学位論文

Studies on seawater CO$_2$ chemistry in the tropical to subtropical Pacific using *Porites* coral boron isotopes for the last deglaciation and the industrial era

（ハマサンゴホウ素同位体を用いた熱帯・亜熱帯太平洋における
産業革命以降・最終退氷期の海水炭酸系に関する研究）

平成 26 年 12 月 16 日 博士（理学）申請
東京大学大学院 理学系研究科
地球惑星科学専攻

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Studies on seawater CO_2 chemistry in the tropical to subtropical Pacific using *Porites* coral boron isotopes for the last deglaciation and the industrial era

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"Carbon is forever"

Mason Inman, *Nature Reports Climate Change* (2008)

Abstract

Boron isotope ratios ($\delta^{11}B$) of biogenic carbonates depend on seawater pH (pH_{SW}). To date, many stony corals have been reared in pH_{SW}-regulated aquariums, and $\delta^{11}B$ of skeletons that grew during the experiment have been measured. While the results clearly revealed pH_{SW}-dependency of $\delta^{11}B$ of coral skeletons, they revealed a large difference between measured $\delta^{11}B$ values and theoretically expected ones, too. In order to reconcile the difference, two approaches have been proposed. One approach regards $\delta^{11}B$ as a recorder of pH of calcification fluid (pH_{CF}), rather than pH_{SW}, because a line of evidence uncovers pH_{CF} is higher than pH_{SW} (biological pH up-regulation). The other approach presumes the difference as $\delta^{11}B$ offsets (empirical corrections). Whichever approaches are employed, however, culturing experiment-based $\delta^{11}B$-pH_{SW} calibrations appear to reconstruct pH_{SW} that conflicts with the CO_2 chemistry observation. Therefore, another means to calibrate $\delta^{11}B$-pH_{SW} is required. To meet the needs, massive *Porites* corals living in the natural environment have large potentials, because they are long-lived and have experienced anthropogenic pH_{SW} decreases since the Industrial Revolution (ocean acidification).

The research objectives of this thesis are (1) to obtain the field-based $\delta^{11}B$-pH_{SW} calibrations and (2) to utilize them in paleoenvironmental studies. It is noteworthy that deep understandings of the $\delta^{11}B$-pH_{SW} relationship will lead to not only a development of tools for carbon cycle studies but also understandings of the corals' response to ocean acidification. Firstly, the $\delta^{11}B$-pH_{SW} calibrations using massive *Porites* corals collected from Chichijima (Ogasawara Islands, Japan) and Tahiti (Society Islands, French Polynesia) were shown (Chapter 2). Secondly, based on pH up-regulation mechanisms, effects of the ocean acidification for the last 100 years on the Chichijima coral calcification were discussed (Chapter 3). Thirdly, a paleoceanographic study using fossil *Porites* corals obtained from Tahiti under the program of Integrated Ocean Drilling Program (IODP) Expedition 310 was shown (Chapter 4). Lastly, the key findings of this thesis were discussed, and future avenues for this research were suggested (Chapter 5).

Boron isotopes - pH calibration using long-lived modern corals (Chapter 2): We measured a 100 year record of $\delta^{11}B$ of *Porites* coral obtained from Chichijima. Previously reported $\delta^{11}B$ values of Tahitian corals were also used after corrections of

different procedure-specific isotopic offsets. Comparing coral $\delta^{11}B$ records with pH_{SW} that was estimated from many CO_2 chemistry data and atmospheric CO_2 records, we established, for the first time, field-based calibrations for Chichijima and Tahiti. Using the established calibration, we reevaluated the previously reported pH_{SW} reconstructions from $\delta^{11}B$ of *Porites* corals obtained from Guam and Hainan islands. The results showed that empirically reconstructed pH_{SW}, as well as partial pressure of CO_2 in the seawater ($pCO_{2\ SW}$), were more in line with CO_2 chemistry observations than those calculated using the culture-based calibration, and that the correction values were different depending on locations.

Effects of recent ocean acidification in the western North Pacific on Porites coral calcification (Chapter 3): To better understanding how organisms and ecosystems will adapt to or be damaged by ocean acidification, field observations are crucial. In this chapter, we showed clear evidence, based on $\delta^{11}B$ measurements, that ocean acidification is affecting the pH_{CF} in *Porites* coral collected at Chichijima. A rapid decline of $\delta^{11}B$ of coral skeleton since 1960 (-0.17 ± 0.07‰/decade) was observed and was compared with pH_{SW} near the Ogasawara Islands over the 20th century. The results indicated that pH_{CF} has been changing sensitively to pH_{SW} and suggested that the calcification fluid of coral will become corrosive to aragonite in the future (pH_{CF} = ca. 8.3 when pH_{SW} = ca. 8.0 in 2050) at an earlier point than previously expected, despite the pH_{CF} up-regulation mechanism of coral.

Marine carbon cycle at the equatorial Pacific during the last deglaciation (Chapter 4): While biogeochemical and physical processes in the Southern Ocean are thought to be central to atmospheric CO_2 rise during the last deglaciation (~80 μatm), the roles of the equatorial Pacific, where the largest CO_2 source exists at present, remains largely unconstrained. In this chapter we showed pH_{SW} and $pCO_{2\ SW}$ variations during this period reconstructed from fossil *Porites* corals obtained at Tahiti based on empirical $\delta^{11}B$-pH_{SW} calibration. The new data, together with recalibrated existing data, indicated that a significant $pCO_{2\ SW}$ increase (pH_{SW} decrease), accompanied by anomalously large marine ^{14}C reservoir ages, occurred following not only the Younger Dryas, but also Heinrich Stadial 1. These findings indicated an expanded zone of equatorial upwelling and resultant CO_2 emission, which may be derived from higher subsurface DIC concentration.

Contents

CHAPTER 1

General Introduction

As general introduction of this thesis, first of all, important parameters that control seawater CO_2 chemistry will be introduced. Secondly, boron isotope systematics in the seawater and the current knowledge of biological incorporations of boron isotopes into calcium carbonates that some marine organisms form will be explained. Thirdly, the oceanography of the tropical-subtropical region of the Pacific discussed in the thesis will be reviewed. Lastly, the carbon cycle since the last glacial period with several key paleoclimatological records will be summarized.

1-1. CO₂ chemistry in seawater

Surface seawater actively exchanges carbon dioxide (CO_2) with the overlying atmosphere (Fig. 1-1):

$$CO_2(air) \rightleftarrows CO_2(aq) \qquad \text{(Eq. 1-1)}$$

The air-sea exchanges of CO_2 are controlled by the partial pressure of CO_2 (pCO_2), gas transfer functions (function of temperature) and wind strength (e.g. Takahashi et al., 2009).
Dissolved CO_2 in seawater is dissociated into bicarbonate ion (HCO_3^-):

$$CO_2 + H_2O \rightleftarrows [HCO_3^-] + [H^+] \qquad \text{(Eq. 1-2)}$$

and it is further dissociated into carbonate ion (CO_3^{2-}):

$$[HCO_3^-] \rightleftarrows [CO_3^{2-}] + [H^+] \qquad \text{(Eq. 1-3)}$$

As proton is emitted during the dissociation above, seawater CO_2 chemistry largely depends on pH (concentration of proton in logarithmic scale: $-\log_{10}[H^+]$) (Fig. 1-2). The saturation state of seawater with respect to aragonite (Ω_{arg}) is defined as:

$$\Omega_{arg} = \frac{[Ca^{2+}] * [CO_3^{2-}]}{K_{SP}} \qquad \text{(Eq. 1-4)}$$

where K_{SP} is a solubility product of aragonite that is a function of temperature, salinity and pressure.

Boron is also a major constituent of seawater CO_2 chemistry (Fig. 1-1), and it exists in two forms, boric acid ($B(OH)_3$) and borate ion ($B(OH)_4^-$), in seawater with pH of ~8 (Fig. 1-2). Boron concentration in seawater is a function of salinity (e.g., Millero, 1979):

$$B_T = [B(OH)_3] + [B(OH)_4^-] = 12.12 * salinity \qquad \text{(Eq. 1-5)}$$

Boric acid reacts with water, producing borate ion and proton:

$$[B(OH)_3] + H_2O \rightleftharpoons [B(OH)_4^-] + [H^+] \qquad \text{(Eq. 1-6)}$$

Dissolved inorganic carbon (DIC) is defined as sum of carbon bearing ions:

$$DIC = [HCO_3^-] + [CO_3^{2-}] + [CO_2(aq)] \qquad \text{(Eq. 1-7)}$$

On the other hand, total alkalinity (TA), excess anions that keep charge balances of seawater, is defined as follows:

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] \qquad \text{(Eq. 1-8)}$$

As relative abundance of borate ion in TA is only a few percent (e.g., 3.8% when DIC = 2,000 μmol/kg, salinity = 35, and temperature = 25 °C), a contribution of borate ion to TA is neglected in general (and in this thesis, too). We can fully calculate CO_2 chemistry when pressure, temperature, salinity, and two of four parameters (DIC, TA, pH and pCO_2) are given (e.g. Zeebe & Wolf-Gladrow, 2001). It should be noted, unless otherwise stated, pH scale is the total hydrogen scale (Gattuso & Hanson, 2011; Riebesel et al., 2010; Robbins et al., 2010; Zeebe & Wolf-Gladrow, 2001), and the dissociation constants are carbonic acid (CO_3^{2-}, HCO_3^-) derived from Lueker *et al.* (2000) and hydrogen sulfate (HSO_4^-) derived from Dickson (1990) in this thesis.

Fig. 1-1. A schematic diagram of seawater CO_2 chemistry in the surface ocean.

Fig. 1-2. (**a**) Concentration of each ion that constitutes CO_2 chemistry. The calculation was made using DIC of 2,000 μmol/kg, salinity of 35, and temperature of 25 °C. (**b**) Enlarged view of **a**. Note that concentration of bicarbonate ion is shown in right axis.

1-2. Boron isotopes in seawater and carbonates

Not only relative abundances of boric acid and borate ion, but also $\delta^{11}B$ of each species are pH-dependent (Fig. 1-3). The following equation is proposed to describe incorporations of boron into biogenic carbonates (Hemming & Hanson, 1992):

$$CaCO_3 + B(OH)_4^- \rightarrow Ca(HBO_3) + HCO_3^- + H_2O \qquad \text{(Eq. 1-9)}$$

As seen in the equation, if borate ion $B(OH)_4^-$ is incorporated into biogenic carbonates preferentially, $\delta^{11}B$ of carbonates ($\delta^{11}B_{carbonate}$) acts as a pH-meter following the equation:

$$pH = pK_B - \log\left(\frac{\delta^{11}B_{SW} - \delta^{11}B_{carbonate}}{\alpha_{3\text{-}4} * \delta^{11}B_{carbonate} - \delta^{11}B_{SW} + 10^3 * (\alpha_{3\text{-}4} - 1)}\right) \qquad \text{(Eq. 1-10)}$$

pK_B is the dissociation constant of boric acid (Dickson, 1990). $\delta^{11}B_{SW}$ is the global average $\delta^{11}B$ of seawater (a recently compiled value is 39.61‰, Foster et al., 2010) and can be regarded as a constant throughout the Quaternary because a residence time of boron in the seawater is long enough (at least ~20 Ma, Spivack & Edmond, 1987). $\alpha_{3\text{-}4}$ is the fractionation factor between trigonal boric acid $B(OH)_3$ and tetrahedral borate ion $B(OH)_4^-$ determined empirically through spectrometric pH measurements of borate buffer solutions containing only ^{11}B or ^{10}B (1.0272, Klochko et al., 2006).

As pioneering works, Vengosh *et al.* (1991) and Hemming & Hanson (1992) demonstrated that $\delta^{11}B$ values of modern marine carbonates, both aragonite and calcite, are roughly in line with the theoretically expected values (Table 1-1). Nowadays, boron isotopes of carbonate materials are measured by mainly two methodologies: thermal ionization mass spectrometry (TIMS) and multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) (Table 1-2). Although $\delta^{11}B$ measurements of biogenic carbonates using secondary ionization mass spectrometry (SIMS, e.g., Allison et al., 2014; Kasemann et al., 2009), high-resolution ICPMS (HR-ICPMS, e.g., Mirsa et al., 2014), and laser ablation ICPMS (LA-ICPMS, e.g., Kaczmarek et al., 2015) has also developed recently, they are omitted here. The TIMS method is further divided into two

ways depending on which ion is used in mass spectrometry, positive (P-TIMS) or negative (N-TIMS). Mcmullen *et al*. (1961) developed the P-TIMS method utilizing $Na_2BO_2^+$ ions (mass of 89 and 88). However, the precision of this methodology was worse than 2–3‰ at that time. After a while Spivack & Edmond (1987) improved the P-TIMS method introducing $Cs_2BO_2^+$ ion (mass of 309 and 308). Up until now, Ishikawa & Nagaishi (2011)'s P-TIMS method using $Cs_2BO_2^+$ ion reports the highest precision (0.08‰, 2σ) for $\delta^{11}B$ measurements of biogenic carbonates, which requires 50–100 ngB for the analysis (equivalent to 2–3 mg of coral aragonite). The N-TIMS method using BO_2^- ion (mass of 43 and 42), developed by Heumann (1982), is characterized by a high sensitivity, namely it requires a little sample amount (< 1 ngB). Although the precision of the N-TIMS method is relatively worse than P-TIMS method (~0.50‰, 2σ), it is suitable for $\delta^{11}B$ measurements of small samples (e.g., foraminifers). Currently, the MC-ICPMS method is the most widely used for $\delta^{11}B$ measurements of biogenic carbonates because of a moderately high precision (~0.25‰, 2σ), a swiftness of sample preparation, and availability of an autosampler (Table 1-2, and references therein). Foster (2008) developed the MC-ICPMS method using a sample-standard bracketing routine, and paved the way to measure $\delta^{11}B$ of 1–3 mg of foraminiferal calcite.

However, there are large gaps between the measured $\delta^{11}B$ of scleractinian corals cultured in pH-regulated aquariums and the theoretical curve of $\delta^{11}B$ of borate ion (Fig. 1-4, Table 1-3) (Holcomb et al., 2014; Trotter et al., 2011; Krief et al., 2010; Raynaud et al., 2004; Hönisch et al., 2004). In order to draw Figs. 1-4 and 1-5, we firstly corrected the analytical procedure-specific isotopic offsets (Kubota et al., 2014, modified after Zeebe & Wolf-Gladrow, 2001):

$$\delta^{11}B_{\text{carbonate-corrected}} = \delta^{11}B_{\text{SW-stacked}} + \frac{\delta^{11}B_{\text{SW-stacked}} + 10^3}{\delta^{11}B_{\text{SW-measured}} + 10^3} * (\delta^{11}B_{\text{carbonate-measured}} - \delta^{11}B_{\text{SW-measured}})$$

(Eq. 1-11)

The differences between $\delta^{11}B$ of biogenic carbonates and theoretically expected ones are ubiquitously seen in scleractinian and deep-sea corals, foraminifers, brachiopods, ostracods, pteropods, gastropods, mollusks, echinoderms, and calcareous algae (e.g.,

Table 1-1 and references therein). The only exception is benthic foraminifers (*Cibicidoides* spp.); their $\delta^{11}B$ values coincide with the theory (Rae et al., 2011). Trotter *et al*. (2011) explained the cause of the difference seen in scleractinian corals as biological modulation of carbonate chemistry in calcification fluid from which the skeleton is produced. McCulloch et al. (2012a, b) extended their idea to deep-sea corals. They regarded $\delta^{11}B$ of both scleractinian and deep-sea corals as a recorder of calcification fluid pH, not seawater pH (Table 1-3). More simply, on the other hand, Hönisch *et al*. (2007) regarded the difference as a "vital effect" and corrected it empirically. This approach is reasonable because what we need in paleoceanography is an empirical proxy.

Fig. 1-3. (**a**) Relative abundance and (**b**) $\delta^{11}B$ of boric acid (red) and borate ion (blue). The calculation was made using the fractionation factor of Klochko *et al.* (2006), dissociation constants (pK_B) of boric acid of Dickson (1990) with salinity of 35 and temperature of 25 °C.

Fig. 1-4. Previously reported δ^{11}B values of cultured scleractinian corals (Table 1-3). Analytical procedure-specific isotopic offsets were corrected using Equation (1-11). The theoretical curve of δ^{11}B of borate ion is also plotted.

a

b

Fig. 1-5. (**a**) An illustration of calcification model proposed by Al-Horani *et al.* (2003). (**b**) Same as **Fig. 1-4**, but only Poritidae corals are shown. Arrows indicate pH_{CF} and ΔpH.

Table. 1-1. A summary of corals of which $\delta^{11}B$ values have documented in literatures.

Genus	Location	References
Scleractinian corals		
Porites (culture)		
massive *Porites* spp.	Eilat (Israel)	Krief et al., 2010
Porites cylindrica	Okinawa (Japan)	Hönisch et al., 2004
Porites (field, modern)		
massive *Porites* spp.	Chichijima (Japan)	This study
massive *Porites* spp.	Moorea (French Polynesia)	Douville et al., 2010; Gaillardet & Allegre, 1995
massive *Porites* spp.	Hainan (China)	Liu et al., 2014
massive *Porites* spp.	Guam (USA)	Shinjo et al., 2013
massive *Porites* spp.	GBR (Australia)	Wei et al., 2009; Pelejero et al., 2005
massive *Porites* spp.	Ishigaki (Japan)	This study (not shown); Kubota et al., 2014; McCulloch et al., 2014; Ishikawa & Nagaishi, 2011; Douville et al., 2010
massive *Porites* spp.	New Caledonia	Douville et al., 2010
massive *Porites* spp.	Luson (Philippines)	This study (not shown)
massive *Porites* spp.	Red sea	Gaillardet & Allegre, 1995
massive *Porites* spp.	Hawaii (USA)	Allison et al., 2014
massive *Porites* spp.	Jarvis (USA)	Allison et al., 2014
massive *Porites* spp.	GBR (Australia)	Vengosh et al., 1991
Porites lutea	New Caledonia	Rollion-Bard et al., 2003
Porites lobata	Hawaii (USA)	Allison et al., 2010
Porites lobata	Fanning (Kiribati)	Hemming et al., 1998
Porites porites	Florida (USA)	Hemming & Hanson, 1992

Continued

Porites (field, fossil)		
–	Tahiti (French Polynesia)	Kubota et al., 2014; Douville et al., 2010
–	Marquesas	Douville et al., 2010
	Papua New Guinea	Kasemann et al., 2009
–	SCS (China)	Liu et al., 2014, 2009
Acropora (culture)		
Acropora nobilis	Okinawa (Japan)	Hönisch et al., 2004
Acropora spp.	New Caledonia	Raynaud et al., 2004
Acropora spp.	New Caledonia	Dissald et al., 2012
Acropora (field, modern)		
Acropora cervicornis	Jamaica	Hemming & Hanson, 1992
Acropora (field, fossil)		
–	Tahiti (French Polynesia)	Gaillardet & Allegre, 1995
–	Red Sea	Gaillardet & Allegre, 1995
–	La Reunion	Gaillardet & Allegre, 1995
–	Mauritius	Gaillardet & Allegre, 1995
–	Saint Thomas (USA)	Gaillardet & Allegre, 1995
Cladocora (culture)		
Cladocora caespitosa	Villefranche (France)	Trotter et al., 2011
Cladocora caespitosa	Villefranche (France)	Rollion-Bard et al., 2011
Cladocora (field, modern)		
Cladocora caespitosa	Levanto (Italy)	Trotter et al., 2011
Cladocora caespitosa	Ischia (Italy)	Trotter et al., 2011
Pocilopora (culture)		
Pocillopora damicornis	Eilat (Israel)	Allison et al., 2014

Continued

Stylophora (culture)		
Stylophora pistilata	Aqaba (Jordan)	Holcomb et al., 2014
Stylophora pistilata	Eilat (Israel)	Krief et al., 2010
Stylophora (field, modern)		
Stylophora pistilata	Eilat (Israel)	Vengosh et al., 1991
Siderastrea (field, modern)		
Siderastrea siderea	Jamaica	Hemming & Hanson, 1992
Montastrea (field, modern)		
Montastrea spp.	Jamaica	Hemming & Hanson, 1992
Agaricia (field, modern)		
Agaricia agaricites	Jamaica	Hemming & Hanson, 1992
Pratygira (field, modern)		
Pratygira spp.	Eilat (Israel)	Vengosh et al., 1991
Fungia (field, modern)		
Fungia spp.	Eilat (Israel)	Vengosh et al., 1991
Goniastrea (field, modern)		
Agaricia agaricites	Sumba (Indonesia)	Gaillardet & Allegre, 1995

Deep-sea corals	
Caryophyllia smithii	McCulloch et al., 2012b
Desmophyllum dianthus	McCulloch et al., 2012b; Anagnostou et al., 2012
Desmophyllum spp.	Kasemann et al., 2009
Enallopsammia rostrata	McCulloch et al., 2012b
Lophelia pertusa	McCulloch et al., 2012b; Rollion-Bard et al., 2011
Madrepora oculata	McCulloch et al., 2012b
Keratoisis spp.	Farmer et al., in press
Corallium spp.	McCulloch et al., 2012b

Table 1-2. A summary of methodologies to measure $\delta^{11}B$ of carbonate materials.

Method	References	
	Corals (aragonite)	**Foraminifers (calcite)**
P-TIMS	This study; Kubota et al., 2014; Holcomb et al., 2014; McCulloch et al., 2012a, b; Trotter et al., 2011; Ishikawa & Nagaishi, 2011; Wei et al., 2009; Pelejero et al., 2005; Gaillardet & Allegre, 1995	
N-TIMS	Farmer et al., in press; Kasemann et al., 2009; Hönisch et al., 2004; Raynaud et al., 2004; Hemming et al., 1998; Hemming & Hanson, 1992; Vengosh et al., 1991	Hönisch et al., 2009; Hönisch & Hemming, 2005; Palmer & Pearson, 2003
MC-ICPMS	This study; McCulloch et al., 2014; Liu et al., 2014; Henehan et al., 2013; Yu et al., 2013; Shinjo et al., 2013; Dissard et al., 2012; Anagnostou et al., 2012; Douville et al., 2010; Krief et al., 2010; Kasemann et al., 2009	Foster & Sexton, 2014; Seki et al., 2009; Foster, 2008

Table 1-3. Previously reported δ¹¹B values of scleractinian corals reared in aquariums with lowerd pH$_{SW}$.

