

# Ocean Acidification: Investigation and Presentation of the Effects of Elevated Carbon Dioxide Levels on Seawater Chemistry and Calcareous Organisms

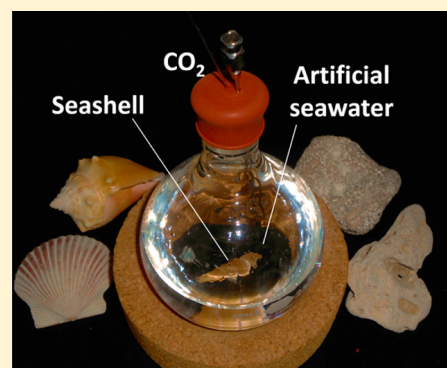
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**S** Supporting Information

**ABSTRACT:** Ocean acidification refers to the process by which seawater absorbs carbon dioxide from the atmosphere, producing aqueous carbonic acid. Acidic conditions increase the solubility of calcium carbonate, threatening corals and other calcareous organisms that depend on it for protective structures. The global nature of ocean acidification and the magnitude of its potential impact on marine ecosystems and the industries they support make it an important and engaging topic to explore in the undergraduate laboratory. In this multiweek experiment, designed for second year analytical and environmental chemistry courses, artificial seawater samples containing pieces of seashell or coral were prepared. One sample was pressurized with carbon dioxide and stirred for 1 week, while the other was stirred without carbonation. Mass and pH measurements and carbonate, bicarbonate, calcium(II), and magnesium(II) titrations were performed on samples before and after treatment. Through data analysis and a rigorous consideration of the acid–base and solubility equilibria involved, students concluded that carbonation significantly decreased seawater pH and caused appreciable seashell and coral dissolution, which raised the bicarbonate and calcium(II) concentrations. Minimal change in the seawater chemistry or carbonaceous material was observed for the noncarbonated sample. Overall, the experience provided a meaningful experimental context for titration analyses and a practical application of the conceptual treatment of a multiequilibrium system. In addition to the experiment, a corresponding oral presentation assignment is presented, in which students produced a video designed to educate a general audience on the topic of ocean acidification by using their experimental results as support. Through this assignment, students reflected on the broader ecological and societal ramifications of ocean acidification and developed the ability to communicate scientific knowledge to a nonscientific audience, a critical collaborative skill for addressing such multifaceted issues.

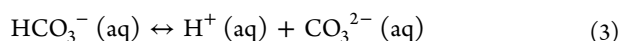
**KEYWORDS:** Second-Year Undergraduate, Analytical Chemistry, Environmental Chemistry, Laboratory Instruction, Hands-On Learning/Manipulatives, Aqueous Solution Chemistry, Equilibrium, Quantitative Analysis, Titration/Volumetric Analysis



In recent years, ocean acidification has gained increasing attention in the scientific community as “the other carbon problem” together with global warming.<sup>1</sup> The earth’s oceans serve as a predominant carbon sink, absorbing roughly one-third of anthropogenic carbon dioxide emissions.<sup>2</sup> Upon dissolving in seawater, carbon dioxide reacts to form carbonic acid (eq 1):



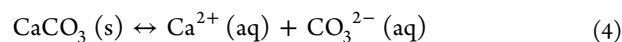
Diprotic carbonic acid may then dissociate to form bicarbonate (eq 2), which may further dissociate to carbonate (eq 3), releasing hydrogen ions and thus increasing acidity:



As atmospheric carbon dioxide levels have risen since preindustrial times, the average pH of the ocean has decreased

by 0.1 unit from 8.2 to 8.1.<sup>3</sup> Because of the logarithmic nature of the pH scale, this represents a 26% increase in ocean acidity.

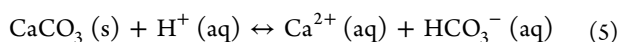
Ocean acidification poses several ecological and societal risks. Increased ocean acidity threatens calcareous organisms, such as corals and other species, that depend on protective shells made of calcium carbonate, which is sparingly soluble in water (eq 4):



According to Le Chatelier’s principle, as the hydrogen ion concentration in seawater increases, eq 3 shifts toward the left to produce bicarbonate while consuming carbonate. The decrease in carbonate concentration causes eq 4 to shift toward the right, resulting in the dissolution of calcium carbonate. The relationships between the predominant species at typical seawater pH may be summarized in the combined eq 5:

**Received:** August 17, 2015

**Revised:** December 22, 2015



Thus, increased ocean acidity may result in the dissolution of calcium carbonate protective structures or hinder their formation.<sup>4</sup> It may also lead to substantial economic impacts for industries like fishing and tropical tourism as the organisms that sustain them are affected.<sup>5,6</sup>

