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

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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 ν1 peak quantified total carbonate ion structural disorder (full-width at half maximum height [FWHM] of ν1) and Mg content (ν1 position, Raman shift). The total structural disorder was then partitioned into Mg-driven and non-Mg driven components (residual ν1 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

Introduction

Environmental and physiological (i.e., vital effects) factors can influence carbonate ion structural disorder (referred to hereinafter as structural disorder) within biogenic calcium carbonates (CaCO3) through the incorporation of elemental impurities as well as growth rate kinetics and organic molecules involved in biogenic calcification. CaCO3 structural disorder involves the orientation of carbonate ions relative to the c (vertical) and a (horizontal) unit-cell axes (Bischoff et al. 1985). Ideally, carbonate ions are symmetrically aligned with their respective basal planes along the a axis; however, deviations from this symmetry occur at varying extents within synthetic and biogenic CaCO3. The incorporation of non-constituent ion impurities (divalent cations with radii differing from Ca) such as Mg, Sr, and Ba results in altered cation-oxygen bond lengths that can rotate carbonate ions out of the basal plane toward the c axis (Bischoff et al. 1985; Urmos et al. 1991; Perrin et al. 2016; Farfan et al. 2018, 2022). Large anions like sulfate (relative to carbonate ions) can also be substituted into the CaCO3 crystal structure and increase structural disorder (reviewed in Vielzeuf et al. 2018). Kinetic effects influenced by growth rate as well as ambient temperature and pressure also promote disorder because rapid crystallization reduces the symmetric alignment of carbonate ions and increases the incorporation of impurities (Watson 2004; Morse et al. 2007; Mavromatis et al. 2013; Farfan et al. 2018, 2022). CaCO3 precipitation rates can be elevated through favorable physicochemical conditions obtained either through

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