(1)pH$_{SW}$	±	pK_B (T, S)	Coral genera	δ¹¹B$_{coral}$ values (‰) measured	(2)corrected	error (‰, 2σ)	pH$_{CF}$	ΔpH	Method	δ¹¹B$_{SW}$ (‰)	Reference
8.22	0.05	8.58 (25.3, 38.0)	*Acropora* spp.	24.0	23.4	0.50	8.42	0.21	N-TIMS	40.3	Reynaud et al., 2004
8.20		8.55 (28.2, 38.0)		23.9	23.3		8.38	0.19			
8.03		8.58 (25.1, 38.0)		22.5	21.9		8.32	0.30			
8.02		8.54 (28.3, 38.0)		22.8	22.2		8.31	0.29			
7.75	0.05	8.57 (27.0, 36.4)	*Acropora nobilis*	21.1	21.0	0.31	8.25	0.50	N-TIMS	39.7	Hönisch et al., 2004
8.00				22.9	22.8		8.37	0.38			
8.20				24.5	24.4		8.48	0.28			
7.75	0.05	8.57 (27.0, 36.4)	*Porites cylindrica*	21.7	21.6	0.31	8.29	0.55	N-TIMS	39.7	Hönisch et al., 2004
8.00				23.5	23.4		8.41	0.42			
8.20				24.9	24.8		8.50	0.31			
8.09	0.05	8.57 (25.0, 40.7)	*Porites* spp.	25.2	25.3	0.25	8.54	0.45	MC-ICPMS	39.5	Krief et al., 2010
7.49				22.0	22.1		8.33	0.84			
7.19				21.0	21.1		8.26	1.07			
8.09	0.05	8.57 (25.0, 40.7)	*Stylophora pistillata*	24.8	24.9	0.25	8.51	0.42	MC-ICPMS	39.5	Krief et al., 2010
7.49				21.8	21.9		8.32	0.83			
7.19				20.7	20.8		8.24	1.05			
8.09	0.02	8.67 (17.6, 38.1)	*Cladocora caespitosa*	25.3	24.8	0.27	8.61	0.52	P-TIMS	40.1	Trotter et al., 2011
7.87		8.64 (20.5, 38.1)		24.3	23.8		8.51	0.64			

Continued

7.17	0.07	8.58	*Stylophora pistillata*	20.4	19.9	0.25	8.18	1.01	P-TIMS	40.1	Holcomb et al., 2014
7.36	0.08	(25.0, 38.0)		21.2	20.8		8.25	0.89			
7.71	0.08			22.2	21.7		8.31	0.60			
7.94	0.04			23.5	23.0		8.40	0.46			

(1) pH scales were integrated into the total hydrogen scale.
(2) Analytical procedure-specific isotopic offsets were corrected using Equation (1-11)

1-2-1. δ^{11}B-pH calibration (1): pH up-regulation

Corals up-regulate pH of calcification fluid (pH$_{CF}$) in order to realize more suitable conditions for calcification (Allison et al., 2014; Holcomb et al., 2014; Hendriks et al., 2015; Venn et al., 2013, 2011; McCulloch et al., 2012a,b; Trotter et al., 2011; Cohen & Holcomb, 2009; Al-Horani et al., 2003). For instance, pH$_{CF}$ is ~1.1 (under the light) and 0.2–0.5 higher than seawater pH (pH$_{SW}$) for *Galaxea fascicularis* and *Stylophora pistillata*, respectively (Venn et al., 2013, 2011; Al-Horani et al., 2003). Recently Allison *et al.* (2014) showed that pH$_{CF}$ of *Stylophora pistillata* directly measured using pH sensitive dye is in an excellent agreement with that estimated from δ^{11}B$_{coral}$. The enzyme Ca^{2+}-ATPase likely plays a key role in this pH up-regulation because it has a function of pumping Ca^{2+} into the calcification fluid and removing two H$^+$, which elevates pH$_{CF}$ and [CO$_3^{2-}$] (Figs. 1-2 and 1-5). Then increases of [Ca^{2+}] and [CO$_3^{2-}$] will lead to more saturated $\Omega_{arg\ CF}$, thus facilitating calcification. In the pH up-regulation, δ^{11}B$_{coral}$ represents pH$_{CF}$, not pH$_{SW}$, and a deviation between them is defined as ΔpH (Trotter et al., 2011) (Fig. 1-5):

$$\text{pH}_{CF} = pK_B - \log\left(\frac{\delta^{11}\text{B}_{SW} - \delta^{11}\text{B}_{coral}}{\alpha_{3\text{-}4} * \delta^{11}\text{B}_{coral} - \delta^{11}\text{B}_{SW} + 10^3 * (\alpha_{3\text{-}4} - 1)}\right) \quad \text{(Eq. 1-12)}$$

$$\Delta\text{pH} = \text{pH}_{CF} - \text{pH}_{SW} \quad \text{(Eq. 1-13)}$$

ΔpH is always positive, namely δ^{11}B$_{coral}$ locates in the left side of the theoretical curve in δ^{11}B-pH cross plot (lessor pH) (Figs. 1-4 and 1-5).

1-2-2. δ^{11}B-pH calibration (2): Empirical correction

On the other hand, Hönisch *et al.* (2007) proposed a more simplified equation by introducing "offset *a* (unit is ‰)" in the δ^{11}B-pH$_{SW}$ calibration equation:

$$\text{pH}_{SW} = pK_B - \log\left(\frac{\delta^{11}\text{B}_{SW} - (\delta^{11}\text{B}_{coral} + a)}{\alpha_{3\text{-}4} * (\delta^{11}\text{B}_{coral} + a) - \delta^{11}\text{B}_{SW} + 10^3 * (\alpha_{3\text{-}4} - 1)}\right) \quad \text{(Eq. 1-14)}$$

The offset *a* has a negative value, namely δ^{11}B$_{coral}$ is plotted above the theoretical curve

(heavier δ^{11}B) (Fig. 1-4).

1-3. Oceanography of the tropical and subtropical Pacific

Study regions discussed in this thesis is the tropical-subtropical Pacific. Modern and fossil corals obtained from Chichijima (Ogasawara Islands, 27°06'N 142°12'E) in the western North Pacific and Tahiti (Society Islands, 17°39'S 149°30'W) in the South Pacific are used. In the following sections, the sea surface temperature (SST) and salinity (SSS) regimes, the ocean current, and then the carbon cycle in the surface ocean of the tropical-subtropical Pacific will be summarized.

1-3-1. Temperature and salinity

In the western equatorial Pacific, the broad warm water mass called the Western Pacific Warm Pool (WPWP) exists (Fig. 1-6). On the other hand, in the eastern equatorial Pacific, there exists the outcrop of cold subsurface water due to inclined thermocline toward the west, called the cold tongue. Cold tongue is formed as a result of the equatorial upwelling and the advection of upwelled subsurface water at the coast off Peru (coastal upwelling) (Talley et al., 2011). Due to the heat transport by Kuroshio Current, the south coast of Japan is kept relatively warm regardless of its latitude. The annual mean temperature of Chichijima is 24.2 °C with the minimum temperature of 20.0 °C in winter (Fig. 1-6). On the other hand, as Tahiti locates in the southern rim of the WPWP, the temperature stays high through the year: the annual mean temperature is 27.4 °C and the seasonal variation is only 2.4 °C (Fig. 1-6). These islands lie in water whose temperature is over 18 °C, that is the distribution limit of *Porites* coral (Fallon et al., 1999). As a result, a cessation of *Porites* coral growth in the coldest season has never been documented (e.g., Chichijima, Felis et al., 2009; Tahiti, Cahyarini et al., 2009).

The Intertropical Convergence Zone (ITCZ) lying several degrees north of the equator brings heavy rain in the regions (Schneider et al., 2014). As a result, the lowest surface salinity in the tropical-subtropical Pacific is observed right bellow the ITCZ (Fig. 1-6) (Talley et al., 2011). Although the amplitude of the meridional ITCZ migration over the equatorial Pacific is small compared to the one over continents, it

migrates towards the warmer hemisphere seasonally: The ITCZ migrates northward (~9°N) in the boreal summer and southward (~2°N) in the austral summer (Schneider et al., 2014). The ITCZ drives the Hadley circulation in the troposphere, and its descending flow of dry air causes the aridification around subtropical regions. It yields positive evaporation-precipitation balances, and thus salinity increases in the subtropical surface water. This is why there exists the salinity maximum near the centers of the subtropical gyre in the North and South Pacific (Fig. 1-6). Another southward branch of rain band stretching towards Tahiti is called the South Pacific Convergence Zone (SPCZ, Fig. 1-6). Although it is the largest rain band in the southern hemisphere (Vincent, 1994), it has a slight influence on salinity variations in Tahiti. In Tahiti, SST is under influences from the WPWP, but salinity is neither affected by the ITCZ nor the SPCZ. The ITCZ also has a strong influence on Southeast Asian monsoon. In summer when the ITCZ migrates northward along the east coast of Eurasian Continent, it brings a heavy rain to the eastern Asia including the southern Japan. Dilution of surface seawater caused by freshwater influx from the surrounding continents is probably a reason why the north subtropical gyre shows the lower salinity than the south subtropical gyre (Fig. 1-6).

Fig. 1-6. (**a,b**) Climatological mean sea surface temperature and salinity. Data is from World Ocean Atlas 2009 downloaded via *http://odv.awi.de/en/data/* and plotted using Ocean Data View software version 4.6.2 (Schlitzer, 2014). WPWP, Western Pacific Warm Pool; ITCZ, Intertropical Convergence Zone; SPCZ, South Pacific Convergence Zone. (**c,d**) Monthly mean sea surface temperature and salinity at Chichijima and Tahiti.

1-3-2. Ocean current

The two islands locate within the subtropical gyre in both hemispheres. The North Equatorial Current (NEC) brings warm, nutrient-poor tropical water to the western Pacific. At ~15ºN, NEC splits into the western boundary current, the Kuroshio Current (Fig. 1-7). Kuroshio flows northward along the continental shelf of East Eurasia Continent, and turns its direction eastward at ~30°N to flow along the south coast of Japan. On the other hand, the South Equatorial Current (SEC) constitutes a northern rim of the subtropical gyre in the South Pacific. Because the SEC extends across the equator, the South Pacific subtropical gyre is more directly connected to the equator than the northern counterparts (Fig. 1-7) (Talley et al., 2011). Between the NEC and the SEC, there exists the Equatorial Counter Current (ECC) that flows eastward. Right bellow the equator, there exists one of the strongest oceanic current in the world, the Equatorial Undercurrent (EUC) that flows eastward along the thermocline (Talley et al., 2011).

(a) Sea surface dynamic height (m)

(b) Surface seawater pCO_2 (µatm)

Fig. 1-7. (**a**) Climatological mean sea surface dynamic height (in units of m relative to the 1,000 m level) with arrows showing major surface ocean currents. Data source is "World Ocean Atlas 2009 > annual". NEC, North Equatorial Current; ECC, Equatorial Counter Current; SEC, South Equatorial Current. (**b**) Distribution of surface seawater pCO_2 in the tropical-subtropical Pacific for the reference year AD 2000 (Takahashi et al., 2009). Arrow indicates atmospheric pCO_2 in 2000 (369.5 µatm). Red and blue colors represent CO_2 sources and sinks, respectively. Data source is "LDEO_Database_V2010 > Gridded_sumflax_2006c". Both data were downloaded via *http://odv.awi.de/en/data/* and plotted using Ocean Data View software version 4.6.2 (Schlitzer, 2014).

1-3-3. Surface pCO$_2$ distribution and CO$_2$ source versus sink

The equatorial Pacific is currently the largest CO$_2$ "source" in the world as indicated by higher pCO$_2$ values than the atmospheric pCO$_2$ (Fig. 1-7) (Takahashi et al., 2009; Gruber et al., 2009; Sarmiento & Gruber, 2006). The direction and magnitude of CO$_2$ flux is mainly controlled by pCO$_2$ difference in the air-sea interface (e.g., Takahashi et al., 2009). The equatorial upwelling brings the nutrient- and DIC- rich cold subsurface water to the surface, which results in enhanced biological productivities. CO$_2$ outgassing from the sea to the air occurs, because biological carbon drawdown in the surface is insufficient due to a shortage of micronutrients such as iron (c.f., high-nutrient low-chlorophyll region; Sarmiento & Gruber, 2006). Seawater CO$_2$ chemistry in the equatorial upwelling region shows stochastic variabilities in seasonal to decadal timescales (e.g., Sutton et al., 2014; Feely et al., 2006, 2002).

On the contrary, the surface seawater in the subtropical gyre in both hemispheres are the modest CO$_2$ "sink" as characterized by the lower pCO$_2$ than the atmospheric pCO$_2$ (Fig. 1-7) (Ishii et al., 2011, 2001; Dore et al., 2009; Takahashi et al., 2009; Gruber et al., 2009; Sabine et al., 2004). In boreal summer, the surface water in the western North Pacific (Chichijima) becomes a weak source of CO$_2$ (Ishii et al., 2001; 2011), but this is not the case for that surrounds Tahiti in austral summer, namely Tahiti is a CO$_2$ sink throughout the year (Kubota et al., 2014). As a deep thermocline inhibits incorporations of subsurface nutrient, the surface seawater surrounding these islands is oligotrophic and can hardly sustain active biological productivities (e.g., Kubota et al., 2014; Ishii et al., 2011, 2001; Midorikawa et al., 2012, 2010). Therefore, the dominant driver of pH$_{SW}$ and pCO$_{2\,SW}$ variability is the seasonal SST around the area (Kubota et al., 2014; Ishii et al., 2011; 2001).

1-4. Carbon cycle since the last glacial period

Although the direct atmospheric observation of atmospheric CO_2 only became possible after AD 1958 (Tans & Keeling, 2014), Antarctic ice and firn cores have recorded atmospheric pCO_2 ($pCO_{2\ atm}$) fluctuations in the past (Fig. 1-8) (Marcott et al., 2014; Rubino et al., 2013; Lourantou et al., 2010; Lüthi et al., 2008). EPICA Dome C ice core has offered the longest $pCO_{2\ atm}$ records over the last 800 thousand years before AD 1950 (ka BP) (Lüthi et al., 2008). In the eastern equatorial Atlantic, the $\delta^{11}B$ of the fossil planktonic foraminifer in the marine sediment core showed that surface seawater pH and pCO_2 (pH_{SW} and $pCO_{2\ SW}$) fluctuations synchronized with $pCO_{2\ atm}$ over the last 800 ka BP (Hönisch et al., 2009; Hönisch & Hemming, 2005). The $\delta^{11}B$ measurements of planktonic foraminifer further extended their records back to 2.1 million years ago (Ma), and they showed that $pCO_{2\ atm}$ periodically fluctuated between 180 and 300 µatm coinciding with global ice sheet retreats and advances (Hönisch et al., 2009). Given that excellent correspondences between the peaks of $pCO_{2\ atm}$ and ice-sheet volume, it is reasonable to think that the relationship has continued over the entire Quaternary (since 2.81 Ma). Therefore, the current $pCO_{2\ atm}$ level (~400 µatm) is not only much higher than that of the late Holocene (~280 µatm) but also that of the Quaternary (Fig. 1-8), and may be so over the last 25 Ma (Beerling & Royer, 2011). Furthermore, the rate of modern $pCO_{2\ atm}$ increase is unprecedentedly higher than that from other periods over the Cenozoic (65 Ma).

To study the carbon cycle for the last ~50 ka (constrained by half-life of radiocarbon and detection limit of the measurement), radiocarbon can be used as a tracer that travels from the stratosphere to the deepsea sediments. In the modern ocean, the oldest seawater, age of ~2,000 years, exists in the deep Pacific Ocean while the average of global surface seawater is ~400 years. Another important tracer studying carbon cycle is stable carbon isotope ($\delta^{13}C$). In general, $\delta^{13}C$ of DIC ($\delta^{13}C_{DIC}$) of the deep seawater has lighter value than that of the surface seawater because sinking particles that are remineralized in the deep sea have lighter $\delta^{13}C$, too (Sarmiento & Gruber, 2006). The sinking particles (marine snow) originate from phytoplanktons living in the surface layer of the ocean. As phytoplanktons selectively incorporate lighter carbon isotope into their bodies, the biological pump transports more ^{12}C than ^{13}C to the deep sea. Therefore the deep seawater that is isolated from the atmosphere for a long time tends to

be older and have lighter $\delta^{13}C_{DIC}$. As a result, modern Pacific deep water has older ages and has lighter $\delta^{13}C_{DIC}$ than those of the Atlantic deep water, as the former and the latter is respectively an exit and an entrance of the global conveyer belt of the seawater (Schmittner et al., 2013; Sarmiento & Gruber, 2006; Broecker & Peng, 1992).

In the following section we will introduce carbon cycles from two recent periods during the Quaternary, "the last deglaciation" and "after the Industrial Revolution", when the earth experienced the rapid increases of $p\text{CO}_{2\,atm}$ through natural and human activities. These two $p\text{CO}_{2\,atm}$ increases occurred in totally different mechanisms (Fig. 1-9). During the last deglaciation, $p\text{CO}_{2\,atm}$ increased as a result of redistribution of carbon among major reservoirs (e.g., deep seawater, terrestrial biomass, and the atmosphere). As $p\text{CO}_{2\,atm}$ increased from 180 to 280 μatm during the last deglaciation, $p\text{CO}_2$ and DIC of the surface layer of the ocean increased, too (Figs. 1-8 & 1-9). TA was probably higher (by ~80 μmol/kg) during the LGM because the salinity was ~1.2 g/kg higher as a result of increased freshwater storage on land (e.g., Adkins et al., 2002). Since the Industrial Revolution, on the other hand, anthropogenic CO_2 has entered into the surface layer of the ocean from the atmosphere, causing DIC increases. The time scale of the CO_2 addition is so fast that the ocean has not reached to the steady state. It is noteworthy that TA remains unchanged since the Industrial Revolution because CO_2 invasion against the ocean does not influence TA (e.g., Zeebe & Wolf-Gradlow, 2001) (Fig. 1-9).

Fig. 1-8. Variations of pCO$_2$ $_{atm}$ in three different time-windows. (**a**) pCO$_2$ $_{atm}$ records of Antarctic ice core (Lüthi et al., 2008). pCO$_2$ $_{atm}$ varied cyclically: ~280 µatm during interglacial and ~180 µatm during glacial periods. Marine Isotope Stages (MIS) are given in Arabic numerals. (**b**) As **a**, but higher resolution records during the last deglaciation (Lourantou et al., 2010). pCO$_2$ $_{atm}$ increased by ~50 µatm during HS1 and ~30 µatm during the YD. HS1, Heinrich Stadial 1; B/A, Bolling/Allerod; ACR, Antarctic Cold Reversal; YD, Younger Dryas. (**c**) pCO$_2$ $_{atm}$ during 1959–2013 are measured at the Mauna Loa Observatory in Hawaii (red) (Tans & Keeling, 2014) and those prior to 1959 are reconstructed records from Antarctic ice core (magenta) (Rubino et al., 2013). After the Industrial Revolution pCO$_2$ $_{atm}$ increased by 120 µatm and reached to 400 µatm nowadays.

Fig. 1-9. A DIC-TA plot of the surface seawater that is well ventilated with the overlying atmosphere. The calculation was made using salinity and temperature of 35.9 and 27.1 °C (climatological values of Tahiti). TA is 2360 μmol/kg at present and was by ~80 μmol/kg higher during the LGM. The LGM DIC was calculated from $pCO_{2\ SW}$ of 180 μatm and the LGM TA. Since the Industrial Revolution, the anthropogenic CO_2 addition have caused DIC increases while keeping TA constant (ocean acidification).

1-4-1. The last deglaciation

Physical and bigeochemical dynamics in the Southern Ocean surrounding Antarctica has proposed to play a central role to control glacial - interglacial $pCO_{2\ atm}$ fluctuations, because carbon reservoirs in the ocean is ~60 times as large as that of the atmosphere (e.g., Martínez-García et al., 2014; Schmitt et al., 2012; Sigman et al., 2010, Sarmiento & Gruber, 2006). The hypothetical carbon stored in the glacial ocean is called "glacial abyssal carbon reservoir". In fact, the existence of extremely aged (depleted in ^{14}C) seawater has been reported through analyzing fossil benthic foraminifer and deepsea corals' skeletons in the last glacial Southern Ocean (Burke & Robinson, 2012; Rose et al., 2010; Skinner et al., 2015, 2009).

During the last deglaciation, climatic shifts from the last glacial to the present interglacial, $pCO_{2\ atm}$ increased by ~50 μatm during Heinrich Stadial 1 (HS1, 17.5–14.6 ka BP), followed by additional ~30 μatm during the Younger Dryas (YD, 12.9–11.5 ka BP) (Fig. 1-8). During HS1 and the YD, both $\delta^{13}C$ of atmospheric CO_2 ($\delta^{13}C_{atm}$) and decay-corrected radiocarbon concentration of atmospheric CO_2 ($\Delta^{14}C_{atm}$) decreased. This supports the hypothesis that the stored carbon in the glacial ocean returned to the atmosphere during these periods (e.g., Schmitt et al., 2012; Skinner et al., 2010; Marchitto et al., 2007; Spero & Lea, 2002). Similarities seen between Antarctic air temperatures and $pCO_{2\ atm}$ strongly suggest the Southern Ocean was the most important place to control glacial - interglacial carbon cycles. To date, different mechanisms have been proposed to explain lower $pCO_{2\ atm}$ during the last glacial and rapid increases in $pCO_{2\ atm}$ during glacial terminations. They are included oceanography-dominant mechanisms such as oceanic and atmospheric circulations (e.g., Kwon et al., 2012; Skinner et al., 2010; Anderson et al., 2009; Toggweiler et al., 2006), Antarctic sea ice and brine rejection feedback (e.g., Bouttes et al., 2011, 2010), biology-dominant mechanisms such as iron fertilization (Martínez-García et al., 2014; Ziegler et al., 2013) and silica leakage (e.g., Matsumoto et al., 2002; Brzezinski et al., 2002), and combination of them (e.g., Sigman et al., 2010; Kohfeld et al., 2005; Archer et al., 2000; Sigman & Boyle, 2000). However, the clear explanation of $pCO_{2\ atm}$ variability has been controversial (e.g., Matsumoto & Yokoyama, 2013; Thomas et al., 2009).

1-4-2. After the Industrial Revolution

Since the beginning of the industrial era (AD 1750), the ocean has absorbed about one quarter of emitted CO_2 as a result of human activities; such as fossil fuel burning, land use changes, and cement production (Ciais et al., 2013; Francey et al., 2013; Le Quéré et al., 2009; Sabine et al., 2005; Key et al., 2004). The extra DIC addition has disturbed the seawater CO_2 chemistry by lowering pH_{SW} and CO_3^{2-} concentrations (Fig. 1-9). This is the phenomenon so-called "ocean acidification" (OA). In the present surface layer of the ocean, pH_{SW} is 8.1 on average, which is a weak alkaline. Thus, OA means that ocean becomes more acidic, not acid liquid (pH < 7). pH_{SW} has decreased by ~0.1 after the Industrial Revolution as most surface seawater is a CO_2 sink (Doney et al., 2014; Gattuso & Hansson, 2011; Feely et al., 2009; Tans et al., 2009; Sabine et al., 2005; Key et al., 2004). This is especially evident that in the North Atlantic Ocean and the Southern Ocean, where deep and intermediate water formations and vigorous biological primary production occur, absorbed CO_2 is efficiently transported into the subsurface (Sallée et al., 2012; Ito et al., 2010; Gruber et al., 2009; Sabine et al., 2004). A large fraction of absorbed CO_2 currently distributes in the interior of the South Pacific Ocean due to its large surface area for air-sea CO_2 exchange and production of Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) that subduct along the pycnocline south of 30 °S (Sallée et al., 2012; Iudicone et al., 2011; Ito et al., 2010). Depending on the future course of CO_2 emission, pH_{SW} is anticipated to further decrease about 0.3-0.4 by the end of this century (Doney et al., 2014; Feely et al., 2009; Tans et al., 2009; Orr et al., 2005; Caldeira & Wickett, 2003).

Numerous culturing experiments conducted in aquariums with lowered pH_{SW} have suggested that many calcifying organisms such as corals, foraminifers and mollusks are generally vulnerable to OA (Hoegh-Guldberg et al., 2011; Pandolfi et al., 2011; Doney et al., 2009; Kleypas & Yates, 2009; Fabry et al., 2008; Gattuso & Hansson, 2008; Orr et al., 2005). This phenomenon is supported by field observations at naturally acidified sites by volcanic CO_2 seeps such as Milne Bay (Papua New Guinea), Iwotorishima (Japan), and Ischia (Italy) that acidified seawater eliminates calcifying organisms and leads to proliferation of non-calcifying organisms such as softcoral and macroalgae (e.g., Inoue et al., 2013; Fabricius et al., 2011; Hall-Spencer et al., 2008).

Due to isotopic dilution by ^{12}C-enriched CO_2 emitted from fossil fuel burning and

deforestation, $\delta^{13}C_{atm}$ is decreasing since the Insudtrial Revolution with an observed acceleration after 1960 (Rubino et al., 2013; Francey et al., 1999). In the same reason outlined in the previous section, burning of fossil fuel and terrestrial biomass will produce lighter $\delta^{13}C_{atm}$ as they are ^{12}C-rich. The phenomenon is called "^{13}C Suess effect" named after its discoverers (Revelle & Suess, 1957). $\delta^{13}C_{DIC}$ of surface layers of the oceans is also decreasing (Schmittner et al., 2013; Keeling et al., 2004; Quay & Stutsman, 2003; Quay et al., 2003, 1992; Gruber et al., 1999). As calcifying organisms that live in the surface layer of the oceans utilize oceanic carbon to secrete their $CaCO_3$ skeleton, it is also decreasing at an simil018 rate with $\delta^{13}C_{atm}$ depending on regional efficiency of CO_2 ventiulation (Dassié et al., 2013; Swart et al., 2010; Nozaki et al., 1978).

