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Investigating the kinetics of clay-catalyzed conversion of anthracene to prebiotically relevant 9,10-anthraquinone.

By

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Abstract

The presence polycyclic aromatic hydrocarbons (PAHs) on the primordial Earth can be attributed to carbonaceous meteorites bombarding planetary surfaces. Subsequently, the PAHs reacted with catalytic clay mineral surfaces to produce quinones that functioned as electron transporters in emergent biological systems. To address this hypothesis, we assessed the kinetics of anthracene (ANTH) conversion to 9,10-anthraquinone (ANTHQ) in the presence of montmorillonite and kaolinite clay (MONT and KAO, respectively) 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 (O₂)). We also tested the respective compounds kinetics in crucibles and reaction tubes over 25, 225 and 250 °C in both a muffle furnace and oven. Based on preliminary results, rates of conversion are concentration independent and display a sigmoidal relationship with temperature. These results suggest a scenario in which meteoritic ANTH and MONT interactions could yield biologically important quinones in prebiotic planetary environments

Introduction

Due to their chemical versatility and ubiquity throughout the interstellar medium, polycyclic aromatic hydrocarbons (PAHs) have long been considered as potential precursors to bioactive molecules. Besides being hypothesized as plausible membranous components (Groen 2012), PAHs have also been considered as the original templating polymers (Ehrenfreund 2006) and have been noted as a predominant component of cosmic materials (Ohishi 2016, Sabbah 2017), especially meteorites. Carbonaceous meteorites contributed large quantities of PAHs to early earth and other planetary environments (Becker 1997). Heavy deposits of three ring PAHs including anthracene have been described in multiple carbonaceous meteorites including the Ivuna (Wing and Bada 1991), Murchison (Gilmour 1994), and Allende (Zenobi 1989) meteorites. In addition to depositing organic material, these meteoritic impacts may have generated areas conducive to organic reactions due to their deposition of trace minerals and introduction of large surface areas (Lunine 2006). Minerals and clays have long been considered a key component of the origin of prebiotically relevant molecules (Pedreira-Segade 2018, Cairns-Smith 2005, Hazen 2005, Laszlo 1987) due to their catalytic capacity. This reactivity would undoubtedly be induced by radiation from the sun (Tirard 2017, Ehrenfreund 2006, Berstein 1999), and thermal radiation from hydrothermal vents (Barge 2017) or volcanic activity of the primordial earth, wherein PAHs undoubtedly resided (Stracquadanio 2003). Insight into the thermodynamic properties of volcanic plumes has previously demonstrated its capacity to catalyze the formation of amines and amino acids (Miller 1953, Parker 2011). Despite this wide experimentation, the exact conditions of the primordial earth in the context of the formation of prebiotically relevant molecules remains unknown (Barge 2018, McKay 2014), calling for further experimentation especially in the context of clay catalysts. To address this knowledge

gap, we assessed the potential of montmorillonite clay (MONT) to catalyze the conversion of anthracene (ANTH) – a low molecular weight PAH commonly detected in meteorites and terrestrial geochemical environments – to 9,10-anthraquinone (ANTHQ), 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 O₂ levels on the kinetics of conversion. Continually, we assessed the kinetics of anthracene (ANTH) conversion to 9,10-anthraquinone (ANTHQ) in the presence of montmorillonite and kaolinite clay (MONT and KAO, respectively) in crucibles and reaction tubes over 25, 225 and 250 °C in both a muffle furnace and oven.

General methods

ACS grade dichloromethane (DCM) and toluene were purchased from Sigma-Aldrich, mixed together in a 1:1 ratio, and stored at -20°C for use in sample extraction. Anthracene, 9,10-Anthraquinone, K10 Montmorillonite (MONT), and Kaolinite (KAO) were purchased from Alfa Aesar and stored in solvent rinsed amber vials at -20°C for the duration of the study. All glassware and reaction vessels were cleaned with Alconox detergent, solvent rinsed in triplicate, and allowed to air dry in covered containers prior to use. Custom reaction tubes were created using disposable 9 inch borosilicate glass pasteur pipettes sealed by a Blazer Piezo micro butane torch to generate a roughly 3 inch sections (Fig. 1) that were filled with PAH:Clay mixtures and wrapped in aluminum foil prior to incubation. Extraction efficiency of all individuals involved in sample generation was established to verify consistency.