The global ecological and economic significance of ocean acidification makes it an important and engaging topic for an undergraduate laboratory experiment. Additionally, ocean acidification is well-suited for undergraduate study because it involves dynamic equilibrium reactions (eqs 1–5), a curricular subject of central importance. More specifically, the treatment of systems of inter-related equilibrium reactions is often a key learning objective of quantitative analysis courses. In this *Journal*, Perera and Bopegedera previously reported an experiment that explored the impact of ocean acidification on calcareous organisms tailored to general/introductory chemistry courses.<sup>7</sup> In their experiment, calcite (representing calcareous biological material) was added to aqueous buffers of varying pH, and the percent mass of dissolved calcite was found to increase with decreasing pH.

The experiment described presently was designed for foundation level analytical chemistry and environmental chemistry students that have completed a two semester general chemistry sequence. It aimed to determine directly how an elevated carbon dioxide level affected artificial seawater chemistry and calcareous material such as seashells and coral in a holistic way. Seashell or coral mass measurements were integrated with pH measurements and titrimetric determinations of carbonate, bicarbonate, calcium(II), and magnesium(II) concentrations to draw final conclusions. A corresponding oral presentation is also described (see assignment sheet in the [Supporting Information](#)), in which students produced a video designed to educate a general audience on ocean acidification by using their experimental results as support.

## ■ EXPERIMENTAL DETAILS

The experiment was conducted by the author using seashell and coral samples and by two lab sections of 11 and eight students from the same quantitative analysis course over three 3 h lab periods using two types of coral samples. It was performed near the end of a major unit on solubility, acid–base, and complexation equilibria. Prior to the experiment, ocean acidification was introduced, and the relevant equilibrium reactions and experimental design were discussed in the lecture component of the course. Sample preparation was performed during the first week and did not take more than 1 h. Thus, it could potentially be completed during the same lab period as a different activity. Carbonate/bicarbonate titrations and pH measurements were made during the second week, while calcium(II)/magnesium(II) titrations and mass measurements were performed in the third week. These two weekly activities consumed the entire 3 h lab period. To accelerate the process and reduce equipment needs, students worked in pairs for the sample preparation and pH and mass measurements. Samples were then subdivided between partners, and titrations were performed individually. An overview of the experiment is given below, while more specific details may be found in the student lab instructions and instructor notes provided in the [Supporting Information](#).

Samples and controls were prepared using artificial seawater prepared in advance by the instructor following a recipe

adapted from Lyman and Fleming.<sup>8</sup> Two 150 mL aliquots were transferred to separate round-bottom flasks. To each flask was added several grams of the same type of seashell or coral. After each flask was sealed with a rubber septum, the artificial seawater in one of the flasks was purged with pure carbon dioxide gas for 20 min while the flask was vented to saturate the solution and pressurize the headspace with carbon dioxide. The other flask was not treated with carbon dioxide. The carbon dioxide exposure was not intended to mimic environmental conditions but rather to produce more substantial chemical changes that could be quantified in a practical time frame. While the seal was maintained, each flask was then magnetically stirred at a moderate rate for 1 week. As a negative control, 150 mL of artificial seawater was set aside for analysis without exposure to seashells or coral or carbonation.

After 1 week of exposure, the calcareous solid in each round-bottom flask was separated from the aqueous solution by Gooch filtration. It was then rinsed with deionized water, dried at 50 °C until the following week, and massed after equilibrating to room temperature. The final mass of each sample was compared to its original mass before treatment.

The pH of both the samples and the control was measured using a pH meter. Carbonate and bicarbonate concentrations were determined via titration with 0.002 M hydrochloric acid to phenolphthalein and methyl red end points, respectively. Finally, the concentrations of calcium(II) and magnesium(II) were determined via EDTA titration following the procedure from Experiment 12 entitled “EDTA Titration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in Natural Waters” found in the online Supporting Information of Harris’ *Quantitative Chemical Analysis*.<sup>9</sup>

## ■ HAZARDS

Proper care must be taken to secure the carbon dioxide gas tank during transport. The tank must be securely fastened to the lab bench when in use. Because many undergraduate students have not previously used gas tanks, the instructor or an experienced teaching assistant should be present to instruct and immediately supervise students when dispensing carbon dioxide. Care should be taken in handling needles for dispensing and venting gas. The needles should be disposed of in a sharps waste receptacle. Oven mitts must be worn when handling items heated in the oven. Safety gloves should be worn when using hydrochloric acid, sodium hydroxide, EDTA, or titration indicators, which may stain the skin. All used chemicals must be collected in labeled waste containers and disposed of according to local regulations and procedures.

