

Technical Report – SCEC award 20172 - Coseismic Chemistry: Developing kinetics of various chemical reactions over earthquake timescales

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Abstract

The mechanical strength and behavior of faults is in part controlled by chemical reactions. However, the chemistry of fault zones during earthquakes is not well understood because many of the important reactions have generally been studied at equilibrium conditions, whereas pressures and temperatures change dramatically over very short times (seconds) during earthquakes. Thus we need to understand the rates of chemical reactions at high temperatures and short timescales in order to calibrate paleoseismic indicators and explore mechanical feedbacks between frictional strength and temperature. We perform short duration experiments with accurate and repeatable temperatures to determine reaction kinetics relevant to earthquake heating. Ultimately, these kinetic parameters will be used to model and understand how the time-varying temperatures during earthquake heating produce the measured chemical signatures in exhumed or drilled faults. Specifically for this project, we focused on the kinetics of biomarker thermal maturity and carbonate dissociation.

Technical Report

Delays due to COVID

Our project was significantly impacted by COVID-19. The shutdown of our university in March 2020 made it impossible to conduct laboratory work for months. Furthermore, as we had just moved to UCSC the summer before, the renovation of our new labs was halted as well. In addition, the switch to online teaching and childcare responsibilities with distance learning significantly impacted the time we could commit to this project. We made progress on the project in the form of literature searches and improving modeling capabilities. We received an extension on the grant into this next year. As the university is now open, we anticipate the work being completed over summer 2021.

Project Goals

The goal of this project is to develop new high-temperature heating experiments of short duration to understand the kinetics of reactions relevant to fault zones during earthquakes. We describe a new rapid heating apparatus that we have constructed to quickly achieve high temperatures and then rapidly quench reactions after very short heating intervals. The experiments described here will be the first we have run with this apparatus. We are not attempting to simulate the temperature history a fault would experience during an earthquake, but rather simulate an accurate and repeatable boxcar function of temperature with rapid rise to run conditions and then a rapid fall to stop the reactions. In this way, we can measure reaction extents over a range of times and temperatures to establish kinetic parameters directly applicable to coseismic conditions. Such information will allow us to couple this reaction to more complicated heating histories as we would expect in fault zones during earthquakes. In order to link these experiments to previous, longer-duration heating experiments, we will start our work with the kinetics of biomarker alteration at earthquake timescales. In this way, we can overlap experimental

conditions to establish the continuity of results from our previous studies (Rabinowitz et al., 2017; Savage and Polissar, 2019; Sheppard et al., 2015). In addition, we will run experiments on carbonate dissociation to explore the kinetics of new systems that have shown to be promising seismic indicators in high velocity friction experiments (De Paola et al., 2011). We anticipate that the data collected during this grant will (i) provide a publishable dataset of kinetic parameters for these reactions, (ii) be immediately applicable to a number published and ongoing studies of fault zones, and (iii) be used as preliminary data in a larger NSF proposal to explore the chemistry of several important reactions in fault zones.

Background

Biomarker thermal maturity

Almost all sedimentary rocks contain some amount of organic material from organic remains such as plants, algae and bacteria. As the rocks are buried and lithified, the organic material can be thermally altered due to burial heating over long time periods (Peters et al., 2004). Thermal alteration can result in the destruction of organic molecules or their less thermally stable isomers, the transformation from less thermally stable to more thermally stable isomers, or creation of new molecules or isomers. Organic thermal maturity can also change over short time periods at high temperatures, such as during earthquakes, lightning strikes, forest fires (Daly et al., 1993; Sakaguchi et al., 2011; Simoneit, 2002), and in fault zones (Savage et al., 2014). Our biomarker methods are motivated from studies of molecular thermal maturity in petroleum systems and are complementary to the vitrinite maturity parameter. Organic thermal maturity does not experience retrograde reaction (Peters et al., 2004), therefore the integrated heating signal of a sample will be preserved. Due to the non-linear increase of the reaction rates with temperature, the organic thermal maturity in a fault zone likely represents the hottest earthquake (which does not necessarily need to be the largest magnitude earthquake, but likely will be) that the fault has experienced (Coffey et al., 2019), although smaller earthquakes can contribute slightly to the signal.