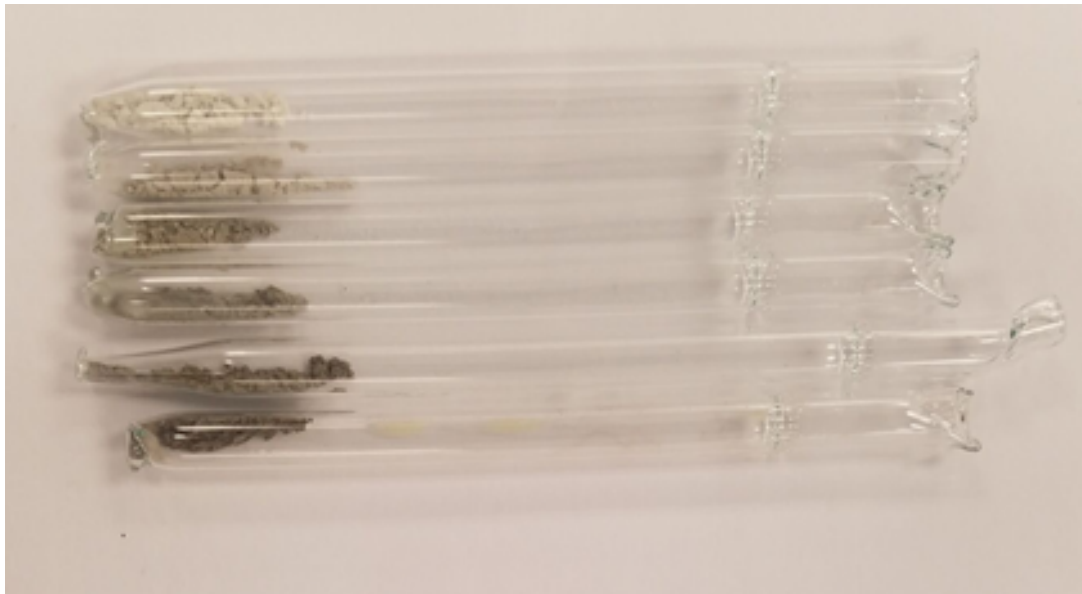


Figure 1: Color change gradient as a function of incubation time. The lightest color corresponds to the shortest incubation time and the darkest color corresponds to the longest incubation time.

Sample preparation and extraction

Stock mixtures (10-30 g) of solid MONT and ANTH 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 ANTH: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 (2-12960 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 ANTH: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 sec each. The extraction mixtures were centrifuged at

3,000 x 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 ANTHQ to the 1X mixture (10 mg 1:25 mg MONT) to ensure each 35 mg aliquot analyzed contained 4 µg of ANTHQ followed by vortexing, solvent extraction, and direct GC-MS determination and quantitation as above. Extraction efficiency was determined to be 89.0 ± 3.0 % (n = 10) and all data were scaled relative to this measurement. To assess the influence of O₂ on conversion, 35 mg aliquots of the 1X mixture were introduced into 15 mL amber gastight septum vials (Restek, Bellfonte, PA). The headspace of each vial was flushed and replaced with either high purity CO₂ 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 CO₂ 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 ANTH to ANTHQ 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.

Stock mixtures of MONT/KAO and ANTH were prepared and stored at -20°C. Aliquots of 35 mg of ANTH:MONT or ANTH:KAO mixtures were introduced into 15 mL covered ceramic crucibles and/or reaction tubes, and incubated in triplicate at the prescribed temperature (25, 225, or 250°C) for the desired duration (2-9000 min) in Fisherbrand™ Gravity Ovens (Fischer Scientific, Waltham, MA, USA). Following incubation, crucibles and reaction tubes were removed from the oven and allowed to cool at room temperature for 10 min. Mixtures were transferred to 10 mL glass culture tubes, 1.5 mL of 1:1 DCM:toluene (v/v) was added, and tubes

were vortexed using a Heidolph Multi Reax Vortexer for 5 minutes at maximum speed.

