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LETTER

Pretreatment of coral aragonite for Mg and Sr analysis: Implications for coral thermometers

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Trace elements (e.g., Sr, Mg, and U) in coral skeletons are widely used as a potential robust paleothermometers. However, there is little consensus among workers on the chemical pretreatment of skeletal samples, which contain small amounts of organic material and inorganic detritus enriched in many metals compared to the skeleton. We tested the analytical effects of chemical treatment on coral aragonite by comparing several chemical treatments for Mg/Ca and Sr/Ca ratios as well as oxygen and carbon isotopic ratios. Our results suggested that the Sr/Ca ratio and stable isotopic ratios are resistant to chemical treatments. However, organic matter or crystal surfaces in corals could absorb more than 40% of magnesium although 60% of magnesium in coral aragonite substitutes for calcium. Our results suggest that it is expedient to remove impurities by the method outlined here, especially before determining Mg/Ca ratios in corals for paleoenvironmental reconstruction.

INTRODUCTION

Coral skeletons provide high-resolution records of climate variability in the tropical oceans during the last several hundred years. Trace element ratios (e.g., Sr/Ca, Smith, 1979; Mg/Ca, Mitsuguchi *et al.*, 1996; U/Ca, Min *et al.*, 1995) as well as oxygen isotopic ratio (e.g., Weber and Woodhead, 1972) in coral skeletons are commonly used as potential robust paleothermometers. However, trace elements are highly susceptible both to pre-existing surface contamination (detritus and organic) and contamination introduced in sample recovery and preparation (Shen and Boyle, 1988). Moreover, recent high-resolution studies using an ion microprobe or laser ablation analysis revealed

micro-scale heterogeneity for trace elements in coral skeletons because the coral organic matrix is enriched in many metals compared to the skeleton (Allison, 1996; Sinclair *et al.*, 1998; Fallon *et al.*, 1999). Therefore, chemical pretreatment steps in sample preparations for coral material are often necessary. We tested the analytical effects of chemical treatment on coral aragonite and compared our results to several chemical treatments used in previous studies.

MATERIALS AND METHODS

Samples

A coral core (3 m long, 5 cm-diameter) was collected by hydraulic drilling apparatus from the

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colonial coral *Montastrea faveolata* at 7 m water depth off La Parguera, Puerto Rico. The coral *Montastrea* is widely used for the paleoclimatic reconstruction in the Caribbean Sea and the Atlantic Ocean. The core was slabbled parallel to the axis of maximum growth and X-rayed to observe density banding. We made a homogeneous powder of crushed coral skeleton from the well preserved lower part of core (i.e., 1700–1705 years) using an agate mortar for 30 minutes.

Chemical pretreatment

We evaluated several cleaning processes (all done under sonication) described in previous works (e.g., Shen and Boyle, 1988; Min *et al.*, 1995; Mitsuguchi *et al.*, 1996): 1) samples not treated, 2) samples rinsed with milli-Q water (the electric conductance was lower than 10–11 Ω), 3) samples washed with 0.005N HNO_3 for fifteen minutes after procedure 2, 4) samples cleaned with a 1:1 mixture of 30% H_2O_2 and 0.1 M NaOH in a 60°C water bath for fifteen minutes after step 3. Next, we assessed the following organic matter removal processes: 4-a) 0.1 M NaOH for 15 min. at 25°C, 4-b) 1:1 mixture of 30% H_2O_2 and 0.1 M NaOH in a 60°C water bath for 15 min., 4-c) 1:1 mixture of 30% H_2O_2 and 0.1 M NaOH in a 60°C water bath for 60 min., 4-d) 1:1 mixture of 30% H_2O_2 and 0.2 M NaOH in a 60°C water bath for 60 min., 4-e) 15% H_2O_2 for 15 min. at 25°C, 4-f) 5% NaClO for 24 hours at 25°C, 4-g) 30% H_2O_2 for 15 min. in a 60°C water bath, 4-h) 30% H_2O_2 for 60 min. in a 60°C water bath. We typically used 3 mg powder samples with 2 ml of rinse solution and also measured the dry weight of any remaining powder after each chemical treatment in order to estimate sample loss.

