




# Investigating the Kinetics of Montmorillonite Clay-Catalyzed Conversion of Anthracene to 9,10-Anthraquinone in the Context of Prebiotic Chemistry

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## Abstract

Carbonaceous meteorites contributed polycyclic aromatic hydrocarbons (PAHs) to the organic inventory of the primordial Earth where they may have reacted on catalytic clay mineral surfaces to produce quinones capable of functioning as redox species in emergent biomolecular systems. To address the feasibility of this hypothesis, we assessed the kinetics of anthracene (**1**) conversion to 9,10-anthraquinone (**2**) in the presence of montmorillonite clay (MONT) over the temperature range 25 to 250 °C. Apparent rates of conversion were concentration independent and displayed a sigmoidal relationship with temperature, and conversion efficiencies ranged from 0.027 to 0.066%. Conversion was not detectable in the absence of MONT or a sufficiently high oxidation potential (in this case, molecular oxygen (O<sub>2</sub>)). These results suggest a scenario in which meteoritic **1** and MONT interactions could yield biologically important quinones in prebiotic planetary environments.

**Keywords** PAH · Anthracene · 9,10-Anthraquinone · Montmorillonite · Kinetics · Prebiotic

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## Introduction

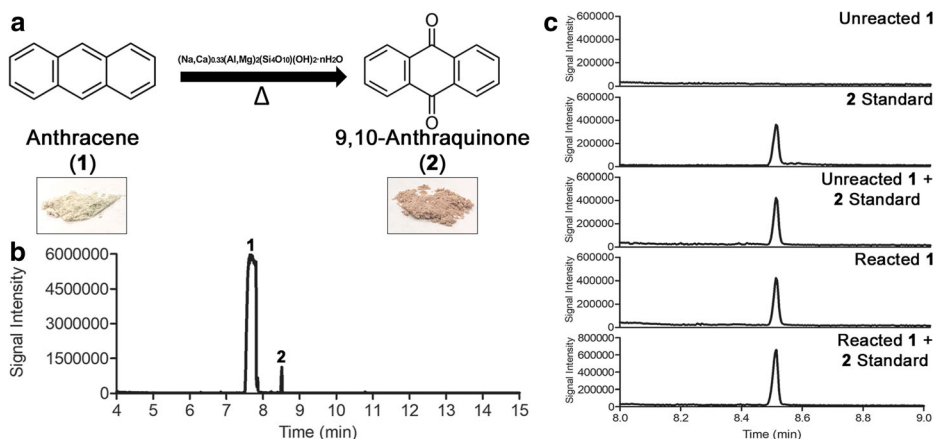
Carbonaceous meteorites are presumed to have contributed significant polycyclic aromatic hydrocarbons (PAHs) to the organic inventory of the primordial Earth and other planetary environments (Ehrenfreund et al. 2006; Gilmour and Pillinger 1994; Sephton 2002; Wing and Bada 1991). These compounds are ubiquitous in the solar system and are thought to have been precursors for the prebiotic synthesis of biomolecules. Owing to their unique planar structure, resonance, and UV absorption capacity, PAHs have been proposed as core constituents of the potentially biologically important tholins detected in the atmosphere of Saturn's moon Titan (Sagan and Khare 1979; Stevenson et al. 2015), scaffolding for prebiotic nucleic acids (Ehrenfreund et al. 2006, e.g. the PAH World), and precursors for prebiotic quinones (Bernstein et al. 1999) crucial for modern-day cellular bioenergetics. Because of their versatile redox properties, the latter have also been suggested as possible primitive stabilizing agents and photochemical pigments within the earliest membrane systems (Deamer 1992; Deamer 1997; Groen et al. 2012). Within meteorite parent bodies during transport, and upon impact with planetary surfaces, PAHs interact with a multitude of phyllosilicate mineral phases (e.g. smectites, and commonly referred to as clays) to produce reactive oxidized products (Watson and Sephton 2015). These phyllosilicate minerals are common in terrestrial environments, and have been detected on the large asteroid-belt object, Ceres, as well as on Mars (Clark et al. 2007; King et al. 1992; Mustard et al. 2008; Rivkin et al. 2006). Cation substitutions in phyllosilicate interlayers control surface charge and cation exchange capacity, and thus their oxidative capacity in soils and sediments. These properties motivate consideration of phyllosilicate minerals as crucial phases for catalyzing the production of potentially important biomolecular precursors from simpler meteorite and crustal constituents in primordial environments (Ehrenfreund et al. 2006; Ferris 2005; Watson and Sephton 2015). Although quinones have been synthesized via modern liquid- and solid-phase approaches and studied extensively for their utility as consumer products, organic and pharmaceutical reagents, and redox species (Madje et al. 2010), we are aware of no studies that have considered the kinetics of clay mineral-catalyzed quinone formation from PAHs.