Fossil fuel-derived carbon is depleted in ^{14}C ("dead" carbon) because millions of years have passed since petroleum and coal was produced. In addition to $\delta^{13}C_{atm}$, ^{14}C in atmospheric CO_2, ^{14}C in DIC, and ^{14}C in living organisms are decreasing faster than the decay rate since the beginning of the industrial era (Druffel, 2002; Nozaki et al., 1978). This phenomenon is called "^{14}C Suess effect" distinguishing it from the ^{13}C Suess effect (Nozaki et al., 1978). After the 1960s, the ^{14}C Suess effect has been overwhelmed by anthropogenic ^{14}C pollution caused by nuclear tests (bomb ^{14}C) (Grottoli & Eakin, 2007; Druffel, 2002; Nozaki et al., 1978).

1-5. Research objectives and thesis structure

The boron isotopes (δ^{11}B) are the most promising proxy to estimate atmospheric pCO$_2$ prior to 800 ka BP and to understand dynamic CO$_2$ chemistry, for example, in the coastal and upwelling regions (e.g., Kubota et al., 2014; Foster et al., 2014; Douville et al., 2010; Palmer & Pearson, 2003). However, there are no δ^{11}B-pH$_{SW}$ calibrations using long-lived corals collected in the natural environment. The needs to establish a field-based calibration equation is that culturing-based calibrations can hardly reconstruct reasonable pH$_{SW}$ that is in line with observations of seawater CO$_2$ chemistry (discussed in detail in Chapter 2). There are many regions where we can estimate pH$_{SW}$ time-series through simple calculations of CO$_2$ chemistry with aid of previous efforts to reconstruct atmospheric CO$_2$ level and to estimate anthropogenic CO$_2$ absorption by the ocean. In such regions past δ^{11}B variations of long-lived corals should be calibrated with already-known pH$_{SW}$ rather than be used to reconstruct pH$_{SW}$.

The primary objective of this thesis is to obtain a field-based δ^{11}B-pH$_{SW}$ calibration. Firstly a methodology to obtain an empirical δ^{11}B-pH$_{SW}$ equation for massive *Porites* corals collected at Chichijima and Tahiti will be introduced (Chapter 2). pH$_{SW}$ variations since the Insudtrial Revolution are estimated from atmospheric pCO$_2$ records, because air-sea pCO$_2$ differences (ΔpCO$_2$) has been kept constant around these islands. Secondly, changes of pH$_{CF}$ of Chichijima coral (estimated from δ^{11}B based on the pH up-regulation) will be discussed, highlighting effects of OA on calcification in particular (Chapter 3). Thirdly, the empirical δ^{11}B-pH$_{sw}$ calibration for Tahiti obtained in Chapter 2 will be applied to δ^{11}B of fossil *Porites* corals in order to reconstruct pH$_{SW}$ and pCO$_{2\,SW}$ during the last deglaciation (Chapter 4). Lastly, the key findings of this thesis will be summarized, and future avenues for this research will be suggested (Chapter 5).

CHAPTER 2

Boron isotopes - pH calibration using long-lived modern corals

Chapter 2 Abstract

Boron isotopes ($\delta^{11}B$) of marine biogenic carbonates can reconstruct pH_{SW}, $pCO_{2\ SW}$, and potentially atmospheric CO_2 concentration in the geological past. To date, $\delta^{11}B$-pH_{SW} calibration has been proposed through culturing experiments of calcifying organisms under artificially acidified seawater. However, as for scleractinian corals, reconstructed pH_{SW} using the culture-based calibration do not agree well with seawater CO_2 chemistry observations. Thus, another approach is needed to establish a more reliable calibration. To attain the purpose, we measured a 100 year record of $\delta^{11}B$ of *Porites* coral obtained from Chichijima, Ogasawara Archipelago, Japan. Previously reported $\delta^{11}B$ values of Tahitian corals were also used after corrections of different procedure-specific isotopic offsets. We compared coral $\delta^{11}B$ records with pH_{SW} variation that was estimated from many CO_2 chemistry data and atmospheric CO_2 records, and established, for the first time, field-based calibrations for Chichijima and Tahiti. Using the established calibration, we reevaluated the previously reported two examples of pH_{SW} reconstructions from $\delta^{11}B$ of *Porites* corals obtained from Guam and Hainan islands. The results showed that empirically reconstructed pH_{SW} as well as $pCO_{2\ SW}$ were more in line with CO_2 chemistry observations than those calculated using the culture-based calibration, and that the correction values were different depending on locations.

2-1. Introduction

There are two motivations to develop past seawater CO_2 chemistry proxy. Firstly, to constrain atmospheric pCO_2 and climate sensitivity of the earth during warmer periods in the past (e.g., Pliocene epoch and Paleocene-Eocene Thermal Maximum) is one of the most important research subjects in paleoclimatology, because these periods are regarded as past-analogs of increasing atmospheric CO_2 level and subsequent global warming (Beerling & Royer, 2011; Seki et al., 2009). Secondly, it is urgently required to understand natural variability of CO_2 chemistry of biogeochemically, ecologically, and economically important regions; such as, equatorial upwelling, eastern boundary current - upwelling system, coral reefs, and estuaries (Hendriks et al., 2015; Kubota et al., 2014; Gruber et al., 2012), and their future responses, vulnerabilities, and resilience to environmental pollution of CO_2 (e.g., ocean acidification).

To date, a lot of studies have reared various genera of corals under artificially acidified seawater and measured $\delta^{11}B$ of coral skeletons to understand $\delta^{11}B$-pH_{SW} systematics (Holcomb et al., 2014; Dissard et al., 2012; Trotter et al., 2011; Krief et al., 2010; Raynaud et al., 2004; Hönisch et al., 2004) (Fig. 1-4, Table 1-3). However, it does not appear that the culture-based $\delta^{11}B$-pH_{SW} (and $pCO_{2\,SW}$) calibration for *Porites* corals can reconstruct reasonable pH_{SW} and $pCO_{2\,SW}$ during the last millennia (Kubota et al., 2014; Liu et al, 2014; Shinjo et al., 2013). For instance, Liu *et al.* (2014) calculated surface pH_{SW} from $\delta^{11}B$ of *Porites* spp. that was collected at Hainan Island (18.2°N, 109.5°E, Fig. 2-2) using a reported pH_{SW}-pH_{CF} relationship for cultured *Porites* coral (Trotter et al., 2011), but the reconstructed pH_{SW} decrease after the Industrial Revolution to the present was as much as 0.3, which is far different from the accepted value of ~0.1 (Doney et al., 2014; Gattuso & Hansson, 2011; Feely et al., 2009; Tans et al., 2009; Sabine et al., 2005; Key et al., 2004). Their reconstruction also indicated that $pCO_{2\,SW}$ in 2000 was 270 μatm when the calculation was made using TA of 2220.4 μmol/kg, SST of 26.9 °C, and SSS of 33.8, but it is unacceptably lower than the reported pCO_2 value of 360 μatm in the same year at the Southeast Asian Time-series Study (SEATS; 18°N, 116°E, Fig. 2-2) (Tseng et al., 2007). Similarly, Shinjo *et al.* (2013) reconstructed pH_{SW} at Guam (13.45°N, 144.76°E, Fig. 2-2) from $\delta^{11}B$ of *Porites* spp. using the same pH_{SW}-pH_{CF} relationship, but not only pH_{SW} values but also its decreasing trend, do not agree with pH_{SW} observation at the Station ALOHA

in Hawaii (Fig. 2-2) (Dore et al., 2009), although these islands are equally located inside of the north subtropical gyre and in weak CO_2 sink region (Fig. 2-1 & 2-2).

Therefore, we have to reconcile the discrepancy in order to use the $\delta^{11}B$-pH_{SW}-pCO_2 calibration in ecological and environmental studies. To establish the calibration, we employed massive *Porites* corals from Chichijima and Tahiti that live in the surface ocean with well-equilibrated atmospheric CO_2 (Fig. 2-1). Massive *Porites* corals, often used in paleoceanography, are characterized for its longevity, which means that they preserve, century-long geochemical records in their skeletons. Thus, in order to calibrate $\delta^{11}B$-pH_{SW}, we measured a 100 year record of $\delta^{11}B$ of long-lived *Porites* coral that was obtained at Chichijima and compared it with independently estimated pH_{SW} variations. In this strategy, the precision of $\delta^{11}B$ measurements are essential, because surface pH_{SW} decreases due to the anthropogenic DIC addition since the Industrial Revolution is 'only' ~0.1 (it is translated into ~1.0‰ in $\delta^{11}B$). As for Tahiti, as we could not obtain modern coral samples, we utilized previously published $\delta^{11}B$ values of *Porites* corals for the calibration (Douville et al., 2010; Gaillardet & Allegre, 1995).

To summarize, the purpose of this chapter is to establish the empirical $\delta^{11}B$-pH_{SW} calibrations in order to use them in paleoclimatology and paleoceanography. In the calibartion, we used a modern long-lived coral collected at Chichijima, two modern corals collected at Moorea (the west of Tahiti), and one fossil coral obtained at Marquesas (dated to 1750 AD) (Fig. 2-1). The difference of $\delta^{11}B$ values from the theoretically expected values, that is the offset *a* in Equation (1-14), are determined in Chichijima and Tahiti regions.

(a) Surface seawater pCO$_2$ (µatm)

(b) Chichijima

(c) Tahiti-Moorea

Fig. 2-1. (**a**) Same as **Fig. 1-7b**, but islands mentioned in this chapter are indicated in diamonds. (**b,c**) A bathymetric map around Chichijima and Tahiti. The modern coral of Chichijima was collected at locations well flushed with open ocean seawater (black diamond).

Fig. 2-2. Climatological mean sea surface dynamic height in the western North Pacific region (in units of m relative to the 1,000 m level). Blue arrows represent Kuroshio and the NEC.

2-2. Material & Methods

2-2-1. $\delta^{11}B$ measurements of Chichijima coral

A *Porites* spp. that lived in 5.6 m deep water was cored in 2002. A sampling location is not a closed environment (e.g., reef flat), but was an opened environment that receives good circulation of open ocean seawater (Fig. 2-1). This justifies the comparison of coral $\delta^{11}B$ variations with open ocean pH_{SW}. After sonification under distilled water, coral skeleton was drilled along the major growth direction and just 1-year resolution sub-samples, from 1873–2002 (one summer to the next summer) were obtained. We discarded the sub-samples from the top 4 years due to geochemical alterations (Felis et al., 2009). We also discarded those prior to 1910 because a previous study reports large climatic regime shift from 1905–1910 (Felis et al., 2009). To prepare 3-year resolution subsamples for $\delta^{11}B$ measurements (typically 3–6 mg of carbonate), we mixed the same amount of annual sample. $\delta^{11}B$ were measured using two methodologies: P-TIMS and MC-ICPMS. Ishikawa and Nagaishi (2011) reports the methodology using the P-TIMS and Tanimizu *et al.* (in prep.) reports that using the MC-ICPMS (Fig. 2-3).

For the P-TIMS method, after removing organic matter using a 30% H_2O_2 for ~12 hours, boron were purified by cation and anion exchange using AG 50W X12 and 1-X4 resin (Bio-Rad, USA). Then, cesium and mannitol were added to produce and stabilize cesium-borate complex. The solution was dried in a 60 °C oven for 12 hours. The obtained material was dissolved in distilled water and 309/308 isotopic ratio were measured using Thermo Finnigan TRITON at Kochi Institute for Core Sample Research. All reported $\delta^{11}B$ values are the average of replicate analyses (2–4 times, Table 2-1). Repeated analysis of the JCp-1 (Okai et al., 2004), homogenized powder of *Porites* coral skeleton collected at Ishigakijima (Fig. 2-1 & 2-2), yielded 24.28 ± 0.14‰ (2σ, n = 14) where boron isotopic ratios of coral samples were expressed as per mil deviations from the values of standard (NIST SRM 951):

$$\delta^{11}B = \left[\frac{(^{11/10}B)_{sample}}{(^{11/10}B)_{std}} - 1 \right] *10^3$$

$$= \left[\frac{(^{309/308}Cs_2BO_2)_{sample} - 0.00079}{(^{309/308}Cs_2BO_2)_{std} - 0.00079} - 1 \right] *10^3$$

(Eq. 2-1)

We used ± 0.14‰ as the analytical uncertainty of $\delta^{11}B$ measurements of Chichijima coral.

For the MC-ICPMS method, the wet chemistry was the same as the P-TIMS method until the ion exchange. After the ion exchange, lithium-spike instead of caesium was added in order for the drift correction during measurements. $\delta^{11}B$ values were measured using a sample-standard bracketing routine on Thermo Finnigan NEPTUNE at Kochi Institute for Core Sample Research without replicate analysis. We used the recommended value of ± 0.25‰ as the analytical uncertainty of $\delta^{11}B$ (Tanimizu et al., in prep.).

Fig. 2-3. Schematic procedures of boron isotope analyses of coral samples.

Table 2-1. Measured $\delta^{11}B$ values for Chichijima coral.

| Sample name | $\delta^{11}B$ values | | | pH_{SW} |
| | P-TIMS | | MC-ICPMS | |
		mean		
OGA02_3Y_1997	23.92	23.84	23.65	8.12
	23.95			
	23.71			
	23.77			
OGA02_3Y_1992	23.88	23.84	23.77	8.12
	23.81			
	23.79			
	23.87			
OGA02_3Y_1987	24.11	24.22	24.39	8.14
	24.26			
	24.30			
OGA02_3Y_1982	23.77	23.89	24.08	8.15
	23.97			
	23.92			
OGA02_3Y_1977	24.24	24.17	23.61	8.14
	24.11			
OGA02_3Y_1972	24.75	24.71	24.99	8.14
	24.69			
	24.70			
OGA02_3Y_1966	24.19	24.16	24.28	8.16
	24.13			
OGA02_3Y_1960	24.48	24.43	24.47	8.16
	24.44			
	24.37			
OGA02_3Y_1954	24.59	24.56	24.57	8.15
	24.54			
OGA02_3Y_1948	24.24	24.28	24.48	8.16
	24.31			

Continued

OGA02_3Y_1942	24.29	24.28	24.75	8.17
	24.26			
OGA02_3Y_1935	24.39	24.38	24.40	8.17
	24.38			
OGA02_3Y_1928	24.86	24.76	25.02	8.18
	24.72			
	24.71			
OGA02_3Y_1921	24.13	24.06	23.87	8.18
	24.03			
	24.01			
OGA02_3Y_1914	24.26	24.41	24.33	8.18
	24.53			
	24.43			

2-2-2. δ^{11}B values of Tahiti and Marquesas corals

In the δ^{11}B-pH$_{SW}$ calibration We also used previously reported δ^{11}B values of corals that were obtained from Moorea, the west of Tahiti, and Marquesas (Fig. 2-1) (Douville et al., 2010; Gaillardet & Allegre, 1995). As these values are determined by different analytical procedures, firstly we corrected the analytical procedure-specific isotopic offset (Foster et al., 2010) using Equation (1-11). We used the recommended value of 39.61‰ for δ^{11}B$_{SW\text{-}stacked}$ (Foster et al., 2010).

2-2-3. pH$_{SW}$ estimation since 1970

Long-term pH$_{SW}$ monitoring sites do not exist in the tropical-subtropical Pacific, except for the Station ALOHA (Dore et al., 2009) and the repeat hydrographic line at 137°E by Japanese Meteorological Agency (JMA) (e.g., Midorikawa et al., 2012, 2010; Ishii et al., 2011, 2001). Thus we estimated pH$_{SW}$ variations from sporadic seawater CO_2 chemistry data that have been measured in the open ocean through research cruises. There are many international programs that measured various CO_2 chemistry parameters (i.e., DIC, TA, pH, pCO$_2$, and fCO$_2$), and the combined data to understand horizontal and vertical distributions, temporal variation, and amount of anthropogenic CO_2 incorporation by the ocean (e.g., WOCE, World Ocean Circulation Experiment; JGOFS; Joint Global Ocean Flux Study; GEOSECS, Geochemical Ocean Sections program; CLIVAR, Climate Variability and Predictability Project). In such efforts, the data compilation by Surface Ocean Carbon Atlas (SOCAT) has large and quality-controlled data sets of fCO$_2$ measurements in the open ocean surface layer. This data set is suitable for the purpose of this thesis because *Porites* corals live in the surface ocean in order to obtain sunlight for photosynthesis. Hence, in this thesis, we used SOCAT fCO$_2$ data (version 2, Bakker et al., 2014) to estimate pH$_{SW}$ variation at Chichijima, Hawaii, Tahiti, and Marquesas. We extracted the data using 1.0° latitude by 5.0° longitude grids centered on Chichijima and Hawaii. As for Tahiti and Marquesas, we enlarged the grids (5° latitude by 10° longitude) to extract the data, because fCO$_2$ data is less abundant in the South Pacific and the equatorial Pacific than in the North Pacific. In the calculation, we used ancillary *in situ* data of SST and SSS to each fCO$_2$ data-point. For grid points where SSS data was not available, we imported

climatological salinity values from the World Ocean Atlas 2005. We estimated TA from TA-SSS relationships from Midorikawa *et al*. (2010) for Chichijima and Kutchinke *et al*. (2014) for Hawaii, Tahiti, and Marquesas, respectively:

$$TA = nTA * SSS / 35 = 2295 * SSS / 35 \qquad\qquad \text{(Eq. 2-2, Midorikawa et al., 2010)}$$

$$TA = 2300 + 66.3 * (SSS - 35) \qquad\qquad \text{(Eq. 2-3, Kuchinke et al., 2014)}$$

Midorikawa *et al*. (2010)'s relationship is based on continuous TA and SSS measurements by JMA at the 137°E line and Kuchinke *et al*. (2014)'s one is based on the compilation of discrete TA and SSS data by GLODAP and CLIVAR. We calculated DIC from fCO$_2$ and assuming TA using CO2Calc software (version 1.0, Robins et al., 2010). Then we normalized DIC at a salinity of 35 (nDIC), and fitted it to an empirical function of the timing of measurement (year), SST, and SSS by multi-parameter regression (See Ishii et al. (2011) for detail):

$$
\begin{aligned}
nDIC &= DIC * 35 / SSS \\
&= f(yr, SST, SSS) \qquad\qquad\qquad \text{(Eq. 2-4)} \\
&= C_0 + C_1 * yr + C_2 * temp + C_3 * temp^2 + C_4 * temp^3 + C_5 * sal + \varepsilon
\end{aligned}
$$

Here yr = year - 1994, $temp$ = SST - T$_{ave}$, and sal = SSS - S$_{ave}$. Average temperature (T$_{ave}$) and salinity (S$_{ave}$) was separately specified for Chichijima, Hawaii, Tahiti, and Marquesas (Table 2-2). The terms $C_0 \sim C_5$ are coefficients of multiple regressions, and ε represents the residual of the fitting (Table 2-2). The polynomial of *temp* in the equation exhibits strong correlation with nDIC and SST (Ishii et al., 2011).

Table 2-2. Parameters of multi-regression analysis.

Parameter	Location			
	Chichijima	**Hawaii**	**Tahiti**	**Marquesas**
C_0	1958.7	1965.9	1934.3	1961.7
C_1	1.15	1.22	0.76	1.07
C_2	-2.22	-3.49	-4.9	-17.5
C_3	0.30	0.76	0.53	-1.44
C_4	-0.05	-0.56	0.26	-2.32
C_5	-12.0	-13.5	1.51	-52.5
T_{ave} (˚C)	24.7	25.0	27.4	27.9
S	34.5	35.0	35.9	35.6
RMSE	6.7	5.8	5.5	7.4
R^2	0.74	0.58	0.54	0.84
N	1034	11205	1440	4314

2-2-4. pH$_{SW}$ estimation since the Industrial Revolution

High-precision seawater CO_2 chemistry measurements are limited to the past 40 years, and Equation (2-4) can overestimate preindustrial pH$_{SW}$ (e.g., preindustrial pH$_{SW}$ at Tahiti is equivalent to ~8.45, Kubota et al., 2014) because of an assumption that nDIC increased linearly with time. Thus we extended pH$_{SW}$ estimation prior to the Industrial Revolution using atmospheric pCO$_2$ records from a continuous observation at the Mauna Loa Observatory (MLO) and air trapped in the Antarctic ice sheet (Tans & Keeling, 2014; Rubino et al., 2013). We used the method modified from Tans (2009), which uses an empirical pH$_{SW}$ estimation equation based on atmospheric pCO$_2$, taking into account the reaction of borate with anthropogenic CO_2:

$$\text{pH}_{SW} = \text{pH}_{\text{pre-industrial}} - b * \log\left(\frac{p\text{CO}_{2\,\text{atm}}}{280}\right) \qquad \text{(Eq. 2-5)}$$

2-3. Results & Discussion

2-3-1. Comparison of $\delta^{11}B$ values measured in different methods

Firstly, we compared $\delta^{11}B$ variation measured by two methodologies: P-TIMS and MC-ICPMS (Fig. 2-4). Both records showed relatively steady values until 1966, and then decreased. It is consistent with the prediction that ocean acidification accelerated after 1960 reflecting atmospheric CO_2 level (Rubino et al., 2013; Francey et al., 1999; Etheridge et al., 1996). A cross-plot reveals that the relationship is not necessarily one to one (Fig. 2-4). Tanimizu *et al.* (in prep) points out that $\delta^{11}B$ value measured by the MC-ICPMS is systematically, ~0.1‰ higher than that measured by the P-TIMS. It is consistent with the fact that measured $\delta^{11}B$ values of JCp-1 in this thesis was 24.36‰ (2σ, n = 4), 0.08‰ higher than that measured by the P-TIMS (24.28 ± 0.14‰, 2σ, n = 14). However, after correcting the offsets, a slight discrepancy between them still remains (Fig. 2-4). There is a possibility that discrepancy may be related to (1) heterogeneity of prepared subsample and (2) isotopic fractionation during the P-TIMS measurements due to isobaric ions interference derived from organic matter in the coral skeleton (Wu et al., 2012; Ishikawa & Nagaishi, 2011), or a combination of the two. To identify the reason for this discrepancy is an important future research theme, but it is beyond the scope of this thesis. In addition, $\delta^{11}B$ variation measured by the MC-ICPMS has larger amplitude than that measured by the P-TIMS. As we did not replicate $\delta^{11}B$ measurements and precision of the MC-ICPMS method is at present worse than the P-TIMS method, we will discuss the P-TIMS data only in the following sections and Chapter 3. $\delta^{11}B$ variation measured by the P-TIMS showed no statistically significant trend from 1907 to 1960, but showed statistically significant decreasing trend after 1960 (-0.17 ± 0.07‰/decade, p = 0.05). It is consistent with the acceleration of ocean acidification after 1960.

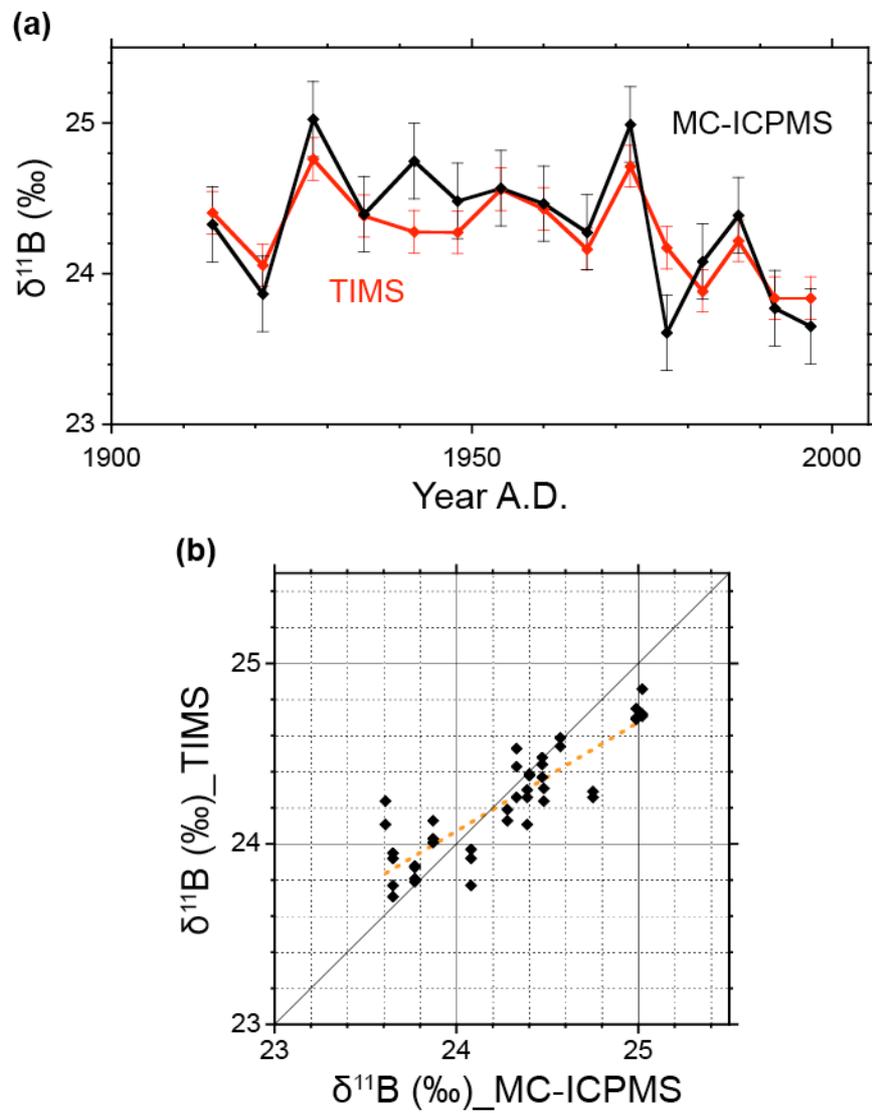**Fig. 2-4.** Comparison of δ¹¹B values of Chichijima coral measured in P-TIMS and MC-ICPMS methods. (**a**) Variation since 1914. (**b**) P-TIMS versus MC-ICPMS. Linear regression line (r = 0.87, p < 0.01, n = 41) and one-to-one line are indicated in yellow and black.

