



Isotopic Fractionations Produced During Direct Air Capture of Carbon Dioxide

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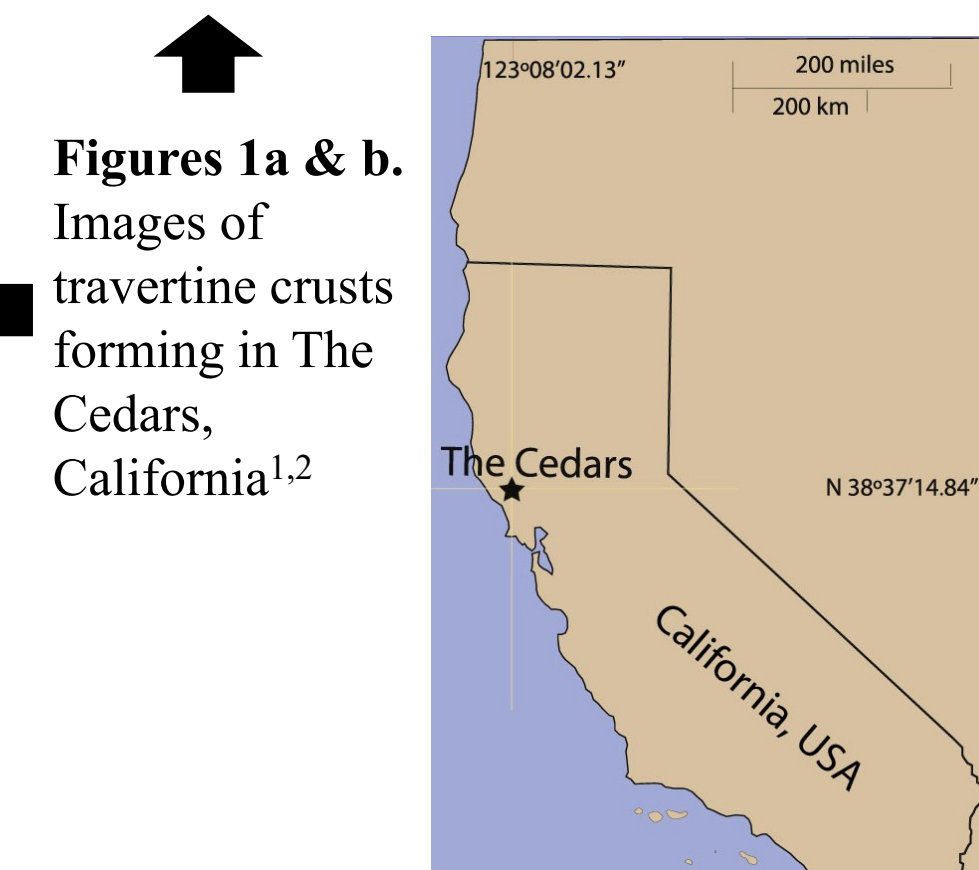
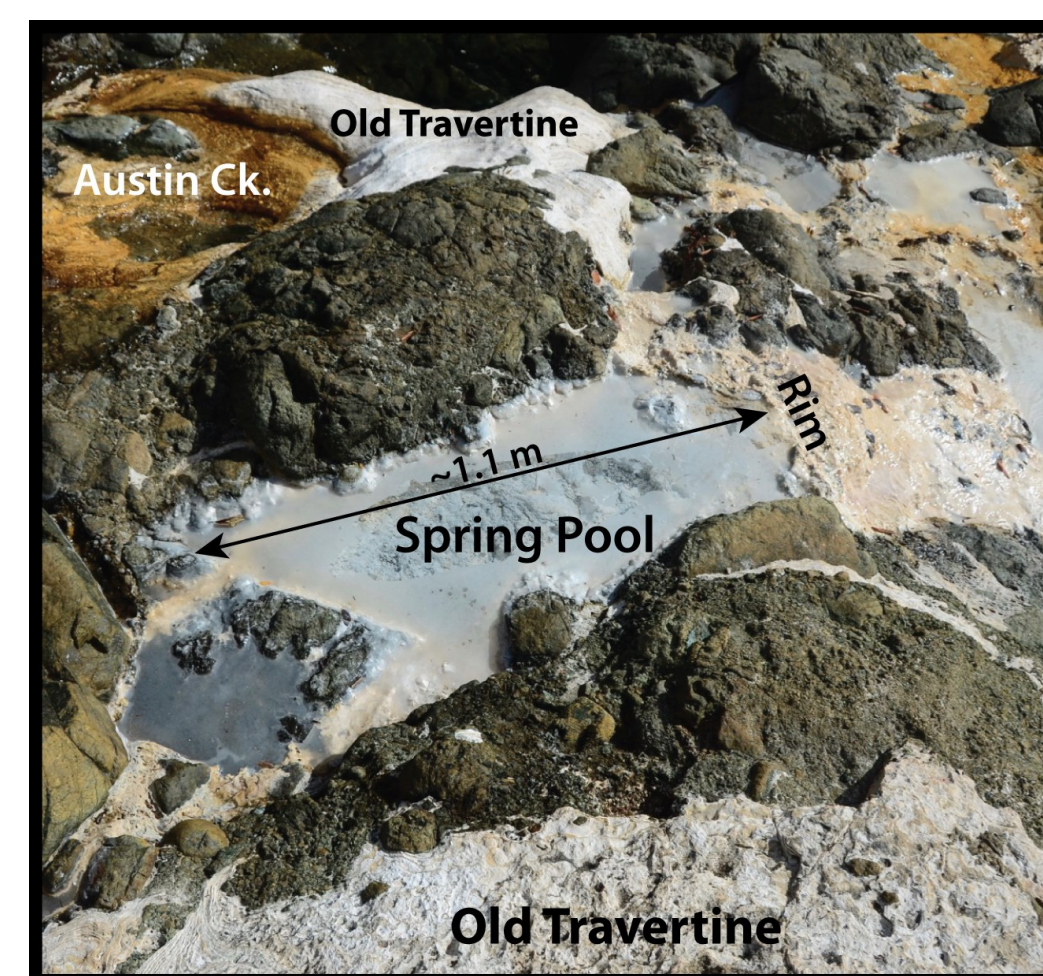
Introduction