To address this knowledge gap, we assessed the potential of montmorillonite clay (MONT) to catalyze the conversion of anthracene (**1**) – a low molecular weight PAH commonly detected in meteorites and terrestrial geochemical environments – to 9,10-anthraquinone (**2**) (Fig. 1a), and quantify the kinetics of conversion over a range of temperatures relevant to the primordial Earth. We also investigated the effects of substrate concentration and reduced O<sub>2</sub> levels on the kinetics of conversion. Though a few studies have reported quinone production on MONT phases in pursuit of more rapid and environmentally benign synthetic routes to useful industrial products (Devi and Ganguly 2008; Singh and Geetanjali 2005), to the best of our knowledge, this is the first reported effort to elucidate the kinetics of MONT-catalyzed conversion of **1** to **2** and to do so in a prebiotic geochemical context.

## Experimental

### General Methods

ACS grade dichloromethane (DCM) and toluene were purchased from Sigma-Aldrich (St. Louis, MO) and used without further purification. Analytical grade Anthracene (**1**) and 9,10-



**Fig. 1** Conversion of anthracene (1) to 9,10-anthraquinone (2) is observed in the presence of MONT at various temperatures, and the insets show the conversion of a cream-colored mixture to a tan-colored mixture following reaction (a). Representative GC-MS TIC of the final solvent extract from a reaction with the 1 peak present at 7.8 min and the 2 peak at 8.5 min (b). GC-MS TICs detailing the formation of 2 and comparison to the authentic 2 standard (c). TICs from top to bottom: unreacted 1; the authentic 2 standard; unreacted 1 spiked with the authentic 2 standard; reacted 1 to produce 2; reacted 1 to produce 2 spiked with the authentic 2 standard

Anthraquinone (2) were purchased from Alfa Aesar (Haverhill, MA), were stored in amber vials at 0 °C throughout the study, and all reactions involving these reagents were shielded from direct exposure to laboratory lighting. K10 Montmorillonite (MONT) was purchased from Alfa Aesar (LOT # 10210586), extracted twice with a 1:1 DCM:toluene (v/v) mixture to remove interferent impurities, and dried completely in vacuo prior to use. After extraction, MONT was determined to have a  $\text{pH} = 3.65 \pm 0.10$  ( $n = 10$ ) using EPA Method 9045D (EPA 2004). After initial cleaning with Alconox detergent, all glassware and reaction vessels were solvent rinsed three times each with DCM and toluene and then allowed to air dry prior to use.

