



Organic thermal maturity as a proxy for frictional fault heating: Experimental constraints on methylphenanthrene kinetics at earthquake timescales

Rachel E. Sheppard^a, Pratigya J. Polissar^{b,*}, Heather M. Savage^b

^a Department of Earth and Environmental Science, Columbia University, United States

^b Lamont–Doherty Earth Observatory of Columbia University, 61 Route 9W, Palisades, NY 10964, United States

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Abstract

Biomarker thermal maturity is widely used to study burial heating of sediments over millions of years. Heating over short timescales such as during earthquakes should also result in measurable increases in biomarker thermal maturity. However, the sensitivity of biomarker thermal maturity reactions to short, higher-temperature heating has not been established. We report on hydrous pyrolysis experiments that determine the kinetic parameters of methylphenanthrene maturation at timescales and temperatures relevant to earthquake heating. Samples of Woodford Shale were heated at temperatures up to 343 °C over 15–150 min. The thermal maturity of the samples as measured by the methylphenanthrene index-1 (MPI-1) increased with heating time and temperature. We find that MPI-1 increases with time and temperature consistent with a first-order kinetic model and Arrhenius temperature relationship. Over the timescales tested here, MPI-1 is strongly affected by maximum temperature and less sensitive to heating duration. Production of new phenanthrene isomers and expulsion of a liquid pyrolyzate also occurred. Differential expulsion of methylphenanthrene isomers affected the apparent maturity of the rock at lower temperatures and may need to be considered for organic-rich fault rocks. Our results demonstrate that the overall MPI-1 reaction extent in both the rock and pyrolyzate are a useful measure of thermal maturity and reflect temperature history during rapid heating.

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1. INTRODUCTION

The kinetics of organic thermal maturity reactions are a function of both time and temperature and occur over a wide range of conditions during earth processes. However, most studies of organic thermal maturity kinetics have focused on longer timescales applicable to burial heating of organic matter and generation of petroleum. There is increasing interest in using organic thermal maturity to study heating processes at much shorter timescales such

as occurs during earthquakes, lightning strikes, bolide impacts, dike intrusions, and drill bit metamorphism (Raymond and Murchison, 1992; Daly et al., 1993; Simoneit et al., 1994; Farrimond et al., 1999; O'Hara, 2004; O'Hara et al., 2006; Bowden et al., 2008; Schimmelmann et al., 2009; Wenger et al., 2009; Parnell et al., 2010; Polissar et al., 2011; Sakaguchi et al., 2011; Fulton and Harris, 2012; Kitamura et al., 2012; Savage et al., 2014). Extrapolation of kinetics determined for slow, burial-heating rates to the short timescales of these processes is highly uncertain.

Here we determine the kinetics of thermal maturation of methylphenanthrene compounds at timescales and temperatures important for shear heating during earthquakes.

* Corresponding author. Tel.: +1 845 365 8400.
E-mail address: polissar@ldeo.columbia.edu (P.J. Polissar).

The frictional work (the product of shear stress and fault slip) done during an earthquake is dissipated as heat, in some cases leading to temperature rise great enough to melt the fault materials (>1000 °C). However, frictional melt is not often detected along faults (Kirkpatrick et al., 2009; Kirkpatrick and Rowe, 2013), potentially due to extreme fault weakening during sliding brought on by various micromechanical processes (Di Toro et al., 2011). Because of a lack of other paleothermometers for faults zones, it is difficult to estimate temperature rise when frictional melt is absent.

Thermal maturity of organic molecules offers a possible alternative to determine temperature rise, and subsequently estimate shear strength and fault slip during an earthquake. Earthquake heating along a fault occurs during the earthquake event, ~1 to 10 s depending on the size of the event and slip velocity. However, heat dissipation occurs over longer timescales, and reaction of chemical compounds should continue as heat dissipates over minutes to hours. These timescales are much shorter than prior experiments on organic thermal maturity reactions. Here we focus on methylphenanthrenes because they appear to be common compounds in geologic faults hosted within sedimentary rocks at burial depths of 1–5 km (Polissar et al., 2011). To our knowledge, these are the first experiments on these compounds in this time/temperature range. We compare our results to previous estimations of methylphenanthrene maturation based on correlations during slow, burial heating of vitrinite. Finally, we discuss potential applications for the results to determine temperature rise on faults during earthquakes.