## ■ RESULTS

The results below represent data obtained by the author for eight trials of the experiment using fragments of the same seashell and eight trials using fragments of the same piece of coral. Student data for two different coral types are presented in the [Supporting Information](#). While the majority of the student results reflect all the same general trends reported by the author, some student data points were discarded because they did not report the coral type, they did not allow sufficient drying time before massing the coral, or they struggled to accurately reach the Eriochrome black T and hydroxynaphthol blue indicator end points in the divalent ion titrations, resulting in anomalous data. The updated instructions now include a sufficient drying period. Students should be encouraged to practice finding the end point several times before analyzing

their samples and to save a solution to use as a color comparison to achieve the best possible divalent ion titration results.

As indicated in Table 1, the pH of the samples decreased slightly after exposure to the seashell and coral without

**Table 1. pH Values for the Artificial Seawater Control, Carbonated, and Noncarbonated Samples**

Sample	Seashell <sup>a</sup>	Coral <sup>a</sup>
Control	7.93	7.93
Carbonated	6.96 ± 0.26	6.73 ± 0.23
Noncarbonated	7.71 ± 0.05	7.80 ± 0.05

<sup>a</sup>Error intervals represent the standard deviation ( $n = 8$ ).

carbonation, while a more substantial decrease was observed with carbonation. This confirmed that carbonation was the predominant cause of acidification.

The seashell mass decreased by  $4.5 \pm 0.2\%$  ( $n = 8$ ) when carbonated and  $0.4 \pm 0.1\%$  ( $n = 8$ ) when not carbonated. The mass of coral decreased by  $10.7 \pm 3.1\%$  ( $n = 8$ ) when carbonated and  $1.4 \pm 0.6\%$  ( $n = 8$ ) when not carbonated. These results indicate that while the seashell and coral dissolved minimally without carbonation, the more acidic conditions of the carbonated samples resulted in much greater dissolution.

The concentration of carbonate was below the limit of detection (one drop of 0.002 M hydrochloric acid titrant to phenolphthalein indicator) for all the carbonated and non-carbonated samples and controls for both the seashell and coral. As shown in Table 2, the bicarbonate concentration was much

**Table 2. Bicarbonate Concentrations and Comparisons for the Artificial Seawater Control, Carbonated, and Noncarbonated Samples**

Sample	Seashell <sup>a</sup>	Coral <sup>a</sup>
Control	$2.10 \times 10^{-3}$ M	$2.10 \times 10^{-3}$ M
Carbonated	$(2.4 \pm 0.5) \times 10^{-2}$ M	$(2.6 \pm 0.2) \times 10^{-2}$ M
(% difference) <sup>b</sup>	1046 ± 245%	1143 ± 94%
Noncarbonated	$(2.11 \pm 0.02) \times 10^{-3}$ M	$(2.4 \pm 0.1) \times 10^{-3}$ M
(% difference) <sup>b</sup>	0.6 ± 1.2%	11 ± 7%

<sup>a</sup>Error intervals represent the standard deviation ( $n = 8$ ). <sup>b</sup>Percent differences were calculated relative to the control.

higher for the carbonated samples than for the untreated control (1046% and 1143% greater for the seashell and coral samples, respectively). The percent increase in bicarbonate concentration was minimal in comparison for the non-carbonated samples (0.6% and 11% greater for the seashell and coral samples, respectively).

**Table 3. Calcium(II) and Magnesium(II) Concentrations and Comparisons for the Artificial Seawater Control, Carbonated, and Noncarbonated Samples**

Sample	Calcium(II) Concentration		Magnesium(II) Concentration	
	Seashell <sup>a</sup>	Coral <sup>a</sup>	Seashell <sup>a</sup>	Coral <sup>a</sup>
Control	$1.01 \times 10^{-2}$ M	$1.01 \times 10^{-2}$ M	$4.86 \times 10^{-2}$ M	$4.86 \times 10^{-2}$ M
Carbonated	$(2.0 \pm 0.4) \times 10^{-2}$ M	$(2.2 \pm 0.1) \times 10^{-2}$ M	$(4.95 \pm 0.08) \times 10^{-2}$ M	$(5.2 \pm 0.2) \times 10^{-2}$ M
(% difference) <sup>b</sup>	96 ± 35%	116 ± 14%	2 ± 2%	6 ± 5%
Noncarbonated	$(1.06 \pm 0.02) \times 10^{-2}$ M	$(1.08 \pm 0.02) \times 10^{-2}$ M	$(4.92 \pm 0.05) \times 10^{-2}$ M	$(4.84 \pm 0.04) \times 10^{-2}$ M
(% difference) <sup>b</sup>	4 ± 2%	6 ± 2%	1 ± 1%	-0.3 ± 0.8%

<sup>a</sup>Error intervals represent the standard deviation ( $n = 8$ ). <sup>b</sup>Percent differences were calculated relative to the control.

