-1}$), and (i–k) nutrient concentrations (NO_3^- , PO_4^{3-} , and Si(OH)_4) ($\mu\text{mol L}^{-1}$) in surface water (9 dbar). Data for 2017 and 2018 was combined.

4. Discussion

4.1. The Effect of the Basal Melting of SGT on the CO_2 System in LHB

The effect of dilution caused by melting of ice shelves and sea ice is known to be one of the important physical processes that affects the CO_2 system in the sea surface of the Antarctic continental margin in the summer (e.g., Arroyo et al., 2019; Legge et al., 2017; Shadwick et al., 2017). We used the fraction of SGT basal meltwater calculated via the $\delta^{18}\text{O}$ and salinity and the relationship between DIC and salinity to quantify the effect of basal melting of the SGT on the CO_2 system parameters in LHB with following equations:

$$\Delta S_{\text{mix}} = -S_{\text{mcdw}} \cdot F_{\text{mw}} \quad (6)$$

$$\Delta \text{DIC}_{\text{mix}} = \text{DIC}_{\text{mcdw}} \cdot \Delta S_{\text{mix}} / S_{\text{mcdw}} = -\text{DIC}_{\text{mcdw}} \cdot F_{\text{mw}} \quad (7)$$

Figure 7. Relationships between (a) DIC and salinity and (b) TA and salinity. Red and blue symbols indicate water samples obtained from pressures >20 dbar and from the surface (9 dbar), respectively.

where ΔS_{mix} and $\Delta \text{DIC}_{\text{mix}}$ represent the change of salinity and DIC, respectively, when SGT basal meltwater and mCDW are mixed. S_{mcdw} and DIC_{mcdw} are salinity and DIC end member values of the mCDW (34.60), respectively. F_{mw} is fraction of meltwater (%).

Figure 7a shows the relationship between DIC and salinity. At subsurface pressures >20 dbar, DIC was well correlated with salinity ($r^2 = 0.84$ and $p < 0.0001$) (red symbols). The slope of the DIC-salinity relationship was 76.9 (standard error of the slope was 1.8 and intercept of the slope was -430.2). Significant biological activity would cause the DIC concentration to deviate from the DIC-salinity line. Such deviations are apparent in the surface water (e.g., blue symbols in Figure 7a for samples collected at 9 dbar). The processes that took place in the surface water are discussed in detail in Section 4.2. Furthermore, the chl.a concentration was as low as $1.0 \mu\text{g L}^{-1}$, except for the surface water (Figure 4c). These results suggest that at subsurface pressures >20 dbar, CO_2 system parameters such as DIC were explained by dilution effects, that is, by the supply of meltwater from the ice shelf/sea ice. The CO_2 system was therefore controlled much more by physical processes than biological processes in most of the water column (>20 dbar). The constant profiles of nDIC (Figure 4d) are also consistent with the dominance of the dilution effect at depths corresponding to subsurface pressures >20 dbar. These conclusions also apply to TA (Figures 4e and 7b). At subsurface pressures >20 dbar, TA was closely correlated with salinity ($r^2 = 0.97$ and $p < 0.0001$) (red symbols in Figure 7b). The slope of the TA-salinity relationship was 65.2 (standard error of the slope was 0.9 and intercept of the slope was 86.1).

