

DISSOLUTION PROCESS OF GLOBIGERINA BULLOIDES  
SHELL (PLANKTIC FORAMINIFERA) OBSERVED BY X-RAY  
MICRO CT BASED ON DISSOLUTION EXPERIMENT AND  
DEEP-SEA SEDIMENT SAMPLES

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## CHAPTER 1

### INTRODUCTION

#### 1. CARBONATE IN MARINE SEDIMENT

There are several types of marine organism, which create calcium carbonate ( $\text{CaCO}_3$ ) in the ocean. The representative ones are pteropoda, coral, foraminifera and coccolithophorid. Among them, pteropoda and coral have aragonite shell/skeleton whereas foraminifera and coccolithophorid have calcite shells. Because calcite is more thermodynamically stable than aragonite [Winland, 1960], calcite shell is relatively well preserved in marine sediment. Therefore, calcium carbonate (calcite) created by foraminifera and coccolithophorid consist most of marine  $\text{CaCO}_3$  sediment. Most  $\text{CaCO}_3$  (calcite) is formed in near surface waters by foraminifera and coccolithophorid and exported to ocean interior. During the  $\text{CaCO}_3$  export from sea-surface to deep-sea sediment, about half of the  $\text{CaCO}_3$  that leaves the surface ocean arrives at marine sediments. Among them, about a third is buried and hence ~13% of the surface exports of  $\text{CaCO}_3$  is lost from the ocean every year [Archer, 1996a; Milliman and Droxler 1996]. Therefore,  $\text{CaCO}_3$  distribution in deep-sea sediment is basically controlled by the coccolithophore and planktic foraminiferal production in the surface water and dissolution in the deep-sea particularly on the seafloor. At first, Arrhenous [1952] investigated  $\text{CaCO}_3$  content in equatorial Pacific. They suggested that variation of  $\text{CaCO}_3$  contents in the sediment has been contributed by  $\text{CaCO}_3$  productivity in the sea

surface. Later, however, several studies revealed that variation of  $\text{CaCO}_3$  content in the sediment is mainly contributed by dissolution of carbonate in the deep-sea [e.g. Berger, 1973; Luz, 1973; Thompson and Saito, 1974; Thompson, 1976; Adelseck, 1977; Volat et al., 1980]. Distribution of  $\text{CaCO}_3$  content in marine sediment is inhomogeneous [e.g., Archer, 1996b]. For example, regions with high  $\text{CaCO}_3$  content are mostly in the shallow oceanic ridges whereas the deep ocean basins are almost completely devoid of  $\text{CaCO}_3$ . In general, sedimentary  $\text{CaCO}_3$  content in the Atlantic Ocean is higher than that of the Pacific Ocean. In particular,  $\text{CaCO}_3$  content is almost zero in the North Pacific below 4000 m. Most  $\text{CaCO}_3$  is dissolved in the deep-sea in the North Pacific regardless of high  $\text{CaCO}_3$  export flux [Dunne et al., 2005].

Dissolution and preservation of  $\text{CaCO}_3$  on the seafloor plays an important role in global climate change [e.g., Broecker, 2006]. The Antarctic ice core records revealed glacial  $p\text{CO}_2$  in the atmosphere was  $\sim 80$  ppm lower than that of during the interglacial periods [Barnola et al., 1987; Petit et al., 1999]. Various hypotheses have been suggested to explain the observed  $p\text{CO}_2$  change in the atmosphere. [e.g., Archer et al., 2000; Boyle, 1988; Broecker and Peng, 1987; Sanyal et al., 1995; Sigman and Boyle, 2000]. However, there is no consensus on the specific drivers of glacial-interglacial  $p\text{CO}_2$  changes. Carbon pool in the deep sea is 60 times as large as the atmosphere [Sigman and Boyle, 2000] and duration of the glacial termination is at millennial time scales [e.g., Matsumoto, 2007] which is equivalent to the thermohaline circulation. In

addition,  $\delta^{13}\text{C}$  of benthic foraminiferal shells revealed that mass of carbon stored as terrestrial biomass was smaller during glacial than during interglacial periods [Shackleton, 1967; Curry et al., 1988]. These results strongly suggest that the deep-sea must have been played a role as carbon reservoir during glacial periods.

