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Raman analysis of octocoral carbonate ion structural disorder along a natural depth gradient, Kona coast, Hawai‘i

Kyle Conner[1,*], Shiv Sharma[1], Ryohei Uchiyama[2], Kentaro Tanaka[3], Naoko Murakami-Sugihara[3], Kotaro Shirai[3], and Samuel Kahng[1]

[1]School of Ocean and Earth Science and Technology, University of Hawai'i at Manoa, Honolulu, Hawaii 96822, U.S.A.
[2]Graduate School of Science, Hokkaido University, Kita-10 Nishi-8 Kita-ku, Sapporo 060-0810, Japan
[3]Atmosphere and Ocean Research Institute, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa-shi, Chiba 277-8564, Japan

Abstract

Both environmental and physiological factors cause carbonate ion structural disorder in biogenic Mg-calcites. A major component of this disorder is driven by the incorporation of Mg through environmental forcing and growth rate kinetics although non-Mg factors (e.g., other cation/anion impurities, organic molecules) also contribute. Understanding the drivers of Mg content in biogenic calcite and its effects on disorder has implications for octocoral Mg paleo-proxies and the stability and diagenetic alteration of their calcitic skeletons. However, prior studies of biogenic Mg-calcites have often been complicated by sampling inconsistencies over space and time and potential intra-sample Mg variability. This study aims to analyze the relative contributing factors of octocoral Mg-calcite structural disorder along gradients of both depth and growth rate. Calcitic octocorals (Coralliidae and Keratoisididae, N = 28) were collected from 221–823 m depths across a natural gradient in biogeochemical parameters (pH: 7.4–7.9, *T*: 5–16 °C) off the Kona coast of Hawai‘i Island and were analyzed using Raman spectroscopy. Samples were collected during the same month, controlling for potential seasonal variability. Raman spectral parameters from the ν_1 peak quantified total carbonate ion structural disorder (full-width at half maximum height [FWHM] of ν_1) and Mg content (ν_1 position, Raman shift). The total structural disorder was then partitioned into Mg-driven and non-Mg driven components (residual ν_1 FWHM). The total structural disorder and Mg content decreased significantly with increasing depth, correlating with temperature and carbonate system parameters. The Mg-temperature relationships from this study were also consistent with prior studies. Non-Mg structural disorder did not correlate to any environmental parameters. When measured across an intra-sample gradient of ontogenetic growth rate, total structural disorder, Mg content, and non-Mg structural disorder increased with growth rate for all but one taxon, demonstrating the kinetic effect of growth rate as well as potential taxon-specific physiological effects. These results provide insight into how environmental and growth rate kinetic effects independently affect different components of carbonate ion structural disorder (Mg content and non-Mg factors). These findings also suggest that Raman spectroscopy may be helpful in quantifying solubility within biogenic calcites.

Keywords: Octocorals, magnesian calcite, carbonate ion disorder, Raman spectroscopy, depth gradient, growth rate kinetics