Chemical and isotopic analyses

Strontium, magnesium and calcium were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) at Hokkaido University. Approximately 1.5 mg of cleaned powder samples were dissolved in 4 ml of 0.5 M nitric acid and introduced into a Leaman Labs—JICP-PS. An internal reference standard solution derived

from the coral skeleton and milli-Q water, was measured after every three analyses in order to correct for low-frequency drift due to changes in room temperature, plasma, and electronics. A correction factor for each sample was calculated using the average value of the reference measurements, similar to the method of Schrag (1999).

For isotopic analysis, powdered samples (0.1 mg) were reacted with 100% phosphoric acid at 70°C with an automated individual-carbonate reaction device (Kiel device) and the $\delta^{18}\text{O}$ of the extracted CO_2 was determined by a coupled Finnigan MAT 251. Isotopic values were expressed relative to the isotopic ratio of the carbon dioxide gas derived from the Pee Dee Belemnite (PDB) in conventional delta notation through NBS-20 standard. The oxygen isotopic values have been expressed in per mil (‰).

The analytical error for fifteen replicate measurements of homogeneous coral powder were 1.7 and 1.3% (of bulk Sr/Ca and Mg/Ca) for Sr/Ca, Mg/Ca and 0.08 and 0.05‰ for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, respectively (2σ ; 95% confidence).

RESULTS AND DISCUSSION

Sr/Ca ratio

Our results indicate that the Sr/Ca ratio of this coral sample is not significantly affected by chemical treatment within the measurement error. However, sample recovery is reduced from one procedure to the next (Fig. 1a). Amiel *et al.* (1973) suggested that strontium in the coral lattice framework replaces calcium and that strontium associated with organic compounds is negligible in aragonite corals. Recently, using an X-ray spectroscopic study of coral skeletons, Greigor *et al.* (1997) found 40% of strontium present as strontianite (SrCO_3) and 60% strontium substituted for calcium in aragonite structures. Their results indicate that mechanisms of strontium incorporation into coral are unexpectedly complex and that the temperature-sensitive partitioning of strontium between seawater and coral skeleton require further works. However, our results confirm, that lattice-bound strontium in coral skel-

