Analyzing Biogenic and Abiogenic Carbonate Dissolution in Ocean-Floor Sediments

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GEOS499: Capstone

Abstract

Around the world today, we see a decrease in ocean pH levels, and this change in pH has potential devastating effects on marine ecosystems. This study examines the role of decreasing pH levels and associated dissolution rates of marine sediments, via analysis of the mineral calcite from biogenic and abiogenic sources; by means of a laboratory experiment setup. The study experimental setup mixed samples of ground biogenic (shells) and abiogenic (ooids) carbonate with aqueous solution at three pH levels (7,6, and 5). Rate and amount of calcite dissolution was measured for each experiment and byproducts of dissolution were analyzed via Ion Chromatography (IC). Data indicates increased dissolution as pH level decreases, which is concurrent with previous research, and IC analysis shows varying concentrations of anions in all samples. While some potentially harmful anions were detected, the concentrations are either in line with normal seawater or the results were inconclusive. More data via further decreasing pH levels will confirm or deny experimental findings.

Research Question

How does dissolution rate of ocean carbonates (biogenic and abiogenic) differ and change with varying pH levels, and what are byproducts of this dissolution?

Project Objectives

- Implement an experiment to examine rates of carbonate dissolution via subjecting samples of ocean sediments to varying pH level solutions to mimic the effects of ocean acidification.
- Analyze the leached components from dissolution via Ion Chromatography.

Background

- Increased concentration of atmospheric CO2 as a result of fossil-fuel burning has led to increased rates and amounts of CO2 into oceans, lowering ocean pH
- Many aquatic species, corals, and ecosystems can only survive in specific pH ranges (Form et al, 2012)

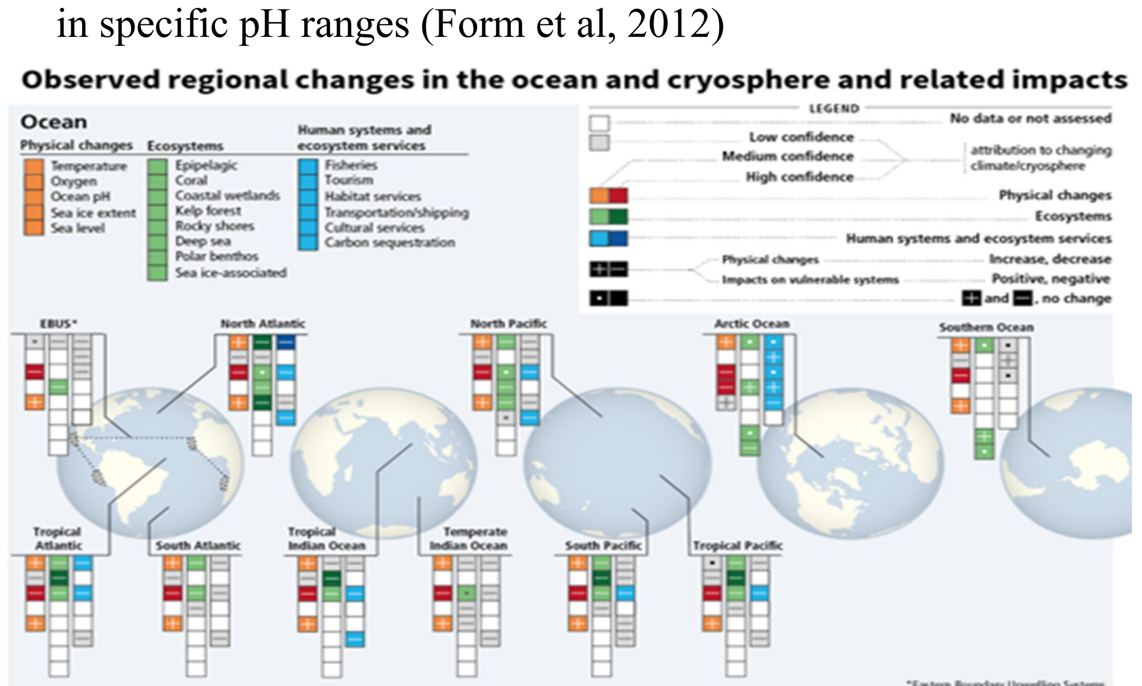

Figure 1: Observed changes to ocean systems around the world. Ocean pH levels are highlighted in the orange column, third block down, with a global trend of declining pH level (IPCC, 2019).