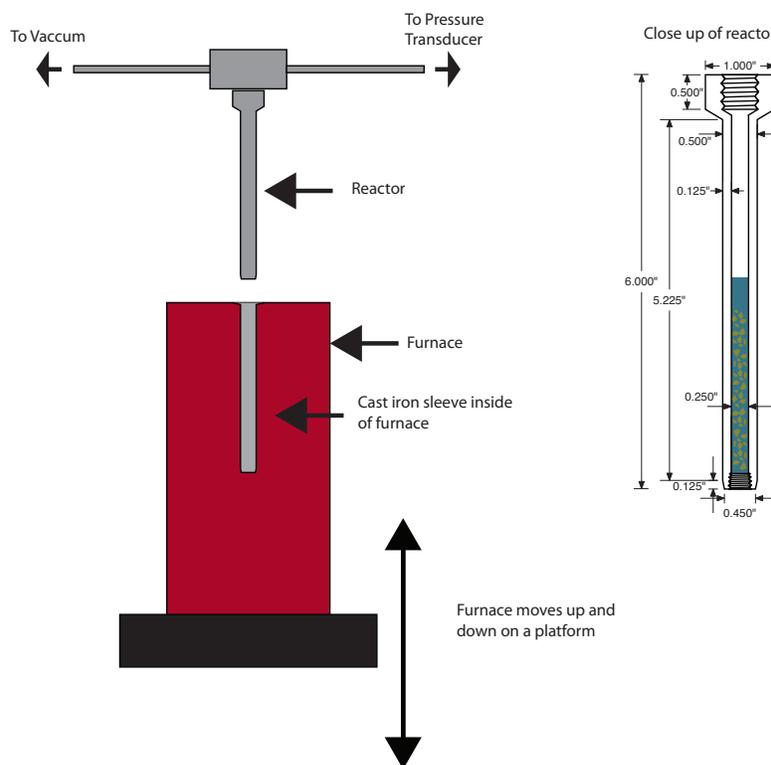
Much of our work to date has been focused on the change in biomarker thermal maturity during earthquakes (Coffey et al., 2019; Polissar et al., 2011; Savage and Polissar, 2019; Savage et al., 2014). We have established that localized slip zones often show an increase in thermal maturity compared to thicker gouge zones, and that this signal is not continuous along the fault, suggesting that temperature rise (and associated weakening) is discontinuous. Furthermore, we have already established the kinetics of several biomarkers at short timescales (60-360 °C, 15 min to days). Some of the biomarkers systems we studied had no established kinetics (e.g. alkenone destruction, *n*-alkane reaction) and others were correlated to more established techniques like vitrinite reflectance (methylphenanthrenes). In the case of methylphenanthrenes, we established that the shorter duration kinetics were faster than those predicted from correlation with vitrinite reflectance. However, due to limitations of our first heating system, we could not achieve high temperatures at timescales shorter than ~15 minutes.

Carbonate Dissociation

Calcium carbonate (CaCO_3) dissociates to calcium oxide (CaO) and carbon dioxide (CO_2) when heated. Previous experiments to determine the temperature at which carbonates begin dissociating were performed at a range of temperatures for 30 minutes at each temperature step

(Rodriguez-Navarro et al., 2009). At 600 °C, some reaction is seen, and by 850 °C the carbonate has completely dissociated to product. These are the values that are generally used to infer earthquake temperature from carbonate dissociation in fault zones (Colletini et al., 2013; Rowe et al., 2012). However, earthquakes occur over much shorter timescales and these temperatures most likely represent a lower bound for heating events of a few seconds. In addition, we expect that there will be large changes in frictional strength associated with this reaction. High velocity friction experiments have invoked that the pressure generated from the CO₂ gas creates low effective friction (Han et al., 2007). The by-product of the reaction will inevitably have different properties as well. CaO, also known as quick lime, rapidly reacts with water (including atmospheric water vapor) to form Ca(OH)₂, or portlandite. Although most earthquakes probably occur in the presence of water, experiments that include the reaction to portlandite are outside the scope of the current proposal.

An additional exploratory aspect of this project will be analysis of carbon and oxygen isotopic fractionation during partial dissociation of carbonates. A detectable isotope effect would provide a means to identify carbonate dissociation in fault zones long after the heating event occurred. Dissociation of carbonates is controlled by both diffusion of CO₂, and reaction kinetics of carbon-oxygen bond dissociation in the carbonate ion (Rodriguez-Navarro et al., 2009). Both processes are known to have mass-dependent isotope effects, and isotopic fractionation in carbonates has been shown to occur experimentally in high-velocity friction experiments (De Paola et al., 2011). While additional factors such as recrystallization, dissolution, and precipitation may be important in the preservation and detection of such a signal in fault zones, these analyses would be a first step towards developing such measurements as a new technique.