The percentage of basal meltwater (F_{mw}) at St. A3 near the SGT ice front was relatively high from the surface ($2.3 \pm 0.3\%$ at 20 dbar) to the subsurface ($0.9 \pm 0.1\%$ at 300 dbar) (Figure 5a). By applying Equations 6 and 7 at St. A3, we calculated $\Delta \text{DIC}_{\text{mix}}$ to be $-51 \pm 7 \mu\text{mol kg}^{-1}$ at 20 dbar and $-21 \pm 3 \mu\text{mol kg}^{-1}$ at 300 dbar (Table 1). In addition, by applying Equations 6 and 7 to TA, we calculated $\Delta \text{TA}_{\text{mix}}$ to be $-54 \pm 7 \mu\text{mol kg}^{-1}$ (20 dbar) and $-22 \pm 3 \mu\text{mol kg}^{-1}$ (300 dbar) at St. A3. Then, by using $\Delta \text{DIC}_{\text{mix}}$ and $\Delta \text{TA}_{\text{mix}}$, we calculated the change of pCO_2 ($\Delta \text{pCO}_{2\text{mix}}$) by using CO2SYS, version 02.05 (Orr et al., 2018). The value of $\Delta \text{pCO}_{2\text{mix}}$ was $-42 \pm 2 \mu\text{atm}$ at 20 dbar and $-21 \pm 1 \mu\text{atm}$ at 300 dbar (Table 1). These results indicate that the supply of freshwater accounted for $2.3 \pm 0.3\%$ and $2.3 \pm 0.3\%$ of the variation of DIC and TA with respect to the initial DIC and TA, respectively and $9.6 \pm 0.4\%$ in the case of pCO_2 (Table 1). The effect of the supply of freshwater from basal melting on the CO_2 system was therefore significant, especially for pCO_2 in seawater.

In LHB, mCDW flows southward and eventually beneath the SGT along a deep layer or trough. A mixture of mCDW and basal meltwater was pumped up by the buoyancy and upwelled above the subsurface layer (Hirano et al., 2020). The distribution of the CO_2 components and

Table 1
 ΔS_{mix} , $\Delta \text{DIC}_{\text{mix}}$, $\Delta \text{TA}_{\text{mix}}$, and $\Delta \text{pCO}_{2\text{mix}}$ for St. A3 at 20 and 300 dbar

	St. A3 at 20 dbar	St. A3 at 300 dbar
ΔS_{mix}	-0.8 ± 0.1	-0.3 ± 0.1
$\Delta \text{DIC}_{\text{mix}} (\mu\text{mol kg}^{-1})$	-51 ± 7	-21 ± 3
$\Delta \text{TA}_{\text{mix}} (\mu\text{mol kg}^{-1})$	-54 ± 7	-22 ± 3
$\Delta \text{pCO}_{2\text{mix}} (\mu\text{atm})$	-42 ± 2	-21 ± 1
Variation S_{mix} (%)	-2.3 ± 0.3	-0.9 ± 0.1
Variation DIC_{mix} (%)	-2.3 ± 0.3	-0.9 ± 0.1
Variation TA_{mix} (%)	-2.3 ± 0.3	-0.9 ± 0.1
Variation $\text{pCO}_{2\text{mix}}$ (%)	-9.6 ± 0.4	-4.8 ± 0.2

Note. The variations are percent changes relative to initial values (%).

Figure 8. Percent decrease of DIC due to influx of basal meltwater from the SGT (ΔC as %) and the average of the SGT basal meltwater fraction ($F_{mw,ave}$) along the (a) deep trough and (b) along the line A.

nutrients in our study were consistent with this circulation pattern. The mCDW is characterized by high concentrations of DIC, TA, and nutrients (Bakker et al., 2008; Hoppema et al., 1997; Whitworth & Nowlin, 1987). At the subsurface (e.g., 300 dbar), DIC, TA, and nutrient concentrations were higher at St. A3 near the ice front than at other stations (Figures 2d–2h, 4a and 4b, and 4g–4i). Furthermore, at St. A3 near the ice front, DIC, TA, and nutrient concentrations were higher at subsurface than at surface.

We calculated the DIC column inventory (20–200 dbar) (mmol m^{-2}) and then examined the decrease of the amount of carbon before and after the influx of meltwater from the SGT (ΔC as %) by using the profiles of DIC and F_{mw} (Figures 8a and 8b). The ΔC was highest ($-1.8 \pm 0.2\%$) near the SGT (St. A3) and decreased to $-1.1 \pm 0.2\%$ at the northern St. G2 (Figure 8a). This variation was followed by F_{mw} (blue symbols in Figure 8a). This result suggests that the supply of meltwater contributed to the carbon standing stock, especially near the SGT. In addition, the ΔC tended to be negatively larger toward the west than toward the east (Figure 8b). This result means that the DIC decreased more toward the west than toward the east due to the supply of basal meltwater from the SGT (Figure 5c). The meltwater volume has been estimated to be larger on the west side of the SGT (Hirano et al., 2020), and the east–west difference of ΔC was consistent with this estimation.