2-3-2. pH$_{SW}$ estimation since 1970

We obtained an empirical regression equation for Chichijima ($R^2 = 0.74$, n = 1,034), Hawaii ($R^2 = 0.58$, n = 11,205), Tahiti ($R^2 = 0.54$, n = 1,440), and Marquesas ($R^2 = 0.84$, n = 4,314) using the parameters summarized in Table 2-2. Root mean squares of ε were 6.7, 5.8, 5.5, and 7.4 μmol/kg, respectively. We used SST and SSS from the Simple Ocean Data Assimilation (SODA version 2.1.6, Carton & Giese, 2008) to estimate monthly values of nDIC for the years 1970–2008, and calculated pH$_{SW}$ and pCO$_{2\ SW}$ from DIC and assuming TA using CO2Calc (Fig. 2-5). Results show that around the studied islands, pH$_{SW}$ is decreasing and pCO$_{2\ SW}$ is increasing at a consistent rate with atmospheric pCO$_2$ since 1970 (Fig. 2-5). Reflecting SST seasonality, cyclic variation is seen in pH$_{SW}$ and pCO$_{2\ SW}$ variation of Chichijima, Hawaii, and Tahtii (Kubota et al., 2014; Ishii et al., 2011, 2002; Dore et al., 2009). Large pH$_{SW}$ and pCO$_{2\ SW}$ seasonality in Chichijima is due to large SST seasonality. On the other hand, Marquesas records show complex variation, reflecting stochastic nature of oceanography in the equatorial Pacific (Sutton et al., 2014; Feely et al., 2002).

In order to evaluate the validity of the empirical regression equation, we compared pH$_{SW}$ and pCO$_{2\ SW}$ time series for Chichijima area with more continuous and abundant measurements at the Line 137°E (Masao Ishii, personal communications). JMA has measured seawater CO$_2$ chemistry repeatedly along this line since 1981. This different data set has two types: one is discrete monthly data for 26.5–27.5°N, 125–145°E (see Midorikawa *et al.* (2012) for detail), and the other is a time series data set for 27°N, 137°E grid point for the years 1993–2010 (Fig. 2-6). We observed only a slight difference in summer between my estimation and the discrete records by JMA (Fig. 2-6). This slight difference is also seen between discrete records and time series data by JMA. A weak biological productivity in summer is a probable cause, because this effect is not reflected in the multiparameter regressions (Masao Ishii, personal communications). Though the time series for 27°N, 137°E grid point (about 500 km west of Chichijima) was estimated using different methodologies from my estimation, these data are in excellent agreement (Fig. 2-6). For instance, it extracts CO$_2$ chemistry data from different areas; it sets different regression parameters; and it uses different SST and SSS data sets (that is, monthly 1° × 1° resolution records from the multivariate ocean variational estimation system (MOVE-G, Usui et al., 2006)). This supports the validity

of pH_{SW} and $pCO_{2\ SW}$ estimation in this thesis, and suggests that the time series from the Ogasawara area may represent the wide range of the western North Pacific.

Using CO_2 chemistry data around Hawaii, we further assessed the reliability of pH_{SW} and $pCO_{2\ SW}$ estimation in this thesis, because there exists continuous pH_{SW} observation since 1988 (i.e., HOT, *http://hahana.soest.hawaii.edu/hot/*). It is important to note that SOCAT v2 data around Hawaii is especially abundant during 2005 and 2009, which enables the comparison in detail. The estimated pH_{SW} time series captures its seasonality quite well (Fig. 2-7). We observed a small underestimation of seasonality in estimated time series compared with pH_{SW} measurements at the Station ALOHA since 1988 (one is directly measured, and the other is calculated from DIC and TA; Dore et al., 2009) (Fig. 2-7). A part of underestimation may be due to biological productivity, as similar to Chichijima. It should be noted that the small discrepancy in pH_{SW} seasonality has a negligible effect on annual mean pH_{SW}.

In order to estimate pH_{SW} and $pCO_{2\ SW}$ differences between Tahiti and Marquesas, we made calculations removing the second term in Equation (2-4). Through this treatment, long-term pH_{SW} decreases and pCO_2 increases are detrended. Since Marquesas is located closer to the equatorial upwelling zone than Tahiti, pH_{SW} ($pCO_{2\ SW}$) is lower (higher) by 0.04 (43.9 µatm) (Fig. 2-8). All calculations considered this offset through this thesis.

Fig. 2-5. pH_{SW} and pCO_2 variation during 1980–2015 in the vicinity of (**a,b**) Chichijima, (**c,d**) Hawaii, (**e,f**) Tahiti, and (**g,h**) Marquesas. Calculations were made using SOCATv2 fCO_2 datasets (black diamonds) (Bakker et al., 2014) and time-series were estimated by multi-regression analysis (gray lines) (Ishii et al., 2011). Atmospheric pCO_2 measured in the MLO is also plotted (red lines) (Tans & Keeling, 2014).

Fig. 2-6. (**a,b**) Comparison of pH$_{SW}$ and pCO$_2$ variation during 1980–2015 in the vicinity of Chichijima (time-series; gray line) with those from the 137°E continuous measurements by the JMA (sporadic data, blue circles; monthly time-series, blue dashed line) (Masao Ishii, personal communication). Atmospheric pCO$_2$ measured at the MLO is also plotted in **b** (a red line) (Tans & Keeling, 2014).

Fig. 2-7. (a) Same as **Fig. 2-5e**, but for years 2005–2009 when data are abundant. Comparison of pH$_{SW}$ time-series with continuous pH$_{SW}$ measurements at the Station ALOHA (directly measured pH$_{SW}$, orange; calculated from DIC and TA, green) (Dore et al., 2009).

Fig. 2-8. Differences of (**a**) pH$_{SW}$ and (**b**) pCO$_2$ between Tahiti and Marquesas for the years 1980–2000. Linear regressions are shown in dashed line.

2-3-3. pH$_{SW}$ estimation since the Industrial Revolution

We used two boundary conditions of pH$_{SW}$ and atmospheric pCO$_2$ for 1994 and the Insudtrial revolution to determine the constant b in Equation (2-5). Firstly we calculated pH$_{SW}$ in 1994 from DIC and TA of GLODAP v1.1 (Key et al., 2004). Secondly, we calculated preindustrial pH$_{SW}$ by subtracting anthropogenic DIC increase of 50 μmol/kg since the Insudtrial Revolution from present DIC (Key et al., 2004; Sabine et al., 2004, 2002). In this calculation TA was kept constant, because CO$_2$ invasion against the ocean does not influence TA (e.g., Zeebe & Wolf-Gradlow, 2001). We determined b as 0.7 (Fig. 2-9). Furthermore, we calculated pCO$_{2 \, SW}$ from pH$_{SW}$ assuming present SST, SSS, and TA (Fig. 2-9). The estimated pCO$_{2 \, SW}$ values in 2000 are 333.1 and 349.5 μatm in Chichijima and Tahiti, respectively (Fig. 2-9). They are consistent with surface pCO$_2$ distribution (Fig. 2-1) (Takahashi et al., 2009). In addition, their rates of increase since 1970 agree well with those of multiparameter regression (Fig. 2-5). Calculated pCO$_2$ increases keeping ΔpCO$_2$ constant in both Chichijima and Tahiti, suggesting that no significant change in biological productivity occurred since the Industrial Revolution despite global climate change (e.g., ocean acidification, global warming, and deoxygenation; Doney et al., 2014; Gruber, 2011).

Fig. 2-9. (**a-d**) Estimated pH$_{SW}$ and pCO$_{2\ SW}$ variation since the Insudtrial Revolution for the surface water surrounding Chichijima and Tahiti. Black points represent atmospheric pCO$_2$ records (Tans & Keeling, 2014; Rubino et al., 2013). Time-resolutions are "just 1 year" for observation at the MLO (Tans & Keeling, 2014) and "several years" for Antarctic ice core records depending on a gas smoothing in the surface layer of ice (Rubino et al., 2013). pH$_{SW}$ and pCO$_{2\ SW}$ calculated from GLODAP v1.1 data for the closet grid to each island are plotted in green diamonds (Key et al., 2004).

2-3-4. δ^{11}B-pH$_{SW}$ calibration and errors

Based on the empirical calibration by Hönisch *et al*. (2007) outlined in Chapter 1, we determined "offset *a*" for Chichijima and Tahiti corals through comparing δ^{11}B and pH$_{SW}$ (Fig. 2-10). We selected the best-fit offset *a* that yielded the minimum chi-square values.

$$\chi^2 = \sum_{i=1}^{N} \left(\frac{pH_{SW-calculated} - pH_{SW-estimated}}{\sigma_i} \right)^2 \qquad \text{(Eq. 2-6)}$$

Here N is the number of measurements and σ is the uncertainty of each data point. In the calculation of pH$_{SW}$ using Equation (1-14), we used the fractionation factor from Klochko *et al*. (2006) and pK_B listed in Table 2-3. As for Marquesas coral, we added 0.04 to the calculated pH$_{SW}$ to compensate for the pH$_{SW}$ difference between Tahiti and Marquesas (Fig. 2-8). Determined *a* values were -5.07 and -5.92 for Chichijima and Tahiti, respectively (Table 2-3). We will use obtained δ^{11}B-pH$_{SW}$ calibration for Tahiti in Chapter 4.

We estimated errors of pH$_{SW}$ estimation derived from the δ^{11}B-pH$_{SW}$ fitting as well as analytical uncertainty. We did not estimate the fitting error of Tahiti-Marquesas calibration, because there are only three data points. We estimated the statistical error of offset *a* (unit is ‰) through finding χ^2 that exhibit ± 1 from the minimum χ^2. We determined them as +0.04 and -0.04 (-5.07 ± 0.04, 1σ). We combined errors derived from δ^{11}B (± 0.07, 1σ, n = 14) and offset *a* using Equation (1-14):

$$\sigma_{pH}(\delta^{11}B \& a) = \sqrt{\left(\frac{\partial pH}{\partial \delta^{11}B} * \sigma(\delta^{11}B) \right)^2 + \left(\frac{\partial pH}{\partial a} * \sigma(a) \right)^2} \qquad \text{(Eq. 2-7)}$$

Here we made the calculation with fractionation factor and δ^{11}B$_{SW}$ as constant (1.0272 and 39.61‰, respectively). When we chose 24.5‰ as a representative value of δ^{11}B, σ_{pH} (δ^{11}B & *a*) is ± 0.006 (1σ). However, it does not consider an error derived from δ^{11}B-pH$_{SW}$ fitting as seen in deviations from the fitted pH$_{SW}$ curve beyond the analytical uncertainty (Fig. 2-10). Thus we regarded a standard deviation of pH anomalies (pH$_{SW-calculated}$-pH$_{SW-estimated}$) as the error derived from the fitting (± 0.020, 1σ, n = 15).

Finally, we calculated a combined error in the pH_{SW} estimation (σ_{pH}):

$$\sigma_{pH} = \sqrt{\sigma_{pH}(\delta^{11}B \,\&\, a)^2 + \sigma_{pH}(\text{fitting})^2}$$

(Eq. 2-8)

The finally obtained error was ± 0.021 (1σ). It indicates that the error derived from the fitting dominates the overall error.

Another way to determine the net error of pH_{SW} estimation is to utilize a probabilistic value in the chi-square fitting. In this, we can regard σ_i as a comprehensive error of $\delta^{11}B$-pH_{SW} proxy. Chosing σ_i in Equation (2-6) that satisfy 95% significance level, we determined σ_i as ± 0.028 (1σ, $\chi^2 = 6.365$, df = 14, p = 0.96) (Fig. 2-11). It is slightly higher than the error determined by the aforementioned procedure (i.e., ± 0.021, 1σ), but it means that there is an only 5% chance that the $\delta^{11}B$-pH_{SW} calibration will reconstruct questionable pH_{SW}.

Results of error estimation indicate that even if we adopt a larger error (± 0.028, 1σ), we can resolve pH_{SW} seasonality (about 0.1 pH unit) with statistical significance from high resolution $\delta^{11}B$ measurements of Chichijima coral. Similarly, if we can collect fossil *Porites* coral from Chichijima in the future (it has never been documented), we can resolve pH_{SW} difference between glacial to interglacial periods (about 0.1 pH unit) from $\delta^{11}B$ measurements of them. We should keep in mind the errors in pH_{SW} reconstruction discussed here. However, needles to say, further efforts to reduce errors and to investigate temporal and inter-colonial variation of offset *a* are necessary to increase applicability of pH_{SW} proxy.

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Fig. 2-10. (a) δ^{11}B-pH$_{SW}$ calibration using modern *Porites* coral collected at Chichijima. Replicated δ^{11}B values during 1914–1997 measured by the P-TIMS is used. Time resolution of each point is three years. Error bars are 2σ of analytical uncertainty. **(b)** δ^{11}B-pH$_{SW}$ calibration using modern and fossil *Porites* corals (Douville et al., 2010; Gaillardet & Allegre, 1995). Modern corals are for the years 1991 and 1950. pH$_{SW}$ calculated from δ^{11}B of fossil coral (1700) that was collected at Marquesas is used after a pH$_{SW}$ correction (add +0.04 pH unit). Time resolution of each point is one or two years (Douville et al., 2010). Error bars are 2σ of analytical uncertainty.

Fig. 2-11. (**a**) Same as **Fig. 2-10a**, but larger error bars are adopted to satisfy 95% confidence level of the chi-square fitting. (**b**) χ^2 and p values when σ_i is 0.028. The maximum p value is 0.96, which satisfies 95% confidence level.

Table 2-3. A summary of *Porites* corals and parameters used in the δ^{11}B-pH$_{SW}$ calibration.

Location	Resolution (years)	Reference	T (°C)	S	pK_B	offset a (‰)
Chichijima	3	This study	24.7	34.5	8.60	-5.07
Tahiti	1 or 2	Douville et al., 2010;	27.4	35.9	8.57	-5.92
Marquesas		Gaillardet & Allegre, 1995	27.9	35.6	8.56	
Hainan	4	Liu et al., 2014	26.9	33.8	8.58	-4.5
Guam	1	Shinjo et al., 2013	28.4	34.4	8.56	-4.0

2-3-5. Location-specific difference of offset *a*

Using offset *a* of -5.07 (for Chichijima coral), we recalculated pH_{SW} and $pCO_{2\ SW}$ from $\delta^{11}B$ of Hainan and Guam corals (Liu et al., 2014; Shinjo et al., 2013) using present SST, SSS, and TA that were calculated from Equation (2-3). The calculated pH_{SW} and $pCO_{2\ SW}$ were more reasonable than the values originally calculated using the pH_{SW}-pH_{CF} relationship of cultured *Porites* corals (Trotter et al., 2011), however most of the calculated $pCO_{2\ SW}$ still remained higher than the atmospheric pCO_2. This indicates that Hainan and Guam are located in CO_2 "source" region, which obviously contradicts with the observed pCO_2 distributions (Fig. 2-1) (Takahashi et al., 2009; Tseng et al., 2006). Instead, suitable *a* values appear to be about -4.5 and -4.0 for Hainan and Guam corals, respectively (Fig. 2-12, Table 2-3). If these values are correct, we can reconcile three issues: (1) pCO_2 values in 2000 for Hainan and Guam areas, (2) pH_{SW} decrease since the Industrial Revolution in Hainan area, and (3) pH_{SW} values and its decreasing trend for the last 60 years in Guam area (Fig. 2-12). Larger $pCO_{2\ SW}$ values than the atmospheric pCO_2 sporadically seen in both Hainan and Guam areas may be due to internal climate variability from interannual to decadal timescales. For instance, monsoonal wind and El Nino - Southern Oscillation (ENSO) can respectively influence CO_2 chemistry in the surface ocean of these areas (Liu et al., 2014; Shinjo et al., 2013).

The difference of offset *a* among locations (i.e., Chichijima, Tahiti, Guam, and Hainan) indicates that there is no ubiquitous calibration equation and paleo-pH_{SW} reconstruction needs *in situ* calibration using one or more modern corals. The reason why there are differences between field-based and culturing-based calibrations is perhaps related to the fact that culture experiments assume severe acidification that can exert a bad influence on coral physiology. In fact, Krief *et al.* (2010) found that skeletal growth of cultured massive *Porites* spp. decreased in acidified seawater. Similarly, many culture experiments on massive *Porites* spp. have reported inhibition of calcification under high pCO_2 level (e.g., Iguchi et al., 2014, 2012). This issue will be further discussed in Chapter 3.

Fig. 2-12. Reconstructed pH_{SW} and $pCO_{2\ SW}$ from $\delta^{11}B$ of *Porites* corals that were collected at Hainan (purple, Liu et al., 2014) and Guam (light blue, Shinjo et al., 2013) since (**a,b**) 1000 and (**c,d**) 1800 to the present. Time-resolutions are 4 years for Hainan coral and 1 year for Guam coral. Calculations were made using Equation (1-14) with *a* values of -4.5 and 4.0, respectively. pH_{SW} seasonality measured at the Station ALOHA (Dore et al., 2009) and atmospheric pCO_{2} records (Tans & Keeling, 2014; Rubino et al., 2013) are also shown.

2-4. Conclusion

We showed that even though there is no monitoring site, we can estimate not only annual variation but also seasonality of pH_{SW} utilizing abundant open ocean CO_2 chemistry measurements using research vessels since 1970. We confirmed the validity of the estimation of time series through comparison with more abundant and continuous measurements at the Line 137°E and the Station ALOHA. We extended pH_{SW} estimation from the recent ~45 years further back to the preindustrial period utilizing atmospheric pCO_2 measurements at the MLO and reconstructions from Antarctic Ice cores. Measured $\delta^{11}B$ of *Porites* coral collected at Chichijima showed no statistically significant trend from 1907 to 1960 and then decreased (-0.17 ± 0.07‰/decade, p = 0.05), being consistent with acceleration of pH_{SW} decrease after 1960 (i.e., ocean acidification). A comparison between obtained pH_{SW} and measured $\delta^{11}B$ variation enabled me to calibrate $\delta^{11}B$-pH_{SW} relationship. We found that offset *a* values of modern corals were different from location to location (i.e., Chichijima, Tahiti, Hainan, and Guam), which means that we must establish the $\delta^{11}B$-pH_{SW} calibration where we collect fossil corals. The newly employed calibration reconciled several discrepancies between CO_2 chemistry observations and pH_{SW} and pCO_2 $_{SW}$ reconstructions using culturing-based $\delta^{11}B$-pH_{SW} calibrations. The field-based calibration proposed by this chapter will become a new means to reconstruct past pH_{SW} and pCO_2 (both seawater and atmosphere), but it is clear that more works are needed to investigate temporal and inter-colonial variation of offset *a*.

CHAPTER 3

Effects of recent ocean acidification in the western North Pacific on *Porites* coral calcification

Chapter 3 Abstract

Marine calcifying organisms such as scleractinian corals are being threatened by rapid ocean acidification (OA) due to the oceanic uptake of anthropogenic CO_2. To better understanding how organisms and ecosystems will adapt to or be damaged by the resulting changes in environments, field observations are crucial. Here we show clear evidence, based on $\delta^{11}B$ measurements, that OA is affecting the pH_{CF} in *Porites* coral collected at Chichijima, one of the Ogasawara Islands, an archipelago located in the western North Pacific Subtropical Gyre. A rapid decline of $\delta^{11}B$ of coral skeleton since 1960 (-0.17 ± 0.07‰/decade) was observed and was compared with pH_{SW} near the Chichijima over the 20th century, as estimated from a large number of shipboard measurements of seawater CO_2 chemistry and atmospheric CO_2. The results indicate that pH_{CF} has been changing sensitively to pH_{SW} and suggest that the calcification fluid of coral will become corrosive to aragonite in the future (pH_{CF} = ca. 8.3 when pH_{SW} = ca. 8.0 in 2050) at an earlier point than previously expected, despite the pH_{CF} up-regulation mechanism of coral.

3-1. Introduction

When CO_2 dissolves in seawater, it becomes a carbonic acid and perturbs the weakly alkaline seawater toward an even less alkaline state. Surface pH_{SW} is considered to have declined by about 0.1 since the beginning of the industrial era, and an additional decline of approximately 0.3 is projected by the end of this century (Doney et al., 2014; Gattuso & Hansson, 2011; Feely et al., 2009; Tans et al., 2009; Orr et al., 2005; Sabine et al., 2005; Key et al., 2004; Caldeira & Wickett, 2003). The impact of OA is thought to manifest earlier in polar oceans than in tropical-subtropical ones (Feely et al., 2009), although it has also been suggested that coral reef ecosystems are more susceptible to a decline of pH_{SW} and saturation state with respect to aragonite (Ω_{ar}) (Hoegh-Guildberg et al., 2011; Pandolfi et al., 2011; Gattuso & Hansson, 2011; Kleypas & Yates, 2009; Doney et al., 2009; Kleypas & Langdon, 2007; Kleypas et al., 1999a,b). As relative changes of seawater Ω_{ar} ($\Omega_{ar\ SW}$) in tropical-subtropical oceans are bigger than in polar oceans (Feely et al., 2009), this will lead to severe consequences. A critical threshold below which reef growth will be hampered is still contested, although is often claimed based on field observations to be 3.3 (Hoegh-Guildberg et al., 2011; Kleypas & Langdon, 2007; Kleypas et al., 1999b). In the surface layers of tropical-subtropical oceans, $\Omega_{ar\ SW}$ is projected to decline as low as 3.3 by 2050, when atmospheric CO_2 level will exceed about 480 µatm (Hoegh-Guildberg et al., 2011; Feely et al., 2009).

To better understand the response of corals under acidified water, we employed long-living corals. As these corals have already been experienced OA over centuries, especially for the last 50 years, after the post-1960s growth of anthropogenic CO_2 emissions. Field-based observations have several advantages compared to culture experiments, since culture experiments often put corals under excessively acidic water (e.g., pH < 7.8) that coral reefs rarely experience in the wild, and will in fact not even experience this century under business as usual CO_2 emissions scenario (e.g., Krief et al., 2010; Hönisch et al., 2004)

To attain the purpose, we chose Chichijima as a study region. The ocean surrounding Chichijima is oligotrophic with limited vertical mixing and low biological productivity (Ishii et al., 2011, 2001). A seasonal change dominates temporal variability in pH_{SW} as is observed as $pCO_{2\ SW}$ (Fig. 3-1), driven mainly by seasonal variation in SST (about 20°C in winter and about 29°C in summer) and in part by variation in the

DIC content (about 1960 µmol/kg in summer and about 1990 µmol/kg in winter at years around 2010 when normalized to salinity of 35). A trend of $p\mathrm{CO}_{2\,SW}$ increase (and pH_{SW} decrease) in the northern subtropical zone of the western North Pacific is nearly tracking the rate of the atmospheric CO_2 increase (Fig. 3-1) (Midorikawa et al., 2012, 2010). These oceanographic characteristics strengthen the reliability of seawater CO_2 chemistry estimation for both seasonal and interannual timescales.

