EVALUATION OF ELEMENT/CA RATIOS AS A SCREENING TECHNIQUE TO QUANTIFY THE AMOUNT OF DIAGENETIC CALCITE IN FOSSIL CORALS

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INTRODUCTION

Fossil corals are widely used as a proxy for past sea level position [1]. The absolute age of a coral can be determined using isotopic dating techniques such as U-Th or radiocarbon [2]. Relative sea level calibration curves derived from the isotopic ages of coral proxies also provide information about eustatic (ice sheet) contribution [2, 3]. Determining how ice sheets reacted to past warming events may lead to better informed predictions of future sea level rise due to global warming [1]. This study focuses on some of the challenges in using coral geochemistry to help reconstruct the timing of past changes in sea level.

BACKGROUND

Scleractinian corals preferentially build their skeleton out of aragonite [4, 5]. Aragonitic coral fossils may undergo alteration via diagenesis to inorganic calcite, a process which complicates accurate isotopic dating [1]. It is imperative that such alteration is detected before compromised material influence data analysis.

Surfaces of fossil corals from (left) Western Australia and (right) Florida Keys.

X-ray diffraction (XRD) is used to determine to what extent this alteration has occurred [2, 3]. Here, we examine a possible alternative method assessing aragonite preservation, which involves analyzing elemental ratios of Mg/Ca and Sr/Ca and comparing them to the calcite percentage determined by XRD. Strontium and magnesium present in seawater have been shown to substitute into the carbonate structure [6] in differing amounts during skeleton-building and re-formation depending on the carbonate mineralogy [7]. The smaller Mg ion more easily substitutes into the trigonal structure of calcite, and the larger Sr ion more easily substitutes into the orthorhombic structure of aragonite. The advantage of this approach is that it is quicker and less intensive than quantitative XRD procedures.

OBJECTIVES

- Measure Sr/Ca and Mg/Ca ratios of powders from corals that have also undergone a quantitative XRD analyses to determine the % calcite and aragonite present
- Assess whether element/Ca ratios are a reliable indicator of % conversion of aragonite to calcite, to save time from having to conduct X-ray diffraction analyses

METHODS

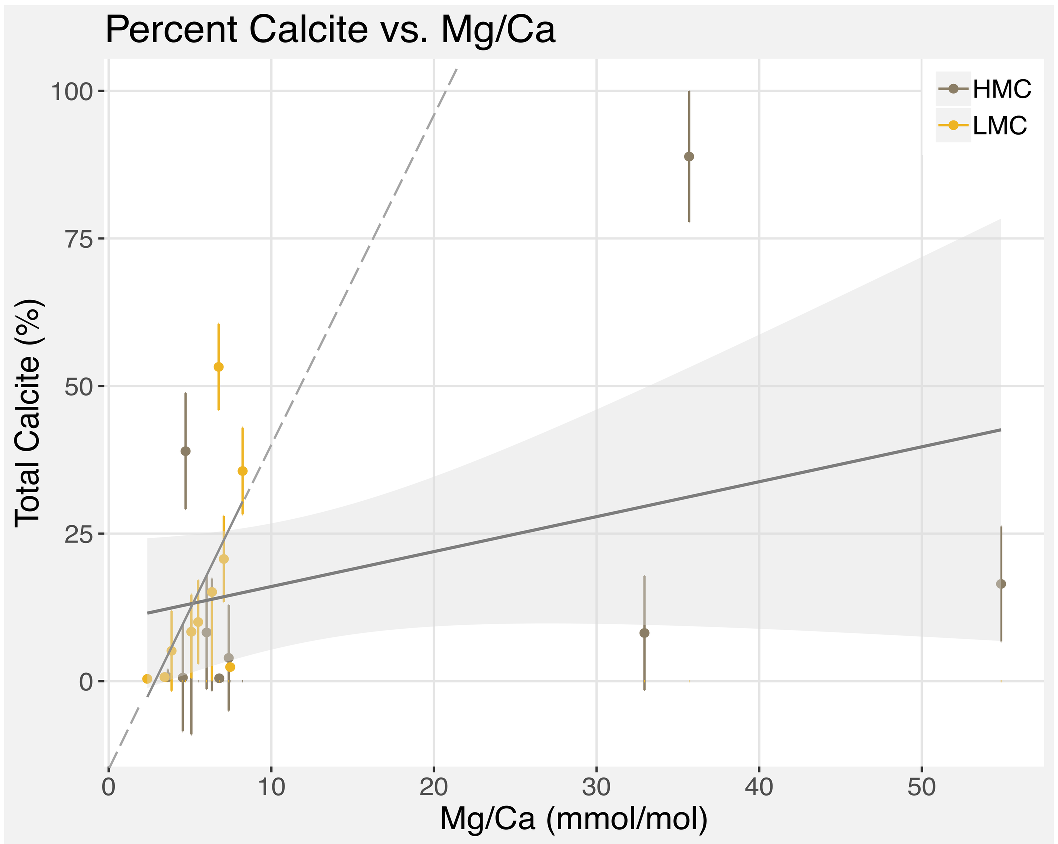
- X-ray diffraction was used to quantify the amount of high-magnesium- (HMC) and low-magnesium-calcite (LMC) relative to total carbonate.
- Inductively-Coupled Mass Spectrometry (ICP-MS) was used to measure element/Ca ratios in samples with a range of calcite composition.
- 20 fossil coral samples collected from the Last Interglacial (~125,000 yrs old) from the Seychelles were examined.

