Raman Analysis of Hawaiian Octocoral Mg-Calcite Lattice Disorder Along a Natural Depth Gradient

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Biogenic Mg-calcites experience varying degrees of molecular disorder in their carbonate ion lattice structure from environmental and vital effects [1]. A primary component of this disorder results from Mg incorporation via environmental forcing and growth rate kinetics although non-Mg components (e.g., growth rate kinetics, organic molecules) also contribute [1]. Understanding the individual drivers of biogenic calcite Mg content and lattice disorder has implications for Mg paleoproxies and mineral stability. This study analyzes the separate effects of physical environmental parameters and growth rate kinetics on lattice disorder and Mg content within calcitic octocoral skeletons. Octocorals (Corallidae and Isididae, N = 28) were collected from 221-823 m 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 analyzed using Raman spectroscopy. Collections were made during the same month to control potential seasonal variability in skeletal growth rate. The Raman spectral peak v_1 was analyzed in terms of its width (full width at half maximum, FWHM) and position (Raman shift) to quantify total lattice disorder and Mg content, respectively [1,2]. Total lattice disorder was then partitioned into Mg-driven and non-Mg driven (residual FWHM) components [3]. Total lattice disorder and Mg content displayed significant positive correlations with environmental parameters (temperature, Ω) while non-Mg disorder displayed no significant patterns. Relative skeletal growth rate can be predicted using branch diameter where thinner branch tips grow faster than thicker branch bases [4]. Intra-sample Raman measurements (under constant environmental conditions) showed increases in Mg content, total lattice disorder, and non-Mg lattice disorder with decreasing branch diameter. These results provide insight into how different forms of lattice disorder are independently driven by environmental and physiological factors. The capacity for FWHM to quantify lattice disorder from sources beyond just Mg demonstrate its potential for quantifying biogenic Mg-calcite solubility.

[1] Bischoff et al. (1985), Am. Min. 71, 581-589. [2] Perrin et al. (2016), Am. Mineral. 101, 2525-2538. [3] Comeau et al. (2018), Glob. Chang. Biol. 24, 4857-4868. [4] Vielzeuf et al.