Chemical reactions that reach equilibrium provide a useful tool for understanding paleoenvironmental conditions. For example, oxygen isotopes (¹⁸O and ¹⁶O) partition themselves between CaCO₃ and H₂O in a way that is temperature-dependent, allowing for paleotemperature reconstructions from carbonate rocks. However, many isotope partitioning reactions in nature do not reach equilibrium, and the products may contain more or less of the heavy isotope (e.g., ¹⁸O) than the equilibrium amount. In this research, we are exploring a case where naturally occurring travertines that grow in high pH (>11) waters are exhibiting abnormally large, non-equilibrium isotopic variations. These large variations make it difficult to understand the paleoenvironmental archive without first understanding the underlying causes.

Geologic Background

Meteoric water travels through ultramafic rocks:^{1,2}

- Calcium is leached from the rocks.
- Carbon is deposited in the rocks.
- Results in carbon-free, high pH solutions
- Upon reaching the atmosphere, solution absorbs CO₂ and produces impressive geologic features including travertine carbonate formations.
- Travertines produced record isotopic carbon signature of the atmosphere.
- Occurs in few parts of the world including The Cedars in Northern California, or the on the Semail Ophiolite in Oman.³



Figures 1a & b. Images of travertine crusts forming in The Cedars, California^{1,2}