Following vortexing, extraction mixtures were centrifuged on a Fisher Scientific accuSpin 8C Clinical Centrifuge at 4,000 x g for 5 min, and the liquid extract was transferred to 1.5 mL screw top autosampler vials for direct GC-MS determination.

GC-MS analysis – solvent extracts

All standards and sample extracts were analyzed using a QP2010 SE GC-MS (Shimadzu, Kyoto, Japan) equipped with an AOC-20i autosampler and Rxi-5ms capillary column (30 m x 0.25 mm with a 0.25 μ m 5% diphenyl 95% dimethyl polysiloxane phase; Restek Corporation, Bellefonte, PA) with helium as the carrier gas. 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 5,000 scans/s.

GC-MS analysis – gases

Using the same GC-MS system described above, sample gases (O₂, CO₂, and Ar) were analyzed by drawing up 100 μ L of the vial headspace into a gastight syringe (Hamilton, Reno, NV) and injecting onto an HP-PLOT Q PT GC column (30 m x 0.32 mm x 20 μ m; 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 GCMS solution 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 were performed with Excel (Microsoft, Redmond, WA).

Results and discussion

Quinones function efficiently as electron transporters within cellular membranes, facilitating the energy transfer required for the functionality of chemiosmotic proton gradients that are responsible for cellular energy production. However, the primordial earth conditions necessary to drive quinone synthesis and later incorporation into biochemical systems on the primordial earth remain unknown (Barge 2018). One possibility is meteorites delivered ANTH to the prebiotic clay mineral surfaces across temperature gradients producing an amount of ANTHQ sufficient to drive emergent biomolecular synthesis reactions on the prebiotic Earth. To investigate this possibility, ANTH was incubated with MONT over a range of prebiotically relevant temperatures (25 – 250 °C) to quantify rates of MONT-catalyzed conversion of ANTH to ANTHQ. ANTH and MONT were chosen as precursor and reaction substrate because they are known constituents of both carbonaceous meteorites and Earth's crust (Watson and Sephton

2015), they could have interacted extensively in the energetic milieu of Earth's Late Heavy Bombardment period (Botta and Bada 2002), and 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 ANTH:MONT (10:25 mg) incubated at all temperatures examined resulted in a color change from cream to tan, reminiscent of the color of pure crystals of ANTHQ. Conversion of ANTH to ANTHQ 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). 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 ANTHQ. To verify peak identity, a certified standard of ANTHQ was injected to confirm retention time and mass spectral library similarity index. Pure ANTHQ was then spiked into solvent extracts of unreacted and reacted ANTH:MONT mixtures to show that ANTHQ eluted at the same retention time as the new peak in the unreacted mixture extracts, that the ANTHQ standard co-eluted with the ANTHQ peak produced in the reacted mixture extracts, and the same MS fragmentation pattern was evident between synthesized and spiked peaks of ANTHQ. These results confirm the conversion of ANTH to ANTHQ in the presence of MONT.

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

Table 1: Rates of apparent conversion of ANTH to ANTHQ over the temperatures and incubation times assessed conducted in triplicate. Data are presented as mean \pm standard deviation, and the goodness of fit is presented

Incubation Temperature (°C)	Linear Range of ANTHQ Detection (min)	ANTHQ Conversion Rate (ng/mg of 1/min)	R ²
25	4320-12960	0.06557 \pm 0.005771	0.9486
50	1440-4320	0.1056 \pm 0.01123	0.9267
75	120-240	1.576 \pm 0.1505	0.9400
100	60-210	5.880 \pm 0.4963	0.9525
125	18-35	13.92 \pm 0.8090	0.9579
150	18-30	23.23 \pm 1.206	0.9377
175	6-21	33.42 \pm 1.615	0.9705
200	6-14	44.04 \pm 2.737	0.9522
225	4-12	49.78 \pm 4.046	0.9380
250	2-12	51.93 \pm 3.940	0.9304

