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Nitrogen isotopes in intra-crystal coralline aragonites

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ABSTRACT

To assess the preservation of the nitrogen isotope composition in reef corals, nitrogen isotopes in a well-preserved Pliocene fossil coral (located in the Tartaro formation on Luzon Island, Philippines (14°N, 121°E)) and in a modern coral (Kochi, Japan (32°N, 132°E)) were analysed using stepwise heating methods. The thermal decomposition of aragonite triggered the largest release of nitrogen at 700 °C for the modern coral and 550 °C for the Pliocene coral. The highest rate of nitrogen gas emission occurred at the aragonite collapse temperature, indicating that organic nitrogen was bound within the intra-crystals of coralline aragonites in both corals. After the aragonite collapsed in both corals, the nitrogen isotope ratios increased due to fractionation and then decreased to values similar to those observed in bulk samples of the modern (+10.1‰) and Pliocene (+4.4‰) corals. These results suggested that fresh organic nitrogen was released due to the decomposition of the internal skeletal structure at higher temperatures (900–1000 °C). Nitrogen isotopes in coral skeletons were preserved in intra-crystal aragonite, even in a Pliocene fossil, and stepwise heating methods were shown to be useful for determining the preservation of coralline nitrogen isotopes.

1. Introduction

The nutrient cycle in surface oceans regulates primary production, which influences the carbon dioxide concentration in the atmosphere. Global warming and cooling have occurred repeatedly over geological time scales and are often accompanied by nutrient concentration changes, especially in the polar and tropical oceans (Sigman and Boyle, 2000). Understanding nutrient circulation changes over geological time scales is useful for predicting future environmental changes. The nitrogen isotope proxy in coral skeletons ($\delta^{15}N_{coral}$) may be applied to fossil corals for the reconstruction of palaeo-nitrogen cycles. Modern and fossil coral skeletons have been used as high-resolution recorders of surface ocean environments at low latitudes (e.g., Gagan et al., 2000; Correge, 2006; Watanabe et al., 2011). The modern $\delta^{15}N_{coral}$ is a record of the high-resolution dynamics of nitrogenous nutrients in surface oceans (Yamazaki et al., 2011a,b). According to the fossil records, corals belonging to the Anthozoa class originated in the Palaeozoic era (Scrutton, 1997), and scleractinian corals appeared in the middle of the Triassic period (~237 Ma) (Stanley and Fautin, 2001). Muscatine et al. (2005) showed that the nitrogen isotope composition in Triassic coral skeletons is similar to that of modern symbiotic coral skeletons. The authors suggested that Triassic corals possessed symbiotic algae and preserved the nitrogen isotope composition in their intra-crystal skeletons. However, few studies have explored the application of nitrogen isotope proxy records in fossil corals over long periods of time because methods that can be used to confirm that organic nitrogen was preserved in intra-crystal coralline aragonites have not yet been developed, even in fossils. In the present study, the preservation of the nitrogen isotope composition in modern and fossil corals was examined using stepwise heating analysis. Stepwise heating methods have been used in the analysis of noble gases and nitrogen in rock samples (e.g., Reynolds et al., 1970; Sano and Pillinger, 1990). This technique has been applied to nitrogen isotopes of modern coral by Uchida et al. (2008) to detect trace nitrogen in coral skeletons. We divided the heating process into seven steps (200 °C to 1000 °C) to determine the aragonite collapse temperature and the nitrogen isotope ratios preserved in extra- and intra-crystalline aragonite. We used well-preserved Pliocene fossil corals (3.5–3.8 Ma) collected from Luzon Island, Philippines, which is located in the western Pacific warm pool. In the middle of the Pliocene epoch, the annual mean temperature was 2–4 °C warmer than that under preindustrial conditions (Haywood and Valdes, 2004; Brierley et al., 2009; Haywood et al., 2009). Pliocene coral specimens may contain nutrient circulation data in tropical warm pools under global-warming-like conditions.

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2. Methods

2.1. Modern coral specimen

To decrypt the $\delta^{15}N_{coral}$ pattern of the Pliocene coral, we compared it with modern $\delta^{15}N_{coral}$ in a living *Porites* coral skeleton from Tatsukushi Bay, Kochi, Japan (32°N, 132°E). We measured modern coral skeletons using the chemical conversion methods described by Yamazaki et al. (2011a) to validate the bulk $\delta^{15}N_{coral}$ values of modern coral skeletons. A rectangular coral skeleton ($10 \times 40 \times 7$ mm) containing 5 annual bands was cut from the coral colony and powdered using an agate mill to obtain a heterogeneous powder. To remove any organic materials attached to the outer crystals, the coral powder was placed in polypropylene tubes, soaked in NaOH (2 N) and placed inside a dry bath (60 °C). Treatment times of 0, 0.5, 1, 2, 3, and 5 h were tailored to capture intra-crystalline nitrogen. During the treatment process, NaOH and coral powder were mixed once every hour using the tube mixer. At each treatment step, the nitrogen isotope content was determined in 5 samples, and those that exhibited a poor recovery rate during the chemical conversion process were excluded from further analysis. The $\delta^{15}N_{coral}$ and total nitrogen content varied widely, especially when the samples were not cleaned (Fig. 1). After 5 h of cleaning, the average $\delta^{15}N_{coral}$ value in the modern coral was $+9.1 \pm 1.5$ (2σ)‰, and the average total nitrogen content was 63 ± 43 (2σ) ppm. The range (2σ) of $\delta^{15}N_{coral}$ and the total nitrogen values were generally in accordance after 1 h and in subsequent steps. The heterogeneity of nitrogen released at every cleaning step was attributed to the spatial distribution of nitrogen components, the seasonal variability of $\delta^{15}N_{coral}$ and of the total nitrogen (Yamazaki et al., 2011b) content and differences in the nitrogen recovery rates throughout the chemical conversion process.