Figure 2. Location of The Cedars, California²

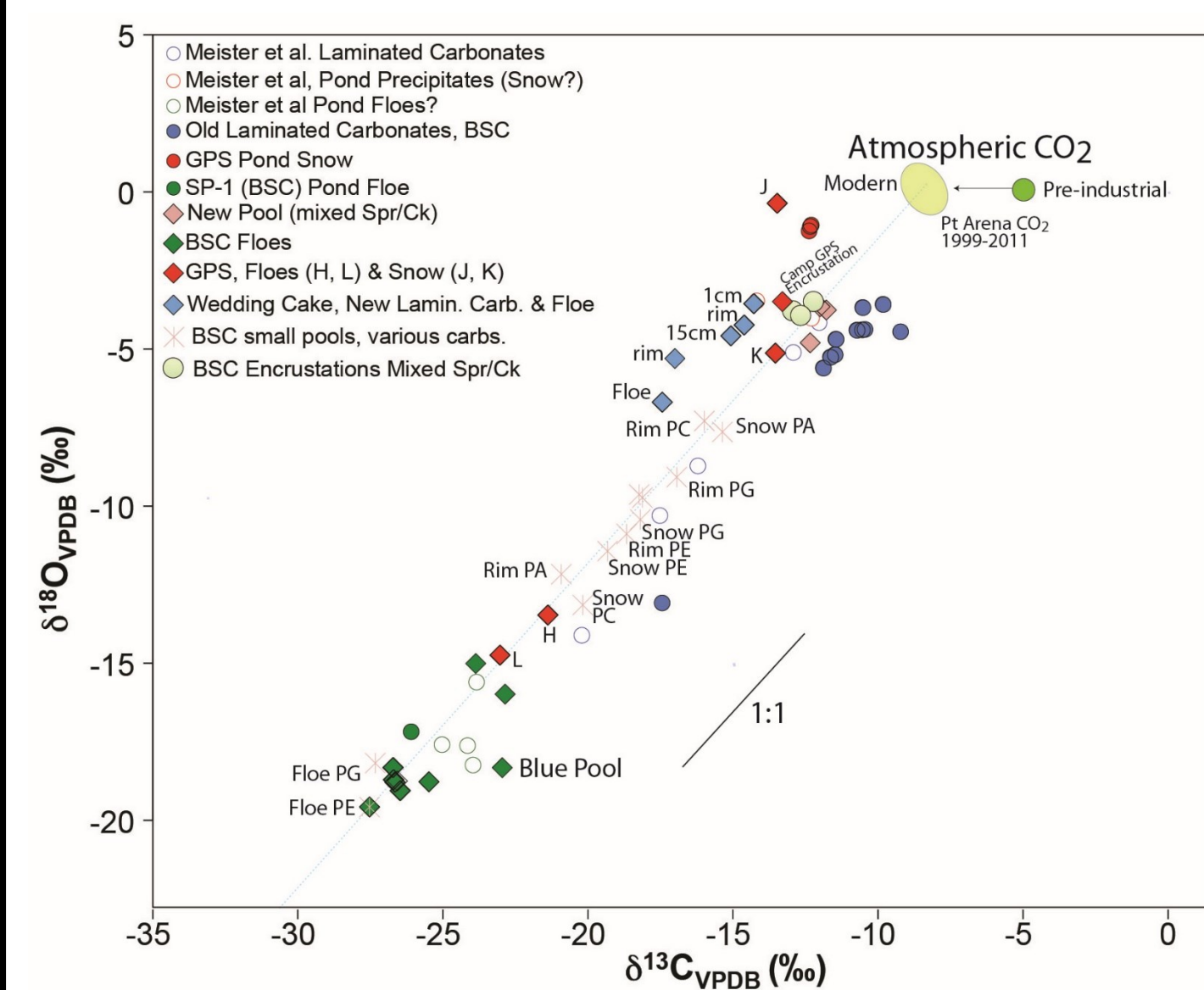


Figure 3. Extreme isotopic variability of different carbonates formed at The Cedars²

- Dataset shows extreme range of fractionation (would expect carbonate data to overlap).
- Carbonate crusts shown in green, bottom left.
- Need to understand what causes such variation.
- Laboratory experiments can be used to control all variables and understand individual impacts.