One possible mechanism to store extra-carbon in the glacial ocean was reviewed in Sigman and Boyle [2000]. In this mechanism, the speciation of  $\Sigma\text{CO}_2$  may shift away from  $\text{CO}_2$  (aq) [Broecker and Peng, 1987].  $\Sigma\text{CO}_2$  or dissolved inorganic carbon (DIC) is represented by:



where the concentration of  $\text{H}_2\text{CO}_3$  is negligible. The speciation of the  $\Sigma\text{CO}_2$  pool helps to maintain a charge balance with the excess of conservative cations over conservative anions in seawater, which called as the alkalinity. As the ratio of alkalinity to  $\Sigma\text{CO}_2$  increases, the  $\Sigma\text{CO}_2$  equilibrium shifts to the right and  $\text{CO}_2$  (aq) drops. As the ratio of alkalinity to  $\Sigma\text{CO}_2$  decreases, the equilibrium shifts to the left and  $\text{CO}_3^{2-}$  drops. Dissolution of  $\text{CaCO}_3$  in the deep-sea sediment elevates the  $\text{CO}_3^{2-}$  in the deep water. When the deep water upwells to the sea-surface, atmospheric  $\text{CO}_2$  is absorbed. Broecker and Peng [1987] expected  $\text{CaCO}_3$  preservation spike during the glacial termination and such preservation maxima were found in the Pacific Ocean [Marchitto et al., 2005]. On the contrary,  $\text{CaCO}_3$  dissolution event occur at the onset of glacial period and major dissolution events were found in the Atlantic Ocean during the marine isotope stages 5d,

5b, and 4 [Broecker, 2006].  $\text{CaCO}_3$  preservation/dissolution events linked to the glacial-interglacial cycles have been reported in the global ocean [Broecker, 1971; Berger, 1973; Thompson and Saito, 1974; Luz and Shackleton, 1975; Farrel and Prell, 1989].

## **2. $\text{CaCO}_3$ DISSOLUTION**

$\text{CaCO}_3$  particles dissolve in the water column and surface sediment.  $\text{CaCO}_3$  distribution in deep-sea sediment depends on the water depth of transition zone in the ocean. Sediments from mid-depth are rich in  $\text{CaCO}_3$  and those from abyssal depths are devoid of  $\text{CaCO}_3$ . These two realms are separated by a transition zone spanning several hundreds of meters in water depth over which the  $\text{CaCO}_3$  content drops toward zero. Upper limit of the transition zone is called lysocline [Peterson, 1966; Milliman, 1977; Metzler et al., 1982]. On the other hand, lower limit of the transition zone is called carbonate compensation depth (CCD). The depth of transition zone basically influenced by deep water properties by thermohaline circulation and it becomes shallow as age of deep water [Broecker and Takahashi, 1977]. Change in the depth of transition zone must have provided the change in DIC and alkalinity of the global ocean. Therefore, dissolution and preservation of calcite play an important role in the global carbon cycle.

There are three possible calcite dissolution processes from upper ocean to sediment. The first one is in water column. Considerable  $\text{CaCO}_3$  dissolution in the

upper 500–1000 m of the ocean mediated by zooplankton activities [Milliman et al., 1999] although the high sinking velocity of sinking particles (greater than 100 m day<sup>-1</sup>) [e.g., Berelson, 2002]. The second one is on the seafloor. This dissolution occurs only at water depth greater than that of lysocline [Broecker, 2006]. The linear relationship between deep water calcite saturation state ( $\Omega$ ) and carbonate dissolution has been suggested in several studies [Broecker and Clark 1999; Broecker and Clark 2001; Johnstone et al., 2010]. The third one is in sediment. CO<sub>2</sub> is released into the pore water during remineralization of organic matter, which leads to CaCO<sub>3</sub> dissolution even if the overlying bottom water is supersaturated [Berger, 1970]. Quantitative models to estimate CaCO<sub>3</sub> dissolution by metabolically produced CO<sub>2</sub> have suggested that the third process plays a significant role in calcite dissolution in case of the molar ratio of organic carbon to CaCO<sub>3</sub> of the deposited material is near 1:1 or greater [Emerson and Bender, 1980; Archer, 1991; Hales, 2003]. In summary, dissolution of ocean calcite mainly occurs on and in the sediment, reflecting the condition of ambient seawater.

Under- and super-saturation of the water column is determined by calcite saturation state ( $\Omega$ ), which is defined as the ratio of the product of the solutes over the product of the solutes at saturation (solubility product)

$$\Omega = [\text{CO}_3^{2-}] [\text{Ca}^{2+}] / [\text{CO}_3^{2-}]_{\text{sat}} [\text{Ca}^{2+}]_{\text{sat}} = [\text{CO}_3^{2-}] [\text{Ca}^{2+}] / K_{sp}$$

where  $[\text{CO}_3^{2-}]_{\text{sat}}$  and  $[\text{Ca}^{2+}]_{\text{sat}}$  are the concentration of the carbonate and dissolved calcium ions in equilibrium with mineral CaCO<sub>3</sub>.  $[\text{CO}_3^{2-}]$  and  $[\text{Ca}^{2+}]$  are observed