To summarize, objectives of this chapter is to gain insights of effects of OA over the last 100 years on the calcification of Chichijima coral based on pH up-regulation mechanisms (Chapter 1). We regarded $\delta^{11}\mathrm{B}$ of Chichijima coral (Chapter 2) as an indicator of pH_{CF}, and compared it with pH_{SW} that was estimated from CO_2 chemistry observation and atmospheric $p\mathrm{CO}_2$ records (Tans & Keeling, 2014; Rubino et al., 2013). We did not discuss Tahiti-Marquesas corals (Chapter 2), because these records do not consist of a single colony (Douville et al., 2010; Gaillardet & Allegre, 1995) and are not suitable to investigate biological responses to the changing environment.

Fig. 3-1. (**a-c**) Time series of pH$_{SW}$, $\Omega_{ar\ SW}$, and pCO$_2$. Monthly atmospheric pCO$_2$ records measured at the MLO are also shown in red line. Dashed horizontal line indicates threshold $\Omega_{ar\ SW}$ for coral reef calcification, 3.3. (**d**) pH$_{SW}$ (red) and pCO$_2$ (blue, seawater; black, atmosphere) variability since the Insudtrial Revolution. Atmospheric pCO$_2$ during 1959–2013 were measured at the MLO (Tans & Keeling, 2014) and those prior to 1959 were reconstructed from trapped air in an Antarctic ice sheet (Rubino et al., 2013). pH$_{SW}$ calculated from GLODAP v1.1 DIC and TA for the year 1994 and 1750 are shown in green diamonds in **a** and **d** (Key et al., 2004).

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3-2. Material and Methods

3-2-1. $\delta^{11}B$ and $\delta^{13}C$ values of Chichijima coral

We used $\delta^{11}B$ values measured in P-TIMS method. We used ± 0.14‰, obtained from repeated analysis of JCp-1 (Chapter 2), as the analytical uncertainty of our $\delta^{11}B$ measurements. We calculated pH_{CF} and ΔpH (that is pH_{CF} minus pH_{SW}) using Equations (1-12) and (1-13). The dissociation constant of boric acid, pK_B, is 8.60 at 24.6 °C and a salinity of 34.8 at Chichijima (Dickson, 1990). WE used $\delta^{11}B_{SW}$ of 39.61‰ (Foster et al., 2010) and α_{3-4} of 1.0272 (Klochko et al., 2006) for the calculation.

We calculated annually averaged $\delta^{13}C_{coral}$ from previously reported monthly records (Felis et al., 2009). We also calculated averages for each 3-year period that corresponded to the same portions of the coral skeleton used for $\delta^{11}B$ analyses. We could not calculate the 3-year averaged data for 1997 because monthly $\delta^{13}C_{coral}$ records were limited until 1994.

3-2-2. Seawater CO$_2$ chemistry

As we did not observe any significant difference between CO$_2$ chemistry time series in the vicinity of Chichijima and those for Line 137°E (Chapter 2), we used the former records. We also calculated Ω_{arg} from regressed nDIC records using CO2calc software (Fig. 3-1).

As pH is temperature-dependent, we evaluated SST effects on pH_{SW} estimation since the Insudtrial Revolution. In all calculations, we kept SSS constant at the present climatological value (34.8), as it had negligible variations less than 0.05 during 1911–1997 (Felis et al., 2009). We calculated past SST from monthly coral Sr/Ca records using equations reported by Felis *et al*. (2009) for the same coral colony:

$$Sr / Ca = \frac{10.33 - 0.051 * SST}{10^3}$$ (Eq. 3-1)

We calculated nDIC from obtained SST and SSS (34.8) using Equation (2-4), where the

term for the linear trend was removed to examine seasonal to inter-annual variations. Then, using CO2calc we calculated de-trended pH_{SW} in combination with assumed TA. We calculated averages for each 3-year period that corresponded to the same portions of the coral skeleton used for $\delta^{11}B$ analyses. We could not calculate the 3-year averaged data for 1997 for the same reason as $\delta^{13}C_{coral}$.

3-3. Results and Discussion

3-3-1. $\delta^{11}B$ variation

Statistically insignificant $\delta^{11}B$ variation is recorded for the period between 1914 and 1954 (p = 0.78), whereas a rapid decrease in $\delta^{11}B$ became evident after 1960 (-0.17 ± 0.07‰/decade, p = 0.05). This trend resembles pH_{SW} evaluated from the atmospheric pCO_2 records (Figs. 3-1 & 3-2). Although we averaged three years of Chichijima coral to minimize effects derived from oceanographic variations that have interannual timescales, we observed some short-term variations that is well beyond the uncertainty of $\delta^{11}B$ measurements (Figs 3-2 & 3-3). For instance, $\delta^{11}B$ values for the mean year of 1921 and 1971 showed negatively and positively pronounced values, respectively. We did not find any correlations with SST proxies (Sr/Ca, U/Ca, and $\delta^{18}O$) that exhibit interannual to decadal variations (Fig. 3-3). (Felis et al., 2011; Felis et al., 2009). The 3-year averaged SST anomaly had a standard deviation of 0.5 °C, and that of the pH_{SW} anomaly was only 0.004 (Fig. 3-4). Therefore, owing to 3-year averaging, we confirmed that effects of past SST changes were negligible in the pH_{SW} calculation. SSS change in the past 100 year is so small (~0.05) that it can hardly influence CO_2 chemistry and coral geochemical records. Furthermore, modern CO_2 chemistry observation does not show any short-term variations because the surface ocean is close to equilibrated state to the atmosphere (Figs. 2-5, 2-6 & 3-1). Thus, rather than the environmental factor, issues related to coral skeleton is suspected as the cause of the short-term variability. Heterogeneity of coral subsamples or existence of drivers in addition to pH_{SW} is one of such possibilities (discussed later in Chapter 5). It should be noted that to identify the cause is beyond the scope of this chapter, and it does not affect the conclusion derived from pH_{CF} and pH_{SW} comparison discussed in the subsequent section.

Fig. 3-2. (**a**) $\delta^{11}B$ records of Chichijima coral. A regression line after 1960 shown in black suggests an acceleration of $\delta^{11}B$ decline (p = 0.05). (**b**) as **Fig. 3-1d** but for the years 1900–2013. (**c**) as **a** but for $\delta^{13}C_{coral}$ (Felis et al., 2009). Annual (line) and 3 year averaged (rectangles) $\delta^{13}C_{coral}$ were calculated from monthly records (Felis et al., 2009). $\delta^{13}C_{coral}$ decreases (a black regression line; p < 0.01) at equivalent rates to $\delta^{13}C_{atm}$ after 1960. (**d**) $\delta^{13}C_{atm}$ during 1981–2012 were measured at the MLO and that prior to 1981 were reconstructed from trapped air in an Antarctic ice sheet (Rubino et al., 2013).

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Fig. 3-3. (**a**) A summary of geochemical records of Chichijima coral ($\delta^{11}B$, this study; others, Felis et al., 2009). LER, Linear Extension Rate. (**b**) A photograph of the coral skeleton taken under soft X-ray (Felis et al., 2009).

Fig. 3-4. Monthly mean (**a**) SST (ºC) and (**b**) resulting pH$_{SW}$ anomalies estimated from coral Sr/Ca paleo-thermometer for the years 1911–1994 (lines). Black circles represent 3-year averages that correspond to portions of skeletons for which δ^{11}B were analyzed.

3-3-2. δ¹³C variation

The stable carbon isotopic ratio (δ^{13}C) previously reported for the same coral ($\delta^{13}C_{coral}$) (Felis et al., 2009) behaves in similar fashion (Fig. 3-2 & 3-3). $\delta^{13}C_{coral}$ keeps steady levels until 1960 (-0.11 ± 0.02‰/decade, $p < 0.01$) followed by a subsequent sharp decrease (-0.25 ± 0.04‰/decade, $p < 0.01$). It is consistent with the δ^{13}C of atmospheric CO_2 ($\delta^{13}C_{atm}$) records corresponding to -0.04 ± 0.01‰/decade ($p < 0.01$) and -0.24 ± 0.01‰/decade ($p < 0.01$) before and after 1960, respectively (Rubino et al., 2013) (Figs. 3-5).

No statistically significant difference of decreasing trends between $\delta^{13}C_{coral}$ and $\delta^{13}C_{atm}$ after 1960 was found ($p = 0.82$). The most important driver of long-term $\delta^{13}C_{coral}$ decrease is probably a $\delta^{13}C_{DIC}$ decrease, that is, the Suess effect (Dassié et al., 2013; Schmittner et al., 2013; Swart et al., 2010; Keeling et al., 2004; Quay & Stutsman, 2003; Quay et al., 2003, 1992; Gruber et al., 1999; Nozaki et al., 1978). Previous studies have estimated that the surface ocean reach to isotopic equilibrium in ~10 years (Schmittner et al., 2013; Gruber et al., 1999). As a first order approximation, therefore, $\delta^{13}C_{coral}$ must have decreased by 1.01‰ since 1910 if CO_2 is efficiently ventilated (Fig. 3-6). In addition to the Suess effect, previous studies have reported that there are other marginal effects derived from, for example, changes of (1) depth (Dassié et al., 2013; Grottoli, 2002, 1999) and (2) pH$_{SW}$ (Krief et al., 2010).

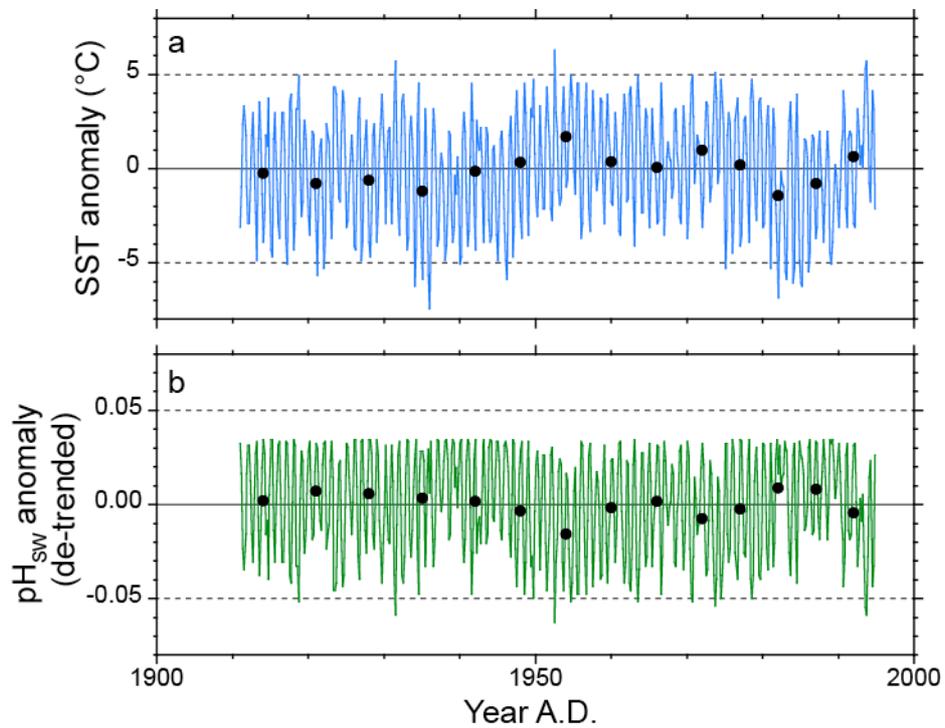The depth effect is almost equivalent to a solar irradiance effect, because the light attenuates with depth and photosynthesis partly control $\delta^{13}C_{coral}$. When the irradiance is sufficient, coral polyp selectively incorporate isotopically "lighter (^{12}C-rich)" carbon from the calcification fluid, leaving "heavier (^{13}C-rich)" carbon to the fluid from which the corals form the skeleton. Thus, a coral living in shallower (deeper) water tend to have a heavier (lighter) $\delta^{13}C_{coral}$. For instance, Dassié *et al.* (2013) found 0.16‰-$\delta^{13}C_{coral}$ decreases per 1-meter increases of habitat depth ($r = 0.88$, $p < 0.01$) in five colonies of massive *Porites* spp. living in Fiji. Glottoli (1999) reported fairly consistent observation for *Porites lutea* ($p < 0.05$) and *Porites compressa* ($p < 0.01$) living in Hawaiian coral reefs, and Glottoli (2002) further demonstrated the depth effect through irradiance-regulated culturing experiments of *P. compressa* ($p < 0.01$). The fact that horizontally cored skeleton of the same Chichijima coral showed systematically ~1.0‰ lighter $\delta^{13}C_{coral}$ values than the vertically cored one (Felis et al., 2009) is also in

line with the depth effect, because a side of massive *Porites* coral becomes the shade where low irradiance and resultant less photosynthetic activities are expected. As Chichijima coral grew ~1.1 m vertically since 1910, the depth effect must have increased $\delta^{13}C_{coral}$ by 0.17‰ (Fig. 3-6).

On the other hand, through culturing experiment of massive *Porites* spp. Krief *et al.* (2010) found that pH_{SW} change, in addition to $\delta^{13}C_{DIC}$ changes, have potential to alter $\delta^{13}C_{coral}$ as a result of physiological response of coral-symbiotic systems. This effect is estimated as -0.4‰ per 0.1 pH_{SW} lowering. Because pH_{SW} decreased by 0.06 since 1910, the pH_{SW} effect must have decreased $\delta^{13}C_{coral}$ by 0.22‰ (Fig. 3-6). As these two additional drivers (depth and pH_{SW}) almost offset each other, we concluded that the Suess effect is the dominant driver of long-term $\delta^{13}C_{coral}$ decrease. Other *Porites* corals collected at the western North Pacific islands such as Ishigakijima, Guam, and Palau also show statistically significant decreasing trends after 1960 (p < 0.01) (Fig. 3-5).

However, it is noteworthy that the decreasing trends of $\delta^{13}C_{coral}$ are different among corals collected from the western North Pacific (i.e., Chichijima, Guam, Ishigaki and Palau) (Fig. 3-5, Table 3-1). For instance, slopes of Ishigakijima and Palau corals were smaller than those of Chichijima and Guam corals (Table 3-1). We found that the depth effect was insufficient to explain the difference in slopes (Table 3-2). Surface seawater observation using reseach ships since 1970s suggest that the decreasing trends of $\delta^{13}C_{DIC}$ depend on how much anthropogenic CO_2 is incorporated from the atmosphere and prisitne seawater is mixed from the subsurface (Gruber et al., 1999). The decreasing trend of $\delta^{13}C_{DIC}$ is steeper in the subtropical ocean than the upweiing regions in the high and low latitudes (Quay et al., 2003, 1992; Gruber et al., 1999). Consequently, a slope of global mean $\delta^{13}C_{DIC}$ changes in the surface ocean between the 1970s and 1990s (-0.16 ± 0.02‰/decade, Quay et al., 2003) is smaller than that of the contemporary atmosphere (-0.24 ± 0.01‰/decade, Rubino et al., 2013). Additionary, through compilation of corals distributed over tropical-subtropical Indo-Pacific regions, Swart *et al.* (2010) confirmed that $\delta^{13}C_{coral}$ are decreasing at a lower rate than $\delta^{13}C_{atm}$. Therefore, the smaller $\delta^{13}C_{coral}$ changes at Ishigaki and Palau are probablly due to a stronger mixing with pristine water that originates from the equatrial upwelling and the NEC and Kuroshio transport (Fig. 2-2). Therefore, the fact that (1) trends of $\delta^{13}C_{coral}$ changes in Chichijima and Guam are identical to that of $\delta^{13}C_{atm}$ (Table. 3-1) and (2) the decreasing trend of $\delta^{13}C_{DIC}$ at the Station ALOHA (HOT, Fig. 2-2) approximately

equals that of $\delta^{13}C_{atm}$ (Table 3-3) further support the key assumption that surface water around these island lying inside of the subtropical gyre is well ventilated in terms of CO_2.

Before 1960, we also found a statistically significant difference of decreasing trends between $\delta^{13}C_{coral}$ and $\delta^{13}C_{atm}$ (p = 0.01). It is presumably due to relatively lower $\delta^{13}C_{coral}$ values during 1945–1960 (A shaded area in Figs. 3-3 & 3-5). In this interval, a linear extension rate (LER) of the skeleton does not change at all (Fig. 3-3) and it is well above "1 cm/yr" bellow which kinetic effects matter (Hayashi et al., 2013; McConaughey, 1989). Also, no clear disturbance in the skeleton is visible (Fig. 3-3). This interval corresponds to when temperature proxies (Sr/Ca, U/Ca and $\delta^{18}O$) suggest relatively warmer condition, however previous studies do not observe any influence of temperature on $\delta^{13}C_{coral}$ (e.g., Hayashi et al., 2013; Suzuki et al., 2005). Another possibility is regionally lowered $\delta^{13}C_{DIC}$ over the western equatorial Pacific during this interval, but no synchronized variation is observed in *Porites* corals collected at Guam, Ishigakijima and Palau (a shaded area in Fig. 3-5) (Osborne et al., 2014; Mishima et al., 2010; Asami et al., 2005). Thus, it might be related to a reduced photosynthetic activity due to some local reason such as temporally increased turbidity. This hypothesis will be tested in future research through analyzing Ba/Ca ratio that is a proxy of terrigeneous materials and/or suspended particles (e.g., Alibert et al., 2003). It should be noted that identification of a single mechanism of interannual to decadal scale $\delta^{13}C_{coral}$ variation is challenging, because they do not always agree among colonies even in the same region (e.g., Fiji, Dassié et al., 2013; Palau, Osborne et al., 2014).

Fig. 3-5. (a) Comparison of Chichijima $\delta^{13}C_{coral}$ and $\delta^{13}C_{atm}$ records during 1911–1994 (Felis et al., 2009; Rubino et al., 2013). Linear regressions before and after 1960 are shown in black lines. All decreasing trends are statistically significant (p < 0.01). **(b)** Compiled $\delta^{13}C_{coral}$ records from the western North Pacific (Chichijima, Felis et al., 2009; Guam, Asami et al., 2005; Ishigakijima, Mishima et al., 2010; Palau, Osborne et al., 2014). Black lines indicate linear regressions of each record during 1960–2000. Slopes of Chichijima and Guam corals are identical to that of $\delta^{13}C_{atm}$, but those of Ishigakijima and Palau are not (Table 3-1).

Fig. 3-6. A simulation of effects of long-term changes of pH_{SW} (Krief et al., 2010), depth (Dassié et al., 2013), and $\delta^{13}C_{DIC}$ (the Suess effect) (Rubino et al., 2013) on $\delta^{13}C_{coral}$. Δ denotes changes relative to a value of the year 1910. The pH_{SW} effect and the depth effect offset each other, consequently the Suess effect dominates net $\delta^{13}C_{coral}$ decreases.

Table 3-1. A summary of δ^{13}C slopes after 1960 of *Porites* corals collected in the western North Pacific.

	δ^{13}C slopes (‰/decade)	error (1se)	df	r	p-values (1)	(2)	Reference
$\delta^{13}C_{coral}$							
Chichijima	-0.25	0.04	33	-0.72	< 0.01	0.80	Felis et al., 2009
Guam	-0.25	0.04	38	-0.70	< 0.01	0.89	Asami et al., 2005
Ishigakijima	-0.14	0.03	33	-0.65	< 0.01	< 0.01	[*]Mishima et al., 2010
Palau#1	-0.13	0.02	39	-0.64	< 0.01	< 0.01	Osborne et al., 2014
Palau#2	-0.16	0.02	39	-0.78	< 0.01	< 0.01	Osborne et al., 2014
$\delta^{13}C_{atm}$							
	-0.24	0.01	26	-0.99	< 0.01	–	Rubino et al., 2013

(1) Statistical significance of δ^{13}C trends after 1960 (Fig. 3-5).
(2) The null hypothesis is "there are no statistically significant difference of decreasing trends between $\delta^{13}C_{coral}$ and $\delta^{13}C_{atm}$ ".
* Unpublished data.

Table 3-2. A summary of *Porites* corals collected in the western North Pacific and expected $\delta^{13}C$ changes during 1960–2000.

Island (Location)	Depth (m)	LER (cm/yr)	[1]$\Delta\delta^{13}C_{Coral}$ (‰)	[2]$\Delta\delta^{13}C_{Depth}$ (‰)	Reference
Chichijima (Northern side)	5.6	1.29	-1.00	0.08	Felis et al., 2012
Guam (Double Reef)	5.8	1.60	-1.00	0.10	Asami et al., 2005
Ishigakijima (Yasurazaki)	5.0	1.65	-0.56	0.11	*Mishima et al., 2010
Palau#1 (Rock Islands)	2.0	2.05	-0.52	0.13	Osborne et al., 2014
Palau#2 (Ulong Channel)	12.0	1.36	-0.64	0.09	Osborne et al., 2014

(1) $\delta^{13}C_{coral}$ change during 1960–2000 calculated from a slope of linear regression of each coral record (Table 3-1).
(2) An predicted $\delta^{13}C$ increase due to a vertical coral growth for 40 years. A reported sensitivity of 0.16‰/m is used for the calculation (Dassié et al., 2013).

* Unpublished data.

Table 3-3. A summary of reported $\delta^{13}C_{DIC}$ changes measured at the Station ALOHA.

Interval	[1]$\Delta\delta^{13}C_{atm}$ (‰/yr)	$\Delta\delta^{13}C_{DIC}$ (‰/yr)	Reference
1988–2002	-0.024	-0.023	Keeling et al., 2004
1990–1999	-0.026	-0.024	Quay et al., 2003
1982–1996	-0.022	-0.025	Gruber et al., 1999

(1) $\delta^{13}C_{atm}$ changes calculated from a slope of linear regression of ice core data (Rubino et al., 2013).

3-3-3. Relationships between $\delta^{11}B$ and $\delta^{13}C$

We observed a significant positive correlation between $\delta^{11}B$ (and pH_{CF}) and $\delta^{13}C_{coral}$ (r = 0.55, p = 0.04). Long-term $\delta^{11}B$ and $\delta^{13}C_{coral}$ decreases are clearly as a result of ocean acidification and the Suess effect, respectively. On the other hand, short-term variability of them is not always correlated (Figs. 3-2 & 3-3). Similarly, those of *Porites* coral collected at Guam do not show any correlated variation in these isotopes annually during 1940–1999, although the long-term decrease trends are apparent (Shinjo et al., 2013; Asami et al., 2005). Therefore, it indicates that short-term $\delta^{11}B$ and $\delta^{13}C_{coral}$ variations are not necessarily controlled by the same mechanism. For instance, Hönisch *et al.* (2004) reports that $\delta^{13}C$ of *P. compressa* depends on the irradiance but $\delta^{11}B$ of it does not. The reason why $\delta^{11}B$ varies in interannual timescales is still unknown, thus further investigations of drivers of short-term $\delta^{11}B$ variability is needed (this issue will be discussed in Chapter 5). Again, we emphasize that short-term variability of $\delta^{11}B$ and $\delta^{13}C_{coral}$ do not affect the conclusion derived from pH_{CF} and pH_{SW} comparison discussed in the subsequent section.

3-3-4. Sensitivity of pH_{CF} to pH_{SW} decrease

We found large differences between pH_{SW} (8.12 to 8.18) and pH_{CF} (8.47 to 8.53) derived from $\delta^{11}B$ of corals and a theoretical curve of $\delta^{11}B$ of borate ion (Fig. 3-7, Table 3-4). One plausible explanation for the fact that pH_{CF} was higher than pH_{SW} is the proposed "pH up-regulation mechanism" (Venn et al., 2013, 2011; McCulloch et al., 2012a,b; Trotter et al., 2011; Cohen & Holcomb, 2009; Al-Horani et al., 2003). Calcification fluid exists between the coral polyp and the underlying skeleton (extracellular), being semi-isolated from the ambient seawater. Corals spontaneously elevate their pH_{CF} to promote calcification processes in which the function of Ca^{2+}-ATPase is playing a key role for pumping H^+ out of and Ca^{2+} into the calcification fluid, which in turn increase pH_{CF} and Ω_{ar} ($\Omega_{ar\ CF}$). *In situ* pH_{CF} measurements using micro-pH electrodes, visualization using pH-sensitive dye, and observation of mineralogy between biologically precipitated and inorganically synthesized aragonite all support the idea of pH up-regulation (Venn et al., 2013, 2011; Cohen & Holcomb, 2009; Al-Horani et al., 2003). It has been anticipated from this mechanism that *Porites*

corals as well as other scleractinian coral genera can maintain their pH_{CF} under ongoing OA (Venn et al., 2013; McCulloch et al., 2012a,b). Therefore, corals are able to raise ΔpH to keep pH_{CF} as high as possible, due perhaps to homeostasis in calcification in their body (Fig. 3-7). The observation that deep-sea corals have larger ΔpH value than reef-building coral is in line with this idea that the system need to overcome to the stress from more corrosive abyssal seawater than the over-saturated surface sea waters (McCulloch et al., 2012b).