Figure 9 is a schematic illustration of these processes and indicates the spatial variation of $p\text{CO}_2$ during the transport from bottom to subsurface within LHB based on calculations using DIC and TA and CO2SYS, version 02.05 (Orr et al., 2018) (see Section 3.1.2). The decrease in $p\text{CO}_2$ from $431 \pm 12 \mu\text{atm}$ (I line, >500 dbar) to $373 \pm 22 \mu\text{atm}$ (A line, 20 dbar) was due to the dilution effect of the SGT basal meltwater, mixing of water masses, and phytoplankton primary production. The foregoing calculation of $\Delta p\text{CO}_{2,mix}$ indicated a decrease of $42 \pm 2 \mu\text{atm}$ due to the supply of basal meltwater (dilution effect). Therefore, 69%–76% of the total decrease of the $p\text{CO}_2$ ($58 \mu\text{atm} = 431 - 373 \mu\text{atm}$) was accounted for by the dilution effect of the SGT basal meltwater. The remaining 24%–31% was presumably accounted for by mixing of water masses (e.g., WW, $p\text{CO}_2 = 373 \pm 22 \mu\text{atm}$) and phytoplankton primary production. The basal melting of the SGT was therefore significant with respect to the decrease of $p\text{CO}_2$ (i.e., impact on CO_2 system) in the LHB water column. An

important implication is that SGT basal melting contributed to the decrease of $p\text{CO}_2$ from super-saturation in the mCDW to under-saturation in surface water with respect to the atmosphere ($390.6 \pm 0.2 \mu\text{atm}$) at Syowa Station, Antarctica during January–February 2017 (Data from National Oceanic and Atmospheric Administration; <https://www.esrl.noaa.gov/gmd/dv/iadv/>). The $p\text{CO}_2$ was calculated from the mole fraction of atmospheric CO_2 after taking into account the saturated water vapor pressure and atmospheric pressure (Figure 9). These results indicate that basal melting of the SGT had a significant effect on CO_2 system in LHB and the potential to decrease the $p\text{CO}_2$ of the seawater. In the particular case of LHB, the decrease of $p\text{CO}_2$ due to basal melting contributed to the shift of the water from a source to a sink of atmospheric CO_2 .

The sea–air CO_2 flux was calculated with following equation:

$$F_{\text{sea-air}} = k\alpha\Delta p\text{CO}_2 \quad (8)$$

where k is the gas transfer velocity (Wanninkhof et al., 2013), α is the CO_2 solubility (Weiss, 1974), and $\Delta p\text{CO}_2$ is the difference in $p\text{CO}_2$ between the sea surface and the atmosphere. A negative flux indicates absorption of atmospheric CO_2 by the ocean. The gas transfer velocity was computed using measured wind speeds. We used the mean wind speed of 14.1 m s^{-1} during our study period at Syowa station (Japan

Figure 9. Schematic illustration of the variation of $p\text{CO}_2$ in Lützow-Holm Bay.

Meteorological Agency; <http://www.data.jma.go.jp/obd/stats/etrn/index.php>) and atmospheric $p\text{CO}_2$ of 390 μatm . In this paper, first, we have estimated the sea–air CO_2 flux by assuming the open water (potential sea–air CO_2 flux). The CO_2 flux was then estimated by assuming that the area percentage of unresolved small leads and cracks were 1%–2% within the sea ice (Steiner et al., 2013).

The estimation of the potential sea–air CO_2 flux by assuming the open water and surface water $p\text{CO}_2$ of 373 μatm (Figure 9), was $-7.8 \text{ mmol m}^{-2} \text{ d}^{-1}$. If there was no dilution by ice meltwater during the transport of mCDW, the surface water $p\text{CO}_2$ was 431 μatm ($p\text{CO}_2$ of mCDW), and potential sea–air CO_2 flux was $+18.7 \text{ mmol m}^{-2} \text{ d}^{-1}$. These estimations indicated that the direction of the potential flux between atmosphere and ocean was changed from positive ($+18.7 \text{ mmol m}^{-2} \text{ d}^{-1}$) to negative ($-7.8 \text{ mmol m}^{-2} \text{ d}^{-1}$) due to mainly by the basal melting, which diluted the surface water and decreased the surface water $p\text{CO}_2$.