2. BACKGROUND

Heating of sediments systematically alters the chemical composition of organic material contained within the rock as thermally unstable compounds break down relative to more stable compounds, and rearrangements of molecules to more stable structures occur. This process of thermal maturation favors generation and preservation of molecules with low H/C ratios, as the ultimate fate of heated organic matter is transformation to graphite and other highly stable, hydrogen-poor structures. Polycyclic aromatic hydrocarbons (PAHs) are an important class of petroleum molecules used to assess thermal maturity. These hydrogen-poor molecules contain conjugated aromatic rings that are the building blocks of graphite and are stable at high temperature.

2.1. Methylphenanthrenes

Methylphenanthrenes are methylated polycyclic aromatic hydrocarbons whose pattern of methylation changes with thermal maturity. Methylation at the 9 and 1 (α) positions increases steric strain in the molecule, causing those isomers to be less stable compared to the 3 and 2 (β) positions (Fig. 1). Consequently, the α isomers 9- and 1-methylphenanthrene (9-MP and 1-MP) are less stable, breaking down at high temperatures, while the β isomers 3- and 2-methylphenanthrene (3-MP and 2-MP) are more

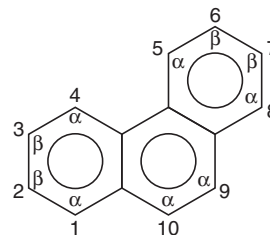


Fig. 1. Molecule structure of phenanthrene and numbering of α (less stable) and β (more stable) methyl positions.

stable at high temperatures (Radke et al., 1982a; Szczerba and Rospondek, 2010). This varied stability at high temperatures forms the basis of the methylphenanthrene index MPI-1, the ratio of stable β -methylphenanthrenes to unstable α -methylphenanthrenes used as a measure of thermal maturity.

Phenanthrene and methylphenanthrenes are created during thermal maturation of organic matter. They are not synthesized by any known organism, but rather formed by alteration of precursor molecules during heating. Methylphenanthrenes have been found in samples of very low thermal maturity (0.4% vitrinite reflectance), suggesting they can be formed early in the maturation process (Szczerba and Rospondek, 2010). Once formed, alteration, destruction and expulsion of phenanthrenes can occur. Alteration includes interconversion of different methylphenanthrenes via isomerization (Szczerba and Rospondek, 2010). Alteration can also occur via transmethylation between phenanthrene and a methyl donor, affecting the relative abundances of phenanthrene and methylphenanthrenes during heating (Szczerba and Rospondek, 2010). Destruction occurs when the triaromatic ring nucleus that defines phenanthrenes is altered through addition or cracking reactions. Expulsion describes the migration of liquid hydrocarbons out of the primary source rock into surrounding sediments. Expulsion can alter both the overall concentration of molecules in the source rock and the relative distribution of molecules by differential expulsion. Migration of fluids through a rock can also leave traces of methylphenanthrenes and other small molecules. The distribution of phenanthrene molecules in a sample therefore reflects the prior heating history of the sample through the creation, alteration, destruction and expulsion of these molecules plus any fluids that may have migrated through the rock.

Previously, the maturation of methylphenanthrenes has only been evaluated at longer timescales (Radke et al., 1982a, 1982b, 2000; Radke, 1988; Armstroff et al., 2006) and the kinetic parameters describing methylphenanthrene maturation have not been determined. Existing estimates for methylphenanthrene maturation rates therefore rely upon an empirical relationship between methylphenanthrene maturity and vitrinite reflectance. The kinetics of vitrinite reflectance are reasonably constrained across laboratory and geologic heating rates (Burnham and Sweeney, 1989; Sweeney and Burnham, 1990). Therefore, vitrinite reflectance can be calculated for most possible

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