New Rapid Heating Apparatus

We have developed a new heating apparatus that can reach operating temperatures of 850°C within 10 seconds (Figure 1). The concept of the design is simple: the reactor is small and thin walled to lower the thermal mass and increase the heating rate. However, the addition of water, such as in the biomarker experiments, requires that the reactor should also be able to safely contain the high pressures produced by water expansion and steam. We have designed

Figure 1. Schematic of rapid heating apparatus.

a vessel out of cast iron with wall thickness of 0.125 inches and internal radius of 0.25 inches. The reactor is plumbed to a vacuum line and a pressure transducer that allows removal of air, addition of helium or other gases, and monitoring of pressure during the experiment. The reactor is heated by an external furnace, but in order to avoid waiting for the furnace to heat up during the experiment, the furnace is pre-heated to the desired temperature. The experiment is started by raising the furnace on a small platform to surround the reactor. In order for the reactor to be thermally well-coupled to the furnace, there is a cast iron sleeve inside the furnace that will be in close contact with the reactor when the furnace is raised. To cool and end the experiment, the furnace is lowered and cold cast iron metal blocks are placed on the reactor until the temperature decreases back to room temperature. All of the mechanical aspects of the system (movement of furnace and cooling blocks) are computer controlled to minimize risk in dealing with extremely hot materials.

Work Plan

Due to delays from COVID-19, this work plan is ongoing.

1) Establish Experimental Techniques

Because these will be the first set of experiments run on the new rapid heating apparatus, there will inevitably be some time spent creating best practices. For instance, in our initial runs, we have found that the quickest way to reach peak temperature is to set the furnace above the desired target temperature and then immediately ramp down the furnace temperature when the experiment starts to avoid overshoot. Rather than trial and error, we will calculate exactly what the overshoot temperature should be set to in order to achieve the fastest ramp up to the target temperature.

2) Experiments on Biomarkers up to 850 °C

To expand on our current biomarker kinetics, we will run ten experiments from 10 seconds to 15 minutes and 350 to 800 °C. The biomarker system we will explore is methylphenanthrenes, which have been documented in various fault zones including the San Andreas and Punchbowl faults. We will run experiments on Woodford shale, a well-characterized, organic-rich shale for which we have previously established kinetics (Sheppard et al., 2015) and shown that these kinetics apply to other rock types such as at the Punchbowl Fault (Savage and Polissar, 2019). In addition to the short timescales, these will be the first experiments to determine kinetic parameters for methylphenanthrene alteration above the critical point of water (374 °C), where the different solvation and other properties of supercritical water could be important.

We will conduct and analyze the heating experiments using techniques we have developed for rapid hydrous pyrolysis of sediments (Sheppard et al., 2015; Rabinowitz et al.; Savage and Polissar, 2019). Shale samples are sieved to a uniform grain size and loaded into the reactor along with a measured portion of de-ionized water. Air is removed and the headspace charged with helium. After the experiment the reaction products are recovered and biomarkers extracted using organic solvents. We will quantify methylphenanthrenes and other compounds by gas-chromatography mass spectrometry in the new Organic

Geochemistry Lab at UCSC. Kinetic analysis will be done following the methods outlined in Savage and Polissar (2019).

3) *Experiments on Calcium Carbonate up to 850° C*

We will conduct ten preliminary experiments to capture the kinetics of carbonate dissociation. Using Icelandic spar (Rodriguez-Navarro et al., 2009), we will grind the rock and sieve to specific grain sizes. Because this reaction involves gas diffusing from grains, we will start with a single grainsize but ultimately explore a range of grain sizes. To start, we will run the experiments dry to isolate the degassing reaction from further reactions involving the creation of portlandite. Samples will be weighed before the experiments and the recovered products will be stored under dry N₂ (to prevent reaction of CaO with atmospheric water vapor) and weighed. Fraction decomposed will be calculated from the mass loss and kinetic analysis will use a first-order form as has been shown to apply to this reaction (Rodriguez-Navarro et al., 2009). We have also budgeted for analysis of the stable carbon and oxygen isotopic composition of the reaction products (and starting materials) to investigate whether there is an isotopic effect during dissociation which may leave a detectable signature in fault zones. These exploratory measurements may lead to a new method for detecting the activation of this process in fault zones (c.f. De Paola et al., 2011). After weighing the samples will be stored under dry N₂ gas until the isotopic measurements are made in the UCSC Stable Isotope Lab.

Intellectual Merit

Localized temperatures generated from frictional heating during earthquakes disrupts the chemical equilibrium in the fault zone. Such disequilibrium can leave chemical signatures of earthquakes in the rock record that help us map fundamental aspects rupture mechanics such as slip localization and propagation. Furthermore, accurate estimates of earthquake temperatures allow us to explore chemo-mechanical feedbacks that impact processes such as dynamic weakening and post-seismic restrengthening.

Broader Impacts

This grant has supported UCSC grad student Julia Krogh. Studies of fault zone temperature rise during earthquakes has led to better understanding of what controls earthquake propagation and arrest.

Publications

None at this time.

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