UNIVERSITY OF MIAMI
ROSENSTIEL SCHOOL of MARINE, ATMOSPHERIC & EARTH SCIENCE

Evaluating the persistence of ichthyocarbonate in sediments from Fiji and the Chagos Archipelago

Jadon Christian[1], Sam Purkis[1], Martin Grosell[2], Alexandra Dempsey[3], Amanda M. Oehlert[1]

[1]Department of Marine Geosciences, University of Miami Rosenstiel School of Marine, Atmospheric, and Earth Science, Miami, FL; [2]Department of Marine Biology and Ecology, University of Miami Rosenstiel School of Marine, Atmospheric, and Earth Science, Miami, FL
[3]Khaled bin Sultan Living Oceans Foundation, Anapolis, MD
For correspondence: jrc362@miami.edu, aoehlert@miami.edu

GEOBIOLOGY AND BIOGEOCHEMISTRY GROUP

1. Introduction

Figure 1: Gulf Toadfish with ichthyocarbonate precipitate

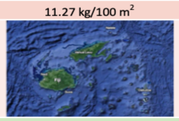
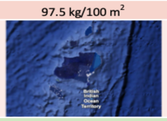
During a process called osmoregulation, a Mg-rich carbonate called ichthyocarbonate is created in the intestines of marine fish and excreted instinctually to the environment (Grosell et al., 2023). Prior studies showed that ichthyocarbonates are highly soluble in seawater and will likely dissolve in open ocean settings (Wilson et al., 2009; Woosley et al., 2012). In shallow marine environments, ichthyocarbonates have been found in fine-grained (< 63 μm) sediments in the Bahamas (Perry et al., 2011), demonstrating their importance in sediment budgets. Recent studies indicate that ichthyocarbonate has a characteristically low $\delta^{13}C$ value (Oehlert et al., 2024) which may be a useful indicator of ichthyocarbonate presence in sediments. **The goal of this study is to evaluate the persistance of ichthyocarbonates in sediments from Fiji and the Chagos Archipelago using morphology, concentration, and composition.**

2. Hypotheses

Fine grained sediments will contain more high magnesium calcite ('HMC', > 4 mol%$MgCO_3$) and lower $\delta^{13}C$ values than coarser size fractions when ichthyocarbonate is present.

Because Chagos Archipelago hosts a large Marine Protected Area (MPA), sediments from Chagos will contain more evidence of ichthyocarbonate than those from Fiji.

3. Materials and Methods

	Fiji (Bruckner et al., 2016)	Chagos (Carlton et al., 2021)
Marine Protected Area	No	Yes
Sediment Type	Mix of Extinct Oceanic Volcanoes and Carbonate	Carbonate
Species Observed during GRE	≥ 483	≥ 784
Fish Biomass	11.27 kg/100 m^2	97.5 kg/100 m^2
Map		

Sediment samples (34) were collected by the Khaled bin Sultan Living Oceans Foundation Global Reef Expedition ('GRE'; Purkis et al., 2019) in Fiji and the Chagos Archipelago. To test our hypotheses, bulk sediment samples were:

1. Wet-sieved with UV-sterilized and filtered seawater using a non-metallic sieve to separate the < 63 μm size fraction
2. The < 10 μm was collected via a settling experiment previously described (Perry et al., 2011)
3. Bulk sediment and < 63 μm size fraction were analyzed for $\delta^{13}C$ values using a MAT 251 as previously (Oehlert and Swart, 2014).
4. Selected samples of the < 10 μm size fraction were examined using SEM-EDS. Selection criteria was the highest difference in $\delta^{13}C$ values between bulk and fine-grained sediments

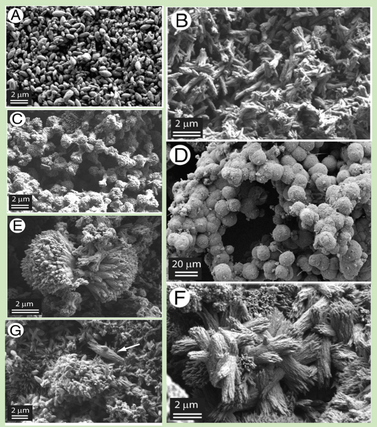


Figure 2: Common morphologies of tropical fish produced ichthyocarbonate crystallites identified in SEM (Perry et al., 2011).