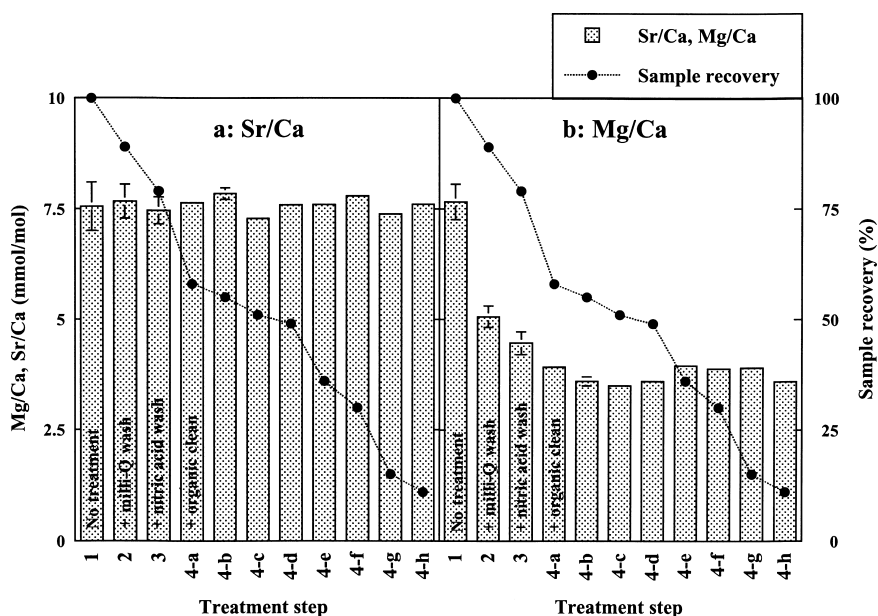


Fig. 1. Sr/Ca (a) and Mg/Ca (b) ratio in the coral skeleton as a function of progressive chemical treatments. Each error-bar represents the range of duplicate samples. Cleaning procedures applied to each sample are summarized as follows (see detailed in text): 1, no treatment; 2, +milli-Q wash; 3, +nitric acid wash; 4, +organic residue step (4-a, 0.1 M NaOH for 15 min. at 25°C; 4-b, 1:1 mixture of 30% H₂O₂ and 0.1 M NaOH in a 60°C water bath for 15 min.; 4-c, 1:1 mixture of 30% H₂O₂ and 0.1 M NaOH in a 60°C water bath for 60 min.; 4-d, 1:1 mixture of 30% H₂O₂ and 0.2 M NaOH in a 60°C water bath for 60 min.; 4-e, 15% H₂O₂ for 15 min. at 25°C; 4-f, 5% NaClO for 24 hours at 25°C; 4-g, 30% H₂O₂, for 15 min. in a 60°C water bath; 4-h, 30% H₂O₂, for 60 min. in a 60°C water bath).

etons has a strong resistance to chemical treatment and that the contribution from strontium in surface adsorption sites and associated with organic compounds is negligible. Therefore, strontium analysis of coral skeletons should give useful results even when chemical pretreatments are rendered difficult or impractical, e.g., when using rapid and high-resolution techniques, such as the ion microprobe or laser ablation.

Mg/Ca ratio

Mg/Ca ratios in corals are significantly affected by chemical treatment, in contrast to Sr/Ca ratios (Fig. 1b). The sample washed with milli-Q water (step 2) showed significantly decreased Mg/Ca ratios (~34%) compared to the untreated samples. Cleaning step 3 (nitric acid wash) gave slightly decreased Mg/Ca ratio (~12%) compared to step 2, and cleaning step 4 (organic residue step)

significantly decreased the Mg/Ca ratio (~19%) compared to step 3 (Fig. 1b). The standard deviation (2σ) of duplicate analysis declined with each procedure, most noticeably at the milli-Q rinse and organic reducing steps. The Mg/Ca ratio decreased with increasing chemical treatment, up to 50% of sample recovery, and levels off between 50 and 20%. Using the relationship between sea surface temperature (SST) and the skeletal Mg/Ca ratio in corals deduced from our previous calibration works ($\text{Mg/Ca (mmol/mol)} = 0.28 (\pm 0.04) \times \text{SST (}^{\circ}\text{C)} - 3.24 (\pm 1.15)$; Watanabe, 1998; Watanabe *et al.*, 2001), the decrease of Mg/Ca ratios from step 4 to step 1, to step 2, and to step 3 can be converted to SST as 14.5°C, 5.2°C, 3.1°C, respectively.

Amiel *et al.* (1973) mentioned that a significant fraction of the magnesium in coral skeleton could occur in adsorbed sites and associated with

organic compounds as well as in the aragonite lattice. This is suggested by Allison *et al.* (1996), who reported elemental anomalies within structurally different features in coral skeleton which may contain different concentrations of the organic matrix enriched in many metals compared to the skeleton.

Our results also suggest that magnesium in coral skeleton could exist in two different phases, first as absorbed magnesium in organic matter or at the surface of the crystal, which are easier dissolved with chemical treatments (i.e., exchangeable and non lattice-bound magnesium), and secondly as lattice-bound magnesium replacing calcium. In this study we estimate that more than 40% of total magnesium in coral aragonite is not lattice-bound and 60% of substitutes for calcium. These results indicate that it is necessary to sufficiently remove non lattice-bound magnesium by chemical pretreatment in order to use Mg/Ca ratio as a reliable paleothermometer. We suggest step 4-b as the best pretreatment method for Mg/Ca analysis because it effectively removes non lattice-bound magnesium, but the sample loss during cleaning is the lowest of the organic removal processes. However, in reality—the method will be applied to different species and core section such as the top with more organics—this experiment does not provide an assessment of the cleaning methods of such sample.

