Trace elements in Japanese precious corals as indicators for habitat and growth characteristics

Dissertation

Trace elements in Japanese precious corals as indicators for habitat and growth characteristics

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ABSTRACT

Japanese precious corals (JPCs) refer to Japanese red coral (*Paracorallium japanicum*), Japanese pink coral (*Corallium elatius*) and Japanese white coral (*Corallium konojoi)* are considered as ecologically as well as economically important natural resources of Japan, and are characterised by slow growth rates compared to other precious corals of other geographical locations. The study reveals that the trace elements in skeletons of precious corals are habitat-specific rather than species-specific. The Mg/Ca and Ba/Ca ratios in skeletons of precious corals, particularly, are the indicators of their habitats and environments. The study also show the spatial distribution of trace elements (S, P, Mg, and Sr) in the skeleton of *P. japonicum*. The distribution pattern of the trace elements, particularly Mg, S and P, illustrates linkage between the trace element distribution and the formation of growth bands in the coral skeleton.

The petrographic method is a popular technique for estimating the age and growth rates of corals based on growth ring density in their axial skeleton. The organic matrix staining (OMS) method, a modified method of petrographic method, has been used for measuring age and growth rate of the Mediterranean red coral (*Corallium rubrum*) by staining the organic matrix in the calcite skeleton. Since the OMS method is based on the concentration of organic matrix in the coral skeleton, this method may not be suitable for coral species with low organic matrix. In the presnt study, growth characteristics and growth rates of three Japanese precious corals (*Paracorallium japonicum*, *Corallium elatius* and *Corallium konojoi*) were determined based on the principles of the petrographic method using a VHX-1000 digital microscope, termed as

VHX-1000 hereafter, without staining the organic matrix in the axial skeleton. Compared to the organic matrix-stained cross-sections (slabs), growth rings in unstained slabs of the Japanese red coral were more clearly visible through the VHX-1000. This may be due to the low concentration of organic matrix in the Japanese precious corals compared to the Mediterranean red coral. Growth rates of Japanese precious corals differ significantly depending on coral species, habitat and environmental conditions. Diametric and linear growth rates of the Japanese red coral (*P. japonicum*) were slower (0.20±0.08–0.27±0.01 and 2.22±0.82–6.66±5.52 mm yr^{-1}, respectively) than the Japanese pink (*C. elatius*; 0.30±0.04 and 2.76±2.09 mm yr^{-1}, respectively) and white (*C. konojoi*; 0.44±0.04 and 7.60±0.75 mm yr^{-1}, respectively) corals. In addition, the diametric growth rate of the Japanese precious corals (*P. japonicum*) is slower (0.24±0.05-0.44±0.04 mm yr^{-1}) than the Mediterranean red coral (*C. rubrum*; 0.20-0.62±0.19 mm yr^{-1}).

Precious corals have been commercially exploited for many centuries all over the world. The skeletons of these corals consist of calcium carbonate, and have been used as amulets or gemstones since ancient times. Different *Corallium* species of Coralidae family (e.g., *C. rubrum*, *C. elatus*, *C. konojoi*, and *P. japonicum*) were collected from different locations of the Mediterranean Sea (off Italy) and Pacific Ocean (off Japan and off Midway Island), and trace elements in their skeletons were analyzed. Results show that trace element concentrations in the skeletons of *Corallium* spp. were attributable to their habitat and origin. In particular, Mg/Ca and Ba/Ca ratios in the skeletons of *Corallium* spp. from the Mediterranean Sea and Japanese and the Midway Islands' waters were found to be habitat-specific. This study also reveals that trace

elements in the skeletons can be used as ecological indicator of the coral's origin, and are expected to play an important part in the cultural study and sustainable management of precious corals. Findings of this study will also be of great relevance to the coral industry to authenticate and identify the habitat and origin of the corals.

This study also investigated the distribution of magnesium (Mg), phosphorus (P), sulfur (S) and strontium (Sr) using micro X-ray fluorescence (μ-XRF), and the speciation of sulfur using X-ray absorption near edge spectroscopy (XANES) along the annual growth rings (AGRs) in the skeleton of Japanese red coral (*Paracorallium japonicum*). The Mg, P and S distribution in μ-XRF mapping images correspond to the dark and light bands along the AGRs in microscopic images of the coral skeleton. μ-XRF mapping data showed a strong positive correlation (r = 0.6) between P and S distribution in the coral skeleton. A contrasting distribution pattern of S and Mg along the axial skeleton of the coral indicates a weak negative correlation (r = -0.2) between these two elements. The distribution pattern of S, P and Mg in the axial skeleton of *P. japonicum* reveals linkage between the trace element distribution and the formation of dark/light bands along the AGRs. S and P were distributed in the organic matrix (OM) rich dark bands, while Mg was distributed in the light bands of the AGRs. XANES analysis showed that inorganic sulphate is the major species of S in the skeleton of *P. japonicum* with a ratio of 1:20 for organic and inorganic sulphate.

学位論文審査結果の要旨

提出学位論文について、各審査委員が個別に審査した後、平成25年7月19日に審査員による予備審査会を実施するとともに、平成25年8月6日に口頭発表会と論文審査委員会を開催し、以下のように判定した。

宝石サンゴは、熱帯や亜熱帯の浅海域に分布する造礁サンゴとは異なる生物種であり、太陽光の届かない海底に生息する。宝石サンゴの骨軸形成過程では、海水中の主要溶存成分から炭酸カルシウムが形成されるが、Ca以外の微量成分も結晶中に取り込まれる。本研究では、宝石サンゴ骨軸の微細構造を解析する新しい方法として、高精度色彩分析による有機色素成分の顕微観察法、及び、電子プローブマイクロアナライザーによる微量無機元素のマッピング分析法を確立し、宝石サンゴの肥大成長速度、伸長成長速度を詳細に明らかにした。また、骨軸中における微量無機元素の濃度を高精度で定量することに成功し、世界の主要生息域から採取した試料の解析から、特にMg、Baの組成比が宝石サンゴの起源を示す科学情報となることを見出した。更に、放射光を利用した軟X線μ-蛍光X線分析/X線吸収端微細構造法により、成長輪に沿った硫黄、リンの2次元分布像を初めて明らかにした。

以上、本研究は、宝石サンゴ骨軸中の微量成分を対象として新しい高感度分析法を開発したものであり、宝石サンゴの生理生態の解明や資源管理に有用な情報を提供する研究として博士（学術）の学位に値するものと判断した。