As depicted in Table 3, the calcium(II) concentration was roughly twice as great in the seashell and coral samples when purged with carbon dioxide than in the untreated control. In contrast, minimal changes were observed for either material without carbonation. Because the calcium carbonate-based seashell and coral represented the only potential sources of additional calcium(II) to the solutions, the calcium(II) concentration increases in the carbonated samples must have been due to their dissolution. Minimal changes in the magnesium(II) concentration were observed for the seashell and coral samples regardless of whether they were carbonated.

## DISCUSSION

This experiment accomplished several pedagogical goals. First, by performing chemical analyses in the context of an experiment of real world importance, student interest and engagement increased, as evidenced by end of semester student evaluations and informal discussions. Titration analyses sometimes become tedious for students when analyzing independent unknown samples. Students' investment in the outcome of the broader experiment motivated them to obtain the best titration data possible. The experience also required students to consider aspects of experimental design, particularly the use of controls, they would not have if the analyses were performed on independent unknowns.

Another major goal accomplished by the experiment was that students came to better understand conceptually how inter-related equilibrium reactions effect one another in a cascading manner and how these effects are governed by equilibrium constants and  $pK_a$  values. Several students commented how the experiment provided a great opportunity to apply and further enhance their understanding of these concepts learned in lecture. As they integrated the results from their analyses, several outcomes were fairly straightforward to account for. It was clear that the pH decreased in the carbonated samples due to the formation of carbonic acid from carbon dioxide and its subsequent dissociation. It was also clear that the coral decreased in mass in the carbonated water as calcium carbonate dissolved to its component ions. This same dissociation would be expected to increase the calcium(II) concentration, which was observed. In comparison, the magnesium(II) concentration did not change substantially upon carbonation because it was not a major component of the seashell or coral.

Explaining the carbonate and bicarbonate titration results presented a greater challenge for students. It was perplexing that while the coral mass and calcium(II) results indicated that some calcium carbonate dissolved in the carbonated sample, the carbonate concentration remained below the detection limit. This required students to consider more closely the conjugate acid/base relationship between bicarbonate/carbo-

nate expressed in eq 3. The pH of all samples and controls was below 8, more than two units below the  $pK_a$  value of 10.3 for bicarbonate. Thus, the equilibrium highly favored the conjugate acid, bicarbonate, over its conjugate base, carbonate, by more than two orders of magnitude. Therefore, even when a significant amount of carbonate from the coral dissolved, it almost quantitatively protonated to form bicarbonate and was not detected.

Another challenge students faced was explaining whether the large increase in the bicarbonate concentration in the carbonated sample was mainly due to the dissociation of carbonic acid (eq 2) or due to the protonation of dissolved carbonate from the coral (eq 3). To account for the later possibility, one must consider that the calcium carbonate of the seashell and coral dissolved with equimolar stoichiometry to calcium(II) and carbonate and that essentially all of the carbonate subsequently protonated to form bicarbonate as described in the previous paragraph. By using the data from Table 3, the calcium(II) concentration, and by inference the bicarbonate concentration, increased by 0.010 and 0.012 M for the seashell and coral samples, respectively, as a result of calcium carbonate dissolution. In total, the bicarbonate concentration increased by 0.022 M for the seashell samples and 0.024 M for the coral samples (Table 2). It was thus deduced that the remainder of the bicarbonate concentration increase, 0.012 M for both the seashell and coral samples, could be attributed to carbonic acid dissociation. Overall, roughly half of the bicarbonate increase in the carbonated samples was attributed to calcium carbonate dissolution, while the other half was attributed to carbonic acid dissociation for both sample types.

A final pedagogical objective accomplished through the associated oral presentation assignment was that students developed aptitude in communicating scientific information to a nonscientific audience. Students also assessed the broader societal implications of ocean acidification, contemplated limitations of scientists in addressing such multifaceted issues, and identified experts in other fields such as government and industry needed to holistically address the issue. The development of these skills better equipped students to engage in the type of broad collaboration required to solve complex, large-scale problems.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: [10.1021/acs.jchemed.5b00676](https://doi.org/10.1021/acs.jchemed.5b00676).

Student data (PDF, DOCX)

Student lab instructions (PDF, DOCX)

Instructor notes; CAS numbers of required chemicals (PDF, DOCX)

Oral presentation assignment sheet (PDF, DOCX)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The University of Mount Union Department of Chemistry and Biochemistry is acknowledged for the provision of facilities and materials. The author thanks Amy McElhinney of the University of Mount Union Department of Biology for contributing coral and seashell samples and three anonymous reviewers whose comments contributed to an improved manuscript.

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