- Marine sediments tend to be rich in minerals that dissolve in acid, like calcite (Bin-Jin et al, 2016).
- As pH levels lower (under pH 7), we could expect to see increased dissolution rates in these sediments (Thomas and Wilson, 1998)
- Dissolution of these sediments could provide an influx of anions into the marine environment, such as; chloride, sulfate, nitrate, and fluoride.
- This area of impact is often neglected in studies that focus on ocean acidification
- Studies like this one could be used to supplement existing research to further quantify survival outcomes of various species in marine ecosystems.

Methods

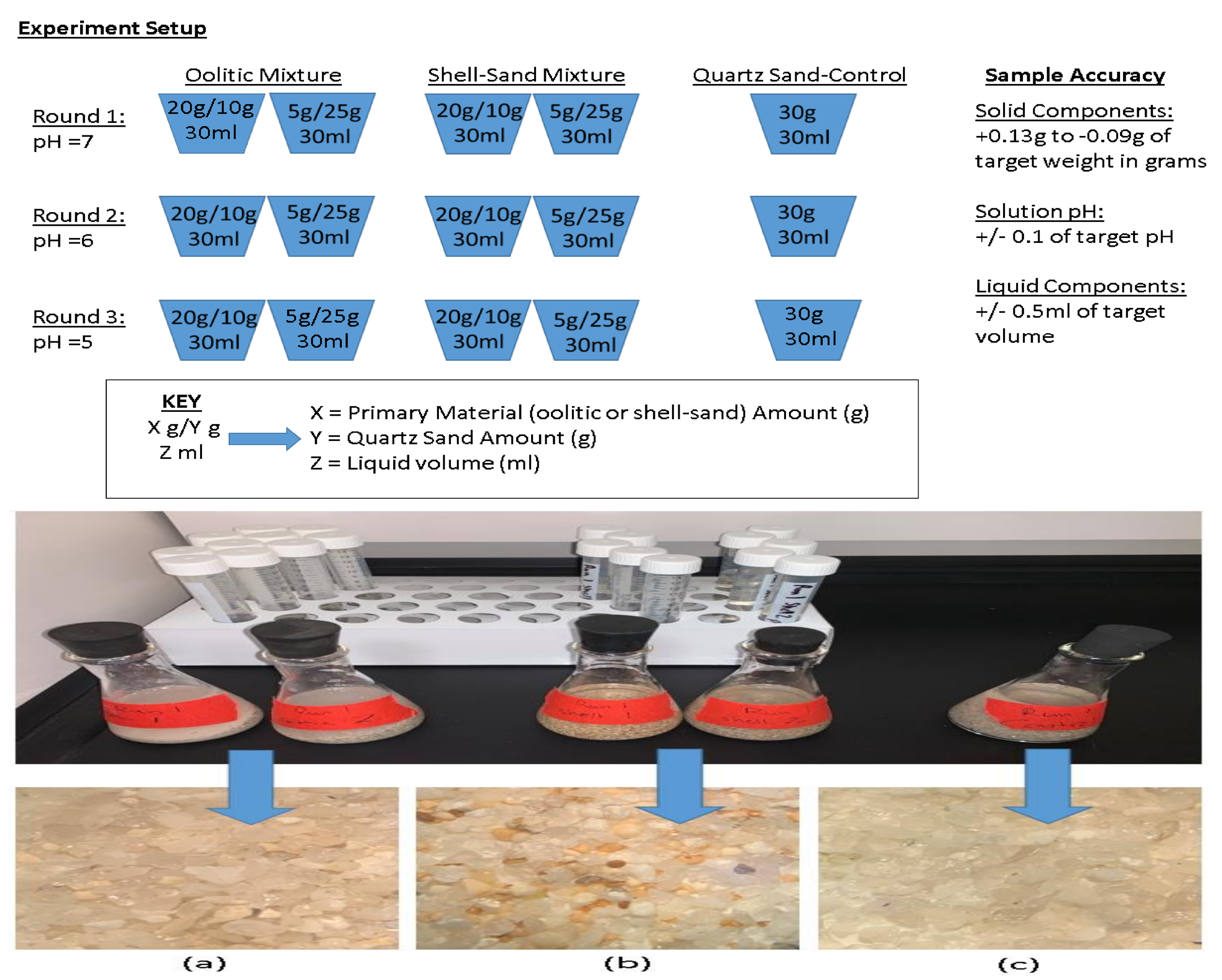

Figure 2: Experimental setup with microscopic view of sediment samples. (a) oolitic limestone with quartz sand, (b) shell-beach sand with quartz sand, (c) quartz sand (control).

Sample Selection

- Abiogenic calcite = ooids, Biogenic calcite = marine shell sands
- Sample identification: abiogenic = Oolitic, biogenic = Shell
- Oolitic: crushed oolitic limestone, sieved via ro-tap down to 0.7mm to 1 mm (coarse/medium sand grain)
- Shell sand: medium to fine grain in size, calcite (from shells)
- Two different mixtures, by weight, for each sample type
- Quartz sand: medium to fine grain in size, no calcite

Dissolution Experiments

- Three rounds utilizing different pH ranges: 7,6, and 5. pH 7 = nano pure water, pH 6/5 = HCl solutions (pH +/-0.1) via serial dilution