Research goal:

Analyze carbonates to understand the processes responsible for the extreme variability and 1:1 covariation of oxygen and carbon isotopes.

Methods

In order to understand the disequilibrium (kinetic) effects, we are simulating the high pH environment in controlled conditions to grow calcium carbonate.

Want high pH to favor:
CO₂ + OH⁻ → HCO₃⁻

HCO₃⁻ → CO₃²⁻ + H⁺
Ca²⁺ + CO₃²⁻ → CaCO₃

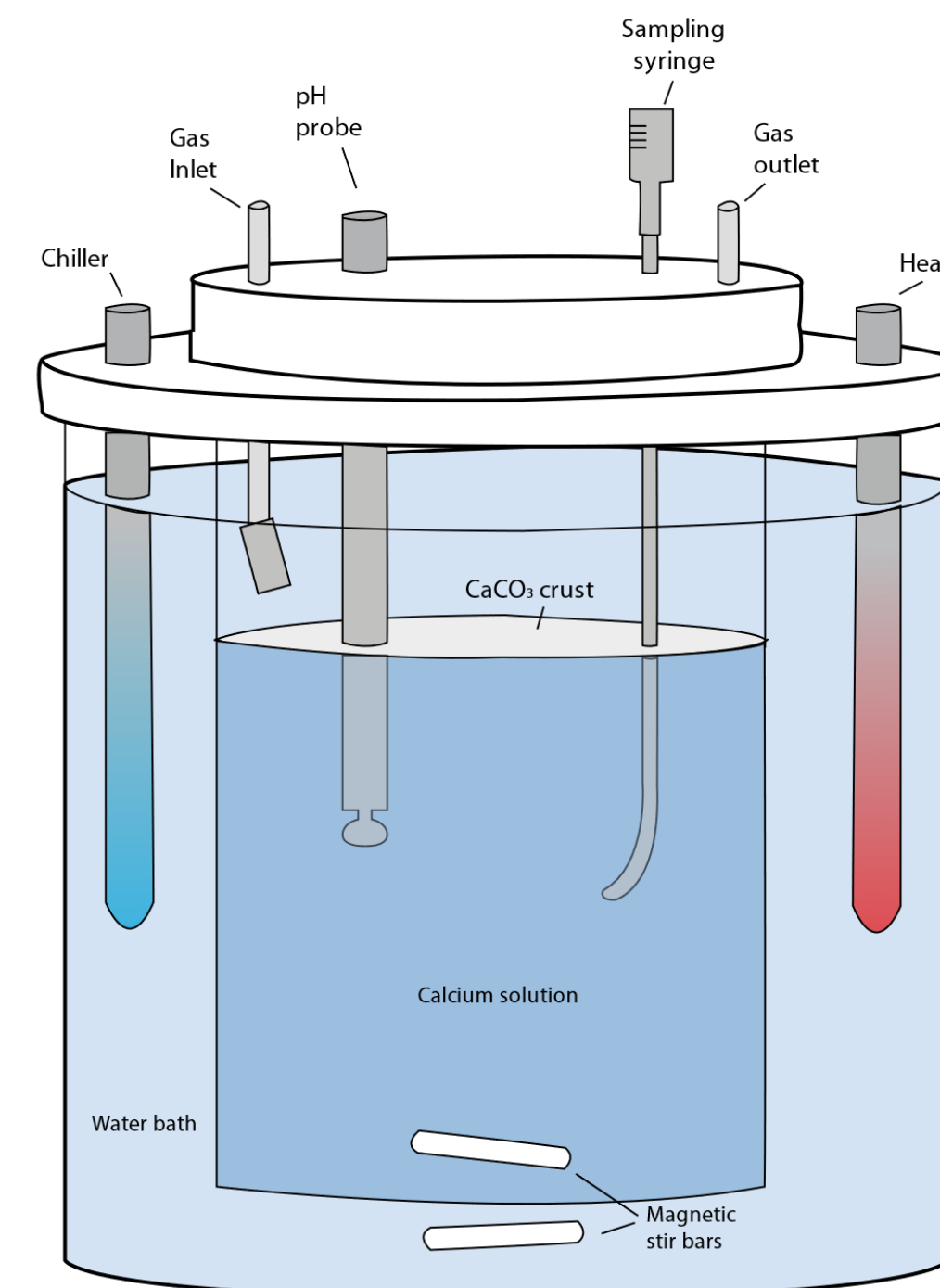


Figure 4. Diagram of the experimental setup

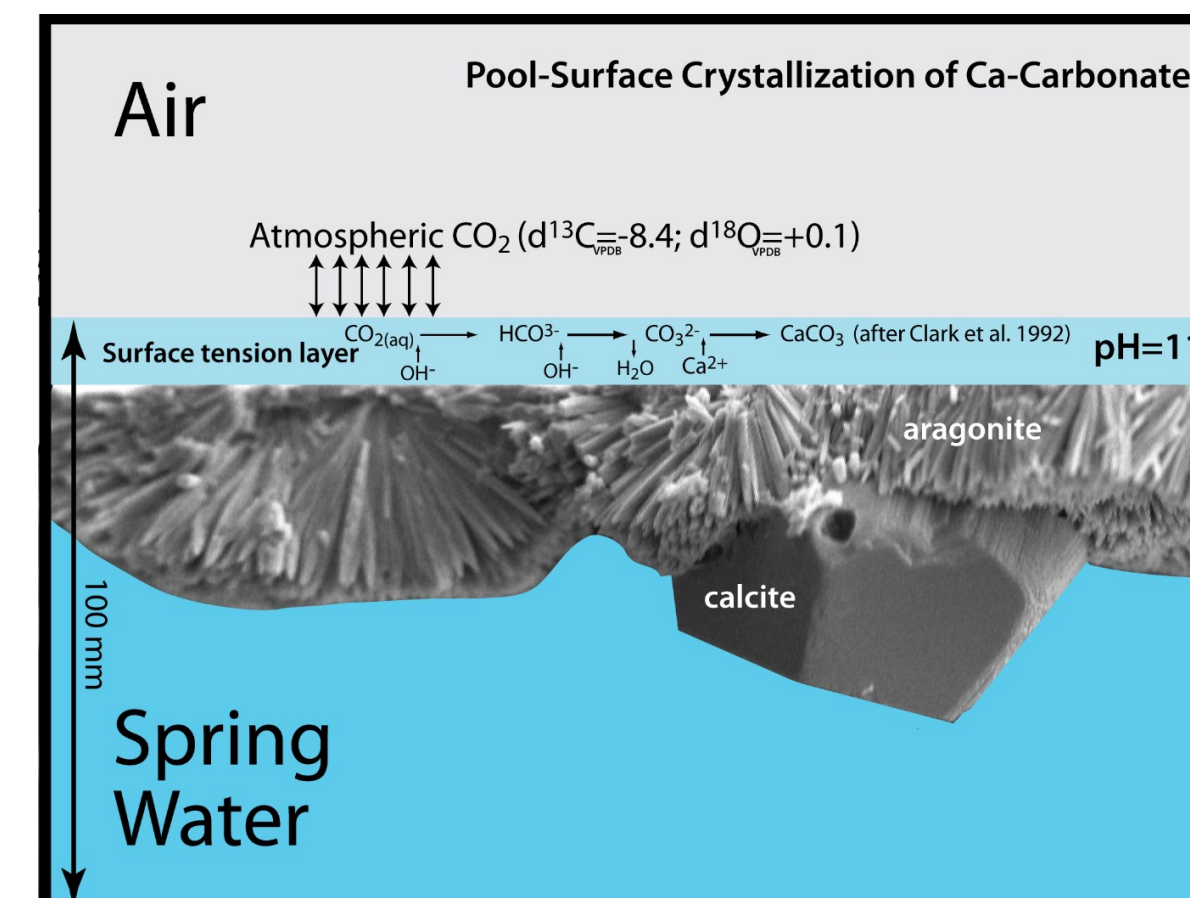


Figure 5. Diagram outlining the relevant reactions and expected carbonate crust formation²