The relationship between pH_{SW} and pH_{CF} for two cultured *Porites* corals (Krief et al., 2010; Hönisch et al., 2004) predict a 0.03 and 0.05 pH_{CF} decline, respectively, per 0.1 pH_{SW} (Fig. 3-7), which suggests that coral $\delta^{11}B$ may not be sensitive enough to detect anthropogenic OA. However, we discovered clear indication of rapid decline in pH_{CF} of the Chichijima coral with the decline of pH_{SW}, which was not found in cultured corals (Fig. 3-7). Although ΔpH values are similar (0.3–0.5) in the present pH_{SW} range of 8.09–8.17 among corals in the field and cultured environments, rates of ΔpH change for both cases are significantly different (p < 0.01) (Fig. 3-7). Furthermore, we found that pH_{CF} change of Chichijima coral is more sensitive than any other previously available scleractinian corals (e.g., *Acropora*, *Stylophora*, and *Cladocora*; p < 0.03) cultured to date, and their pH_{CF} were estimated from $\delta^{11}B$ (Fig. 3-8) (Holcomb et al., 2014; Trotter et al., 2011; Krief et al., 2010; Raynaud et al., 2004; Hönisch et al., 2004). If the relationships between pH_{SW} and pH_{CF} in Chichijima coral are used to project future response to OA, pH_{CF} is about 8.3 and about 7.9 when $\Omega_{ar\ SW}$ is 3.3 (pH_{SW} = c.a. 8.04) and 2 (pH_{SW} = c.a. 7.78), respectively (Fig. 3-7). The magnitude of pH_{CF} decrease is dramatically higher in Chichijima coral than in that predicted from cultured corals (i.e., 8.4–8.5 when $\Omega_{ar\ SW}$ = 3.3 and 8.3–8.4 when $\Omega_{ar\ SW}$ = 2).

Because pH up-regulation demands significant energy for calcification, keeping constant ΔpH (Fig. 3-7) seems reasonable from a biological adaptation point of view (McCulloch et al., 2012a,b; Kleypas & Yates, 2009; Cohen & Holcomb, 2009). However, lower pH_{CF} under OA leads to slower calcification of corals, which will make their skeletons more susceptive to bio-erosions, leading to disadvantages in competition with other organisms such as grazers, burrowers, and macroalgae (Crook et al., 2013; Pandolfi et al., 2011). Given that Ca^{2+} concentration in calcification fluid is almost same as that in seawater (< 10% change, Cohen & Holcomb, 2009), sensitive pH_{CF} decrease will lead to faster $\Omega_{ar\ CF}$ decrease, as it is pH_{CF} that regulates $\Omega_{ar\ CF}$. Thus, it is

reasonable to believe that OA overwhelms or disables their pH_{CF} homeostasis rather than the coral spontaneously regulate their pH_{CF} (Hoegh-Guldberg et al., 2007). The observation of one-to-one relationship between pH_{CF} and pH_{SW} suggests the relationship in current pH ranges (8.1–8.2) is more straightforward than previously thought (Chapter 2). Therefore, it not only strengthens the reliability of coral $\delta^{11}B$ as pH_{SW} proxy (Chapter 4; Kubota et al., 2014), but also will pave the way for studying OA using coral $\delta^{11}B$ in diverse coral reef settings.

Fig. 3-7. (**a**) $\delta^{11}B$ values of Chichijima *Porites* spp., cultured *Porites* spp. (Krief et al., 2010), and cultured *Porites cylindrica* (Hönisch et al., 2004) with the theoretical curve of $\delta^{11}B$ of borate ion in the seawater (Klochko et al., 2006). (**b**) A crosss plot of pH_{CF} versus pH_{SW}. Regression lines are shown for each coral record. Dashed vertical lines indicate pH_{SW} when $\Omega_{ar\,SW}$ become 3.3, 2, and 1 that were calculated using present SST, SSS, and TA. (**c**) as **b** but for pH_{CF} versus ΔpH.

Fig. 3-8. Sensitivities of pH_{CF} against "0.1 pH_{SW} decrease" for Chichijima coral and the cultured scleractinian corals. Error bars are 1 se.

Table 3-4. Measured δ^{11}B values of Chichijima coral, estimated pH$_{SW}$, and calculated pH$_{CF}$ from δ^{11}B values.

Sample name	δ^{11}B$_{P\text{-TIMS}}$ ave.	pH$_{SW}$	pH$_{CF}$	ΔpH
OGA02_3Y_1997	23.84	8.118	8.47	0.36
OGA02_3Y_1992	23.84	8.124	8.47	0.35
OGA02_3Y_1987	24.22	8.130	8.50	0.37
OGA02_3Y_1982	23.89	8.137	8.48	0.34
OGA02_3Y_1977	24.17	8.144	8.49	0.35
OGA02_3Y_1972	24.71	8.150	8.53	0.38
OGA02_3Y_1966	24.16	8.155	8.49	0.34
OGA02_3Y_1960	24.43	8.160	8.51	0.35
OGA02_3Y_1954	24.56	8.162	8.52	0.36
OGA02_3Y_1948	24.28	8.164	8.50	0.34
OGA02_3Y_1942	24.28	8.167	8.50	0.33
OGA02_3Y_1935	24.38	8.168	8.51	0.34
OGA02_3Y_1928	24.76	8.170	8.53	0.36
OGA02_3Y_1921	24.06	8.173	8.49	0.31
OGA02_3Y_1914	24.41	8.175	8.51	0.33

3-3-5. Environmental stressors for Chichijima corals and implications for future coral reefs

Future pH_{SW} and pH_{CF} levels will likely decrease until CO_2 emission ceases completely, since the residence time of anthropogenic CO_2 in the surface seawater is on a century-long scale (Zeebe, 2012; Gattuso & Hansson, 2011; Feely et al., 2009; Tans, 2009; Orr et al., 2005; Caldeira & Wicket, 2003). In the western North Pacific, $\Omega_{ar\,SW}$ has already reached the threshold value of 3.3 in winter and annual average $\Omega_{ar\,SW}$ will also reach 3.3 by the year 2035, given linear extrapolation of the current trend (-0.01/year, Ishii et al., 2011) (Fig. 3-1). In addition to pH_{SW} and $\Omega_{ar\,SW}$, temperature is another important factor for corals since coral-dinoflagellate symbiosis is strongly temperature-dependent. Coral bleaching will occur upon dinoflagellate release if temperature exceeds corals' thermal tolerance, which sometimes leads to mortality as corals heavily depend organic carbon supplied by symbiotic organisms (Pandolfi et al., 2011; Kleypas & Yates, 2009). The coral reefs of the Ogasawara Islands are being threatened by regional warming. Recently, mass bleaching events struck coral reef communities in summer of 2003 and 2009 (Biodiversity Center of Japan, 2009). Moreover, the core top—the most recent potion of the coral skeleton—analyzed in this study (1998–2002) showed unsystematic behaviors of its trace element based paleo-thermometer (Sr/Ca and U/Ca ratios) (Felis et al., 2009). These phenomena are likely related to thermal stresses due to regional warming (Yamano et al., 2011), yet we also speculate that ongoing OA is another potential stressor, as $\Omega_{ar\,SW}$ is already close to its threshold value of 3.3 (Fig. 3-7). One modeling study predicts that coral reefs will disappear from the coastal regions of Japan earlier than the mid-21st century due to simultaneous degradation of living conditions in higher and lower latitudes, that is, acidification in the north and warming in the south, although there is the possibility of northward migration and adaptation (or even eventual evolution) of corals as well as uncertainties in the threshold of their responses to temperature and $\Omega_{ar\,SW}$ (Yara et al., 2012).

Most coral reefs, including those at Chichijima, receive good circulation from open ocean seawater. Open oceans will acidify more rapidly than isolated reefs, which are characterized by a long residence time of seawater that is buffered by dissolution of reef sediments, mitigating acidification (Eyre et al., 2014; Andersson et al., 2014; Kleypas &

Yates, 2009). If the sensitivity of Chichijima coral to OA can be regarded as representative of that of other corals, it follows that many coral reefs surrounding oceanic islands in the wider subtropics might be in more danger than originally thought. Thermal stratification of seawater projected in a high-CO_2 scenario will also deteriorate nutrient availability for corals, which likely increases coral vulnerability since poorly nourished corals are more susceptible to OA (Pandolfi et al., 2011). Ecological regime shifts, such as from coral- to macroalgae- or soft coral- dominated reefs, are possible when environmental stresses exceed a given threshold (Inoue et al., 2013; Fabricius et al., 2011; Kleypas & Yates, 2009; Hall-Spencer et al., 2008).

However, we note that there are large uncertainties in predicting the thresholds for each coral colony and each coral reef community on both global and regional scales. This is because global and local stressors interact with each other in a highly complex fashion (e.g., OA, global warming, destructive fishing, sediment influx) and coral response can vary within and among coral species (Pandolfi et al., 2011; Hoegh-Guldberg et al., 2007). For example, *Porites* coral from Guam (Shinjo et al., 2013) display high sensitivity to the Suess effect (a large $\delta^{13}C_{coral}$ decrease) but little sensitivity to OA (a slight $\delta^{11}B$ decrease), and opposite trends are seen in *Porites* coral from Hainan Island (Liu et al., 2014). To date, many studies have attempted to learn how massive *Porites* corals respond to OA, but results contradict significantly each other (e.g., Iguchi et al., 2014, 2012; Comeau et al., 2014; Crook et al., 2013; Déath et al., 2012, 2009; Cooper et al., 2012; Fabricius et al., 2011). Through culturing experiments under artificially acidified seawater, it is shown that the corals had different responses to OA: Comeau et al. (2014) found no evidence of negative effects of OA on *Porites* spp., whereas Iguchi *et al*. (2014, 2012) found a significant calcification rate decrease of *Porites australiensis* even under a modest acidification, that is ~0.1 pH_{SW} decrease after industrialization. From a field observation on naturally acidified CO_2 seep sites in Mexico, Crook *et al*. (2013) reports that *Porites asteroides* living in $\Omega_{ar\ SW}$ of less than ~2 have low-density skeletons and are prone to biological erosion in spite of ample time for acclimation. Similarly, Fabricius *et al*. (2011) found that massive *Porites* corals living in the CO_2 seep sites in Papua New Guinea have lower calcification rates compared with those living in the natural seawater ovdr the Indo-Pacific region. Past 400-years reconstructions using massive *Porites* corals living in the Great Barrier Reef, the northeastern Australia suggest recent steep decreases of calcification rates, densities,

and growth rates of the corals after 1960s (Déath et al., 2012, 2009). On the contrary, however, calcification rate of massive *Porites* corals living in the western Australia (17–28°S) have increased recently, which may relate to global warming's positive effect (Cooper et al., 2012).

These observations suggest that corals living in natural environments may have different responses to OA depending on the environmental factors of individual reefs. Therefore, more field-based studies using the δ^{11}B technique are needed to understand how corals have adapted to OA, before corals disappear due to physical, chemical, and biological erosions (Pandolfi et al., 2011; Hoegh-Guldberg et al., 2007).

3-4. Conclusion

We used δ^{11}B values of *Porites* coral collected at Chichijima (Ogasawara Archipelago) to estimate pH_{CF} changes for the last 100 years. δ^{11}B values showed a decline and its rate of decrease was accelerated after 1960 (-0.17 ± 0.07‰/decade, p = 0.05). The observation was in line with pH_{SW} decrease (i.e., OA) estimated from atmospheric pCO$_2$ increase. ΔpH remained almost constant values, suggesting pH_{CF} has decreased overcoming homeostasis of calcification fluid. Importantly, a rate of pH_{CF} decrease was significantly faster (ca. 0.2 pH_{CF} / 0.1 pH_{SW} decrease) than those of two *Porites* corals that have cultured under the artificially acidified seawater (ca. 0.03–0.05 pH_{CF} / 0.1 pH_{SW} decrease). We also found a significant positive relationship between coral δ^{13}C and δ^{11}B, indicating these phenomenons were originated from anthropogenic sources. In association with global warming, OA will perhaps lead to significant consequences because a pH_{CF} decrease and a resultant $\Omega_{ar\,CF}$ decrease will likely make coral's calcium carbonate skeletons more vulnerable to erosions. As winter $\Omega_{ar\,SW}$ is already bellow a threshold value of 3.3 in the western North Pacific, it suggests that many coral reefs including Chichijima's are more in danger than we thought.

CHAPTER 4

Marine carbon cycle at the equatorial Pacific during the last deglaciation

Chapter 4 Abstract

While physical and biogeochemical processes in the Southern Ocean are thought to be central to atmospheric CO_2 increases during the last deglaciation, the roles of the equatorial Pacific, where the largest CO_2 source currently exists, remains largely unconstrained. In this chapter we present pH_{SW} and $pCO_{2\ SW}$ variations from fossil *Porites* corals collected from Tahiti based on a newly calibrated $\delta^{11}B$-pH_{SW} proxy. The new data, together with recalibrated existing data, indicate that significant $pCO_{2\ SW}$ increases (pH_{SW} decreases), accompanied by anomalously large marine ^{14}C reservoir ages, happened following not only the Younger Dryas, but also Heinrich Stadial 1. These findings indicate an expanded zone of equatorial upwelling and resultant CO_2 emission, which may be caused by higher subsurface DIC concentration.

4-1. Introduction

Atmospheric pCO$_2$ increased by ~80 µatm during the last deglaciation, with ~50 µatm released during Heinrich Stadial 1 (HS1, from 17.5 to 14.6 kyr), followed by an additional ~30 µatm during the Younger Dryas (YD, from 12.9 to 11.7 kyr) (Lourantou et al., 2010). While the Southern Ocean is generally considered to be central to the deglacial CO$_2$ rise (e.g., Siani et al., 2013; Matsumoto & Yokoyama, 2013; Burke & Robinson, 2012; Yokoyama & Esat, 2011; Skinner et al., 2010; Rose et al., 2010; Anderson et al., 2009; Toggweiler et al., 2006), the contribution from other oceanic regions remains largely uninvestigated (Foster & Sexton, 2014; Henehan et al., 2013; Yu et al., 2013; Douville et al., 2010; Foster, 2008; Palmer & Pearson, 2003). Information on pCO$_{2\ SW}$ is needed to directly constrain past air-sea CO$_2$ exchange. It can be reconstructed from δ^{11}B of marine carbonates, pH$_{SW}$ proxy (Hönisch et al., 2007). Regions where surface seawater CO$_2$ is out of equilibrium with the atmosphere are ideal for such studies. Thus, the equatorial Pacific is particularly well suited because it represents the largest global CO$_2$ source at present (e.g., Sutton et al., 2014; Takahashi et al., 2009; Gruber et al., 2009; Feely et al., 2006, 2002). Corals living in tropical to subtropical regions are good archives for paleo-CO$_2$ studies because they can be dated precisely using U-series radiogenic isotopes (Yokoyama & Esat, 2011; Deschamps et al., 2012), unlike foraminifers that may be affected by ^{14}C marine reservoir ages (R).

Two previous studies have attempted to reconstruct equatorial Pacific pH$_{SW}$ and pCO$_{2\ SW}$ changes. Palmer & Pearson (2003) showed increased CO$_2$ emission during the last deglaciation in the western equatorial Pacific (WEP) from δ^{11}B measurements on the planktonic foraminifer (*Globigerinoides sacculifer*) in a sediment core recovered from offshore Papua New Guinea (ERDC-92, Fig. 4-1). Douville *et al*. (2010) performed δ^{11}B on fossil corals collected from the Marquesas (9.5ºS 139.4ºW, Fig. 4-1). They also demonstrated that CO$_2$ emission increased at the end of the YD. However they did not observe a significant CO$_2$ release during HS1. It complicates interpretation of the equatorial Pacific's contribution to deglacial atmospheric CO$_2$ rise. Integrated Ocean Drilling Program Expedition 310 (IODP Exp. 310, Camoin et al., 2007) drilled the outer reef slope at Tahiti (17.6ºS 149.5ºW, Fig. 4-1) recovering fossil corals from an open ocean environment spanning HS1. Therefore, we can assess the issue. Furthermore,

previous estimation was based on out-of-date fractionation factor between boric acid and borate ions reported by Kakihana *et al.* (1977). Thus we refined the calibration (Chapter 2) and obtained the new pH_{SW} and $pCO_{2\ SW}$ estimations since the last glacial maximum (LGM).

Fig. 4-1. $pCO_{2\ SW}$ in the equatorial Pacific and vertical sections from 60 ºS to 30 ºN of the South Pacific. (**a**) $pCO_{2\ SW}$ for the reference year AD 2000 in which red and blue colours represent CO_2 sources and sinks, respectively (Takahashi et al., 2009). Vertical sections of (**b**) oxygen, (**c**) silicate, (**d**) DIC, and (**e**) $\Delta^{14}C$. Data source is "World Ocean Atlas 2009 > annual" for oxygen and silicate, "Global Alkalinity & TCO_2 > annual" for DIC (Goyet et al., 2000), and "GLODAP Gridded Data" for $\Delta^{14}C$ (Key et al., 2004). All data were downloaded via *http://odv.awi.de/en/data/* and plotted using Ocean Data View software version 4.6.2 (Schlitzer, 2014). Inverted black triangles represent locations of Tahiti and Marquesas. The star and diamond indicate the locations of cores MV99-MC99/GC31/PC08 (Basak et al., 2010; Marchitto et al., 2007) and V21-31 (Stott et al., 2009), respectively. SAMW, Subantarctic Mode Water; AAIW, Antarctic Intermediate Water; EUC, Equatorial Undercurrent.

4-2. Material and Methods

4-2-1. δ^{11}B-pH$_{SW}$ calibration

The way of δ^{11}B-pH$_{SW}$ calibration used for Tahiti and Marquesas areas is described in Chapter 2. Using the new calibration methodology we calculated pH$_{SW}$ from both previously reported and newly obtained δ^{11}B values considering a local difference of pH$_{SW}$ between Tahiti and Marquesas (Fig. 2-8). We further calculated pCO$_2$ from obtained pH$_{SW}$ values from δ^{11}B using CO2calc software under assumptions of constant SST, SSS, and TA. We did not include the δ^{11}B values of *G. sacclifer* (Palmer & Pearson, 2003) here due to large uncertainties in the δ^{11}B-pH$_{SW}$ calibration (e.g., Henehan et al., 2013; Foster, 2008).

4-2-2. δ^{11}B analysis of Tahitian fossil corals

The δ^{11}B values of fossil *Porites* spp. that were obtained under the program of IODP Exp. 310 were measured using the P-TIMS method according to the protocol of Ishikawa and Nagaishi (2011). Fossil corals were screened for diagenetic alteration with X-ray diffraction (XRD) and geochemical analyses (e.g., Mg/Ca, Hathorne et al., 2011), and visual using a Scanning Electron Microscope (SEM) (Inoue et al., 2010). We conducted bulk sampling along the growth axis, and time resolution of each sample is several years (1 - 8 years) depending on growth rate of each coral (Inoue et al., 2010). We used typically 6 mg of carbonate for the δ^{11}B measurement. After removals of organic matter using 30% H_2O_2 for ~12 hours, we purified boron by cation and anion exchange and then δ^{11}B were measured using the P-TIMS (Thermo Finnigan TRITON) at Kochi Institute for Core Sample Research. All reported δ^{11}B values are the mean of duplicate analyses (Table 4-1). Repeated analysis of the JCp-1 yielded 24.21 ± 0.18 ‰ (2σ, n = 18) (Okai et al., 2004). We used ± 0.14‰ as the analytical uncertainty of δ^{11}B measurements.

Table 4-1. The δ¹¹B values of *Porites* corals and calculated pH$_{SW}$ and pCO$_2$ (after Kubota *et al.* (2014)).

Location	¹Sample ID	²Cal. age (Years BP) Reference	1σ	δ¹¹B values (‰) ³mean		2σ	Reference	⁴pH	2σ	pCO$_2$ (μatm)	2σ	ΔpCO$_2$ (μatm)
Fossil												
Tahiti	310-M0005B-3R-1W_58-67 (3116500)	Inoue et al., 2010	74	26.29 26.32	26.31	0.18	This study	8.213	0.013	251	11	-12
Tahiti	310-M0005C-8R-2W_0-5 (3116758)	Inoue et al., 2010	52	26.13 26.12	26.12	0.18	This study	8.200	0.014	261	10	-7
Tahiti	310-M0007A-18R-1W_76-90 (3113922)	Deschamps et al., 2012; Durand et al., 2013	10	26.04 25.98	26.01	0.18	This study	8.191	0.014	268	11	8
Tahiti	310-M0007A-18R-1W_28-58 (3113876)	Deschamps et al., 2012; Durand et al., 2013	10	25.64 25.68	25.66	0.18	This study	8.163	0.014	292	13	32
Tahiti	310-M0007B-21R-1W_0-20 (3114984)	Deschamps et al., 2012; Hathorne et al., 2011	28	25.49 25.47	25.48	0.18	This study	8.149	0.014	304	13	42
Tahiti	310-M0018A-18R-1W_40-50 (3125580)	Durand et al., 2013	31.5	26.39 26.24	26.31	0.18	This study	8.214	0.013	250	10	11
Tahiti	310-M0018A-18R-1W_50-63 (3125582)	Durand et al., 2013	31.5	25.51 25.56	25.54	0.18	This study	8.154	0.014	300	12	61
Tahiti	310-M0009D-7R-1W_11-28 (3105506)	Deschamps et al., 2012; Durand et al., 2013; Asami et al., 2009	36	25.73 25.65	25.69	0.18	This study	8.166	0.014	289	12	50
Tahiti	310-M0023A-6R-1W_48-62 (3101822)	Asami et al., 2009	49	25.58 25.80	25.69	0.18	This study	8.166	0.014	289	12	43
Tahiti	310-M0024A-11R-1W_77-90 (3111904)	Deschamps et al., 2012; Durand et al., 2013	12.5	26.20 26.23	26.21	0.18	This study	8.206	0.014	256	11	28
Tahiti	310-M0024A-11R-1W_60-75 (3111884)	Deschamps et al., 2012; Durand et al., 2013	12.5	24.82 24.77	24.79	0.18	This study	8.093	0.015	359	15	131
Tahiti	310-M0024A-11R-2W_25-61 (3111958)	Felis et al., 2012; Durand et al., 2013; Dechamps et al., 2012	25	25.82 25.73	25.78	0.18	This study	8.173	0.014	283	12	55
Tahiti	310-M0024A-12R-2W_140-150 (3112030)	Deschamps et al., 2012	29	26.10 25.82	25.96	0.18	This study	8.187	0.014	271	11	43

Continued

Location	Original sample code			Reference				Reference					
Tahiti	310-M0024A-12R-2W_62-80 (3112024)	15075	29	Deschamps et al., 2012	26.04 / 26.09	26.07	0.18	This study	8.195	0.014	265	11	37
Tahiti	310-M0024A-13R-1W_32-41 (3112052)	15149	15.5	Deschamps et al., 2012; Durand et al., 2013	25.14 / 25.21	25.18	0.18	This study	8.125	0.015	327	13	99
Tahiti	Ta P8-348	12910	30	Bard et al., 1996		25.9	0.25	Douville et al., 2010	8.149	0.020	304	18	66
Tahiti	Ta P8-353	13335	30	Bard et al., 1996		26.6	0.25	Douville et al., 2010	8.203	0.019	259	15	21
Marquesas	Eiao DR16(3)	8990	130	Cabioch et al., 2008		26.0	0.25	Douville et al., 2010	8.179	0.020	267	18	11
Marquesas	Eiao DR16(5)	9110	130	Cabioch et al., 2008		26.3	0.25	Douville et al., 2010	8.203	0.019	245	16	-11
Marquesas	Eiao DR12(1)	9590	180	Cabioch et al., 2008		26.2	0.25	Douville et al., 2010	8.195	0.019	253	16	-6
Marquesas	DW1281 75a2	11470	90	Paterne et al., 2004		24.8	0.25	Douville et al., 2010	8.077	0.022	375	27	112
Marquesas	DW1281 75a2	11470	90	Paterne et al., 2004		24.5	0.25	Douville et al., 2010	8.050	0.023	408	29	145
Marquesas	Hiva Oa DR10(2)	12420	100	Cabioch et al., 2008		26.2	0.25	Douville et al., 2010	8.195	0.019	253	16	8
Marquesas	Eiao DR11bis(4)	13410	190	Cabioch et al., 2008		25.6	0.25	Douville et al., 2010	8.147	0.021	298	20	60
Marquesas	Eiao DR8(1)	14560	180	Cabioch et al., 2008		26.1	0.25	Douville et al., 2010	8.187	0.020	260	18	21
Marquesas	Hiva Oa DR14bis(1)	15450	150	Cabioch et al., 2008		26.1	0.25	Douville et al., 2010	8.187	0.020	260	18	35
Marquesas	Hiva Oa DR8bis(1)	15460	110	Cabioch et al., 2008		26.4	0.25	Douville et al., 2010	8.211	0.019	239	16	14
Marquesas	Hiva OaDR5	20720	200	Cabioch et al., 2008		27.1	0.25	Douville et al., 2010	8.263	0.018	197	14	10

Modern		**(AD)**											
Moorea	COM2	*(1991)*		Gaillardet & Allegre, 1995		25.3	0.30		8.096	0.025	356	25	-15
Moorea	MOO 3A-1-02	*(1950)*		Douville et al., 2010		25.8	0.25		8.145	0.023	308	20	-10
Marquesas	Nuku Hiva DR6(1)	250	30 *(1700)*	Cabioch et al., 2008		26.2	0.25	Douville et al., 2010	8.205	0.022	244	18	-17

(1) Original sample code of IODP Exp. 310 and sample code in individual laboratories.