- Round 1 = pH 7, Round 2 = pH 6, Round 3 =pH 5
- Each round lasts 48 hours, samples then dried for 48 hours
- Room temperature, hand mixed for 10 seconds (for pre/post IC sample), under laboratory fume hood
- Quantify dissolution via changes in weight, pre vs. post

Ion Chromatography Analysis

- Conducting anion analysis: focused on sulfates, nitrates, and fluoride
- Samples taken before (right after adding solution) and after dissolution experiment (after 48-hour period)
- 30 samples, 3 blanks, and 5 standards created via serial dilution; 1 pre and 1 post IC sample per each dissolution group, each round

Results: Dissolution

Biogenic (Shell)

- Largest sample dissolution: Round 3 Shell 1, loss of 14.25% (4.28g)
- Smallest sample dissolution: Round 2 Shell 2, loss of 0.10% (0.03g)
- Largest total combined dissolution with pH 5 solution of 4.93g
- Round 1 Shell 1 post increased in mass by 0.11g (experimental error)

Abiogenic (Oolitic)

- Largest sample dissolution: Round 1 Oolitic 1, loss of 4.20% (1.26g)
- Smallest sample dissolution: Round 2 Oolitic 2, loss of 1.07% (0.32g)
- Highest average overall dissolution across all runs

Quartz Sand (Control)

- Largest sample dissolution: Round 3 Control, loss of 0.87% (0.26g)
- Smallest sample dissolution: Round 1 Control, loss of 0.13% (0.04g)
- Lowest average overall dissolution across all runs