Procedure:

1. In a sealed beaker we flush a CaCl₂ solution with N₂ gas to remove all atmospheric carbon.
2. Once sufficiently flushed (pCO₂ reaches less than ~30ppm), we add NaOH with KCl to reach and maintain a high pH, greater than 11.
3. We then begin administering an N₂-CO₂ gas mixture at a controlled flow rate.
4. Depending on experimental parameters, experiments will run for 2-5 days.

Varied parameters include:

- A. CaCl₂ concentration
- B. Experimental temperature
- C. CO₂ concentration administered
- D. CO₂ flow rate

Analysis:

- Once a calcium carbonate crust has formed, the crystals are filtered, washed with DDI water, dried, and analyzed for the isotopic signatures of the carbon and oxygen.
- Isotopic analyses are also performed on the water and gas from which the minerals formed.
 - Samples from the reaction solution are taken before and after the experiment to be analyzed for calcium concentration.
 - Dissolved Inorganic Carbon and Total Alkalinity can also be analyzed from the experimental solution.
 - Scanning Electron Microscope (SEM) images are taken to understand the mineralogy and morphology of the final product.

Findings and Ongoing Work

In our first experiment, we used a pure CaCl₂ solution and brought it to high pH by adding NaOH. The atmosphere was held constant at 200 ppm CO₂. Over the course of 7 days, we grew a surface veneer of carbonate crystals and the pH dropped from 11.0 and leveled off at around 8.4. The drop in pH is a result of both CO₂ uptake and CaCO₃ precipitation and ultimately results in cessation of the reaction.

