

## 論文の内容の要旨

### 論文題目

Studies on seawater CO<sub>2</sub> 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)

氏名 窪田 薫

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Boron isotope ratios ( $\delta^{11}\text{B}$ ) of biogenic carbonates depend on seawater pH ( $\text{pH}_{\text{SW}}$ ). To date, many stony corals have been reared in  $\text{pH}_{\text{SW}}$ -regulated aquariums, and  $\delta^{11}\text{B}$  of skeletons that grew during the experiment have been measured. While the results clearly revealed  $\text{pH}_{\text{SW}}$ -dependency of  $\delta^{11}\text{B}$  of coral skeletons, they revealed a large difference between measured  $\delta^{11}\text{B}$  values and theoretically expected ones, too. In order to reconcile the difference, two approaches have been proposed. One approach regards  $\delta^{11}\text{B}$  as a recorder of pH of calcification fluid ( $\text{pH}_{\text{CF}}$ ), rather than  $\text{pH}_{\text{SW}}$ , because a line of evidence uncovers  $\text{pH}_{\text{CF}}$  is higher than  $\text{pH}_{\text{SW}}$  (biological pH up-regulation). The other approach simply presumes the difference as  $\delta^{11}\text{B}$  offsets (empirical corrections). Whichever approaches are employed, however, culturing experiment-based  $\delta^{11}\text{B}$ - $\text{pH}_{\text{SW}}$  calibrations appear to reconstruct  $\text{pH}_{\text{SW}}$  that conflicts with the CO<sub>2</sub> chemistry observation. Therefore, another means to calibrate  $\delta^{11}\text{B}$ - $\text{pH}_{\text{SW}}$  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  $\text{pH}_{\text{SW}}$  decreases since the preindustrial period (ocean acidification).

The research objectives of this thesis are (1) to obtain the field-based  $\delta^{11}\text{B}$ -pH<sub>SW</sub> calibrations and (2) to utilize them in paleoenvironmental studies. It is noteworthy that deep understandings of the  $\delta^{11}\text{B}$ -pH<sub>SW</sub> 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  $\delta^{11}\text{B}$ -pH<sub>SW</sub> calibrations using massive *Porites* corals collected from Chichijima (Ogasawara Islands, Japan) and Tahiti (Society Islands, French Polynesia) was 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  $\delta^{11}\text{B}$  of *Porites* coral obtained from Chichijima. Previously reported  $\delta^{11}\text{B}$  values of Tahitian corals were also used after corrections of different procedure-specific isotopic offsets. Comparing coral  $\delta^{11}\text{B}$  records with pH<sub>SW</sub> that was estimated from many CO<sub>2</sub> chemistry data and atmospheric CO<sub>2</sub> records, we established, for the first time, field-based calibrations for Chichijima and Tahiti. Using the established calibration, we reevaluated the previously reported pH<sub>SW</sub> reconstructions from  $\delta^{11}\text{B}$  of *Porites* corals obtained from Guam and Hainan islands. The results showed that empirically reconstructed pH<sub>SW</sub>, as well as partial pressure of CO<sub>2</sub> in the seawater ( $p\text{CO}_2$  SW), were more in line with CO<sub>2</sub> 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  $\delta^{11}\text{B}$  measurements, that ocean acidification is affecting the pH<sub>CF</sub> in *Porites* coral collected at Chichijima. A rapid decline of  $\delta^{11}\text{B}$  of coral skeleton since 1960 ( $-0.17 \pm 0.07\%$ /decade) was observed and was compared with pH<sub>SW</sub> near the Ogasawara Islands over the 20th century. The results indicated that pH<sub>CF</sub> has been changing sensitively to pH<sub>SW</sub> and suggested that the calcification fluid of coral will become corrosive to aragonite in the future (pH<sub>CF</sub> = ca.

8.3 when  $\text{pH}_{\text{SW}} = \text{ca. } 8.0$  in 2050) at an earlier point than previously expected, despite the  $\text{pH}_{\text{CF}}$  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  $\text{CO}_2$  rise during the last deglaciation ( $\sim 80 \mu\text{atm}$ ), the roles of the equatorial Pacific, where the largest  $\text{CO}_2$  source exists at present, remains largely unconstrained. We showed  $\text{pH}_{\text{SW}}$  and  $p\text{CO}_2 \text{ sw}$  variations during this period reconstructed from fossil *Porites* corals obtained at Tahiti based on empirical  $\delta^{11}\text{B-pH}_{\text{SW}}$  calibration. The new data, together with recalibrated existing data, indicated that a significant  $p\text{CO}_2 \text{ sw}$  increase ( $\text{pH}_{\text{SW}}$  decrease), accompanied by anomalously large marine  $^{14}\text{C}$  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  $\text{CO}_2$  emission, which may be derived from higher subsurface DIC concentration.