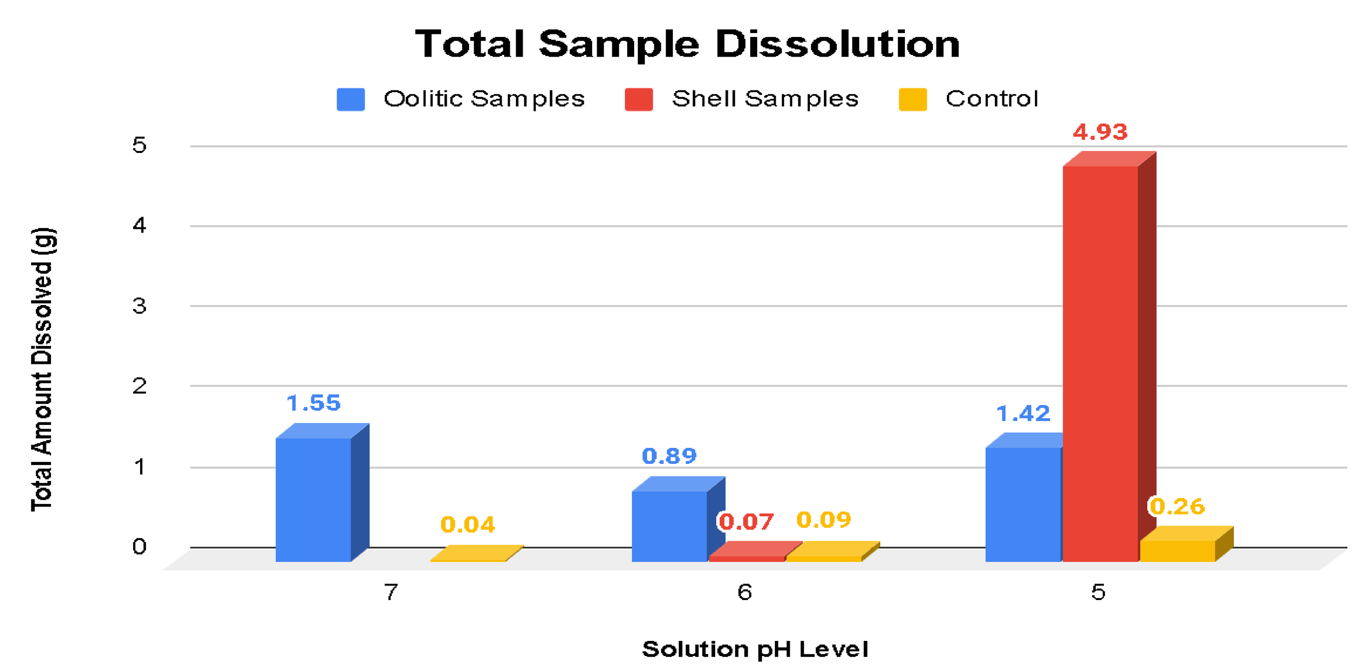

Figure 3: Total dissolution rate data from all sources and all rounds. The Shell sample data is missing for Round 1 (pH 7) due to an erroneous measurement due to experimental error.

Results: Ion Chromatograph Analysis

- Primary anions detected: Chloride, sulfate, nitrate
- Highest total concentration for all samples: Chloride (varying amount)
- Second highest total concentration: Sulfate at 75.96 mg/l (R3C Post)
- Nitrate: detected in all sample, concentrations varying from ~2 mg/l to ~8 mg/l
- Sulfate: detected in all samples, concentrations ranging from ~20 mg/l for Round 1 , to ~75 mg/l for Round 3, highest for control
- Fluoride: detected in all samples, lowest concentrations in Round 3 samples, reaching 0 mg/l for R3S2 Post