### Sample Preparation and Extraction

Stock mixtures (10–30 g) of solid MONT and 1 were made in 0.5X (5 mg 1:25 mg MONT), 1X (10 mg 1:25 mg MONT), and 2X (20 mg 1:25 mg MONT) concentrations by combining the reagents in a sealed amber vial under ambient atmosphere and vortexing the mixture on the maximum setting for 30 min. Aliquots of 35 mg of 1:MONT mixtures were introduced into 15 mL covered ceramic crucibles, which were incubated in triplicate at the prescribed temperature (25–250 °C) for the desired duration (2–12,960 min) in Fisherbrand™ Gravity Ovens (Fischer Scientific, Waltham, MA, USA). Following incubation, crucibles were removed from the oven and allowed 10 min to cool to room temperature. The 1:MONT mixtures were transferred from the crucibles to 10 mL glass culture tubes, 1.5 mL of 1:1 DCM:toluene (v/v) was added to extract the organics, and the tubes were vortexed at the maximum setting in three pulses of 30 s each. The extraction mixtures were centrifuged at 3000  $\times g$  for 3 min to pellet the remaining MONT, and the liquid extract (adjusted to 1.5 mL final volume) was transferred to 1.5 mL screw top autosampler vials for direct GC-MS determination. Extraction efficiency was assessed by spiking a sufficient quantity of pure 2 to the 1X mixture (10 mg 1:25 mg MONT) to ensure each 35 mg aliquot analyzed contained 4  $\mu\text{g}$  of 2 followed by vortexing, solvent extraction, and direct GC-MS determination and quantitation as above. Extraction efficiency was determined to be  $89.0 \pm 3.0\%$  ( $n = 10$ ) and all data were scaled

relative to this measurement. To assess the influence of O<sub>2</sub> on conversion, 35 mg aliquots of the IX mixture were introduced into 15 mL amber gastight septum vials (Restek, Bellefonte, PA). The headspace of each vial was flushed and replaced with either high purity CO<sub>2</sub> or Ar through the septum. Complete removal of oxygen was verified using GC-MS (see method below), such that the peak corresponding to molecular oxygen ( $m/z = 32$ ), which was present in atmospheric air samples and absent in samples of pure CO<sub>2</sub> and Ar, was not observed following incubation of the samples at 100 °C for 180 mins. This temperature and time were chosen because conversion of 1 to 2 was easily detected and septum integrity was maintained. After incubation in amber vials, the samples were extracted and analyzed identically to those incubated in ceramic crucibles.

### GC-MS Analysis – Solvent Extracts

A standard curve of **2** was created via dilution from a 2 mg/mL stock solution in toluene such that 2.5–750 ng of compound was analyzed in triplicate via GC-MS (Fig. 2a). All standards and sample extracts were analyzed using a QP2010 SE GC-MS (Shimadzu, Kyoto, Japan) equipped with an AOC-20i autosampler and Rxi-5 ms capillary column (30 m × 0.25 mm with a 0.25 μm 5% diphenyl 95% dimethyl polysiloxane phase; Restek Corporation, Bellefonte, PA). Helium was used as the carrier gas. The GC injector temperature was maintained at 250 °C and operated in the splitless mode with a helium flow rate of 1.15 mL/min. The initial GC column temperature was set to 110 °C, held for 1 min, and then ramped to 300 °C at 20 °C/min with a 5 min hold at 300 °C. The MS was operated in the electron impact ionization mode at 70 eV and 0.1 kV detector voltage. The ion source and MS interface temperatures were maintained at 250 °C and 290 °C, respectively. Mass spectra were obtained in the full scan mode, with the mass range 28–700 amu scanned at a rate of 5000 scans/s.