4. Geochemical Results

Key Findings: Bulk sediments from Chagos have a similar range in $\delta^{13}C$ values compared to those from Fiji (~ 3.5 ‰). Bulk and < 63 μm size fraction are more often different in samples from Chagos (Fig. 3) than Fiji (Fig. 4). BIOT-9, 18, and 64 and FJ-2, 72, and 152 had the largest difference in $\delta^{13}C$ values with decreasing sediment grain size, and thus, were selected for Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM-EDS).

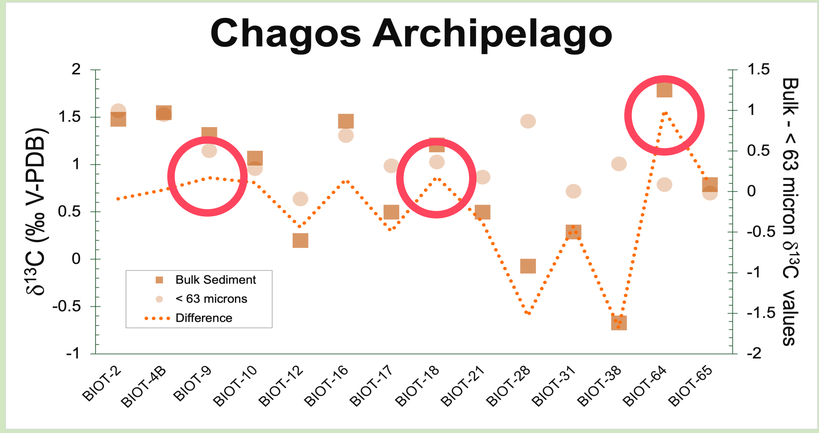


Figure 3: Chagos Archipelago $\delta^{13}C$ values from the bulk and < 63 μm samples (left axis) plotted with the calculated difference between the size fractions (right axis). The largest differences selected for SEM-EDS analysis are emphasized with red circles.

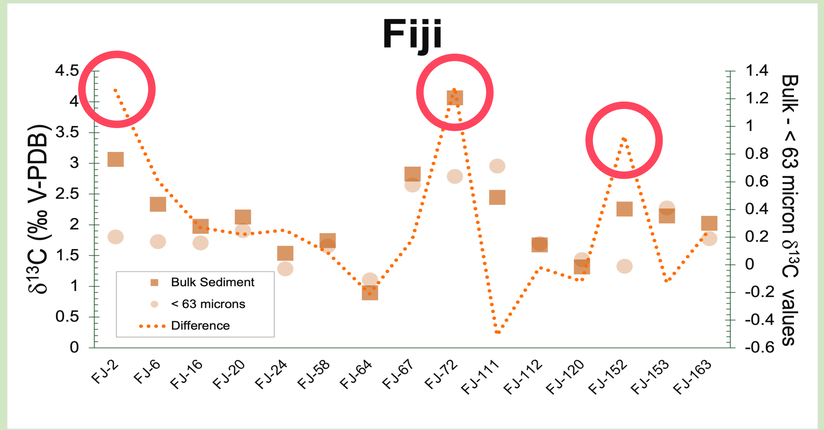


Figure 4: Fiji $\delta^{13}C$ values from the bulk and < 63 μm samples (left axis) plotted with the calculated difference between the size fractions (right axis). The largest differences are emphasized with red circles, indicating samples selected for SEM-EDS analysis.

5. SEM-EDS Results

Key Observations: Evidence of ichthyocarbonate was rare. The < 10 μm size fraction of sediments from Fiji contained morphological and compositional evidence of ichthyocarbonate (Fig. 5), but no evidence was observed in the 3 samples from Chagos Archipelago (Fig. 6).

