<div align="center">論文内容の要旨</div>

論文題目　Mg-calcite dissolution in coral reefs estimated by laboratory experiment and field observation
（室内実験及び現場観測におけるサンゴ礁砂地の Mg-calcite 溶解）

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The ocean is a large carbon reservoir and more than 30% of the CO_2 emitted into the atmosphere by human activities is taken up by the oceans (Sabine et al., 2004), lowering the pH of surface water and decreasing the saturation state of minerals (Kleypas et al., 2006). Future uptake of CO_2 by the ocean is predicted to reduce seawater pH by 0.3 to 0.5 units over the next few decades (Caldeira and Wickett, 2003), which is called ocean acidification. Previous studies have mainly investigated the effects of elevated $p\text{CO}_2$ on the net production and calcification of marine organisms. On the other hand, carbonate dissolution will occur in polar regions and in the deep sea where saturation state with respect to carbonate minerals (Ω_a) will be <1 by 2100. Recent reports demonstrate nocturnal carbonate dissolution of reefs, despite a Ω_a (aragonite saturation state) value of >1. This is probably related to the dissolution of reef carbonate (Mg-calcite), which is more soluble than aragonite. However, the threshold of Ω_a for the dissolution of natural sediments has not been clearly determined. Moreover, Mg-calcite dissolution at sand area in coral reefs under natural conditions (such as tidal change, current, photon flux and temperature so on) have not

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been understood. Originally, previous studies considered that Mg-calcite dissolution occur between seawater in the water column and surface of the sediment. However, A_T increase measured at sediment-water interface is determined by the A_T profile in the sediment and diffusion coefficient caused by physical factor such as current and tidal change. It is important to understand the mechanism of controlling the profiles of O_2 or A_T, and to estimate diffusion coefficient under natural hydrodynamic condition. In this study, (1) by laboratory experiment, the dissolution system with conditions reproducing those of a natural coral reef was designed, and the dissolution rates of aragonite in corals and of Mg-calcite excreted by other marine organisms were measured, under conditions of $\Omega_a > 1$, with controlled seawater pCO_2. And (2) the *in-situ* Mg-calcite dissolution rate under natural condition was measured by different two methods, flow-controlled chamber experiment and eddy covariance (EC) technique. All observation were conducted at Shiraho Reef, Ishigaki Island, and samples used by laboratory experiment were gathered at the same site.

1. Laboratory Experiment

By laboratory experiment, dissolution of bulk carbonate sediments occurs at Ω_a values of 3.7 to 3.8. Mg-calcite derived from foraminifera and coralline algae dissolves at Ω_a values between 3.0 and 3.2, and aragonite starts to dissolve when $\Omega_a = 1.0$. And dissolution rate increased with Ω_a decreased. Nocturnal carbonate dissolution of coral reefs occurs mainly by the dissolution of foraminiferans and coralline algae in reef sediments. The solubilities of foraminiferans and coralline algae obtained by this study reflected not the biogenic "best-fit" solubility, but Plummer and Mackenzie (1974) solubility.

2. Flow-controlled chamber experiment

In order to understand relationship between dissolution rate and Ω_a, chamber experiment which can control flow rate were designed and conducted. Data showed that there were no significant differences in

dissolution/calcification rate between high-flow and low-flow. Also, threshold of net dissolution at sand area was Ω_a = 3.0-3.2. This value was nearly equal to threshold of foraminifera and coralline algae determined by laboratory experiment. While dissolution rate increases as Ω_a decreased from my laboratory experiment, dissolution rate did not change similarly from my chamber experiment. This means that surface of the sediment does not be affected by high pCO_2 in water column. Even when pCO_2 in the water column increases, pCO_2 in the sediment does not change. Therefore, A_T increased by A_T flux caused by the sediment. Hence, understanding of sediment profile under natural condition is important.

3. Dissolution flux estimated by profile of sediment and eddy coraviance

O_2 and carbonate profiles were measured by microelectrode and pore water analysis. Between 0 and 10 mm depth, micro organism respiration consumed oxygen and produced CO_2, pH decreased at night. On the contrary, O_2 increased by the photosynthesis at day time. Deeper than at least 10 mm, O_2 was depleted even during the day time. On the other hand, Ω_{fora} was always constant at the value of 1.0. Both organic reaction such as respiration and inorganic Mg-calcite dissolution occur and keep Ω constant in the sediment.

At the same time, DO fluxes measured by EC were 4.95-5.66 mmol m^{-2} hr^{-1} uptake at night and 14.44-23.99 mmol m^{-2} hr^{-1} production at day time. This is because that photosynthesis by microalgae on the upper part of sediment produced O_2, and on the contrary, respiration during night time consumed O_2. The average DO uptake at flood tide was about three times higher than that at ebb tide. At Shiraho reef area, DO flux would be influenced not by the current but by some physical or biological process which are different flood tide and ebb tide. Also, diffusion coefficient at night was calculated from DO flux observed by eddy correlation and O_2 profile, and night average diffusion coefficient was as 3.44×10^{-4} cm^2 s^{-1}. This value was 30-100 times higher than molecular diffusion. Diffusion coefficient observed by this study was nealy equal to previous studies and it is caused by wave and current driven by unidirectional flows.

4. Discussion

Carbonate chemistry was summarized by A_T-C_T diagram. When it was steady state at night time and DO flux corresponds to respiration rate between 0-10mm layer, AT profile and AT flux at sediment-water interface can be estimated. The exact understanding and estimation on Mg-calcite dissolution can be shown not by the reaction between water column and surface of the sediment but by the profile in the sediment and diffusion coefficient. Moreover, once threshold of Mg-calcite dissolution occur, estimated A_T flux will increase drastically.

Mg-calcite dissolution is understood by diffusion coefficient and profile in the sediment from this study. By this new finding, A_T flux at sediment-water interface can be estimated whatever seawater in the water column will change by ocean acidification. Buffer effect of Mg-calcite dissolution at sand area should be taken into account for model projection.