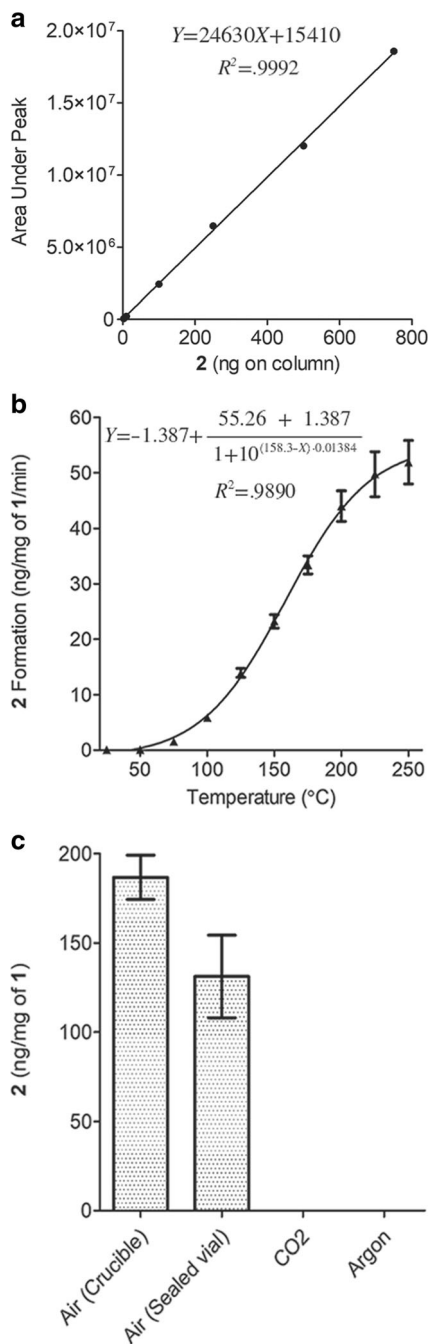
### GC-MS Analysis – Gases

Using the same GC-MS system described above, sample gases (O<sub>2</sub>, CO<sub>2</sub>, and Ar) were analyzed by drawing up 100 μL of the vial headspace into a gastight syringe (Hamilton, Reno, NV) and injecting onto an HP-PLOT Q PT GC column (30 m × 0.32 mm × 20 μm; Agilent, Santa Clara, CA). Helium was used as the carrier gas. The GC injector temperature was maintained at 250 °C and operated in the split mode (10:1 split ratio) with a helium flow rate of 1.44 mL/min. GC analysis was performed isothermally at 60 °C for 3 min. The MS was operated in the electron impact ionization mode at 70 eV and 0.1 kV detector voltage. The ion source and MS interface temperatures were maintained at 260 °C and 270 °C, respectively. Mass spectra were obtained in the full scan mode, with the mass range 10–100 amu scanned at a rate of 476 scans/s.

### Data Analysis

Analysis of total ion chromatograms (TICs) and mass spectra generated for all standards and samples was performed using GCMSsolution software (Version 4.11; Shimadzu, Kyoto, Japan). Compounds were identified by comparison of their mass spectra with those of reference compounds in the NIST/EPA/NIH Mass Spectral Library (NIST 11, Version 2.0, Gaithersburg, MD). All statistical analysis and graphing of data was performed with Excel (Microsoft, Redmond, WA) and Prism (GraphPad, San Diego, CA) software. Images were prepared with Photoshop CS6 software (Adobe, San Jose, CA).

**Fig. 2** Quantitation curve created with the authentic 2 standard generated over the concentration range of 2.5 to 750 ng on-column in triplicate (a). The apparent rates of conversion of 1 to 2 display a sigmodial relationship with reaction temperature (b). The amount of conversion of 1 to 2 in the presence or absence of molecular oxygen in sealed vials (c). All conditions were assessed in triplicate and data is presented as the average  $\pm$  standard deviation. The equation of the fitted line and the goodness of fit are displayed above the line