Some previous workers have mentioned that the coral Mg/Ca ratio does not appear to be an accurate proxy for SST compared to Sr/Ca because of non-thermal affects (e.g., Fallon *et al.*, 1999; Schrag, 1999). However, they are mostly detected in the case of direct microscale analysis using the ion probe or laser ablation (e.g., Allison, 1996; Fallon *et al.*, 1999) or when analyses are conducted without removal of organic treatment (Schrag, 1999). If chemical treatments are performed before these type of analysis, Mg/Ca ratio may still be useful for paleotemperature reconstruction, particularly of the relatively large dependence of the Mg/Ca ratio in corals on temperature ($3\text{--}4\text{ }^{\circ}\text{C}^{-1}$; e.g., Mitsuguchi *et al.*, 1996; Watanabe *et al.*, 2001), compared to that of Sr/Ca

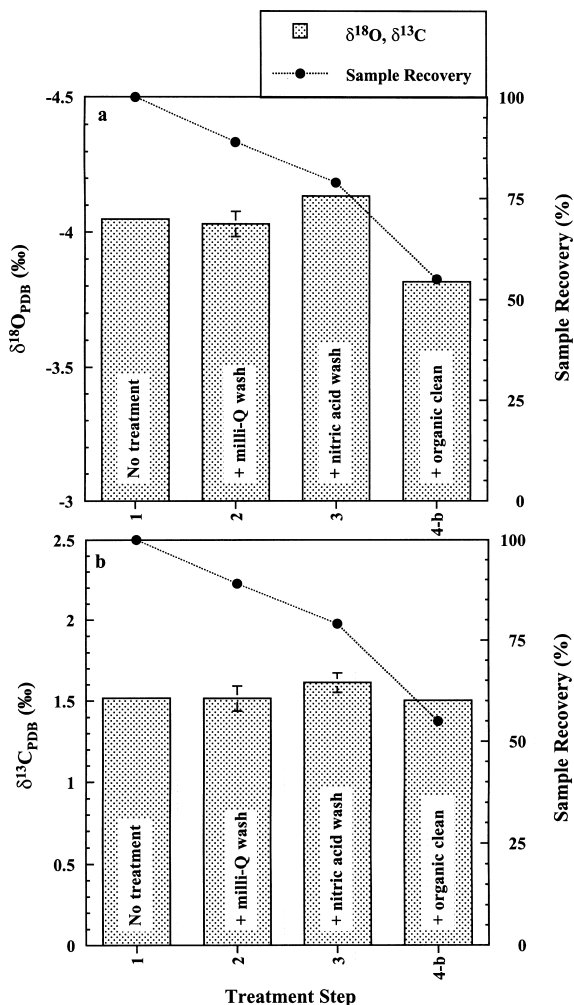


Fig. 2. Oxygen (a) and carbon (b) isotopes in coral skeleton as a function of progressive chemical treatments. Each error-bar represents the range of duplicate samples. Cleaning steps used for each sample, detailed in text, are summarized as follows: 1, no treatment; 2, +milli-Q wash; 3, +nitric acid wash; 4, + organic residue step.

($0.6\text{--}0.8\text{ }^{\circ}\text{C}$; e.g., Beck *et al.*, 1992; de Villiers *et al.*, 1994; Gagan *et al.*, 1998).

Isotopic ratio

Oxygen and carbon isotopes in coral skeleton are not significantly affected by chemical treatment and sample recovery (Figs. 2a and b), although in step 4 a slight decrease in oxygen iso-

topic ratios was observed (Fig. 2a). This may be a result of temperature effects rather than that of H_2O_2 treatment because oxygen isotope ratios of powdered samples kept in a bath of 60°C increased by approximately 0.2–1‰ (Watanabe, 1998) but not during H_2O_2 treatment (Boiseau and Juillet-Leclerc, 1997). Our results suggest that chemical pretreatment of coral aragonite skeletons does not affect the microscale heterogeneity of the isotopes.

CONCLUSIONS

Mg/Ca ratios in coral aragonite decreased significantly with chemical treatments while Sr/Ca as well as oxygen and carbon isotopic ratios are not significantly affected. Our results suggest that 60% of magnesium in coral aragonite substitutes for calcium but more than 40% of the magnesium in coral is associated with organic matter or absorbed onto surfaces of the crystal. However, Mg/Ca may still be a robust paleothermometer considering the relatively large dependence on temperature compared to Sr/Ca. We nevertheless suggest performing effective chemical pretreatment before elemental analysis, especially for magnesium analysis of corals.

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