It has been argued that leads and cracks within sea ice are hot spots for gas exchange between the air and surface water (Else et al., 2013; Loose et al., 2009, 2016; Steiner et al., 2013; Zemmelen et al., 2008). In LHB, land-fast ice is sometimes broken up (Aoki, 2017; Ushio, 2006), crack formation frequently occurs (Nomura, Aoki, et al., 2018). Because it is difficult to estimate the area of the small leads and cracks from the satellite when small leads and cracks is $<20 \text{ m}$ width scale, the sea–air CO_2 flux at the small leads and cracks was estimated on the assumption that the

area percentage of unresolved small leads and cracks were 1%–2% within the sea ice (Steiner et al., 2013). The estimation of the sea–air CO_2 flux at the small leads and cracks (by assuming surface water $p\text{CO}_2$ of 373 μatm) was -0.2 to $-0.1 \text{ mmol m}^{-2} \text{ d}^{-1}$, indicating that the magnitude of the negative CO_2 flux decreased from $-7.8 \text{ mmol m}^{-2} \text{ d}^{-1}$ (assuming the open water) because we have simply multiplied the area percentage of 1%–2% for small leads and cracks to estimate. However, it is said that an open crack acts as an active site for gas exchange between the ocean and atmosphere (Loose et al., 2009, 2016): Observations indicated that gas exchange in cracks and small leads could be much higher than that in open water condition. Loose et al. (2009) examined the tank experiment by simulating a partial ice cover, and they showed the enhancement of the gas exchange rate relative to no ice cover. Therefore, the gas transfer may not scale linearly with the fraction of open water and gas exchange in cracks and small leads could be much higher than that in open water condition because the circulation processes such as current and convection under the ice enhance the gas exchange rate (Loose et al., 2016). Although our estimation of the sea–air CO_2 flux at the small leads and cracks (-0.2 to $-0.1 \text{ mmol m}^{-2} \text{ d}^{-1}$) was low as compared to that in open water ($-7.8 \text{ mmol m}^{-2} \text{ d}^{-1}$), the magnitude of the CO_2 flux at the small leads and cracks could be much higher than that in the open water due to the enhancement of the gas exchange rate by the circulation processes under the ice.

There have even been discussions about CO_2 exchange processes in areas covered by sea ice. Although it has been assumed that sea ice is impermeable to CO_2 exchange, recent studies have proposed that CO_2 exchange may occur through sea ice (e.g., Delille et al., 2014; Nomura, Granskog, et al., 2018). During the early period of ice growth, the brine in sea ice becomes super-saturated with respect to atmospheric CO_2 as the temperature decreases and salinity increases (e.g., Papadimitriou et al., 2003). Brine channels can thus emit CO_2 to the overlying air and, if the ice permeability is sufficiently high (up to $+12 \text{ mmol m}^{-2} \text{ d}^{-1}$) (Geilfus et al., 2012; Nomura et al., 2006; Nomura, Granskog, et al., 2018). Furthermore, during the period of ice melt, sea ice brine may take up atmospheric CO_2 because the brine becomes under-saturated with respect to the atmosphere due to algal productivity and dilution by meltwater (up to $-5.2 \text{ mmol m}^{-2} \text{ d}^{-1}$) (Delille et al., 2014; Nomura et al., 2013; Nomura, Granskog, et al., 2018). During the season of ice melting, the brine volume fraction at the bottom of the sea ice increases. Water exchange processes between the sea ice and under-ice water are therefore important (e.g., Nomura et al., 2009). The undersaturated water beneath the sea ice observed in this study may therefore affect brine $p\text{CO}_2$ and thereby the process of gas exchange with atmosphere.