(2) Calendar age of fossil corals. For 310-M0005B-3R-1W_58-67 and 310-M0005C-8R-2W_0-5, dating was conducted by ^{14}C dating method (Inoue et al., 2010).

(3) Boron isotope values for this study are average values of duplicate analysis. Those for Douville *et al.* (2010) are mainly of replicate analysis.

(4) pH for Marquesas were added by 0.04 after calculation for comparison. pK_B for Tahiti-Moorea and Marquesas are listed in **Table 2-3.**

4-2-3. Marine ^{14}C reservoir age compilation

We compiled published ^{14}C (radiocarbon years) and U/Th ages of fossil corals obtained during IODP Exp. 310 in order to calculate residual radiocarbon activities (Δ^{14}C) and R. We verified that the exact same samples were selected via sample ID and core photographs (Camoin et al., 2007). In some cases different part of the skeleton of the same coral was dated. Given that coral lifetimes are generally less than several decades, temporal gaps derived from sub-sampling are negligible in the calculations of Δ^{14}C and R. We did not use ^{14}C ages from either microbialite or encrusting coralline algae (Seard et al., 2010). We made calculation using an original radiocarbon data (^{14}C$_{age}$) before a local R correction (Burr et al., 2009; Adkins & Boyle, 1997).

$$\Delta^{14}C_{marine} = \left(\frac{e^{-\frac{^{14}C_{age}}{8033}}}{e^{-\frac{(U/Th)_{age}}{8266}}} - 1 \right) * 10^3 \quad (\text{‰}) \qquad \text{(Eq. 4-1)}$$

$$R = 8033 * \ln\left(\frac{\Delta^{14}C_{atm} + 10^3}{\Delta^{14}C_{marine} + 10^3} \right)$$
$$= {}^{14}C_{age(marine)} - {}^{14}C_{age(atm)} \qquad \text{(Eq. 4-2)}$$

Atmospheric Δ^{14}C (Δ^{14}C$_{atm}$) from IntCal13 (Reimer et al., 2013a) was used to calculate R.

In order to calculate R, we also used other ^{14}C and U/Th datasets for fossil corals from the equatorial Pacific islands that include Tahiti (Bard et al., 1998), Marquesas (Paterne et al., 2004), Kiritimati (Fairbanks et al., 2005) and Mururoa (Bard et al., 1998) (Fig. 4-1). R$_{diff}$ denotes differences between calculated R and modern R (235 ± 110 for Tahiti, Reimer et al., 2009; 390 ± 60 for Marquesas, Paterne et al., 2004; 335 ± 100 for Kiritimati, Fairbanks et al., 2005; 300 ± 100 for Mururoa, Bard et al., 1998). We estimated that accumulated R$_{diff}$ uncertainties are the sum of errors in ^{14}C dating, U/Th dating, and modern R estimation.

4-3. Results and Discussion

4-3-1. pH$_{SW}$ and pCO$_{2\,SW}$ reconstructions

Using the revised calibration, we reconstructed pH$_{SW}$ from new δ^{11}B measurements on Tahitian corals, as well as from previously reported data from both the Marquesas and Tahiti (Douville et al., 2010), and the overall result is consistent with the WEP foraminifer δ^{11}B variations (Palmer & Pearson, 2003) (Fig. 4-2). The oldest coral sample, dated to 20.7 ka BP during the LGM, exhibits a relatively high pH (8.26). From 15.5 to 9.0 ka BP, pH$_{SW}$ is generally constant within uncertainty (8.15 - 8.22) and consistent with the preindustrial value of 8.20. Four notable pH excursions are associated with HS1 and the YD. Two of IODP Exp. 310 samples exhibit anomalously low pH at the end of HS1 (8.13 at 15.15 ka and 8.09 at 14.99 ka BP), in addition to those at end of the YD at the Marquesas (Douville et al., 2010). The low pH$_{SW}$ following HS1 had been previously undetected at this location. Calculation of pCO$_{2\,SW}$ reveals deglacial values significantly above those of the atmosphere (Fig. 4-2). Conversely, ΔpCO$_2$ during last glacial and the early Holocene was nearly zero.

Results from a different portion of the same 14.99 ka BP coral sample deviate by as much as 1.4 ‰, which corresponds to 0.11 in pH$_{SW}$ and 100 µatm in pCO$_{2\,SW}$ (310-M0024A-11R-1W_77-90 and 310-M0024A-11R-1W_60-75, Table 4-1). Considering the average ~4 year temporal resolution of each sample, these excursions occurred abruptly and persisted for several years, which differs from modern observations that show no clear interannual or decadal variability (Fig. 2-5). This enhanced variability, which is also observed in Sr/Ca derived SST results from another *Porites* colony recovered from IODP Exp. 310 (Felis et al., 2012), may relate to Tahiti's location at the rim of equatorial upwelling cell (Fig. 4-1). Taken together, pCO$_{2\,SW}$ records indicate that the equatorial Pacific became a larger CO$_2$ source during the last deglaciation with excursions at the end of HS1 and the YD.

Fig. 4-2. Deglacial $\delta^{11}B$, pH_{SW} and pCO_2 variations in the equatorial Pacific. (**a**) Reported $\delta^{11}B$ values of planktonic foraminifera from ERDC-92 core (Palmer & Pearson, 2003). Age model is from the original publication. (**b**) pH_{SW} reconstructed from $\delta^{11}B$ of fossil *Porites* spp. Green and red circles are from Tahiti by Douville *et al.* (2010) and this study, respectively. Blue circles are from Marquesas by Douville *et al.* (2010) after correction by +0.04 pH units. (**c**) pCO_2 $_{SW}$ around the equatorial South Pacific Ocean (same colors as **b**). Atmospheric pCO_2 are also shown on the GICC05 timescale (Lourantou et al., 2010). All error bars are 2σ. LGM, Last Glacial Maximum; HS1, Heinrich Stadial 1; ACR, Antarctic Cold Reversal; B/A, Bølling/Allerød; YD, Younger Dryas.

4-3-2. Marine ^{14}C reservoir ages

Compiled R throughout the equatorial Pacific resembles pCO$_2$ variability (Figs. 4-3 and 4-4). Larger and more variable values of R are evident in Tahiti during HS1 and the YD, and enhanced R variability is also seen in the Marquesas (Figs. 4-3 and 4-4). Paterne *et al*. (2004) sub-sampled different parts in the same fossil coral skeleton and analyzed both ^{14}C and U/Th. They observed no difference in U/Th dates, but a much larger difference in ^{14}C. Possibilities of either a diagenetic alteration or a change in R were suggested. The latter is more probable because a large variation in R is also suggested from Vanuatu coral at 11.7 - 12.4 ka (~ 400 years; during the YD, Burr et al., 1998).

R$_{diff}$ during the Holocene suggests no substantial change (Fig. 4-3 & 4-4). Reported R$_{diff}$ data around the upwelling zone during the LGM are so sparse that it is unclear if R$_{diff}$ during that period was same as present. However, the above-mentioned observation that ΔpCO$_2$ is essentially equivalent to zero during the Holocene and the LGM suggests R$_{diff}$ during the LGM is also near zero due to good ventilation. Large scatters seen in the last glacial corals of Mururoa and Tahiti may relate to Heinrich events 2 and 3 (Reimer et al., 2013a).

There are large differences between IntCal09 and IntCal13 Δ^{14}C$_{atm}$ data sets prior to 15.5 ka BP. This is partly because the previous version of Intcal09 curve heavily relied on Cariaco Basin varve sediment records in the equatorial Atlantic, whose assumption that local R was kept constant is highly questionable (Reimer et al., 2013a, b; Southon et al., 2012). The latest version of Intcal13 curve omitted a part of Cariaco Basin records, and instead adopted Lake Suigetu ^{14}C records whose chronology is anchored by Hulu Cave calendar ages through ^{14}C wiggle-matching (Reimer et al., 2013a, b; Bronk-Ramsey et al., 2012). Therefore, we must keep in mind that if the IntCal curve is updated in the future, estimation of R prior to 15.5 ka BP may change, too (this issue will be further discussed in Chapter 5).

Fig. 4-3. (**a**) Time series of atmospheric Δ^{14}C (black line: IntCal13 (Reimer et al., 2013a); gray line: Intcal09 (Reimer et al., 2009). (**b**) Differences between modern and past R around the equatorial Pacific Ocean. All data are from fossil corals (red: offshore Tahiti (this study); orange: reef crest of Tahiti barrier reef (Bard et al., 1998), blue: Marquesas (Paterne et al., 2004); light blue: Kiritimati (Fairbanks et al., 2005); black: Mururoa (Bard et al., 1998)). Horizontal gray dashed line represents 'R$_{diff}$ = 0'. All error bars are 1σ.

Fig. 4-4. Differences between modern and deglacial pCO_2 and R (ΔpCO_2 and R_{diff}). The last deglaciation is characterized by larger and more variable pCO_2 and R values. (**a**) Atmosphere-ocean ΔpCO_2 based on Tahiti and Marquesas corals and Antarctic ice core (Lourantou et al., 2010). Figure legend is same as **Fig. 4-2**. (**b**) R_{diff} around the equatorial Pacific Ocean calculated from fossil corals (legends are same as **Fig. 4-3**). Horizontal dashed lines represent $\Delta pCO_2 = 0$ and $R_{diff} = 0$.

4-3-3. SSS effects on TA and pCO$_2$ $_{SW}$ calculations

Reduced sea level during the last glacial is thought to have increased global salinity by ~1.2 g/kg (Adkins et al., 2002). During the LGM, which likely exhibited the largest magnitude change in TA relative to present, if the local TA-SSS relationship remained unchanged, TA at Tahiti would have increased by 79.6 mmol/kg (Eq. 2-3, Kutchinke et al., 2014). This would only result in a 0.007 reduction in pH$_{SW}$ and a 12.1 µatm increase in pCO$_2$ $_{SW}$ (Table 4-2). Therefore, we neglected SSS changes during the last deglaciation throughout this chapter.

Table 4-2. Evaluation of SSS and TA changes on pCO$_{2 \text{ SW}}$ calculation.

	SSS	pK_B	δ^{11}B (‰)	[1]pH$_{SW}$	TA (μmol/kg)	pCO$_{2 \text{ SW}}$ (μatm)
Present SSS	35.9	8.562	26	8.192	2359.7	268.7
LGM SSS & TA	37.1	8.556	26	8.185	2439.2	280.8
Differences	1.2	-0.007	0	-0.007	79.6	12.1

(1) Calculated from δ^{11}B value of fossil coral.

4-3-4. SST effects on pCO$_{2\text{ SW}}$ reconstructions

Determination of past pH$_{SW}$ and pCO$_{2\text{ SW}}$ requires knowledge of paleo-SST because these parameters, as well as the dissociation constant of boric acid (pK_B), are temperature dependent (Robins et al., 2010; Hönisch et al., 2007; Zeebe & Wolf-Gladrow, 2001; Dickson, 1990) such that a 10 °C decrease in temperature corresponds to an approximate 0.1 unit increase in pH$_{SW}$. Temperature reconstructions (MARGO Project Members, 2009; Kiefer & Kienast, 2005) from the tropical and subtropical Pacific indicate relatively little change from modern values within the temporal range of our data. A compilation of SST records obtained from marine sediments indicates an overall increase from LGM to present, without major reversals during the YD or HS1, and with a total change of 2 °C from 15 ka (Kiefer & Kienast, 2005).

However, coral SST reconstructions indicate lower temperatures (2 - 4 °C) during the last deglaciation and early Holocene at Tahiti (Felis et al., 2012; DeLong et al., 2010; Asami et al., 2009). Therefore, we recalculated pCO$_{2\text{ SW}}$ considering the coldest reported SST to estimate the maximum range of pCO$_{2\text{ SW}}$ change. For this, we used SST results from IODP Exp. 310 corals that indicate SST was cooler by 3.5 °C at 15.0 ka BP (HS1) (Felis et al., 2012), 2.1°C at 14.2 ka BP Bølling/Allerød (B/A) (Asami et al., 2009), 3.4˚C at 12.4 ka BP (YD) (Asami et al., 2009), 3.2 °C at 9.5 ka BP during the Holocene (DeLong et al., 2010) (Fig. 4-5). Because there are no LGM SST data from this region, we employed a 5 °C LGM change (Stute et al., 1995; Guilderson et al., 1994) (Fig. 4-5). Note that this does not consider the possibility of changes in either seawater Sr/Ca through time or Sr/Ca-SST sensitivity as discussed in previous studies (Gagan et al., 2012; Felis et al., 2012; DeLong et al., 2010; Asami et al., 2009) and therefore represents maximum potential SST change.

Positive ΔpCO$_2$ during the last deglaciation (Fig. 4-5) is clearly insensitive to a large potential SST decrease. Carbon dioxide emission from the equatorial Pacific, as well as anomalously higher pCO$_2$ at ends of HS1 and the YD, persist (Fig. 4-5). we also note that only a slight lowering of LGM SST (1 – 3˚C), the accepted equatorial Pacific range (MARGO Project Members, 2009; Kiefer & Kienast, 2005), results in an estimated LGM ΔpCO$_2$ that is nearly identical to that of the Holocene (under modern

SST conditions, Kiefer & Kienast, 2005) (Fig. 4-5). This implies the surface seawater was in near CO_2 equilibrium state during these periods.

Fig. 4-5. Evaluation of influence of SST change on pCO_2 estimation. (**a**) Estimated SST differences compared to the preindustrial era using the most extreme potential decrease. The absolute minimum reported SST values from the equatorial Pacific were used for calculation of lower limits of uncertainty in **b** and **c**. (**b**) pCO_2 difference between the surface water at Tahiti and Marquesas and the atmosphere. Horizontal dashed line represents '$\Delta pCO_2 = 0$'. (**c**) Calculated pCO_2 of the surface water around the equatorial South Pacific Ocean assuming the same SST to the present (legends are same as **Figs. 4-2 and 4-4**) and atmospheric pCO_2 on the GICC05 timescale (black line) (Lourantou et al., 2010).

4-3-5. Mechanisms to explain higher $\Delta p\mathrm{CO_2}$ during the last deglaciation

$p\mathrm{CO_2}$ variability in subtropical oligotrophic water can be explained by mixing of water masses that exhibit distinctly different DIC concentrations. A southward migration of the ITCZ that partly controls thermocline depth is hypothesized during Heinrich Events including HS1 and the YD (e.g., Deplazes et al., 2014; Broccoli et al., 2006; Zhang & Delworth, 2005). At present, the ITCZ does not seem to directly affect surface $p\mathrm{CO_2}$ variability (Fig. 4-1) because there is no indication of a latitudinal migration of the $p\mathrm{CO_2}$ maxima in accordance with the ITCZ migration (Feely et al., 2006, 2002), and if it is displaced southward, the locus of equatorial upwelling remains at the equator due to the influence of inter-hemispheric asymmetry of Coriolis force (e.g., Talley et al., 2011; Gruber & Sarmiento, 2011). Enhanced upwelling (shallower thermocline, La Niña-like conditions) or increased subsurface DIC (and TA?) concentration are more likely to drive $p\mathrm{CO_2}$ variability based on sedimentary evidence from the equatorial Pacific for higher nutrient content, e.g., enhanced biogenic opal export production and lower $\delta^{13}\mathrm{C}$ (TT013-PC72, ODP Site 1240 and TR163-19; Fig. 4-1) (Pena et al., 2013, 2008; Hayes et al., 2011; Spero & Lea, 2002). Semi-conservative radiogenic neodymium isotopes (εNd) from sediment cores at the eastern equatorial Pacific (EEP) (ODP Site 1240) and off Baja California (MV99-MC99-GC31/PC08) indicate stronger subsurface water transport from the south (Pena et al., 2013; Basak et al., 2010) (Fig. 4-1). Covariation of geochemical properties between the Southern Ocean and the equatorial Pacific suggest a subsurface connection during the last deglaciation (e.g., Pena et al., 2013, 2008; Hayes et al., 2011; Basak et al., 2010; Loubere & Bennet, 2008; Bostock et al., 2004; Spero & Lea, 2002). Thus, $p\mathrm{CO_2}$ variability may be explained by an increase in DIC in the upwelled, subsurface water masses as opposed to physical processes alone.

4-3-6. A similarity between R_{diff} and pCO$_2$ variability

Water mass subduction along the subantarctic front, mainly off Chile (Bostock et al., 2013), forms Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) that upwells at the equatorial Pacific via the Equatorial Undercurrent (EUC) (Fig. 4-1). SAMW and AAIW are characterized by higher/lower concentrations of oxygen/silicic acid (Fig. 4-1). It is suggested that the abyssal DIC reservoir around the Southern Ocean increased during the last glacial period (Burke & Robinson, 2012; Skinner et al., 2010; Rose et al., 2010; Sikes et al., 2000), which would have contributed to lower atmospheric pCO$_2$. Carbon dioxide was released to the surface through deep ocean ventilation during HS1 and the YD (Siani et al., 2013; Matsumoto & Yokoyama, 2013; Burke & Robinson, 2012; Yokoyama & Esat, 2011; Skinner et al., 2010; Rose et al., 2010; Anderson et al., 2009; Toggweiler et al., 2006), however export production was insufficient to fully compensate the increased carbon flux (Foster & Sexton, 2014; Horn et al., 2011). This is consistent with residual radiocarbon content (Δ^{14}C) of intermediate water at the EEP (V21-30, Stott et al., 2009) and off Baja California (MV99-MC99-GC31/PC08, Marchitto et al., 2007) that indicates anomalously older water was incorporated into SAMW/AAIW (Fig. 4-1), as well as with depleted δ^{13}C of surface and lower thermocline dwelling foraminifers from sediment cores at both equatorial (TT013-PC72, ODP Site 1240 and TR163-19) and South Pacific sites (Pena et al., 2013, 2008; Hayes et al., 2011; Loubere & Bennet, 2008; Bostock et al., 2004; Spero & Lea, 2002). Moreover, enhanced export production of biogenic opal suggest more silicic acid was transported via the EUC to thermocline water at the equatorial Pacific (V19-30 and TT013-PC72) without being consumed completely within the Southern Ocean (Horn et al., 2011; Hayes et al., 2011; Anderson et al., 2009). Stronger Ekman transport in association with sea ice retreat and a poleward shift of southern westeries is suggested to be a driver (Anderson et al., 2009; Toggweiler et al., 2006).

A similarity between R_{diff} and pCO$_2$ variability during the last deglaciation supports an interpretation that older DIC was incorporated to subtropical surface water through mixing with SAMW/AAIW (Siani et al., 2013). Yet, further work is still needed to fully understand both the physical and biogeochemical dynamics in the Southern Ocean and the equatorial Pacific (Matsumoto & Yokoyama, 2013).

4-3-7. Did the equatorial Pacific contribute to the deglacial CO_2 rise?

Positive ΔpCO_2 indicates CO_2 flux from the ocean to the atmosphere (e.g., Takahashi et al., 2009). Previous studies (Douville et al., 2010; Palmer & Pearson, 2003) indicated that the equatorial Pacific contributed to deglacial CO_2 rise, however the timing of anomalously higher pCO_2 events recorded in radiogenically dated fossil corals do not systematically correspond to those of atmospheric CO_2 rise recovered from Antarctic ice core on the GICC05 timescale (Lourantou et al., 2010) (Fig 4-2). Moreover the new calibration reveals a modest CO_2 emission continued through the Bølling/Allerød/Antarctic Cold Reversal when no atmospheric CO_2 increase is observed (Figs. 4-2, 4-3, and 4-5). Though we demonstrate that the equatorial Pacific became a larger CO_2 source during the last deglaciation, it is too early to conclude its exact contribution to atmospheric CO_2 rise. The Southern Ocean is suggested to be central in CO_2 degassing due to its connectivity with the deep seawater, vast surface areas, and strong wind (Siani et al., 2013; Matsumoto & Yokoyama, 2013; Burke & Robinson, 2012; Yokoyama & Esat, 2011; Skinner et al., 2010; Rose et al., 2010; Anderson et al., 2009; Toggweiler et al., 2006). Furthermore, the contribution of other oceanic basins and the terrestrial biosphere should be further evaluated (Ciais et al., 2012; Yu et al., 2010). More evidence spanning the YD and the early part of HS1, in particular the sharp rise in atmospheric CO_2 and the sudden drop of $\delta^{13}C$ of CO_2 (Schmitt et al., 2012; Lourantou et al., 2010), as well as more spatial coverage is needed.

4-4. Conclusion

In order to assess equatorial Pacific's contribution to deglacial CO_2 rise, we measured $\delta^{11}B$ of fossil corals that were obtained at Tahiti. After procedure-specific isotopic corrections and location-specific pH_{SW} and $pCO_{2\ SW}$ difference corrections, $pCO_{2\ SW}$ were calculated from $\delta^{11}B$ values of both newly obtained and previously reported fossil corals using the new calibration established in Chapter 2. Reconstructed $pCO_{2\ SW}$ showed larger values than the atmospheric pCO_2 during the last deglaciation and near equilibrium condition during the LGM and the Holocene. These observations indicate that during the last deglaciation the equatorial Pacific became larger CO_2 source than the present. A compilation of marine ^{14}C reservoir ages in the surface seawater also

became larger during the last deglaciation, suggesting that a mixing with subsurface seawater characterized as higher DIC and older ages was stronger. More $p\text{CO}_2\,_{\text{SW}}$ reconstructions using fossil corals as well as marine sediment cores will reveal how glacial abyssal carbon had escaped to the atmosphere.

CHAPTER 5

General conclusion and future perspectives

5-1. General conclusion

In this thesis, a new approach of the δ^{11}B-pH$_{SW}$ calibration using massive *Porites* corals living in the natural environment was showd (Chichijima and Tahiti) (Chapter 2), and two application studies through δ^{11}B measurements of modern and fossil corals collected from Chichijima (Chapter 3) and Tahiti (Chapter 4). The key findings of this thesis are summarized as follows.