To further assess MONT-catalyzed conversion of ANTH to ANTHQ, the effect of substrate concentration was examined ANTH:MONT mixtures were prepared with 0.5X (5:25

mg) and 2X (20:25 mg) concentrations of ANTH and incubated at 100 °C, 175 °C, and 250 °C to measure conversion. Rates of conversion of the 0.5X and 2X mixtures were not significantly different (t-test; $p > 0.05$) from those observed in the 1X (10:25mg) mix used for all other conversion experiments conducted at the same temperatures (Table 2). The influence of O₂ on conversion of ANTH to ANTHQ was also assessed by incubating the 1X mixture in sealed gastight vials from which air was evacuated and then replaced with either carbon dioxide (CO₂) or argon (Ar) gas. Under quasi-anoxic conditions, no conversion of ANTH to ANTHQ was observed following incubation at 100 °C for 180 mins. Comparable conversion of ANTH to ANTHQ was observed between aerobic experiments conducted in sealed vials and ceramic crucibles. These results demonstrate that changes in the ratio of ANTH:MONT do not alter conversion kinetics under the conditions assessed, and that O₂ is required to drive the reaction. We thus conclude that the MONT-catalyzed conversion of ANTH to ANTHQ is governed by pseudo zero-order kinetics under these conditions.

Table 2 The apparent rate of conversion of ANTH to ANTHQ determined by varying the amount of ANTH while keeping the amount of MONT constant. Data are presented as the average \pm standard deviation. R² goodness of fit values are in parentheses.

Incubation Temperature (°C)	ANTHQ Conversion Rate at Different Ratios of ANTH:MONT (ng/mg of 1/min)		
	0.5X	1X	2X
100	6.626 \pm 0.6254 (0.9182)	5.880 \pm 0.4963 (0.9525)	5.753 \pm 0.4802 (0.9349)
175	33.77 \pm 3.720 (0.9217)	33.42 \pm 1.615 (0.9705)	36.77 \pm 4.195 (0.9165)
250	50.45 \pm 3.194 (0.9727)	51.93 \pm 3.940 (0.9304)	51.62 \pm 6.378 (0.9035)

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 ANTHQ production in other than isolated microenvironments may appear limited. However, there is increasing evidence that the primordial atmosphere was likely redox neutral to moderately oxidizing (Shaw 2008). 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. > 3.5x10⁹-year-old) magma melts suggest that the early atmosphere would have contained oxidized gases (e.g. CO₂, SO₂, and H₂O). 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, including significant O₂ reservoirs, capable of driving the prebiotic conversion of ANTH to ANTHQ and quinone analogs. For example, water and titanium oxide (TiO₂; a terrestrial mineral ore) may undergo photocatalytic conversion to O₂ in the presence of near UV photons (Narita et al. 2015). Other oxidants (e.g. hydrogen peroxide (H₂O₂)) have been detected in the Martian atmosphere (Clancy et al. 2004; Encrenaz et al. 2004) and are hypothesized to arise via heterogenous catalysis on Martian hydrated mineral surfaces (Zent 1998). Mineral-catalyzed (Borda et al. 2001) and atmospheric photochemical production (Liang et al. 2006) of H₂O₂ from H₂O have also been proposed as plausible pathways for producing prebiotic oxidants, with the conversion of ANTH to ANTHQ in the presence of H₂O₂ 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 Maritan 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 ANTH conversion to ANTHQ under the conditions assessed are unclear, informed by e.g. resonance spectroscopic studies of ANTH 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 ANTH (from the 9 and 10 carbons) to produce a radical cationic ANTH intermediate with strong affinity for O₂. The absence of detectable conversion of ANTH to ANTHQ observed in the sealed vials incubated with CO₂ 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 ANTH to ANTHQ in ANTH-contaminated soils (Li et al. 2014). Additionally, Watson and Sephton (Watson and Sephton 2015) reported some ANTHQ production upon heating ANTH 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 Al₂O₃; 5.2% w/w Fe(III) as Fe₂O₃), 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.

Furthermore, ANTH was incubated with non-extracted or extracted MONT/KAO over prebiotically relevant temperatures (25, 225, 250 °C) to quantify rates of MONT/KAO-catalyzed conversion of ANTH to ANTHQ. ANTH, MONT, and KAO were chosen as precursor and reaction substrates because they are known constituents of both carbonaceous meteorites and Earth's crust (Watson and Sephton 2015; Clark 2007) and 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 typically found in hydrothermal systems (Barge and White 2017).