RESULTS

- Percent HMC, LMC, and total calcite were plotted respectively vs. Mg/Ca and Sr/Ca and a linear model was created using R.
- Figure 1 and Figure 2 include all of the data and are color-coded to indicate HMC and LMC.
- Plots which isolate LMC (Mg/Ca) and HMC (Sr/Ca) are shown in accordance with the most statistically significant results. HMC data for Mg/Ca and HMC data for Sr/Ca were less conclusive.
- Statistical analysis implies that the models may be more accurate when HMC and LMC are isolated than when they are plotted together.

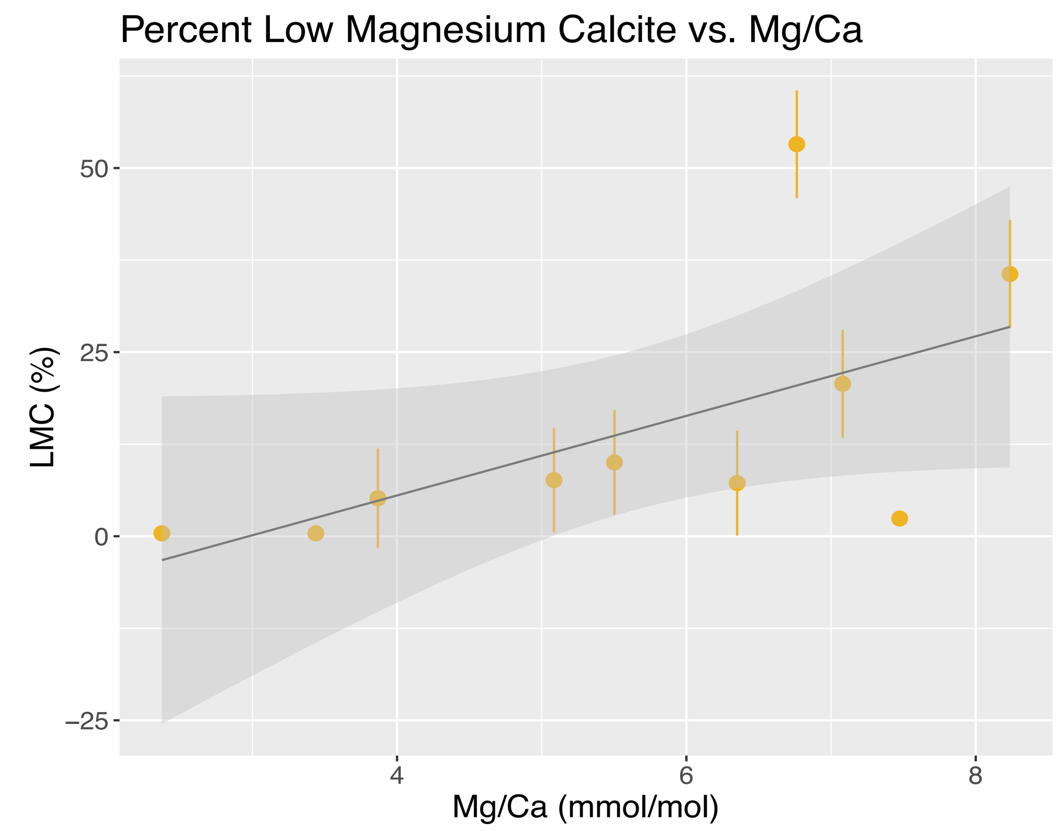
Mg/Ca

Figure 1



- **Mg/Ca does not appear to be a good predictor of % conversion of aragonite to calcite because there are two phases of calcite present (HMC and LMC), and each has a different relationship with Mg/Ca content.**

