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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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https://doi.org/10.15017/1441030

出版情報:九州大学,2013,博士(理学),課程博士 バージョン: 権利関係:全文ファイル公表済

CHAPTER 1

INTRODUCTION

1. CARBONATE IN MARINE SEDIMENT

There are several types of marine organism, which create calcium carbonate (CaCO₃) 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 CaCO₃ sediment. Most CaCO₃ (calcite) is formed in near surface waters by foraminifera and coccolithophorid and exported to ocean interior. During the CaCO₃ export from sea-surface to deep-sea sediment, about half of the CaCO₃ that leaves the surface ocean arrives at marine sediments. Among them, about a third is buried and hence $\sim 13\%$ of the surface exports of CaCO₃ is lost from the ocean every year [Archer, 1996a; Milliman and Droxler 1996]. Therefore, CaCO₃ 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 CaCO3 content in equatorial Pacific. They suggested that variation of CaCO₃ contents in the sediment has been contributed by CaCO₃ productivity in the sea

surface. Later, however, several studies revealed that variation of CaCO₃ 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 CaCO₃ content in marine sediment is inhomogeneous [e.g., Archer, 1996b]. For example, regions with high CaCO₃ content are mostly in the shallow oceanic ridges whereas the deep ocean basins are almost completely devoid of CaCO₃. In general, sedimentary CaCO₃ content in the Atlantic Ocean is higher than that of the Pacific Ocean. In particular, CaCO₃ content is almost zero in the North Pacific below 4000 m. Most CaCO₃ is dissolved in the deep-sea in the North Pacific regardless of high CaCO₃ export flux [Dunne et al., 2005].

Dissolution and preservation of CaCO₃ on the seafloor plays an important role in global climate change [e.g., Broecker, 2006]. The Antarctic ice core records revealed glacial pCO₂ in the atmosphere was ~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 pCO₂ 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 pCO₂ 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, δ^{13} 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 ΣCO_2 may shift away from CO_2 (aq) [Broecker and Peng, 1987]. ΣCO_2 or dissolved inorganic carbon (DIC) is represented by:

$$\Sigma \text{CO}_2 = [\text{CO}_2(\text{aq})] \longleftrightarrow [\text{H}_2\text{CO}_3] \longleftrightarrow [\text{HCO}_3^-] \longleftrightarrow [\text{CO}_3^{2^-}].$$

where the concentration of H_2CO_3 is negligible. The speciation of the ΣCO_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 ΣCO_2 increases, the ΣCO_2 equilibrium shifts to the right and CO_2 (aq) drops. As the ratio of alkalinity to ΣCO_2 decreases, the equilibrium shifts to the left and $CO_3^{2^2}$ drops. Dissolution of CaCO₃ in the deep-sea sediment elevates the $CO_3^{2^2}$ in the deep water. When the deep water upwells to the sea-surface, atmospheric CO_2 is absorbed. Broecker and Peng [1987] expected CaCO₃ preservation spike during the glacial termination and such preservation maxima were found in the Pacific Ocean [Marchitto et al., 2005]. On the contrary, CaCO₃ 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]. CaCO₃ preservation/dissolution events linked to the glacial-interglacial cycles have been reported in the global ocean [Broecker, 1971; Berger, 1973; Thompson and Saito, 1974l Luz and Shackleton, 1975; Farrel and Prell, 1989].

2. CACO₃ DISSOLUTION

CaCO₃ particles dissolve in the water column and surface sediment. CaCO₃ distribution in deep-sea sediment depends on the water depth of transition zone in the ocean. Sediments from mid-depth are rich in CaCO₃ and those from abyssal depths are devoid of CaCO₃. These two realms are separated by a transition zone spanning several hundreds of meters in water depth over which the CaCO₃ 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 CaCO₃ 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⁻¹) [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 (Ω) 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. CO₂ is released into the pore water during remineralization of organic matter, which leads to CaCO₃ dissolution even if the overlying bottom water is supersaturated [Berger, 1970]. Quantitative models to estimate CaCO₃ dissolution by metabolically produced CO₂ have suggested that the third process plays a significant role in calcite dissolution in case of the molar ratio of organic carbon to CaCO₃ 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 (Ω), which is defined as the ratio of the product of the solutes over the product of the solutes at saturation (solubility product)

$$\Omega = [CO_3^{2^-}] [Ca^{2^+}] / [CO_3^{2^-}]_{sat} [Ca^{2^+}]_{sat} = [CO_3^{2^-}] [Ca^{2^+}] / Ksp$$

where $[CO_3^{2^-}]_{sat}$ and $[Ca^{2^+}]_{sat}$ are the concentration of the carbonate and dissolved calcium ions in equilibrium with mineral CaCO₃. $[CO_3^{2^-}]$ and $[Ca^{2^+}]$ are observed

carbonate and calcium ions concentrations. *Ksp* is the solubility product, which is contributed by temperature, salinity, pressure, pH and nutrient. When $\Omega > 1$, seawater is supersaturated with respect to mineral CaCO₃. Conversely, when $\Omega < 1$, seawater is undersaturated. Because $[Ca^{2+}]$ in the ocean has long residence time of 10⁶ yr, it can be assumed to be constant in a time scale shorter than 10⁴ yrs. The carbonate saturation state (Ω), therefore, is mainly determined by the $[CO_3^{2-}]$ and *Ksp*. Numbers of proxies using planktic foraminiferal shell to reconstruct past $[CO_3^{2-}]$ in the deep-sea have been proposed.

3. CALCIUM CARBONATE DISSOLUTION PROXIES USING PLANKTIC FORAMINIFERAL SHELLS

Proxies for CaCO₃ 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 $[CO_3^{2^-}]$.

Size-normalized shell weight of planktic foraminifera, which was firstly proposed by [Lohman, 1995], is the most widely used method to reconstruct past $[CO_3^{2-}]$. 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 Villers, 2005]. This method is based on empirical calibration of bottom water $[CO_3^{2-}]$ or $\Omega_{calcite}$ 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 CaCO₃ 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 CaCO₃ 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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