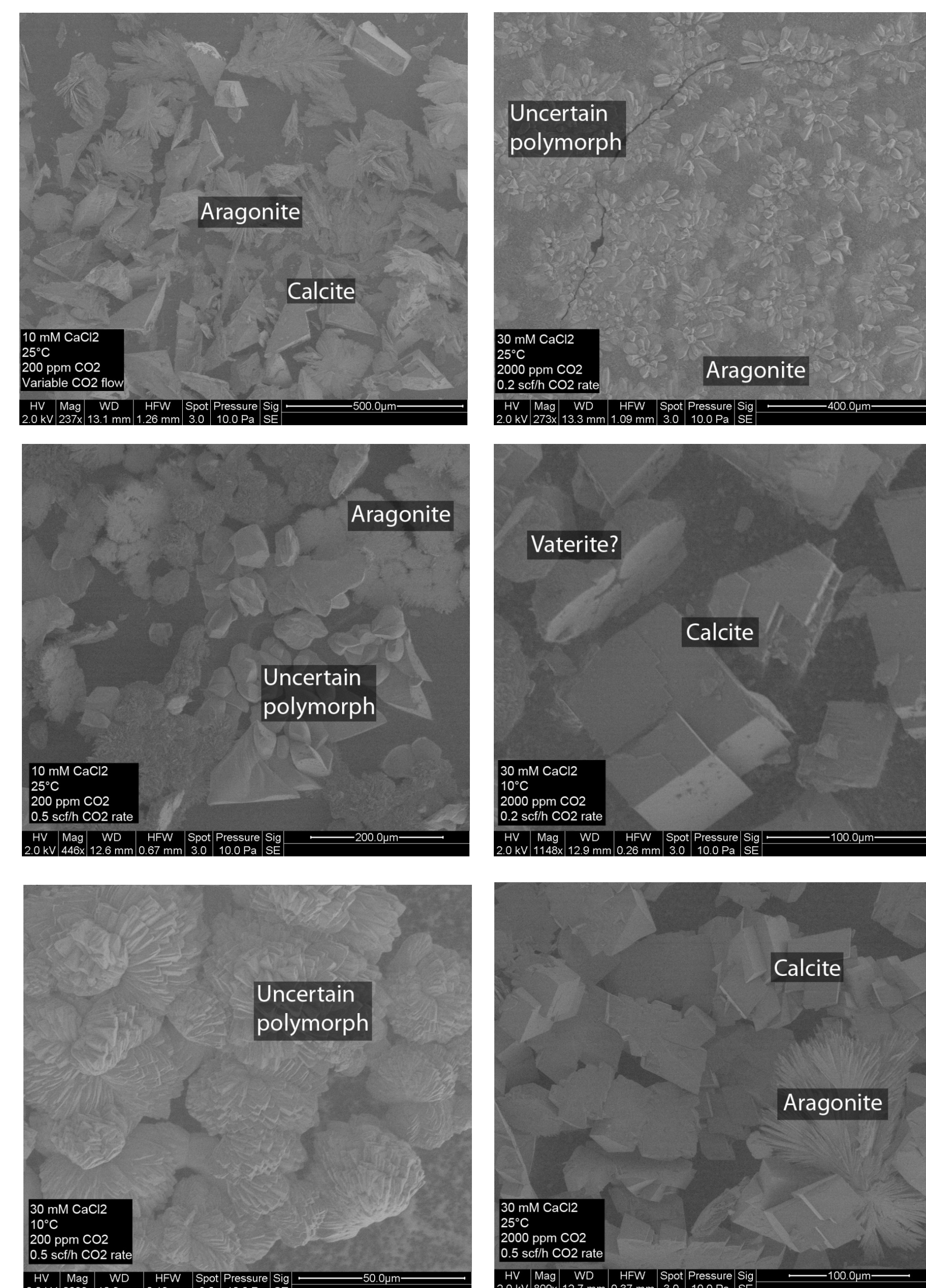
The first experiment yielded results that are comparable to isotopic fractionations found in nature but with the complication that it occurred at variable pH.

In subsequent experiments, we added KCl to help buffer the pH. This worked really well for maintaining constant pH but the pCO₂ of the headspace was lower than the gas tank value because the CaCO₃ was growing too rapidly at high pH. This led to isotopic distillation of the CO₂, which explains the apparent small isotopic fractionations.

We addressed this by increasing the gas flow rate and are awaiting isotopic results.

Ten experiments have been conducted thus far, half of which have been analyzed isotopically. As more data is collected, we will continue to narrow down the parameters that control fractionation.

Results



Figures 6a-f. SEM images of carbonates grown.

Our experiments yield three different polymorphs of CaCO₃: calcite, aragonite, and vaterite.