## Results and Discussion

Extant biochemical systems have evolved to rely on electron carriers that function via facile changes in redox potentials. Members of the quinone class are efficient at moving electrons

between components of the electron transport chain within cellular membranes, which facilitates the transfer of energy to create chemiosmotic proton gradients for cellular energy production and homeostasis. However, despite their ubiquity in prokaryotic and eukaryotic processes, the evolutionary underpinnings of quinone synthesis in prebiotic environments and subsequent incorporation into biochemical systems remain unknown. One possibility is that prebiotically available pools of 1 (e.g. from meteorites) could have reacted on clay mineral substrates across diverse temperature gradients to produce labile inventories of 2 (and other quinone analogs) sufficient to drive emergent biomolecular redox systems on the prebiotic Earth. To investigate this possibility, 1 was incubated with MONT over a range of prebiotically relevant temperatures (25–250 °C) to quantify rates of MONT-catalyzed conversion of 1 to 2. 1 and MONT were chosen as precursor and reaction substrate because 1) they are known constituents of both carbonaceous meteorites and Earth's crust (Watson and Sephton 2015) 2) they could have interacted extensively in the energetic milieu of Earth's Late Heavy Bombardment period (Botta and Bada 2002) and 3) their analytical simplicity permits rapid assessment of conversion kinetics via a single extraction with direct GC-MS determination of reaction products. The temperature range assessed accounts for a potentially cool (25 °C) environment, while also evaluating higher temperatures typical for hydrothermal systems (Barge and White 2017; Martin et al. 2008).

Mixtures of 1:MONT (10:25 mg) incubated at all temperatures examined resulted in a color change from cream to tan (Fig. 1a), reminiscent of the color of pure crystals of 2. Conversion of 1 to 2 within the specified time periods (Table 1) was evidenced by the elution of a new peak at a retention time of 8.5 min in all generated total ion chromatograms (TICs; Fig. 1b). Comparison of the constituent ions of the new TIC peak in all sample extracts to the National Institute of Standards and Technology (NIST) Mass Spectral Library consistently produced >95% similarity index outputs for 2. To verify peak identity, a certified standard of 2 was injected to confirm retention time and mass spectral library similarity index (Fig. 1c). Pure 2 was then spiked into solvent extracts of unreacted and reacted 1:MONT mixtures to show 1) that 2 eluted at the same retention time as the new peak in the unreacted mixture extracts, 2) that the 2 standard co-eluted with the 2 peak produced in the reacted mixture extracts, and 3) the same MS fragmentation pattern was evident between synthesized and spiked peaks of 2. These results confirm the conversion of 1 to 2 in the presence of MONT.

Serial dilutions of the authentic 2 standard were prepared to generate a standard quantitation curve over the range 2.5–750 ng injected on-column (Fig. 2a). This range was selected to encompass both the linear range of analyte response and the concentrations produced under all conditions assessed. Rates of conversion of 1 to 2 exhibited a sigmoidal relationship with temperature such that the highest incubation temperature assessed yielded the greatest rate of 2 production (expressed in ng of 2 formed per mg of 1 reacted per minute; Fig. 2b, Table 1). The observed sigmoidal kinetics may be explained in part by saturation of catalytic sites on the MONT with increasing incubation temperature, or perhaps by some level of cooperativity within the system. Computed conversion efficiencies ranged from 0.027 to 0.066% at the latest time point in the linear range of 2 conversion at each temperature. 2 was not detected when 1 was incubated without MONT at any temperature, demonstrating that incubation with MONT is required for the temperature-dependent conversion of 1 to 2. No conversion of 1 to 2 was detected in unreacted 1:MONT mixtures after three months of incubation at 4 °C.

To further assess MONT-catalyzed conversion of 1 to 2, the effect of substrate concentration was examined. 1:MONT mixtures were prepared with 0.5X (5:25 mg) and 2X (20:25 mg) concentrations of 1 and incubated at 100 °C, 175 °C, and 250 °C to measure conversion. Rates

**Table 1** Rates of apparent conversion of 1 to 2 over the temperatures and incubation times assessed conducted in triplicate