(1) *pH$_{SW}$ estimations are possible when CO$_2$ ventilation is good and abundant CO$_2$ chemistry data is available.*

Even if seawater CO_2 chemistry measurements are limited or do not exist at all, in some cases we can calculate past variations of pH$_{SW}$ and pCO$_2$ $_{SW}$ by utilizing atmospheric CO_2 records. Thus it is critical to check whether a study region is near the air-sea CO_2 equilibrium state or not. Additionally, we should not neglect international efforts that quantified the ocean's anthropogenic CO_2 absorption by ship based measurements and model simulations.

(2) *The δ^{11}B-pH$_{SW}$ calibration using cultured corals is not feasible to reconstruct reasonable pH$_{SW}$ variations.*

The pH$_{SW}$ reconstructions should be conducted using field-based δ^{11}B-pH$_{SW}$ calibration. It may be related to the fact that culturing experiments are basically conducted under heavily acidified seawater causing physiological stresses on corals. In addition, empirical equations are different depending on the sites in question (i.e., Chichijima, Tahiti, Guam, and Hainan), which means that the equation that can be ubiquitously applicable does not exist, and a regional calibration using one or more modern corals must be conducted. Thus, further δ^{11}B measurements of corals living in the natural environment are required to achieve more accurate pH$_{SW}$ reconstructions.

(3) *Past 100 years' ocean acidification has been negatively influencing calcification of Porites coral living in Chichijima through pH$_{CF}$ decreases.*

It can be highlighted that a rapid decrease of pH$_{CF}$ after 1960 is clearly seen. It was found that pH$_{CF}$ decreases of the Chichijima coral are significantly more sensitive to pH$_{SW}$ decreases than the other scleractinian corals cultured under the artificially

acidified seawater. These findings suggest that even 0.1 pH unit acidification has potential to cause substantial impacts on coral calcifications. This is the controvercial view that corals can keep homeostasis in calcification fluids. The $\delta^{13}C_{coral}$ has been decreasing at a consistent rate with $\delta^{13}C_{atm}$ since 1960 (the Suess effect). A significant positive relationship between $\delta^{13}C$ and $\delta^{11}B$ indicates that these phenomenons are from anthropogenic origin.

(4) *The equatorial Pacific became a larger CO_2 source during the last deglaciation.*

   The CO_2 purging events at Tahiti at 15.15 and 14.99 ka BP were discovered. These were analogous to the previously reported event found from Marquesas at 11.5 ka BP. The ^{14}C marine reservoir ages in the equatorial Pacific showed larger values during the last deglaciation than the present values, and a reasonable explanation for this is a stronger mixing with subsurface seawater characterized by higher DIC and older ages. A part of glacial carbon reservoir emerged in the Southern Ocean might have been incorporated into SAMW and AAIW, and then appeared in the equatorial Pacific.

5-2. Future perspectives

5-2-1. Perspectives on δ^{11}B-pH systematics

A part of the δ^{11}B interannual variabilities over analytical uncertainties from the Chichijima coral (Fig. 2-10) may be due to "heterogeneity of subsamples of coral skeleton" or "interannual variation of offset *a*", because such a large variation is unexpected from the δ^{11}B theoretical curve and seawater CO_2 chemistry (Figs. 2-5 & 2-9). The quantities of subsamples for δ^{11}B measurements were only a fraction (~0.1%, preliminary result) of the entire skeleton drilled to obtain three-year averages of environmental records. The heterogeneity of subsamples potentially biases δ^{11}B values, because pH$_{SW}$ changes by 0.1 seasonally at Chichijima (δ^{11}B seasonalities are perhaps ~1‰). Relatively smaller seasonalities of pH$_{SW}$ at Tahiti (and Marquesas) may partly explain why the fitting of coral δ^{11}B values and pH$_{SW}$ are better than that of Chichijima (Fig. 2-10). Thus, methodologies to drill the carbonate skeleton and to mix coarse grain subsamples are important to be developed. Another possible explanation of the large interannual δ^{11}B variabilities found in the Chichijima coral is the annual variation in offset *a* (measured δ^{11}B - theoretical δ^{11}B), more correctly ΔpH (= pH$_{CF}$ - pH$_{SW}$). Given the fact that not only *Porites* corals but also other genus of corals have different offset *a* and ΔpH (Figs. 1-4, 3-5 & 5-1), it is reasonable to assume that these parameters can vary from seasonal to decadal timescales. For instance, Dissald *et al*. (2012) found that light intensity could influence δ^{11}B of *Acropora* spp. through modifications of pH$_{CF}$. As for branching *P. cylindrica* and *P. compressa*, Hönisch *et al*. (2004) did not find any effect of water depths, nutrient levels, and temperatures on δ^{11}B. Strictly speaking, however, potential environmental factors (e.g., irradiance, temperature, salinity, and growth rate) that may control δ^{11}B of massive *Porites* corals have not been fully investigated yet. Hence through culturing experiments of massive *Porites* corals, effects of these environmental factors must be evaluated further to better understandings of δ^{11}B-pH systematics. There seem other controlling factors in addition to pH$_{SW}$, because not only the Chichijima coral but also *Porites* spp. collected in Guam showed interannual variabilities over analytical uncertainties (Fig. 5-1). Shinjo *et al.* (2013) did not find any correlations between δ^{11}B and ENSO index. Furthermore, these large interannual pH$_{SW}$ variations are unrealistic considering good ventilation of CO_2 in this

region. It is proposed that future works should quantify relative importance of pH_{SW} and other factors.

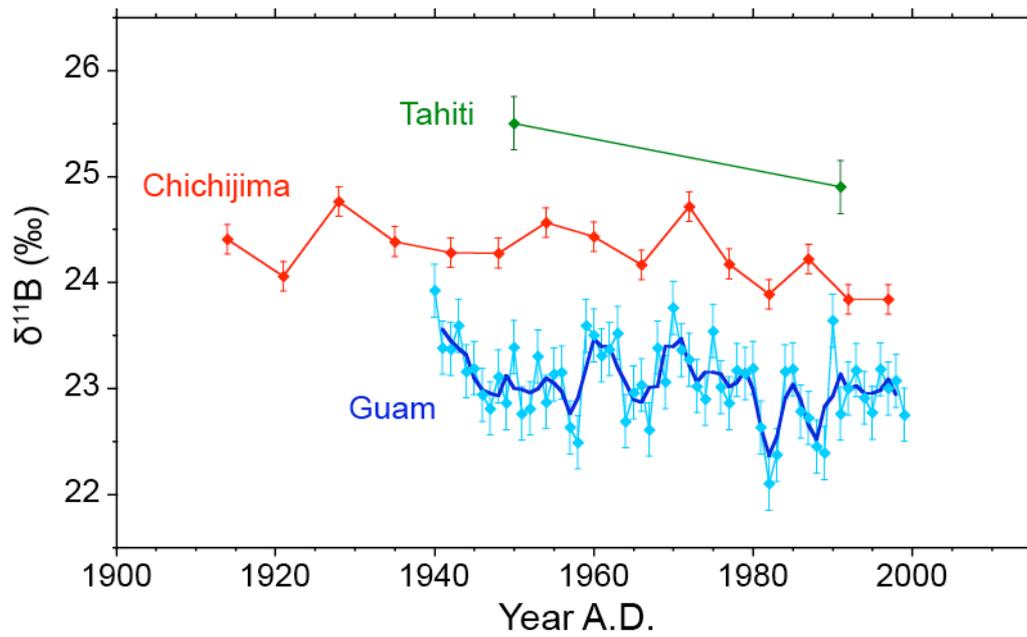**Fig. 5-1.** Comparison of $\delta^{11}B$ records of *Porites* spp. collected from Chichijima, Tahiti (Gaillardet & Allegre, 1995; Douville et al., 2010), and Guam (Shinjo et al., 2013). In Guam coral records, blue line represents three-year moving averages of annual records (light blue). Error bars are analytical uncertainties (2σ).

5-2-2. Direction of δ^{11}B-pH$_{SW}$ calibration using long-lived calcifying organisms

For future research, the new calibration procedures proposed by this thesis should further be applied to massive *Porites* corals from other areas for more comprehensive understanding of δ^{11}B-pH systematics. In this section, points needed to be adressed will be briefly described, and then near-future directions of our studies will be introduced.

(1) *Corals that are more than ~50 years old should be used.*

It is after 1960 when ocean acidification accelerated, thus δ^{11}B of corals that were more than 50 years old could record pH$_{SW}$ decreases. To date, only massive *Porites* spp. has been studied but other long-lived scleractinian corals such as *Favia* spp., *Diploria* spp., and *Siderastrea* spp. are also candidates for this research. In addition, potential of other surface living calcifiers such as coralline algae, sclerosponges, and mollusks should be investigated.

(2) *A well-ventilated area should be selected as a study region.*

The field-based δ^{11}B-pH$_{SW}$ calibration requires independent pH$_{SW}$ estimations. Open ocean seawater is well equilibrated with the overlying atmosphere in terms of CO_2. Thus, even around the coast of large continents, a region where seawater is well mixed with open ocean seawater should be selected as a study area. Ocean acidification occurs at a similar rate in the global surface ocean as far as CO_2 is well ventilated (e.g., Takahashi et al., 2014; Midorikawa et al., 2010; Lenton et al., 2010; Tans, 2009; Dore et al., 2009; Bates, 2007). It should be noted that there are many locations such as coastal regions, marginal seas, upwelling regions, and large coral reefs where CO_2 chemistry is far from the air-sea CO_2 equilibrium (e.g., Hendriks et al., 2015; Gruber et al., 2012; Hofmann et al., 2011). Such regions are not suitable for the calibration work.

Although long-lived massive *Porites* corals are very rare, inter-colonial variability often exist in coral skeletal geochemistry. Thus, we are going to measure two colonies *Porites* spp. collected from Kikaijima in 2009 (28.32°N 129.97°E). One coral is ~230 years old and the other coral is ~430 years old. Importantly the latter records preindustrial oceanic environments (Kawakubo et al., 2013). We believe that Kikaijima is one of the best study regions because these corals were collected from the environment that satisfies aforementioned prerequisites. Furthermore, as the island is close to Chichijima, we can evaluate the location-specific difference between two islands.

5-2-3. Paleoclimatological perspectives

Several important issues have been unsolved in paleoceanography since the last glacial period. First, even though pH_{SW} and $pCO_{2\ SW}$ reconstructions require past sea temperature changes, SST in the equatorial region during the LGM are in disagreement among proxies from myriad studies. Therefore, much more works are needed to constrain the LGM SST, as well as to estimate SST in less explored area such as the central Pacific. The second issue is a scarcity of R reconstructions at the equatorial Pacific during the LGM (Fig. 4-3). One critical reason is little evidence of coral reef growth during the LGM (Marshall & McCulloch, 2002). It substantially limits our knowledge about R. What is worse, there is no promising marine sediment cores that enables R estimation from ^{14}C measurements of planktonic foraminifer in association with independent age models (e.g., Reimer et al., 2013b). Recent success of coral reef drilling by IODP Exp. 325 at the world heritage site of the Great Barrier Reef, the northeastern Australia, must improve our understandings of past R variabilities, because it recovered many fossil corals dated to the LGM (Yokoyama et al., 2011). The third issue is about the IntCal curve (atmospheric $\Delta^{14}C$ records) during the glacial period. The IntCal curve is defined as "*the result of a community effort to produce the best calibration sets from the currently available data*" (Reimer et al., 2013a), thus there is the possibility of future revisions. The latest version of IntCal13 (especially, Lake Suigetu sediments and Hulu Cave speleothem data sets) are based on the hypothesis that dead carbon fraction (DCF) of Hulu Cave speleothem, a dilution effect by ^{14}C-depleted carbon derived from $CaCO_3$ bedrock, is absolutely constant through times. Whereas the DCF is constant from 12.55 ka BP to the present (Southon et al., 2012), it still remains unknown if it applies prior to 12.55 ka BP. In fact, a growth rate of Hulu Cave speleothem changes before and after ~19 ka BP (Southon et al., 2012), which is perhaps due to changes of a residence time of fresh water flowing through the bedrock. Residence time changes can influence the DCF estimation (Reimer et al., 2013b). Therefore, further efforts are necessary to establish the robust IntCal curve that does not require the reservoir corrections (i.e., R and DCF).

In terms of atmospheric CO_2 reconstructions, ice cores have provided invaluable records since 800 ka BP. Recently Marcott *et al.* (2014) published the highest resolution

CO_2 records so far during the last deglaciation through the analyses of West Antarctica Divide ice core (WDC) (Fig. 5-2). Intriguingly it revealed, for the first time, sudden CO_2 purge events (10–15 µatm increase in 200 years) beginning at 16.3 ka BP (during HS1), as well as previously reported events at 14.6 ka BP (the end of HS1) and 11.7 ka BP (the end of the YD) (Fig. 5-2). In marine CO_2 purge events found at the equatorial Pacific, one in Marquesas happened 230 years after 11.7 ka event (11.47 ± 0.09 ka BP, Douville et al., 2010). The other marine CO_2 events found at Tahiti (15.15 and 14.99 ka BP, this study) do not coincide with any major atmospheric CO_2 events, but it happened 350–510 years after slight $pCO_{2\,atm}$ increases at 15.5 ka BP (Fig. 5-2). One hypothesis to explain these observations is; it takes several hundred years for the upwelling of DIC-rich water in the Southern Ocean to emerge in the equatorial Pacific via SAMW and AAIW transport. However, this hypothesis should be tested with more spatial coverage of $pCO_{2\,SW}$ reconstructions around the equatorial Pacific region.

As seen in different reconstructions of the timing and the duration of these atmospheric CO_2 events from different Antarctic ice cores (e.g., WDC, EDC, Byrd, and Siple Dome) (Fig. 5-2), ice cores suffer from smoothing of the atmospheric CO_2 signal in the firn and large uncertainties in age determinations of gas trapped in the ice (e.g., Marcott et al., 2014; Pedro et al., 2012; Lourantou et al., 2010). Hence, modern and fossil corals, which are dated very accurately using U-series and preserve high-resolution records, have great potential to reveal fine structures of CO_2 events that might have occurred in a short period of time (decade to centuries): such as rapid CO_2 increases during the last deglaciation (Marcott et al., 2014) and during Heinrich events in the glacial period (e.g., Ahn & Brook, 2014), and rapid CO_2 decreases at ~1600 AD (e.g., Rubino et al., 2013).

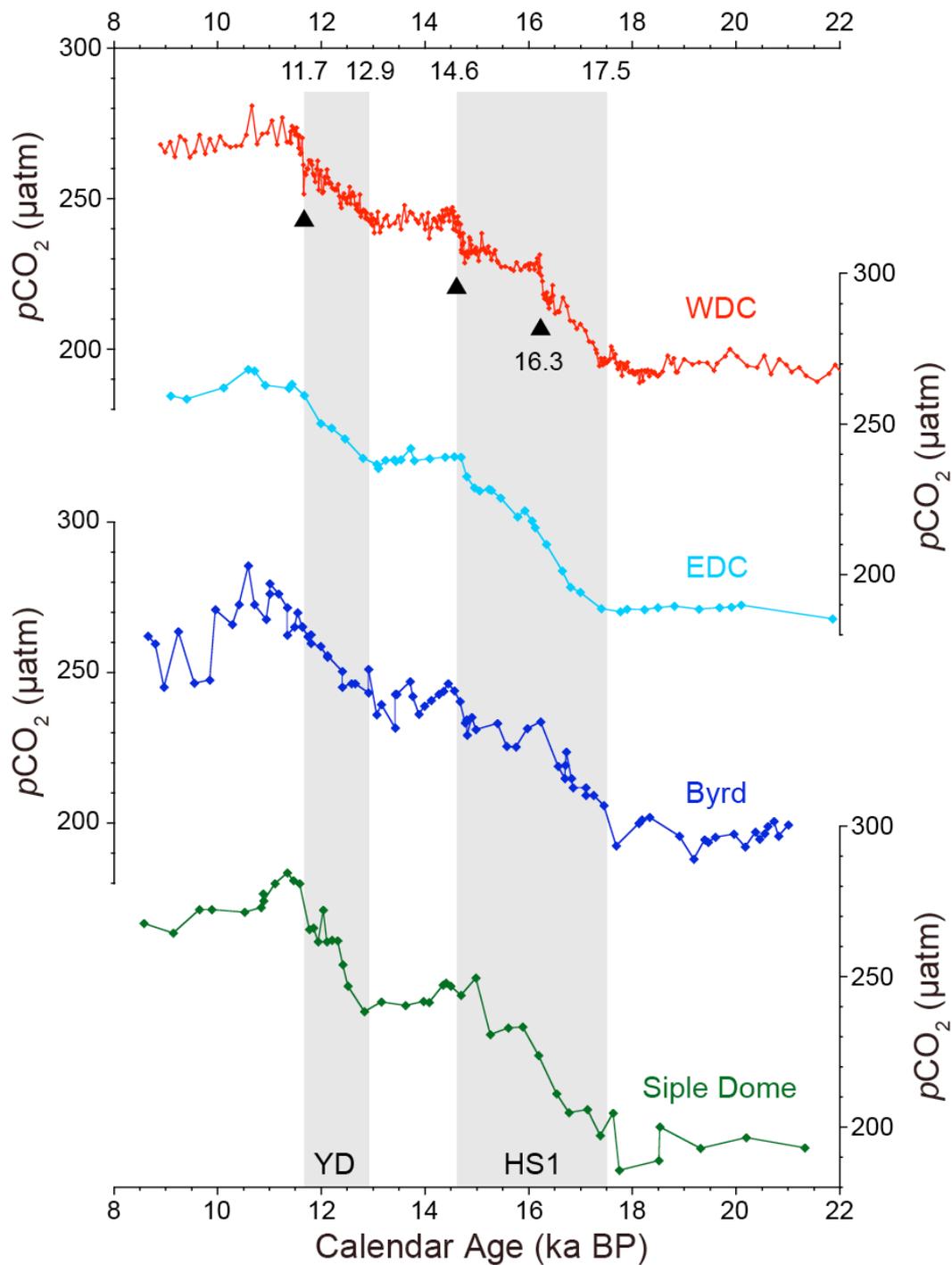**Fig. 5-2.** Atmospheric $p\mathrm{CO_2}$ records of Antarctic ice cores. Gass-ice age models are WDC06A−7 for WDC (Marcott et al., 2014); GICC05 for EDC (Lourantou et al., 2010), Byrd (Pedro et al., 2012), and Siple Dome (Pedro et al., 2012) ice cores. All replicated analyses are averaged. YD, Younger Dryas; HS1, Heinrich Stadial 1; WDC, West Antarctica Divide ice core; EDC, EPICA Dome C.

Acknowledgements

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Appendix A. Abbreviation

Abbreviation	Definition
AAIW	Antarctic Intermediate Water
ACR	Antarctic Cold Reversal
ALOHA	A Long-Term Oligotrophic Habitat Assessment
B/A	Bølling/Allerød
CLIVAR	Climate Variability and Predictability
DCF	Dead Carbon Fraction
DIC	Dissolved Inorganic Carbon
ECC	Equatorial Countercurrent
EDC	EPICA Dome C
EEP	Eastern Equatorial Pacific
EUC	Equatorial Undercurrent
GICC05	Greenland Ice Core Chronology 2005
GLODAP	Global Data Analysis Project
HS1	Heinrich Stadial 1
IODP	Integrated Ocean Drilling Program (International Ocean Discovery Program)
IPCC	Intergovernmental Panel on Climate Change
ITCZ	Intertropical Convergence Zone
JGOFS	Joint Global Ocean Flux Study
JMA	Japanese Meteorological Agency
LER	Linear Extension Rate
LGM	Last Glacial Maximum
MC-ICPMS	Multicollector-Inductively Coupled Plasma Massspectrometry
MLO	Mauna Loa Observatory
MOVE-G	Multivariate Ocean Variational Estimation–the global
NEC	North Equatorial Current
SAMW	Subantarctic Mode Water
SCS	South China Sea
SEC	South Equatorial Current

Continued

SOCAT	Surface Ocean CO_2 Atlas
SODA	Simple Ocean Data Assimilation
SPCZ	South Pacific Convergence Zone
SSS	Sea Surface Salinity
SST	Sea Surface Temperature
TA	Total Alkalinity
TIMS	Thermal Ionization Mass Spectrometry
TTO	Transient Tracers in the Oceans
WDC	West Antarctica Divide ice core
WEP	Western Equatorial Pacific
WOCE	World Ocean Circulation Experiment
WPWP	Western Pacific Warm Pool
YD	Younger Dryas

Appendix B. A script used to extract SOCAT v2 data set.

```
$intxt="./SOCATv2_TropicalPacific.tsv";
$outtxt="./SOCATv2_TropicalPacific_ogw.csv";
$"=",";
#-=-=#-=-=#-=-=#-=-=#-=-=#-=-=#-=-=#-=-=#
# set range : if not use, set extra large (or small) value (ex. -999 or 999)
$latmin=26.6;
$latmax=27.6;
$lonmin=139.7;
$lonmax=144.7;
$yrmin=1960;
$yrmax=2014;
#-=-=#-=-=#-=-=#-=-=#-=-=#-=-=#-=-=#-=-=#
# "¥" must be translated into "back slash".

if(-f $outtxt){
    print "¥n$outtxt exist! Overwrite it¥n";
    print " yes -> y // no -> any other key¥n";
    $yesno=<STDIN>;
    chomp($yesno);
    if($yesno ne "y"){exit;}
}
open(IN,"<$intxt");
print "Read $intxt¥n";
#
#
for($i=1;$i<=627;$i++){
    $header=<IN>;
#    print $header
}
$label=<IN>;
chomp($label);
```

```perl
@olabel=("Expocode","Yr","Mon","Day","Hour","Min","Longitude","Latitude","Temp
","Sal(measured)", "Sal(WOA05)","fCO2_rec","WOCE_flag");
open(OUT,">$outtxt");
        print OUT "@olabel\n";
while(<IN>){
  chomp;
  @indat=split("\t");
  if($indat[22]<0){next;}                       # fco2<0
  if($indat[10]<$latmin || $indat[10]>$latmax){next;}
  if($indat[9]<$lonmin || $indat[9]>$lonmax){next;}
  if($indat[3]<$yrmin || $indat[3]>$yrmax){next;}


        printf OUT "%14s", $indat[0];           #Expocode
        printf OUT ",%5d", $indat[3];           #year
        printf OUT ",%2d", $indat[4];           #month
        printf OUT ",%2d", $indat[5];           #day
        printf OUT ",%2d", $indat[7];           #hour
        printf OUT ",%2d", $indat[8];           #min
        printf OUT ",%9.4f", $indat[9];         #longitude
        printf OUT ",%9.4f", $indat[10];        #latitude
        printf OUT ",%7.3f", $indat[13];        #temperature
        printf OUT ",%7.3f", $indat[12];        #salinity (measured)
        printf OUT ",%7.3f", $indat[17];        #salinity (WOA05)
        printf OUT ",%7.2f", $indat[22];        #fco2_rec
        printf OUT ",%2d", $indat[24];          #WOCE_flag
        printf OUT "\n"
}
close(IN);
close(OUT);
print "Output $outtxt\n";
```

Appendix C. A script used to draw bathymetrical map of Fig. 2-1.

```
range=142.05/142.35/27/27.25
#size is in cm scale
size=6
reso=f
file=Ogasawara_bathymetry
xy=Ogasawara_coral_location


grdcut ETOPO1_Bed_c_gmt4.grd -R${range} -G${file}.grd
makecpt -Cocean -T-2000/0/50 -Z > ${file}.cpt
#
grdimage ${file}.grd -R${range} -JM${size} -C${file}.cpt -E100 -P -K > ${file}.eps
#
grdcontour ${file}.grd -JM${size} -C50 -W0.5 -L-500/-50 -A50tf6 -O -K >> ${file}.eps
pscoast -R${range} -JM${size} -D${reso} -W1 -A -G220 -O -K -Lf142.2/27.3/27.3/5k >> ${file}.eps
psscale -Ba500g500f500 -C${file}.cpt -D3c/-1c/6c/0.3ch -O -K >> ${file}.eps
psxy ${xy}.txt -JM -R -W -Sd6p -Gblack -O -K >> ${file}.eps
#pstext ${xy}.txt -JM -R -O -Gblue -D0.2/0 >> ${file}.eps
psbasemap -R${range} -JM -Ba0.1f0.1/a0.1f0.1WSne -O >> ${file}.eps
```