Coral calcifying fluid aragonite saturation states derived from Raman spectroscopy

THOMAS M. DECARLO[1,2], JUAN P. D'OLIVO[1,2], STEEVE COMEAU[1,2], TARYN FOSTER[3], CHRISTOPHER E. CORNWALL[1,2], MICHAEL HOLCOMB[1,2], MALCOLM T. MCCULLOCH[1,2]

[1]UWA's Oceans Institute and School of Earth Sciences
[2]ARC Centre of Excellence for Coral Reef Studies, The University of Western Australia
[3]Australian Institute of Marine Science

Quantifying the saturation state of aragonite (Ω_{Ar}) within the calcifying fluid of corals is critical for understanding their biomineralisation process and sensitivity to ocean acidification. Recent advances in microscopy, microprobes, and isotope geochemistry allow determination of calcifying fluid pH and $[CO_3^{2-}]$, but characterisation of Ω_{Ar} (where $\Omega_{Ar} = [Ca^{2+}][CO_3^{2-}]/K_{Ar}$) has proved elusive. Here we present a new technique for deriving Ω_{Ar} based on Raman spectroscopy. First, we show a strong dependence of Raman peak width on Ω_{Ar} (ranging from 10 to 34) in abiogenic aragonite crystals. Next, we analysed the international standard JCp-1, which is a ground *Porites* coral skeleton, and validate our Raman-derived Ω_{Ar} (12.3 ± 0.3) by comparison to published skeletal Sr/Ca, Mg/Ca, B/Ca, δ^{44}Ca, and δ^{11}B data. Finally, we demonstrate that our Raman technique can detect changes in calcifying fluid Ω_{Ar} as illustrated by annual oscillations in a field-collected coral. Together, these data strongly support the applicability of Raman spectroscopy as a tool to quantify coral calcifying fluid Ω_{Ar}. Raman measurements are rapid (≤ 1 s), high-resolution (1 μm), precise (derived Ω_{Ar} ± 1-2 per spectrum), and do not require sample preparation; making the technique well suited for investigations of the sensitivity of corals to ocean acidification in natural and laboratory settings. We will also present calcifying fluid Ω_{Ar} from laboratory-cultured corals exposed to a range of carbonate chemistry treatments, show potential applications to other marine calcifiers including coralline algae and sclerosponges, and discuss the implications of our findings for understanding mechanisms of resilience to ocean acidification.