Figure 10. Relationships between nDIC and nTA for surface water (9 dbar) samples (blue circles) and winter water (20–400 dbar) samples (gray circles). Red square indicates the average of the nDIC and nTA for winter water (20–400 dbar) samples. Solid lines indicate photosynthesis/respiration (green line, slope = -0.15), the precipitation/dissolution of calcium carbonate (gray line, slope = 2.0) and CO_2 exchange (black line, slope = 0).

4.2. The Effect of Primary Production on the CO_2 System in LHB

The CO_2 system parameters are changed by various processes, including photosynthesis and respiration, gas exchange (CO_2 release and uptake), and carbonate mineral dissolution and formation (Anderson & Sarmiento, 1994; Zeebe & Wolf-Gladrow, 2001). Here, we discuss the processes that occurred in the ice-covered area (including open water area shown in Figure 1) of LHB by using the relationship between nDIC and nTA in seawater.

Figure 10 shows the relationship between nDIC and nTA in LHB. For the subsurface winter water (WW: $T < -1.5^\circ\text{C}$) (Ohshima et al., 1996) at 20–400 dbar (gray circles), nDIC were relatively constant ($2204 \pm 7 \mu\text{mol kg}^{-1}$) than those in surface water (9 dbar) ($2141 \pm 37 \mu\text{mol kg}^{-1}$). In addition, nTA were constant ($2318 \pm 2 \mu\text{mol kg}^{-1}$ for nTA). These results suggest that processes such as respiration, gas exchange, and carbonate mineral dissolution and precipitation were not significant during the transition from winter to summer. These results are consistent with the relationship between DIC and salinity (Figure 7a) and TA and salinity (Figure 7b). The good correlations between DIC and salinity ($r^2 = 0.84$ and $p < 0.0001$ for DIC) and TA and salinity ($r^2 = 0.97$ and $p < 0.0001$ for TA) are consistent with the conclusion that dilution effects were significant and that other process such as photosynthesis, respiration, gas exchange, and carbonate mineral dissolution and precipitation had only minor effects on CO_2 system.

However, in the case of the surface water (9 dbar) (blue circles in Figure 10), the data deviated from the WW (20–400 dbar) nDIC and nTA data (red square). Furthermore, the relationship between nDIC and nTA for surface water (9 dbar) (slope = -0.13 , standard error = 0.03) was similar to the lines for biological processes (slope = $-16/106 = -0.15$) and gas exchange (slope = 0) (Figure 10). In addition, there was only a poor correlation between DIC and salinity ($r^2 = 0.13$ and $p = 0.004$) but a relatively high correlation for TA ($r^2 = 0.92$ and $p < 0.0001$). Other process such as photosynthesis, respiration, and gas exchange may therefore relate in the case of surface water. Here, we have examined the effect of gas exchange processes on the relationships between nDIC and nTA. If gas exchange occurs, nDIC changes, but nTA remains constant (slope = 0) (Zeebe & Wolf-Gladrow, 2001). The nDIC increases when atmospheric CO_2 enters the ocean, whereas nDIC decreases when the ocean releases CO_2 to the atmosphere. In this study, the pCO_2 of WW at the surface of the ocean was $378 \pm 20 \mu\text{atm}$, a value that is below the winter atmospheric pCO_2 of $391.4 \pm 0.5 \mu\text{atm}$ at Syowa Station, Antarctica during June–August 2017 (Data from National Oceanic and Atmospheric Administration [<https://www.esrl.noaa.gov/gmd/dv/iadv/>], and pCO_2 calculated as described in Section 4.1). This pCO_2 of $378 \pm 20 \mu\text{atm}$ is reasonable for the WW when compared to the pCO_2 obtained near LHB in winter ($349.9 \pm 6.4 \mu\text{atm}$) (Nomura et al., 2014) (both data represent lower pCO_2 in seawater than that in the air).

