Video Article

An Experimental Protocol for Studying Mineral Effects on Organic Hydrothermal Transformations

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URL: https://www.jove.com/video/58230
DOI: doi:10.3791/58230

Keywords: Environmental Sciences, Issue 138, Hydrothermal experiments, minerals, organic-mineral interaction, organic geochemistry, silica tube, gas chromatography

Date Published: 8/8/2018

Citation: Yang, Z., Fu, X. An Experimental Protocol for Studying Mineral Effects on Organic Hydrothermal Transformations. *J. Vis. Exp.* (138), e58230, doi:10.3791/58230 (2018).

Abstract

Organic-mineral interactions are widely occurring in hydrothermal environments, such as hot springs, geysers on land, and the hydrothermal vents in the deep ocean. Roles of minerals are critical in many hydrothermal organic geochemical processes. Traditional hydrothermal methodology, which includes using reactors made of gold, titanium, platinum, or stainless-steel, is usually associated with the high cost or undesired metal catalytic effects. Recently, there is a growing tendency for using the cost-effective and inert quartz or fused silica glass tubes in hydrothermal experiments. Here, we provide a protocol for carrying out organic-mineral hydrothermal experiments in silica tubes, and we describe the essential steps in the sample preparation, experimental setup, products separation, and quantitative analysis. We also demonstrate an experiment using a model organic compound, nitrobenzene, to show the effect of an iron-containing mineral, magnetite, on its degradation under a specific hydrothermal condition. This technique can be applied to study complex organic-mineral hydrothermal interactions in a relatively simple laboratory system.

Video Link

The video component of this article can be found at https://www.jove.com/video/58230/

Introduction

Hydrothermal environments (*i.e.*, aqueous media at elevated temperatures and pressures) are ubiquitous on Earth. The hydrothermal chemistry of organic compounds plays an essential role in a wide range of geochemical settings, such as organic sedimentary basins, petroleum reservoirs, and the deep biosphere[1,2,3]. Organic carbon transformations in hydrothermal systems occur not only in pure aqueous medium but also with dissolved or solid inorganic materials, such as Earth-abundant minerals. Minerals have been found to dramatically and selectively influence the hydrothermal reactivity of various organic compounds,[1,4,5] but how to identify the mineral effects in complex hydrothermal systems still remains as a challenge. The goal of this study is to provide a relatively simple experimental protocol for studying mineral effects on hydrothermal organic reactions.

The laboratory studies of hydrothermal reactions traditionally use robust reactors that are made of gold, titanium, or stainless steel[6,7,8,9]. For example, gold bags or capsules have been favorably used, because gold is flexible, and it allows the sample pressure to be controlled by pressurizing water externally, which avoids generating a vapor phase inside the sample. However, these reactors are expensive and could be associated with potential metal catalytic effects[10]. Hence, it is imperative to find an alternative method with low cost but high reliability for these hydrothermal experiments.

In recent years, reaction tubes made of quartz or fused silica glass have been more frequently applied to hydrothermal experiments[11,12,13]. Compared to precious gold or titanium, quartz or silica glass is considerably cheaper but also the strong material. More importantly, quartz tubes have shown little catalytic effects and can be as inert as gold for the hydrothermal reactions[11,14]. In this protocol, we describe a general method for conducting small-scale hydrothermal organic-mineral experiments in thick-walled silica tubes. We present an example experiment using a model compound (*i.e.,* nitrobenzene) in the presence/absence of an iron-oxide mineral (*i.e.,* magnetite) in a 150 °C hydrothermal solution, in order to show the mineral effect, as well as to demonstrate the effectiveness of this method.

Protocol

1. Prepare the Sample for Hydrothermal Experiment

1. Choose the size of the quartz or silica glass tubes, *e.g.,* 2 mm inner diameter (ID) x 6 mm outer diameter (OD) or 6 mm ID x 12 mm OD, and determine the amounts of organic compounds and minerals to use. In this work, the amounts of nitrobenzene and magnetite (Fe_3O_4) to load into the silica tube (*e.g.,* 2 mm ID x 6 mm OD) are 3.0 µL and 13.9 mg, respectively.