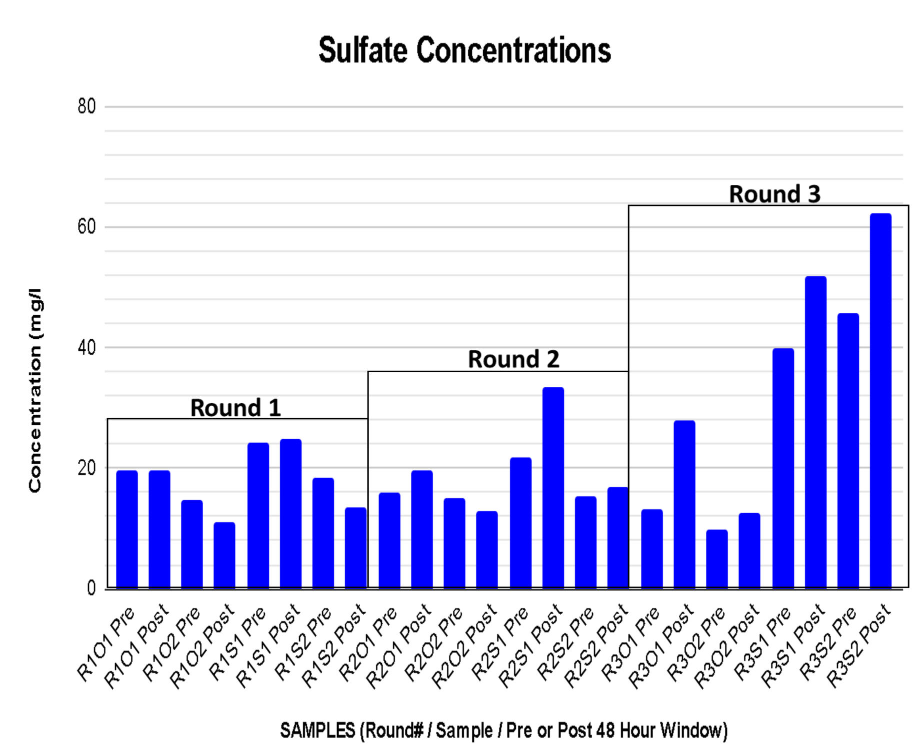

Figure 4: Sulfate IC data for all samples, pH 7 = Round 1, pH 6 = Round 2, pH 5 = Round 3.

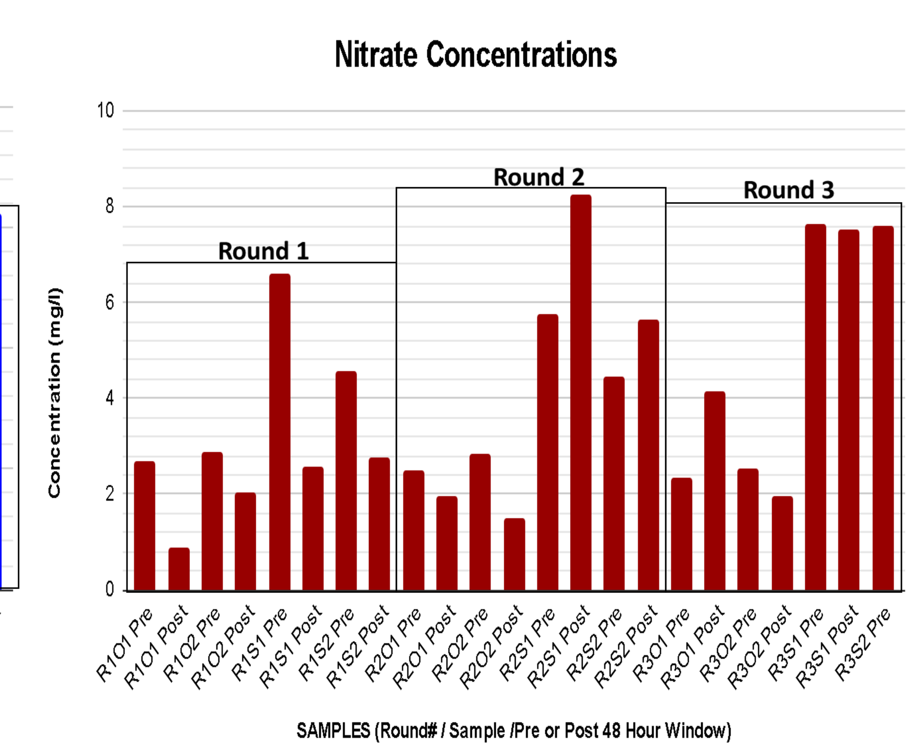

Figure 5: Nitrate IC data for all samples, pH 7 = Round 1, pH 6 = Round 2, pH 5 = Round 3.