The relationship between the pCO_2 of seawater (sw) and the air in winter (pCO_2 of sw $<$ pCO_2 of air) suggests that surface water has the potential to take up CO_2 from the atmosphere, and nDIC should therefore increase from winter to summer (our observation period) if gas exchange occurs. However, plots of the nTA versus nDIC of surface water (9-dbar depth) deviated in the direction of CO_2 release for WW (Figure 10), which is the opposite direction for CO_2 uptake. Furthermore, the sea ice that covered LHB throughout the year would have prevented gas exchange between the ocean and atmosphere, but with the caveat that gas exchange may occur through sea ice and small leads and cracks (see Section 4.1) (Nomura, Granskog, et al., 2018). The estimation of the DIC increase by the uptake of CO_2 through the small leads and cracks ($-0.2 \text{ mmol m}^{-2} \text{ d}^{-1}$) was small ($< 1.2 \mu\text{mol kg}^{-1}$), which is based on the assumption that mix layer depth is 20 dbar and the period is 120 days (from winter to our study period). Our results therefore suggest that the effect of gas exchange processes on CO_2 system was minor.

The contribution of the precipitation/dissolution of calcium carbonate (ikaite) was apparently small in this study because no nTA versus nDIC data were consistent with the slope for precipitation/dissolution of calcium carbonate (slope = 2.0), except for the a few data points (Figure 10) (Dieckmann et al., 2008; Nomura et al., 2013; Rysgaard et al., 2012, 2013). If the precipitation of ikaite occurs with the formation of sea ice from autumn to winter, the nDIC and nTA in the brine should decrease relative to WW along a line with a slope of 2.0. Dissolution of ikaite during the ice-melting season, however, should cause the nDIC and nTA to increase in brine and in the water under the ice. Most of our data (Figure 10) deviated from the relationship expected for biological processes (slope = −0.15), there were a few data points that fell along the line describing this relationship and a few data points were similar to the slope line for precipitation/dissolution of calcium carbonate (slope = 2.0) (shown by gray dotted arrow). These results suggest that some of the under-ice water was affected by ikaite dissolution caused by the supply of meltwater from sea ice. The fact that a few data points were obtained mainly from open-water area samples (Figures 1b and 1c), and data indicated relatively low salinity (33.7) and high nTA ($2338 \mu\text{mol kg}^{-1}$) as compared to that in the ice-covered area (Figures 6b and 6f), supporting the sea ice melt and the dissolution of calcium carbonate. The ocean surface of LHB is basically covered with thick land-fast sea ice throughout the year (Aoki, 2017; Ushio, 2006). In the austral autumn of 2016, however, large areas of land-fast ice broke up (Aoki, 2017), and the ocean surface was covered by relatively new and thin (1–2 m) land-fast ice. Ikaite formation is known to occur more efficiently within new ice (Rysgaard et al., 2013). The relatively young age of the sea ice should have facilitated ikaite formation in the new ice during the winter of 2016, and we indeed detected some evidence of ikaite dissolution during the summers of 2018 (Figure 10).

Overall, our results suggest that biological modification of the nDIC and nTA of the surface water in LHB was a possible explanation for the fact that variations of nDIC and nTA occurred along a line with a slope of −0.15 is consistent with biological processes. We concluded that gas exchange and ikaite formation/dissolution did not have a significant effect on CO_2 system. The implication is that the DIC concentration and TA at the surface changed because of phytoplankton photosynthesis between the previous winter and the summer. In particular, the magnitude of the changes of DIC and TA were larger in the open water area of LHB than in areas covered with sea ice (Figures 1 and 9). In addition, the very high sea surface chl.a concentration (up to $31 \mu\text{g L}^{-1}$) (Figure 6h) suggests that phytoplankton were actively fixing carbon in the surface waters of LHB.

5. Conclusion

Oceanographic observations made during the summers of 2017 and 2018 off the SGT in LHB, an ice-covered bay in East Antarctica, revealed that the CO_2 system at subsurface pressures >20 dbar was strongly influenced by the dilution effect of SGT basal melting and the inflow of mCDW. Dilution by SGT basal meltwater reduced the partial pressure of CO_2 in the mCDW from 431 to 387 μatm . The water then became a sink rather than source of atmospheric CO_2 . In contrast, within the surface layer of LHB, the CO_2 system was strongly influenced by biogeochemical processes.

Data Availability Statement

All data used in this study are available in Table S1 of the supporting information and data archive system (<https://ads.nipr.ac.jp/dataset/A20200727-002>, and <https://ads.nipr.ac.jp/dataset/A20200727-003>).

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