Mixtures of non-extracted/extracted ANTH:MONT and non-extracted/extracted KAO:ANTH(25:10 mg) incubated at all temperatures examined resulted in a color change from cream to tan/dark brown (Fig. 1). During initial method and experimental conception, a discrepancy between extracted and non-extracted clay catalyzed conversion of ANTH to ANTHQ was noted. Although the reasons for this disparity remain unknown, all further experimentation was carried with non-extracted clays due to their higher production of ANTHQ.

Based on preliminary results, we hypothesize that rates of conversion of ANTH to ANTHQ when exposed to KAO, will exhibit a sigmoidal relationship with temperature (Fig. 3) such that the highest incubation temperature assessed yielded the greatest rate of ANTHQ production, as previously observed in previous experiments. Our results also suggest that KAO produces less ANTHQ than MONT. This finding may be due in part to KAO's smaller specific

area (15-20 m²/g) compared to MONTs large 500-750 m²/g specific area (Laszlo 1987). The oven also produces more ANTHQ than the muffle furnace and the reason for this observation still eludes us. Finally, ANTH:MONT produce ANTHQ at 25C over a 6 day time course (Fig. 2), which is indicative of a biologically relevant temperature that these reactions can occur. 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 ANTHQ.

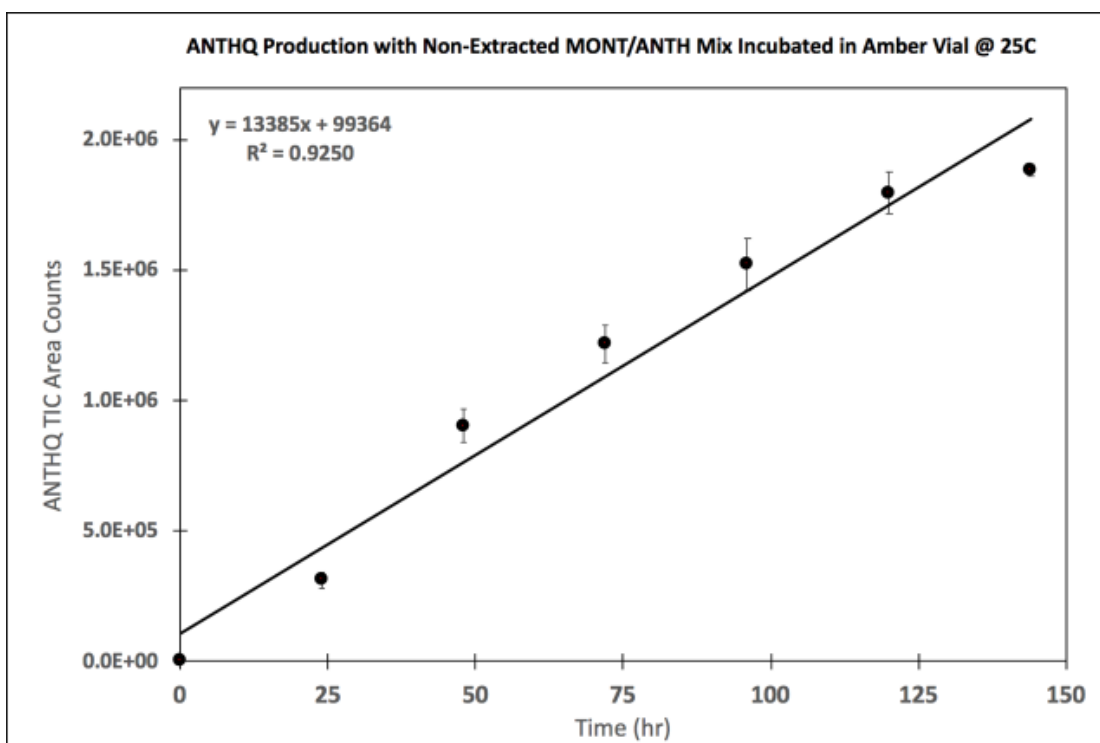


Figure 1: Non-extracted MONT:ANTH mixture incubated for 6 days in an amber vial at 25C.