NOTE: The large diameter tubes allow easier loading of the materials but require more efforts of tube sealing.
2. Cut the clean silica glass tubing into small pieces with ~30 cm in length using a tube cutter. Seal one end of the tube closed using an oxyhydrogen torch with an appropriate flame head.
CAUTION: Follow the safety procedures for using the oxyhydrogen torch.
3. Weigh the predetermined amount of the starting organic compound on a 0.1 mg-scale balance (if it is solid) and transfer it into the silica glass tube using a weighing paper. If the compound is liquid (*e.g.*, nitrobenzene in this case), use a microliter syringe (*e.g.,* 10 µL) to transfer it into the small silica tube. Add the weighed minerals into the silica tube through a Pasteur pipette, and then add deionized and deoxygenated water (*e.g.*, 0.3 mL). Use 18.2 MΩ·cm deionized water and deoxygenate it by sonication.
4. Connect the silica tube to a vacuum line (~1 cm ID) with a closed valve. Immerse the tube in a Dewar flask filled with liquid nitrogen for ~3 min until the organics and water are completely frozen.
CAUTION: Follow the safety procedures for transferring and using liquid nitrogen.
5. When the tube remains immersed in liquid nitrogen, open the vacuum valve and remove the air from the headspace of the tube.
NOTE: This process should last until the pressure drops below 100 mtorr on the pressure gauge of the vacuum pump.
6. Switch off the valve, remove the tube from the liquid nitrogen, and let the tube warm up to room temperature. Gently tap the bottom of the tube to release the remaining air bubbles from solution to headspace.
7. Repeat the above freeze-pump-thaw cycle for two more times and keep the tube in liquid nitrogen before sealing the other end of the tube. Close the vacuum line and use the oxyhydrogen flame to make the entire tube closed.
NOTE: When the tube undergoes hydrothermal experiments, the headspace volume of the tube will decrease due to liquid water expansion. For example, the density of water reduces about 30% from room temperature to 300 °C. Calculate and leave enough headspace volume when sealing the tube.

2. Set Up the Hydrothermal Experiment

1. After the sealing steps, put the silica tube into a small steel pipe (~30 cm in length and 1.5 cm in diameter) with loose screw caps, in order to prevent damage from any pressure building or tube failure inside the pipe.
2. Place the pipe in a well temperature-controlled furnace or oven and heat it up to the desired temperature (*e.g.,* 150 °C in this work). Use a thermocouple inside the oven to monitor the temperature through the hydrothermal reaction.
3. As soon as the reaction time is reached (*e.g.,* 2 h in this work), quench the silica tube by quickly putting the pipe into an ice water bath.
NOTE: The quenching process takes less than 1 min to cool down to room temperature, which avoids potential retrograde reactions.

3. Analyze the Sample after the Experiment

1. Open the silica tube using a tube cutter, and quickly transfer all the products (*e.g.*, ~0.3 mL in small silica tube) into a 10 mL glass vial using a Pasteur pipette.
2. Extract the organic products with 3 mL dichloromethane (DCM) solution that contains 8.8 mM dodecane as an internal standard for gas chromatography (GC). Cap the vial and shake it by hands for 2 min and vortex it for 1 min.
NOTE: This helps to facilitate the extraction of organic products into the organic phase. Also, rinse the transferring pipet and inside walls of the silica tube with DCM to ensure products recovery. For samples with high mineral contents, sonicate them in the DCM solution for better extraction.
3. Allow the mineral particles to settle down in the extraction solution (*i.e.*, DCM with dodecane) for 5 min. Use a Pasteur pipette to carefully transfer ~1 mL of the sample from the DCM layer (*i.e.,* the bottom layer) into a GC vial.
4. Analyze the organic product distribution using GC with a poly-capillary column (*e.g.,* 5% diphenyl/95% dimethylsiloxane) and a flame ionization detector. Set up the GC oven with a program to start at 50 °C and hold for 8 min, increase at 10 °C/min to 220 °C and hold for 10 min, increase at 20 °C /min to 300 °C and hold for 5 min. Set the injector temperature to 300 °C.
NOTE: The GC program needed to be changed based on the type of organic compounds being analyzed.
5. Build the GC calibration curves by plotting the peak area ratio of the analyte to the internal standard versus the concentration of the analyte.
6. Calculate the reaction conversion based on the concentrations of the starting organic material before and after the reaction, *i.e.*, conversion % = ([initial] – [final]) ⁄ [initial] ×100%. Use the conversions to determine if the mineral facilitates or slows down the hydrothermal organic transformations.

