

## 1. Introduction

The concentration of carbon dioxide (CO<sub>2</sub>), a major greenhouse gas, has been increasing in the atmosphere because of anthropogenic activities such as fossil fuel burning (IPCC, 2007b; WDCGG, 2007). The current concentration of CO<sub>2</sub> in the atmosphere is approximately 100 ppm higher than that during the preindustrial era, i.e. early 18<sup>th</sup> century (280 ppm; IPCC, 2007a). To predict future atmospheric CO<sub>2</sub> concentrations on the basis of emission scenarios and the potential alteration of carbon cycles caused by climate change, the processes that control the flux of CO<sub>2</sub> and its temporal variability among global carbon reservoirs, including the atmosphere, the terrestrial biosphere and the oceans, must be understood.

The oceans are the important sinks for anthropogenic CO<sub>2</sub>. The latest estimate of ocean CO<sub>2</sub> uptake is  $2.2 \pm 0.5 \text{ GtC yr}^{-1}$  (IPCC, 2007b). Recent model simulation revealed that uptake of anthropogenic CO<sub>2</sub> by the oceans will lower the average pH of surface seawater by approximately 0.1 compared with the pH in 1750 (Caldeira and Wickett, 2003). The increase in CO<sub>2</sub> concentration in the ocean's surface layer affects the chemical equilibrium in seawater. As CO<sub>2</sub> concentrations increase, surface waters become more acidic, and the concentration of carbonate ion consequently decreases. This change in chemical equilibrium reduces the capacity of the ocean to take up additional CO<sub>2</sub> (Sabine et al., 2004). Moreover, model simulations have indicated that anthropogenic ocean acidification might impact calcifying organisms at high latitudes, particularly in the Southern Ocean, within the next few decades, not centuries as suggested previously (Orr et al., 2005). Therefore, monitoring ocean acidification and its influence on biogeochemical processes by means of field observations is highly important.

At the hydrogen ion concentration range of seawater observed in the oceans, CO<sub>2</sub> predominantly exists as hydrogencarbonate (HCO<sub>3</sub><sup>-</sup>) or carbonate (CO<sub>3</sub><sup>2-</sup>) ions. The concentrations of these ions are determined by mass balance, charge balance and the acid–base equilibrium within the carbonate system in seawater. This carbonate system can be described by four measurable parameters: CO<sub>2</sub> partial pressure (*p*CO<sub>2</sub>), total inorganic carbon (TCO<sub>2</sub>), hydrogen ion concentration ([H<sup>+</sup>]) and total alkalinity (TA). The hydrogen ion concentration, usually reported as pH (= -log [H<sup>+</sup>]), determines the ratio of carbonate to TCO<sub>2</sub> and the ratio of hydrogencarbonate to TCO<sub>2</sub>. Given two of these four parameters, one can calculate the remaining two from the thermodynamic relationships between the parameters (e.g., Lee and Millero, 1995).

We have been observing *p*CO<sub>2</sub> in the atmosphere and in near-surface seawater (i.e., air in which CO<sub>2</sub> gas exchange between a great excess of near-surface water has attained the equilibrium) for more than two decades and TCO<sub>2</sub> in seawater for more than a decade, mainly in the western Pacific Ocean and the equatorial Pacific Ocean (Inoue, 1995; Inoue, 2000; Ishii et al., 2001; Midorikawa et al., 2005). We aimed

to describe the temporal and spatial variations of these parameters and to understand the factors that control them. In addition, we started to measure pH in seawater with high comparability and precision in the late 1990s to describe the variability in the carbonate system not only in surface waters but also at greater depths. We continually improve our methods to measure these parameters precisely.

Midorikawa et al. (2005) reported that  $p\text{CO}_2$  values in the atmosphere and in surface waters in the western subtropical North Pacific Ocean increased at rates of  $1.60 \pm 0.03 \mu\text{atm yr}^{-1}$  and  $1.6 \pm 0.2 \mu\text{atm yr}^{-1}$ , respectively between 1984 and 2003. This rate of increase in oceanic  $p\text{CO}_2$  corresponds to an annual change in pH of  $-0.002 \text{ yr}^{-1}$  at a constant TA of  $2300 \mu\text{mol kg}^{-1}$ . Therefore, a pH measurement precision of 0.002 or better is required to monitor long-term oceanic acidification (DOE, 1994).

Seawater pH was formerly measured by a potentiometric method using a pair of glass and Ag/AgCl reference electrodes (e.g., Grasshoff, 1976) based on the operational definition of pH in the absence of seawater-based reference material. However, because of experimental problems such as the fluctuation in electrode sensitivity and residual liquid junction potential, a precision better than  $\pm 0.01$  was rarely achieved, even with very careful measurements (Dickson, 1993). For more precise measurements, a spectrophotometric method has been developed (Byrne et al., 1988; Dickson, 1993). In this study, we constructed an automated apparatus with a flow-type spectrophotometric cell in a closed circuit. Using this apparatus, we achieved the precision of  $\pm 0.0002$  for on board measurements. The reproducibility of measurements and the effects of sample storage were also examined.

## 2. Methods and materials

### 2.1 Principles

In the spectrophotometric method, pH is determined by measuring the visible absorption spectra of seawater samples containing indicator. Our method was based on that described by Clayton and Byrne (1993), who used *m*-cresol purple as an indicator dye.

At the pH range of seawater (7.4–8.2), the predominant pair of acid ( $\text{HI}^-$ )<sup>1</sup> and base ( $\text{I}^{2-}$ )<sup>1</sup> forms of *m*-cresol purple are in equilibrium with each other (Eq. (1)):




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<sup>1</sup> Though the net charges of the acid form and the base form of *m*-cresol purple are 0 and  $-1$ , respectively, we express these ions as  $\text{HI}^-$  and  $\text{I}^{2-}$  for the sake of convenience, as such notation is conventional for dibasic acids.