carbonate and calcium ions concentrations.  $K_{sp}$  is the solubility product, which is contributed by temperature, salinity, pressure, pH and nutrient. When  $\Omega > 1$ , seawater is supersaturated with respect to mineral  $\text{CaCO}_3$ . Conversely, when  $\Omega < 1$ , seawater is undersaturated. Because  $[\text{Ca}^{2+}]$  in the ocean has long residence time of  $10^6$  yr, it can be assumed to be constant in a time scale shorter than  $10^4$  yrs. The carbonate saturation state ( $\Omega$ ), therefore, is mainly determined by the  $[\text{CO}_3^{2-}]$  and  $K_{sp}$ . Numbers of proxies using planktic foraminiferal shell to reconstruct past  $[\text{CO}_3^{2-}]$  in the deep-sea have been proposed.

### **3. CALCIUM CARBONATE DISSOLUTION PROXIES USING PLANKTIC FORAMINIFERAL SHELLS**

Proxies for  $\text{CaCO}_3$  dissolution have been proposed based on planktic foraminiferal shells. Planktic foraminiferal assemblage in the sediment is the one. Planktic foraminiferal shells have a variety of morphology and some of them are fragile and prone to dissolution [Ruddiman and Heezen 1967; Berger, 1968]. Berger (1968) proposed dissolution index based on empirically ranked planktic foraminiferal species. Similarly, benthic foraminifera have normally thick and smooth shells that are more resistant to dissolution than those of planktic foraminifera. Thus, planktic to benthic foraminiferal ratio in the sediment has been suggested as dissolution proxy [Arrhenius, 1952; Parker and Berger, 1971; Thunell, 1976; Peterson and Prell, 1985]. However, the

proxies based on foraminiferal assemblage require regional calibration. Further, the results depend on the initial makeup of the foraminiferal population in the sediment. Ratio of foraminifera fragments to whole shells is widely used as calcite dissolution index [Peterson and Prell, 1985; Wu and Berger, 1989]. Advantage of the fragment ratio is simplicity. However, its determination is often subjective and it also depends on initial make-up of the foraminiferal assemblages. These methods are not calibrated against present-day pressure-normalized  $[\text{CO}_3^{2-}]$ .

Size-normalized shell weight of planktic foraminifera, which was firstly proposed by [Lohman, 1995], is the most widely used method to reconstruct past  $[\text{CO}_3^{2-}]$ . Shell wall thickness is able to be estimated. The linear relationship between size-normalized shell weight and bottom-water calcite saturation state were suggested [Broecker and Clark, 2001; de Villiers, 2005]. This method is based on empirical calibration of bottom water  $[\text{CO}_3^{2-}]$  or  $\Omega_{\text{calcite}}$  with average weight of clean shells of selected species picked up from narrow size ranges in core-top samples [e.g., de Villiers, 2005]. However, Barker and Elderfield [2002] showed that the thickness of the foraminifera shell walls varies with growth conditions. Spero et al [1997] found strong correlations between shell weight and both water temperature and carbonate ion concentration, the warmer the water and the higher its carbonate ion concentration, the thicker the shells. Therefore, size-normalized shell weight technique has an uncertainty due to initial shell weight variation depending on carbonate saturation state in the



surface water.

As described above, available proxies for CaCO<sub>3</sub> dissolution have a common problem that no proxies can estimate amount of dissolved foraminiferal shell quantitatively. A reason for the problem is limited understanding of dissolution process of planktic foraminiferal shell. In the previous studies, scanning electron microscope (SEM) has been employed for dissolution process observation of planktic foraminiferal shell. SEM observations of the shell surface structure and cross sectional structure of foraminiferal shell wall in marine sediment were performed [e.g., Bonneau et al., 1980; Volber and Henrich, 2002]. Bé et al [1975] performed a laboratory dissolution experiment and observed dissolution process of planktic foraminiferal shell by SEM. However, SEM observation is restricted to shell surface or cross section surface and dissolution process of internal structure have not been clarified yet.

#### **4. GOAL OF THIS STUDY**

Goal of this study is to understand the dissolution process of planktic foraminiferal shell and to develop a novel proxy to measure amount of dissolved shell quantitatively. In Chapter 2, a laboratory dissolution experiment of planktic foraminiferal shells in pH controlled under-saturated water was performed. Dissolution process of foraminiferal shells was observed by X-ray CT scanner and the novel proxy

for  $\text{CaCO}_3$  dissolution was proposed. In Chapter 3, knowledge on dissolution of planktic foraminiferal shell was applied to foraminiferal shells in deep-sea sediments.

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