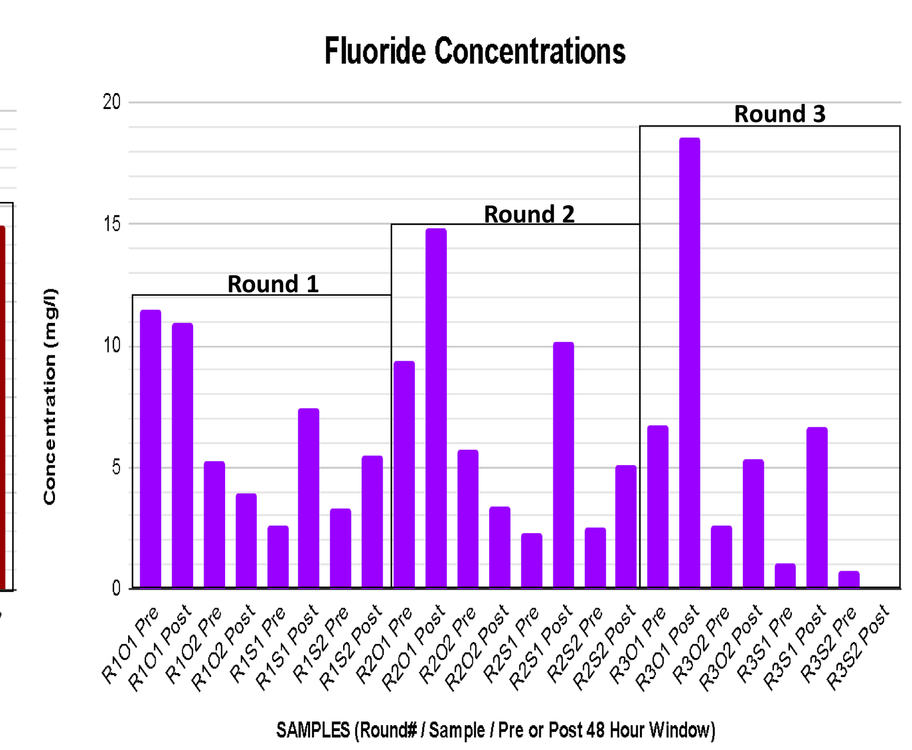

Figure 6: Fluoride IC data for all samples, pH 7 = Round 1, pH 6 = Round 2, pH 5 = Round 3.

Discussion

Experimental Design

- Experimental applicability, not recreating marine environment: temperature, mixing, natural processes, variables not addressed, and experimental accuracy regarding potential errors
- Homogeneity for all samples: no data on potential impurities
- No data on chloride due to utilization of HCl solution

Dissolution

- Trend of increasing dissolution for biogenic calcite
- Abiogenic dissolution: data shows varying rate -Potential error with Round 1

Ion Chromatography Analysis

- Increasing exponential trend of sulfates: past research shows potential harm to marine environments (Giri and Swart, 2019)
- Nitrate concentration is low to average, comparable to past studies examining seawater (Achterberg et al, 2008)
- Presence of fluoride: found in seawater settings, primarily from biogenic carbonate (Fujioka et al, 2013)
- Sulfate concentrations show trend of increasing concentration with lowering pH level
- Trend of decreasing fluoride concentration; possible interaction with hydrogen ions from the original HCl solution
- Some samples show higher concentrations pre vs post

Conclusions

- More data! An additional round with a pH of 4 would confirm or deny potential trends
- A larger scale version of this experiment would lead to more concrete data
- Nitrate IC data is inconclusive; results in general are mixed
- Sulfate concentration: concurrent with research indicating higher concentrations from biogenic carbonate sources (Giri and Swart, 2019)
- Source of fluoride: according to prior research; presence presumed from biogenic carbonate source (Fujioka et al, 2013)
- Fluoride concentration: inconclusive; lowering trend likely due to interaction with hydrogen ions
- While research shows potential side effects of larger concentrations of nitrate, sulfate, and fluoride; results from this experiment are inconclusive for ecosystem health effects

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