論文内容の要旨

論文題目：Elemental fractionation in biogenic calcium carbonate

（生物源炭酸塩の微量元素変動）

氏名　　白井　厚太朗

The stable isotopic ratio and minor and trace element compositions in marine biogenic calcium carbonate, such as coral skeleton and bivalve shells, are useful tools for the paleoclimate reconstruction. However, these chemical compositions are also affected by biological processes (vital effect). For the accurate paleoclimate reconstruction, understanding the vital effect mechanism is essential. This study present new data and discuss the elemental incorporation mechanisms by biological processes, mainly based on the micro-scale elemental distributions.

To develop the analytical procedure using a high lateral resolution secondary ion mass spectrometer (Nano-SIMS NS50) installed at the Ocean Research Institute, the University of Tokyo, the chemical compositions of four natural calcium carbonate samples were analyzed by three analytical methods. Concentrations of minor (Mg and Sr) and trace (Ba and U) elements were first analyzed by inductively coupled plasma mass spectrometry (ICP-MS) after chemical dissolution and calibrated against a standard dolomite. Their homogeneities were checked by in situ laser ablation (LA) ICP-MS with 10~20 spots. The carbonate samples were measured by using a high lateral resolution secondary ion mass spectrometer (NanoSIMS NS50). A ~4 nA O^- primary beam was used to sputter a 5~6- μ m diameter crater on the sample

surface and secondary positive ions were extracted for mass analysis using an accelerating voltage of 8 kV and a Mattauch-Herzog geometry. Multi-collector system was adjusted to detect $^{26}Mg^{+}$, $^{43}Ca^{+}$, $^{88}Sr^{+}$, $^{138}Ba^{+}$, $^{238}U^{16}O^{+}$ and $^{238}U^{16}O^{2+}$ ions at the same time. Resolving power of 2500~5000 at 10% peak height was attained by entrance slit set at 40 μ m and each exit slit at 50 μ m with adequate flat topped peaks. Observed $^{26}Mg^{+}$, $^{43}Ca^{+}$, $^{88}Sr^{+}$, $^{138}Ba^{+}$, and $^{238}U^{16}O^{2+}$ ratios agreed well with those measured by LA-ICP-MS, confirming their reported precision and accuracy.

. To evaluate the relationship among chemical compositions, environmental factors and the vital effect, minor and trace elements of modern deep-sea corals were measured in bulk individuals and skeletal micro-structure. Deep-sea corals hold great potential as a key to important aspects of paleoceanography for at least two reasons, 1) they offer temporal high resolution records of deep-sea environment, because they have growth banding structures, 2) and they are good samples for studying vital effects, because the deep-sea environment does not change over short time scales. However, the relationship between the chemical composition of deep-sea coral skeletons and environmental factors is not well understood. The oxygen isotopes and chemical compositions of deep-sea corals were measured in this study. Among the bulk individuals, $\delta^{18}O$ value and Sr/Ca ratio show a negative but weak correlation with ambient temperature. On the other hands, the Mg/Ca ratio has a positive, weak correlation with the temperature. Large variations were found among samples collected from similar temperature. The variation is up to 3.8‰ for $\delta^{18}O$, 0.9 mmol/mol for Sr/Ca ratios, and 0.78 mmol/mol for Mg/Ca ratios among samples with ambient average temperature within 1°C. This variation may be due to a large vital effect. The centers of calcification (COCs), which was formed at high calcification rate, has lower Sr/Ca, U/Ca and higher Mg/Ca ratios than surrounding fasciculi. This chemical distribution supports the model that elemental incorporation derived from Rayleigh fractionation. This suggests that calcification rate is a very important factor for the chemical composition in deep-sea corals and is one of the most significant mechanisms of the vital effect. Because of the large vital effect, further investigations are essential to use the deep-sea coral as a temperature proxy.

To investigate the elemental incorporation mechanism into coral skeletons, chemical and isotopic compositions of *Acropora nobilis* skeleton were analyzed at various spatial resolutions. Branching corals *Acropora* consist of fast-growing axial corallite and slowly

growing radial corallite at the visible scale. On the other hands, at the micro-scale, there are several types of skeletal elements precipitated under different calcification rate. The chemical profiles of both axial and radial corallite along with growth axes were measured by conventional ICP-MS and Stable Isotope Mass Spectrometry. The tip and basal parts of *Acropora nobilos* skeletons were also analyzed at micro-scale. The Mg/Ca, Sr/Ca, Ba/Ca, and U/Ca ratios were measured in ~8μm diameter spots by using NanoSIMS, and Mg, Sr, Ca, and S distributions were analyzed by Electtron Probe Micro Analyzer (EPMA), with a spatial resolution of ~2μm. Based on the elemental distribution obtained by EPMA, the *Acropora*'s skeleton are composed of more than three types of the skeletal elements, "Framework", "Infilling" and High Mg Low S" skeletons. Observation of skeletal structure revealed that the skeletal porosity decreased with distance from the tip, since "Infilling" skeletons filled the voids of "Framework" skeletons. Micro-scale elemental analyses (EPMA and NanoSIMS) revealed that "Infilling" skeletons have lower Mg/Ca and higher Sr/Ca and U/Ca than "Framework" skeletons. Since the "Infilling" skeletons were probably formed under the slower calcification rate than "Framework" skeletons, the elemental fractionation pattern between two skeletal elements is consistent with the Rayleigh fractionation model. The chemical profiles of axial corallite along with the growth were significantly affected by the proportions of "Infilling" skeletons.

To evaluate the effects of hydrothermal and/or biological activity on trace element/Ca ratios in the bivalve shell, the chemical compositions in the cross sections of deep-sea mussel (*Bathymodiolus platifrons*) shell were analyzed by using micro analytical technique. The Mg/Ca, Sr/Ca, Mn/Ca, and Ba/Ca ratios were measured in ~8 μm diameter spots by using NanoSIMS, and Mg, Sr, Ca, and S distributions were analyzed by Electtron Probe Micro Analyzer, with a spatial resolution of ~2μm. After these analyses, shell microstructures were observed by SEM to evaluate the relationship between elemental distributions and shell microstructure. The inner aragonitic layer is composed of three kinds of shell micro-structures. The organic-rich layer and etch-resistant minerals were interlaminated sporadically among ordinary deposited nacreous layers. All elements showed large variations associated with shell microstructure changes, implying that they are mainly controlled by biological processes. Comparing with the nacreous layers, Mg, Sr, Ba, and S were concentrated in intracrystalline organic materials located at organic-rich layers. In contrast, Mn/Ca variations were primarily coupled with shell microstructure; with the low Mn/Ca in etch-resistant minerals. Such element

profiles are not consistent with the expected variation from temperature and/or environmental change around hydrothermal vents, indicating that these element ratios are not direct hydrothermal proxies. To use trace element/Ca ratios as paleoceanographic proxies, observation of shell structures and evaluation of the vital effect are essential.

At the micro-scale, chemical compositions show large heterogeneity associate with skeletal micro-structures, indicating that the biological effects are dominant. Both deep-sea coral and branching coral, the Rayleigh fractionation may be the dominant process affecting the micro-scale elemental distribution. In the case of deep-sea hydrothermal mussel, localized organic materials are the main controlling factors for the micro-scale elemental distributions.