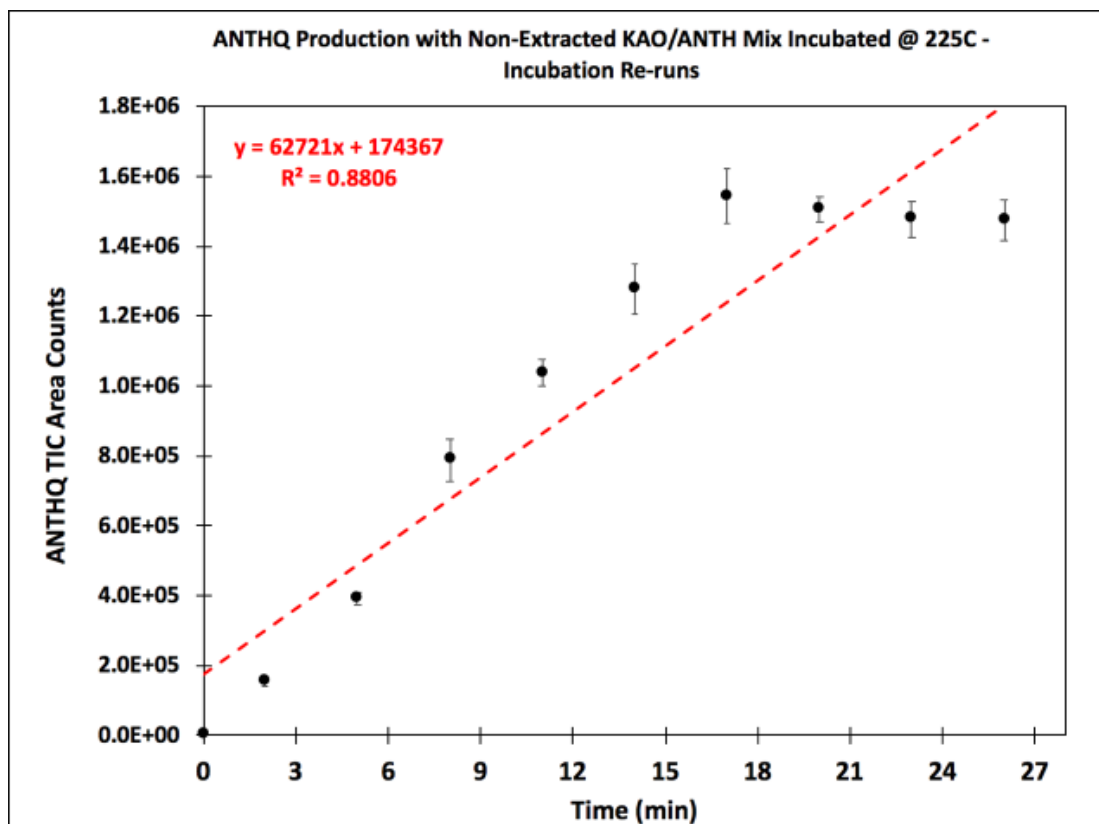


Figure 2: Non-Extracted KAO:ANTH mixture ANTHQ production as a function of time at 225C.

Conclusion

In summary, we conclude that apparent MONT-catalyzed rates of conversion of ANTH to ANTHQ are sigmoidal and concentration independent with respect to incubation temperature, conversion efficiencies ANTH to ANTHQ are in the range of 0.027 to 0.066 %, and conversion of ANTH to ANTHQ does not occur in the absence of MONT or O₂ at any temperature examined. We hypothesize that interactions of ANTH and MONT in the presence of abiotic O₂ could have contributed appreciable ANTHQ and quinone analogs to the organic inventory of the prebiotic Earth that could have driven the emergence of primitive biomolecular redox systems. Continually, we observed that the custom reaction tubes resulted in higher yields of ANTHQ, MONT results in a higher conversion of ANTH to ANTHQ than KAO does, and the oven

resulted in a higher conversion of ANTH to ANTHQ than the muffle furnace did. We hypothesize that continued longitudinal studies will show a sigmoidal relationship between conversion and temperature. Ongoing studies are being completed to determine the rate of conversion between different anthracene species and other prebiotically relevant clays.

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