Incubation temperature (°C)	Linear range of 2 detection (min)	2 Conversion rate (ng/mg of 1/min)	R <sup>2</sup>
25	4320–12,960	0.06557 ± 0.005771	0.9486
50	1440–4320	0.1056 ± 0.01123	0.9267
75	120–240	1.576 ± 0.1505	0.9400
100	60–210	5.880 ± 0.4963	0.9525
125	18–35	13.92 ± 0.8090	0.9579
150	18–30	23.23 ± 1.206	0.9377
175	6–21	33.42 ± 1.615	0.9705
200	6–14	44.04 ± 2.737	0.9522
225	4–12	49.78 ± 4.046	0.9380
250	2–12	51.93 ± 3.940	0.9304

Data are presented as mean ± standard deviation, and the goodness of fit is presented

of conversion of the 0.5X and 2X mixtures were not significantly different (*t*-test; *p* > 0.05) from those observed in the 1X (10:25 mg) mix used for all other conversion experiments conducted at the same temperatures (Table 2). The influence of O<sub>2</sub> on conversion of 1 to 2 was also assessed by incubating the 1X mixture in sealed gastight vials from which air was evacuated and then replaced with either carbon dioxide (CO<sub>2</sub>) or argon (Ar) gas. Under quasi-anoxic conditions, no conversion of 1 to 2 was observed following incubation at 100 °C for 180 mins (Fig. 2c). Comparable conversion of 1 to 2 was observed between aerobic experiments conducted in sealed vials and ceramic crucibles. These results demonstrate that changes in the ratio of 1:MONT do not alter conversion kinetics under the conditions assessed, and that O<sub>2</sub> is required to drive the reaction. We thus conclude that the MONT-catalyzed conversion of 1 to 2 is governed by pseudo zero-order kinetics under these conditions.

Deducing rational mechanisms to account for the emergence of oxidized biomolecular precursors on the prebiotic Earth is challenging as consensus regarding the precise composition of the primordial atmosphere is lacking (Holland 2006; Kasting 1993; Zahnle et al. 2010). Under the reducing conditions proposed by Miller and Urey (Miller 1953; Miller and Urey 1959), for example, the relevance of aerobic MONT-catalyzed 2 production in other than isolated micro-environments may appear limited. However, there is increasing evidence that the primordial atmosphere was likely redox neutral to moderately oxidizing (Shaw 2008). Indeed, in support of the latter state, studies of the oxygen fugacity (Frost and McCammon 2008) and rare-earth element ratios of zircon crystals (Trail et al. 2011) in ancient (e.g. > 3.5 × 10<sup>9</sup>-year-old) magma

**Table 2** The apparent rate of conversion of 1 to 2 determined by varying the amount of 1 while keeping the amount of MONT constant

Incubation temperature (°C)	2 Conversion rate at different ratios of 1:MONT (ng/mg of 1/min)		
	0.5X	1X	2X
100	6.626 ± 0.6254 (0.9182)	5.880 ± 0.4963 (0.9525)	5.753 ± 0.4802 (0.9349)
175	33.77 ± 3.720 (0.9217)	33.42 ± 1.615 (0.9705)	36.77 ± 4.195 (0.9165)
250	50.45 ± 3.194 (0.9727)	51.93 ± 3.940 (0.9304)	51.62 ± 6.378 (0.9035)

Data are presented as the average ± standard deviation. R<sup>2</sup> goodness of fit values are in parentheses