Representative Results

To demonstrate how to use this approach to study hydrothermal organic-mineral interactions, a simple experiment using a model compound, nitrobenzene, was conducted with mineral magnetite (Fe_3O_4) at a hydrothermal condition of 150 °C and 5 bars for 2 h. To show the mineral effect, an experiment of nitrobenzene without mineral was also performed under the same hydrothermal condition. As shown in **Figure 1a**, two silica tubes were made following the protocols prior to the hydrothermal experiment. The sealed tube with no mineral was clear, and the tube with magnetite exhibited a black mineral color inside. The starting concentrations of nitrobenzene were both 0.1 M (in 0.3 mL deionized and deoxygenated water) and the added magnetite was 13.9 mg. After the hydrothermal process, the tube with no mineral showed no color change, whereas the tube with magnetite turned into a brown color (**Figure 1b**), which implies an oxidation reaction from magnetite to hematite (Fe_2O_3). Based on gas chromatography analysis, the effect of magnetite was revealed by the nitrobenzene conversions between the experiments (**Figure 2**). In the no-mineral experiment, the calculated conversion for nitrobenzene was 5.2%; however, in the presence of magnetite, the nitrobenzene conversion was 30.3%, which increased by a factor of 6. Additionally, duplicate but independent experiments were conducted, in which one standard deviation was calculated to be 2.1% and 1.4% for the no-mineral and magnetite experiments, respectively (**Figure 2**). These results suggest that magnetite, probably through redox reactions, can significantly promote the reaction of nitrobenzene at given hydrothermal conditions. This protocol was found to be successful with relatively high reproducibility in quantifying hydrothermal organic degradation under the influence of minerals.

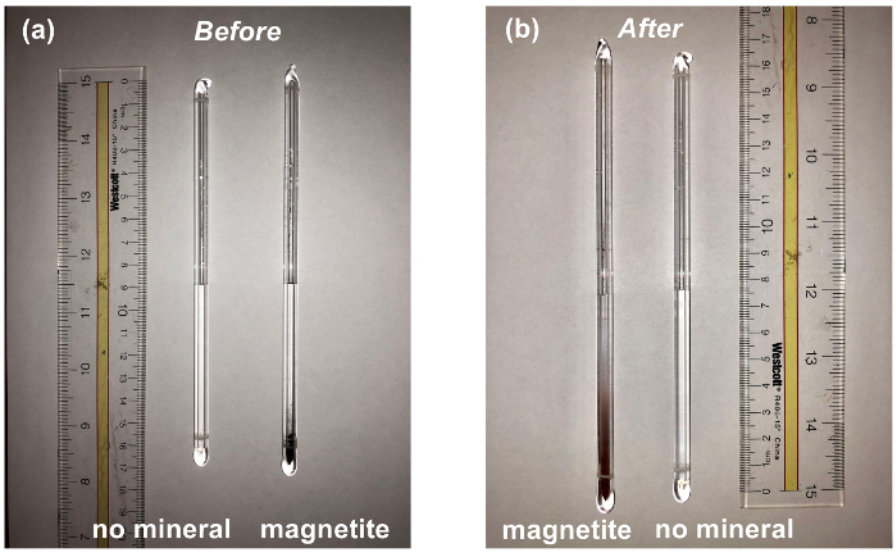

Figure 1: Example experiment with nitrobenzene in the presence or absence of magnetite. (**a**) Silica glass tubes before the hydrothermal experiment; (**b**) silica glass tubes after the hydrothermal experiment. Note that there is a color change in the silica tube with magnetite. Please click here to view a larger version of this figure.