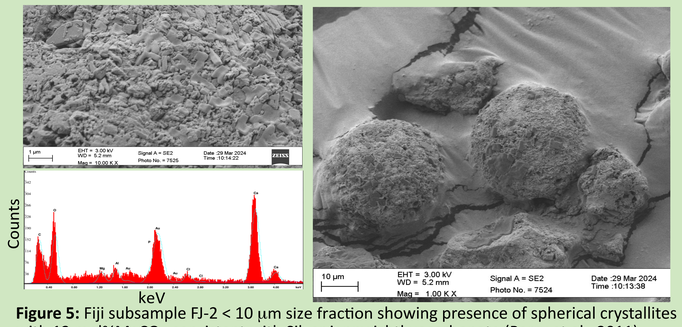


Figure 5: Fiji subsample FJ-2 < 10 μm size fraction showing presence of spherical crystallites with 12 mol%$MgCO_3$ consistent with Silver jenny ichthyocarbonate (Perry et al., 2011).

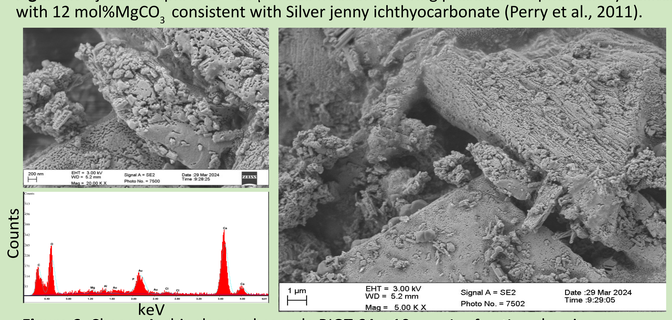


Figure 6: Chagos Archipelago subsample BIOT-64 < 10 μm size fraction showing no morphological evidence for presence of ichthyocarbonate, confirmed by EDS which indicated < 4 mol%$MgCO_3$, consistent with low-magnesium calcite.

6. Interpretations and Conclusions

Results indicate that using a decrease in $\delta^{13}C$ values alone is not sufficient to consistently identify samples with ichthyocarbonate in the < 10 μm size fraction. Similar ~ 1.0 ‰ changes between bulk and ~ < 63 μm size fraction were observed in sediments from both atolls, but only sediments from Fiji contained morphological and compositional evidence of ichthyocarbonate.

- **Decreasing $\delta^{13}C$ values with decreasing grain size should be one criteria for selecting samples. Since ichthyocarbonate is comprised of high magnesium calcite, X-ray diffraction would be a complimentary.**

Although our dataset was limited (3 samples per atoll), preliminary results indicate that the establishment of an MPA is not an overarching control on ichthyocarbonate persistence in shallow marine sediments.

- **Further analysis is warranted to develop a more robust SEM-EDS dataset.**
- **Fine grained sediment from Chagos were often low-magnesium calcite, and exhibited a pitted surface (Fig. 6, upper left).**
- Despite a more heterogeneous mineralogical **composition indicated by EDS analysis (Fig. 7), fine grained sediment collected from Fiji contained morphological and compositional evidence that supports the interpretation of ichthyocarbonate persistence (Fig. 5).**

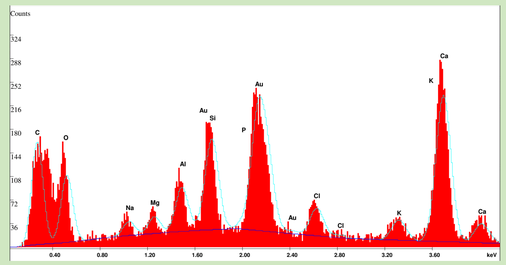


Figure 7: EDS from subsample FJ-72 < 10 μm suggesting an increase in mineralogical diversity (note peaks for Si, Al, K) in the finest fraction of Fiji's sediments compared to Chagos (Fig. 6).

7. Acknowledgements & References

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