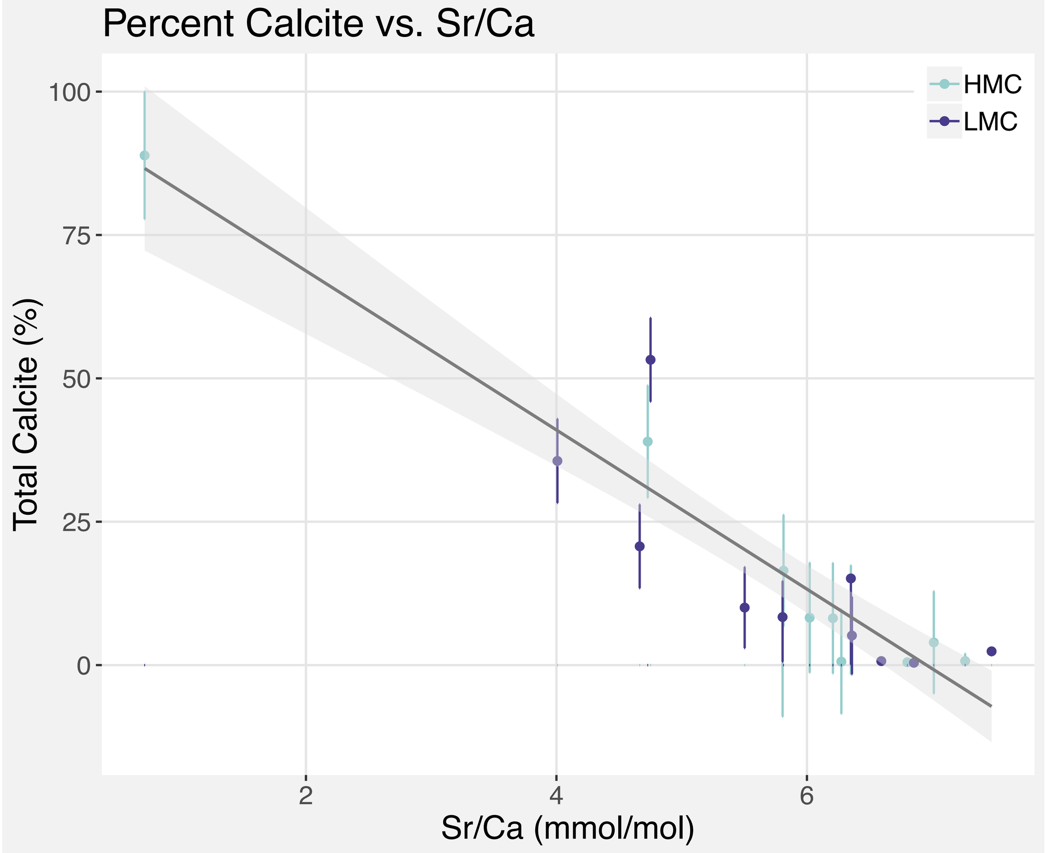
Figure 2



- **Percent LMC (as determined by XRD) in the samples generally increases with Mg/Ca (R^2 = .2703, p = .07).**
- **Because of the scattered distribution of this data, Mg/Ca is not a precise predictor of LMC content.**