Figure 7. Image of the carbonate crust of a finished experiment

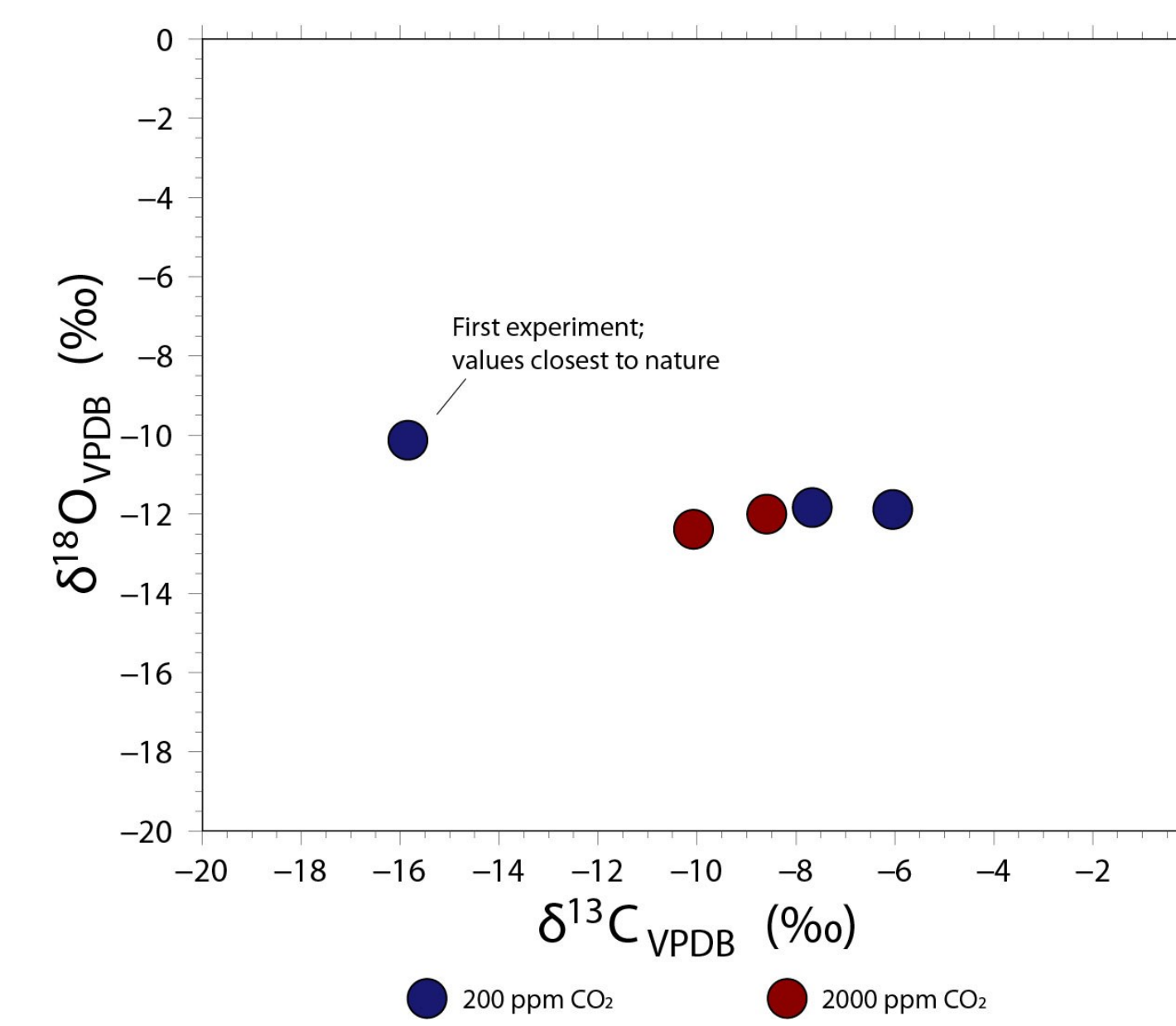


Figure 8. Isotopic fractionation of carbon and oxygen in the first five experiments

At both CO₂ concentrations, the isotopic fractionation is smaller than at The Cedars because of isotopic distillation of the CO₂ in the small headspace.

Carbon Sequestration

Carbon dioxide constitutes ~400 ppm of the atmosphere. Although it is a minor component of the atmosphere, it is a large contributor to the greenhouse effect. Human activities are adding CO₂ to the atmosphere at an unprecedented rate and there are efforts to find ways of removing CO₂ from the atmosphere.⁴

The most permanent form of CO₂ removal and storage is in the form of carbonate minerals. A promising byproduct of this research is to assess the potential for carbonate growth to sequester atmospheric carbon.

In addition to the isotopic experiments, we are conducting open-air experiments to quantify carbonate mineral growth rate and assess whether it can be enhanced by changing solution chemistry and experiment geometry.

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Acknowledgments

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