2.2. Fossil coral specimen

Porites specimens were excavated from the Tartaro formation located on Luzon Island, Philippines (14°N, 121°E). A previous study on the nanofossil assemblages showed that the age of the fossils was approximately 3.5–3.8 Ma (Watanabe et al., 2011). The well-preserved fossil coral was selected by conducting a diagenetic alteration test using X-ray radiography, X-ray diffraction analysis, micro-analysis of thin sections via high-energy synchrotron X-ray diffraction, scanning electronic microscopy observations, and optical microscopy observations (Watanabe et al., 2011). Oxygen isotopes ($\delta^{18}O$) were preserved without diagenetic alteration from aragonite to calcite. We used a fossil coral without diagenetic alterations to determine the intra-crystalline nitrogen content using stepwise heating methods.

2.3. Stepwise heating methods

Cubic samples of modern and fossil corals were obtained from each colony, cleaned using milli-Q water in an ultrasonic bath for 20 min and dried in an oven (40 °C) for 2 days. Rectangular samples $5 \times 3 \times 3$ mm in size, which captured approximately 1 year of calcification, were used to adjust the estimated quantity of nitrogen to the mass spectrometer. The sample weights of modern and fossil corals were 17.89 and 17.93 mg, respectively. Each cubic sample was loaded into a double-walled quartz glass tube and placed overnight in a furnace equipped with a resistance wire under vacuum. A solid cube sample was used to reduce blank effects. Each sample was heated stepwise to temperatures of 200, 450, 550, 700, 800, 900, and 1000 °C over 4 days (2 steps/day). After the sample was heated for 90 min at each step, the nitrogen and argon gases released from the samples were directed to a purification vacuum line designed to measure molecular nitrogen at the sub-nanomole level (Takahata et al., 1998). The procedure used for the purification of nitrogen gas is shown in Fig. 2. Carbon dioxide (CO_2) and water (H_2O) were trapped using liquid nitrogen (cold trap 1). Carbon monoxide, hydrocarbons, and hydrogen were then oxidised to CO_2 and H_2O using pure oxygen produced by a copper oxide finger heated to 850 °C and a platinum foil catalyst heated to 1000 °C. To resorb excess oxygen, the copper oxide furnace was cooled to 600 °C and finally to 450 °C. In this deoxidised state and in the presence of the platinum foil catalyst, nitrogen oxide gas was deoxidised to nitrogen gas (N_2). CO_2 and H_2O were adsorbed in cold trap 2 during the cooling of the copper oxide finger. A quadrupole mass spectrometer (QMS; HAL201, Hiden Analytical) was used to determine the sample size introduced to the mass spectrometer. The dilution process was repeated to obtain the proper sample volume. To detect the isotopes of trace nitrogen gas at the sub-nanomole level, we used the high-sensitivity static vacuum mass spectrometer (a modified VG3600, VG Micromass Ltd.) at the Atmosphere and Ocean Research Institute at the University of Tokyo. Nitrogen gas calibrated to nitrogen in air ($\delta^{15}N = 0\%$) was analysed before and after each sample. Repeated analysis of the standard over the course of 20 days showed that the overall reproducibility was 0.25% (Takahata et al., 1998). After the most recent sample

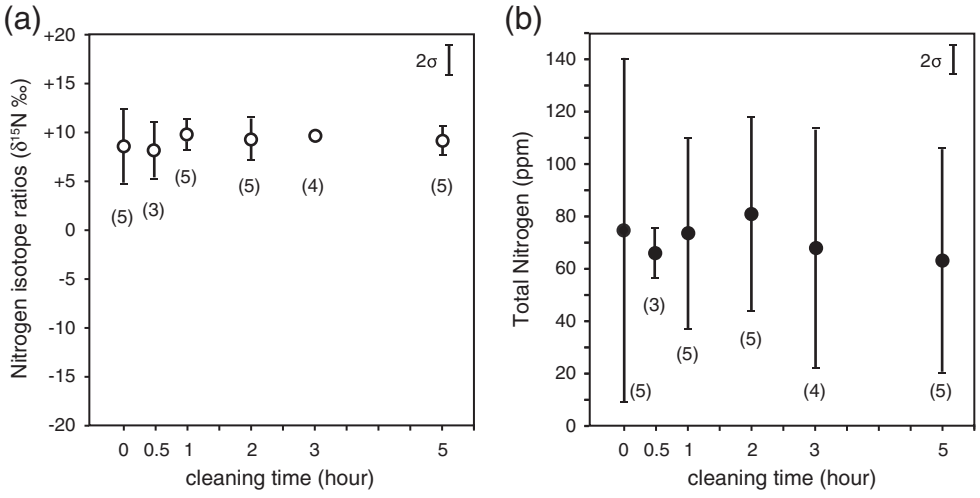

Fig. 1. The (a) $\delta^{15}N_{coral}$ and (b) total nitrogen content in a modern coral analysed by the chemical conversion methods reported by Yamazaki et al. (2011a). To analyse the nitrogen released by intra-crystalline organic matter, the modern coral powder was soaked in hot NaOH (60 °C, 2 N) before cleaning (for 0, 0.5, 1, 2, 3, and 5 h). The number in parentheses is the number of samples at each step. The error bar shows the uncertainty (2σ) at each cleaning time.