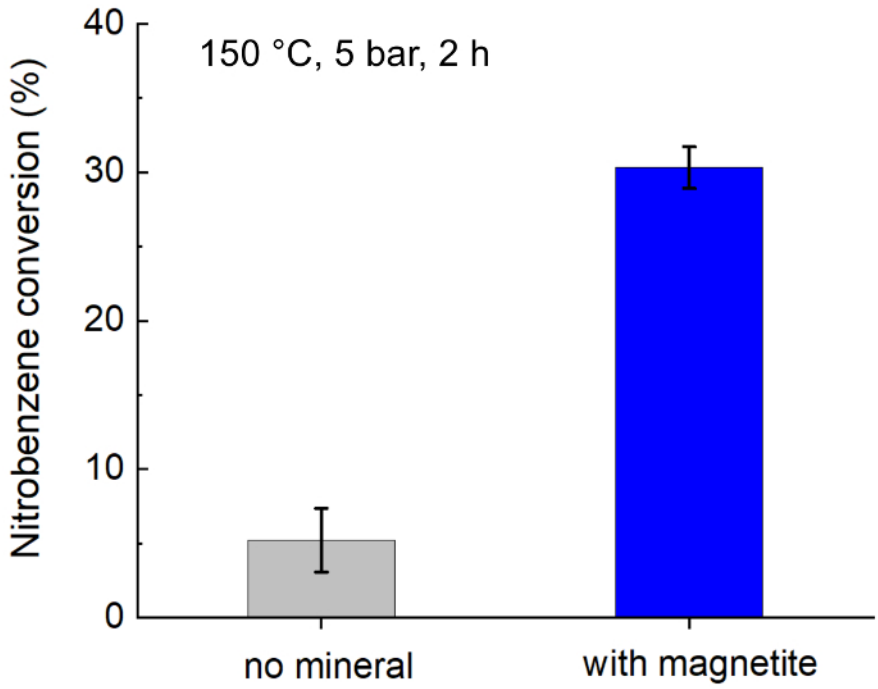

Figure 2: Experimental results of nitrobenzene conversion after 2 h under hydrothermal conditions at 150 °C and 5 bar. The reaction conversions are calculated by the amount of nitrobenzene reacted after the reaction. Error bars are one standard deviation of the mean of duplicate experiments. The difference between the no-mineral and magnetite experiments clearly shows the mineral effect on hydrothermal degradation of nitrobenzene. Please click here to view a larger version of this figure.

Discussion

In this study, we used nitrobenzene with mineral magnetite as an example to demonstrate how to evaluate mineral effects on hydrothermal organic reactions. Although the experiments are carried out in small silica glass tubes, highly reproducible results are observed in the magnetite experiments, *i.e.*, 30.3 ± 1.4% in nitrobenzene conversion, which suggests the effectiveness and the reliability of this hydrothermal protocol. In the no-mineral experiments, the conversion of nitrobenzene is 5.2 ± 2.1%, which shows a lower reproducibility than the mineral experiment. The relatively high uncertainty in the no-mineral experiment could be due to the low conversion of the starting material, considering the µL (or mg) of samples used in the small tube. To improve reproducibility for low-conversion reactions, silica tubes with larger internal volume are suggested.

This protocol could be particularly useful for small-scale experiments when the amount of sample is limited, or the cost of chemical is high. Both mineral and non-mineral hydrothermal experiments can be conducted by this protocol.

As described earlier, this hydrothermal protocol has certain advantages over other traditional methods, such as low cost of reaction tubes, facile operation procedures, and low or negligible catalytic effect[11,14]. However, due to the limited mineral strength and stability, quartz tubes may cause failure at temperatures above 450 °C or pressures above 400 bar[15], which may not be suitable for long-duration hydrothermal experiments near or above the critical point of water. Another limitation of this method is that, at high temperature (*e.g.,* > 400 °C), quartz may also be subject to dissolution, which could produce dissolved silica species that interfere organic hydrothermal reactions. Since the dissolution of silica may also be influenced by the solution pH, the presence of salts, acids or bases, the tube survival temperature could be lower than that in the pure water system, and these factors should also be considered in high-temperature experiments. In addition, compared to flexible reactor materials such as gold, silica tubes are usually associated with a headspace volume that cannot be reduced by applying external pressure, which could allow some gas-phase reactions to occur.

Furthermore, the volume of liquid inside the silica tube could be critical in determining the success of the experiment. Based on the thermodynamics calculation using SUPCRT92[16], for example, the saturation pressure of water (P_{sat}) can reach more than 85 bar at 300 °C, and the volume of liquid water inside the silica tube can expand by 30%. To survive at high temperatures and pressures, thicker silica glass tubes (*i.e.,* ID/OD ratio <0.3) with larger headspace should be used. Even with the same diameter, silica tubes from different manufacturers may cause failure at different temperatures. Therefore, the temperature and pressure restrain for each type of the silica tubes should be thoroughly tested before use. Note that borosilicate glass is excluded from this hydrothermal protocol because it is reactive and typically cannot handle temperatures above 300 °C. In addition, loading the organic compounds that are "sticky" or viscous into narrow silica tubes may be challenging, in which case large diameter tubes (*e.g.,* 6 mm ID x 12 mm OD) would be recommended.

Disclosures

The authors have nothing to disclose.

Acknowledgements

We thank the H.O.G. group at Arizona State University for developing the initial methodology of these hydrothermal experiments, and in particular, we thank I. Gould, E. Shock, L. Williams, C. Glein, H. Hartnett, K. Fecteau, K. Robinson, and C. Bockisch, for their guidance and helpful assistance. Z. Yang and X. Fu were funded by startup funds from Oakland University to Z. Yang.

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