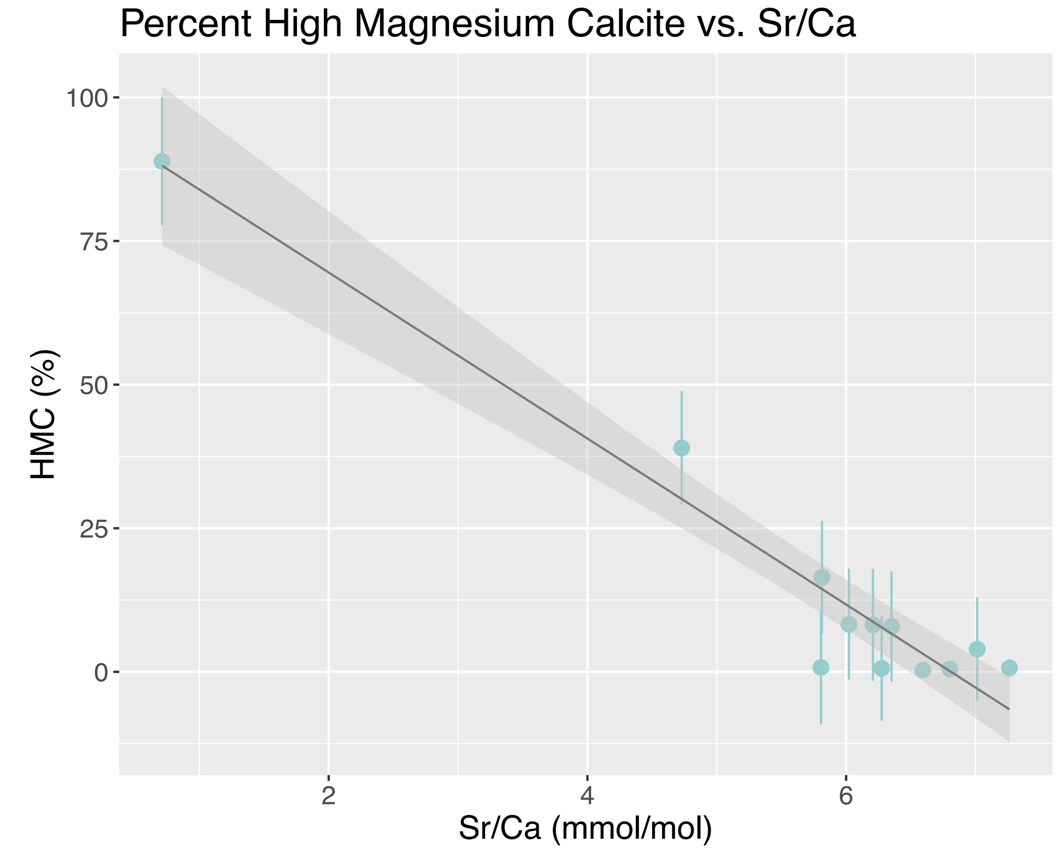
Sr/Ca

Figure 3



- **Sr/Ca appears to be a good predictor of % conversion to aragonite to calcite based on the strong negative, linear trend that fits the relatively concentrated spread of data.**

Figure 4



- **Percent HMC in the samples decreases as Sr/Ca increases (R^2 = .9335, p= 2.0e-08). Sr/Ca seems to be a better predicter of HMC than LMC.**

CONCLUSIONS

- As predicted, the percent calcite in a sample increases as Mg/Ca increases and the percent calcite decreases as Sr/Ca increases.
- However, **the presence of two phases of calcite (HMC & LMC) complicates the relationship** between % calcite and Mg/Ca content.
- Even within the %LMC and Mg/Ca relationship (Figure 2), the scatter is large enough that Mg/Ca is not a precise predictor of % calcite present.
- **The relationship between Sr/Ca and % calcite is more consistent** between the two different phases of calcite present because the Sr content is primarily controlled by the amount of aragonite present.
- However, as with the case of Mg/Ca, the scatter between Sr/Ca and % calcite is large enough that Sr/Ca is not a precise predictor of calcite content.
- One possibility is that **Sr/Ca could be used to screen the corals** and then corals with Sr/Ca higher than some threshold (e.g. 0.6), could be measured on XRD for a more precise assessment of calcite content.
- This approach of using element/Ca ratios to screen corals for aragonite preservation (instead of having to conduct quantitative XRD) is not robust given the high scatter observed and due to the complication of multiple phases of calcite present.

FURTHER STUDY

- This analysis is limited to samples from one particular location and begs the question of how consistent these relationships are at other sites with different diagenetic histories.
- We hope to apply this technique to submerged corals, where there may not be LMC present, to see if this approach might be more effective in that environment.

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