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Developing a reliable laser ablation ICP-MS method for I/Ca measurements in corals

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Corals are unique archives of continuous, time-resolved climate variability. Several element-to-calcium ratios (e.g., Sr, Mg, Ba, U) have been established as proxies for environmental conditions such as temperature, pH, and salinity. The I/Ca ratio has been proposed as a proxy for localized oxygen depletion [1]. It is not clear how the heterogeneity in coral materials impact the proxy signal. Laser ablation ICP-MS offers the potential for rapid, high-resolution analysis of elemental ratios in corals, but several challenges arise when measuring iodine with microbeam techniques. These include iodine's high ionization potential, low natural abundance, and lack of suitable standards. We (1) test three different reference materials in search for a suitable working standard (2) explore the effects of different laser settings, (3) develop a protocol for micro-sampling I/Ca ratios in corals. We find that the repeatability and precision in measuring iodine, as well as Sr, Mg and U, is improved using biogenic standard JCp-1(a *Porites sp.* coral reference material) compared to synthetic calcite standard USGS MACS-3. In sections of *Porites* sp. coral differences in I/Ca ratio are observed between structural features and changes in density which might be related to patterns of growth. Variability in I/Ca values along transects has a moderate positive relationship with U/Ca, a moderate to weak positive relationship with Sr and Ba, and no relationship with Mg/Ca.

[1] Sun, Robinson, Parkinson, Stewart, Lu, Hardisty, Liu, Kershaw, LaVigne & Horner (2023) *Front. Mar. Sci.* **10,** 1-13.