melts suggest that the early atmosphere would have contained oxidized gases (e.g. CO<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>O). This uncertainty notwithstanding, the atmosphere and surface environments of the primordial Earth experienced intense solar radiation fluxes, which could have produced an inventory of oxidant species, perhaps including localized O<sub>2</sub> reservoirs, capable of driving the prebiotic conversion of 1 to 2 and quinone analogs. For example, water and titanium oxide (TiO<sub>2</sub>; a terrestrial mineral ore) may undergo photocatalytic conversion to O<sub>2</sub> in the presence of near UV photons (Narita et al. 2015). Other oxidants (e.g. hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)) have been detected in the Martian atmosphere (Clancy et al. 2004; Encrenaz et al. 2004) and are hypothesized to arise via heterogeneous catalysis on Martian hydrated mineral surfaces (Zent 1998). Mineral-catalyzed (Borda et al. 2001) and atmospheric photochemical production (Liang et al. 2006) of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub>O have also been proposed as plausible pathways for producing prebiotic oxidants, with the conversion of 1 to 2 in the presence of H<sub>2</sub>O<sub>2</sub> being reported in controlled lab studies (Charleton and Prokopchuck 2011; Estrada et al. 2011). Production of reactive oxygen species via photocatalytic oxidation of organic matter pools in terrestrial desert soils has also been reported, which has subsequently informed theoretical predictions regarding the abiotic production in analogous Martian surface environments (Georgiou et al. 2015). Our findings, along with the results of previous studies, permit a number of plausible geochemical scenarios in which PAHs could undergo conversion to quinones in prebiotic environments.

While details of the underlying mechanism of 1 conversion to 2 under the conditions assessed are unclear, informed by e.g. resonance spectroscopic studies of 1 interactions with cation-exchanged clays (Soma et al. 1985), we can reasonably hypothesize that metal cations (e.g. Fe(III), Al(III)) sequestered in the MONT interlayers likely abstract pi electrons from the most reactive (i.e. least electron dense, least resonance stabilized) center ring of 1 (from the 9 and 10 carbons) to produce a radical cationic 1 intermediate with strong affinity for O<sub>2</sub>. The absence of detectable conversion of 1 to 2 observed in the sealed vials incubated with CO<sub>2</sub> and Ar provide additional support for such a mechanism. Recent work with Fe(III)-exchanged smectite clays has also shown the capacity of interlayer Fe(III) cations to facilitate conversion of 1 to 2 in 1-contaminated soils (Li et al. 2014). Additionally, Watson and Sephton (Watson and Sephton 2015) reported some 2 production upon heating 1 with Fe(III)-exchanged MONT at 120 °C in a study of the catalytic potential of cation-exchanged MONT to produce the macromolecular organics of chondrites from simpler aromatics. They invoked a similar mechanism to account for this result. However, the MONT used in the present study was enriched in Al(III) relative to Fe(III) by more than three-fold (i.e. 17.0% w/w Al(III) as Al<sub>2</sub>O<sub>3</sub>; 5.2% w/w Fe(III) as Fe<sub>2</sub>O<sub>3</sub>), suggesting that higher concentrations of Al(III) in the MONT interlayers may similarly influence conversion kinetics under the conditions assessed. Despite the substantially reduced oxidation potential of Al(III) ( $E^\circ = -1.66$  V) relative to Fe(III) ( $E^\circ = 0.77$  V), efficient coordination of Al(III) with aromatics in environmental and biological systems has been reported (Martell et al. 1996), which lends support to this idea. These interactions with metal cations in clay under a neutral to moderately oxidizing prebiotic atmosphere provide plausible mechanistic conditions for the catalytic conversion of PAHs under mild to more extreme temperature regimes to form a labile pool of potentially bioactive quinones in prebiotic environments.

## Conclusions

In summary, we conclude that 1) apparent MONT-catalyzed rates of conversion of 1 to 2 are sigmoidal and concentration independent with respect to incubation temperature, 2) conversion



efficiencies of 1 to 2 are in the range of 0.027 to 0.066%, and 3) conversion of 1 to 2 does not occur in the absence of MONT or O<sub>2</sub> at any temperature examined. We hypothesize that interactions of 1 and MONT in the presence of abiotic O<sub>2</sub> could have contributed appreciable 2 and quinone analogs to the organic inventory of the prebiotic Earth that could have driven the emergence of primitive biomolecular redox systems. Work is ongoing to assess the efficacy of other putative prebiotic oxidizers (e.g. H<sub>2</sub>O<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and ClO<sub>4</sub><sup>-</sup>) to convert PAHs to potentially bioactive quinones in the presence of MONT and other clay mineral types.

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