Survivability of 1-Chloronaphthalene During Simulated Early Diagenesis: Implications for Chlorinated Hydrocarbon Detection on Mars

Samuel H. Royle1, Jonathan Tan1, Samuel P. Kounaves1,2, and Mark A. Sephton1

1Impacts and Astromaterials Research Centre, Department of Earth Science and Engineering, Imperial College London, London, UK, 2Department of Chemistry, Tufts University, Medford, MA, USA

Abstract All missions to Mars have attempted to detect organic molecules have detected simple chlorohydrocarbons, the source of which has yet to be firmly established. This study assessed the likelihood of these chlorinated molecules being indigenous to the sedimentary units in which they were detected or if they were chlorinated during analysis. The survivability of 1-chloronaphthalene was examined via hydrous pyrolysis experiments and its dechlorination kinetics were determined. The results of these experiments were used to model the survivability of this simple chlorohydrocarbon under Mars-relevant diagenetic conditions using the Sheepbed mudstone unit as a case study. It was found that 1-chloronaphthalene was rapidly dechlorinated under Noachian conditions, and thus, the detected Martian chlorohydrocarbons are unlikely to be ancient and probably formed within the rover’s sample handling chain during analysis.

Plain Language Summary The search for past or present life on Mars is centered on the detection of organic molecules. Most attempts to detect organic molecules on Mars have only found simple chlorinated compounds. The source of these chlorinated compounds has not been firmly established. It has been hypothesized that chlorinated organic compounds could form on the Martian surface via reactions between chlorine-bearing salts and organic compounds delivered by meteorites. This study examined the ability of simple chlorinated organic molecules to survive the high pressures and temperatures associated with burial over geological time scales. Our aim was to calculate whether chlorinated molecules detected on Mars could be ancient and preserved in the rock units, or if they formed during the analysis process, as other studies have assumed. It was found that, on a warmer ancient Mars when the sediments the chlorinated molecules were detected in were deposited, the increased surface temperatures would have promoted the loss of chlorine relatively rapidly, and the intact chlorinated organic molecules would not have survived the burial and exhumation processes to the present day. The chlorinated organics detected on Mars are therefore likely to have been formed recently, most probably through reactions with chlorine-bearing salts when heated during analysis.

1. Background

All three landed missions to Mars which have attempted to detect organic compounds have found chlorinated organic molecules. Viking Lander 1 detected chloromethane at levels of 15 ppb while Viking Lander 2 detected dichloromethane at 2–40 ppb (Biemann et al., 1976, 1977), reanalysis also suggests that Viking Lander 1 detected chlorobenzene at 0.08–1.00 ppb (Guzman et al., 2018). The Sample Analysis at Mars (SAM) instrument suite on board the Curiosity rover has detected chloromethane, dichloromethane, trichloromethane, chloromethylpropene, chlorobenzene (150–300 ppb), 1,2-dichloropropane (~70 ppb), 1,2-dichloroethene, and 1,1- and 1–2-dichlorobutane (below quantification limit; Freissinet et al., 2015; Glavin et al., 2013), Figure 1.

Attempts to explain the sources of these compounds have resulted in numerous interpretations. Originally, the Viking data were thought to show terrestrial contamination from residual cleaning products, as chlorinated solvents had been used in the cleaning of the spaceflight hardware (Biemann et al., 1976, 1977). This conclusion did not sufficiently explain the absence of these compounds in the blanks, nor why the two landers detected different compounds. After the discovery of perchlorate (ClO4−) in the Martian soil by the Phoenix lander (Hecht et al., 2009; Kounaves et al., 2010), the Viking results were reinterpreted as indigenous organic materials reacting with perchlorates during thermal volatilization (Guzman et al., 2018;
Navarro-González et al., 2010). Chloromethane and chloromethylpropene detected by SAM have been attributed to Martian chlorine from perchlorate decomposition reacting with terrestrial organic carbon from MTBSTFA, a chemical known to have leaked from a derivatization cup inside the SAM instrument suite (Glavin et al., 2013). Terrestrial benzene or toluene derived from Tenax® on the gas chromatograph (GC) hydrocarbon trap may explain part of the detected chlorobenzene (Glavin et al., 2013; Miller et al., 2015). However, chlorobenzene was detected above instrument background levels during Evolved Gas Analysis, where samples do not pass through the Tenax® hydrocarbon trap. This indicates that there must also be a Martian carbon source (Freissinet et al., 2015; Miller et al., 2015). A temperature dependence of the chlorobenzene detection recently identified in the Viking Lander 2 data is also indicative of a Martian carbon source (Guzman et al., 2018). Furthermore, a source of Martian organic carbon has recently been confirmed with the detection of complex macromolecular organic matter by MSL (Eigenbrode et al., 2018).

Therefore, there are two clear competing hypotheses in the literature for the sources of the organic carbon contribution to the chlorinated hydrocarbons:

1. It is a terrestrial contaminant chlorinated during analysis (Miller et al., 2015);
2. It has a Martian source and has been chlorinated during analysis (Freissinet et al., 2015).

There is also a third possibility: (3) indigenous organic compounds are chlorinated prior to analysis due to in situ reactions with oxychlorine species produced during both the formation and breakdown of perchlorate on the Martian surface (Kounaves, Carrier, et al., 2014). Although perchlorate (ClO4−) salts and other stable Cl− minerals present in the Martian soil (Hecht et al., 2009; Kounaves, Chaniotakis, et al., 2014) may have little direct effect on organic molecules under ambient Mars conditions, the effects of UV sunlight, X-rays, galactic cosmic rays (GCR), and solar energetic particles will both form and destroy perchlorate. These processes will produce a variety of highly reactive species such as chlorite radicals (ClO2−), hypochlorite (ClO−), chlorine, and chlorine dioxide (ClO2; Góbi et al., 2016; Quinn et al., 2013) along with other, as yet undetected oxychlorine species (Carrier, 2017). Thus, a variety of reactive intermediary oxychlorines may always be present in the Martian surface (and shallow subsurface) regolith (Carrier & Kounaves, 2015; Schuttlefield et al., 2011) and available to react with organic compounds (Kounaves, Carrier, et al., 2014). These processes could produce indigenous chlorinated organic compounds (e.g., Hawkins et al., 2003; Hayatsu et al., 1971) in the uppermost Martian regolith.

To test whether this third hypothesis was feasible, it was necessary to investigate the stability of simple chlorinated organic molecules under Mars-relevant conditions. If these chlorinated molecules were found to be stable under relevant Martian diagenetic conditions, there would be a strong possibility that chlorinated compounds found in the Martian regolith were ancient, rather than formed recently via the SAM sample handling chain on board Curiosity.

Assuming any fossil organic indigenous chlorohydrocarbons were codeposited with the sediments that host them, they would have had to survive the geological history of the rock unit from which they were extracted. For this study, the Sheepbed mudstone member of the Yellowknife Bay formation in Gale crater was taken as a case study, as this is where the greatest variety of chlorohydrocarbons have been detected (Freissinet et al., 2015), and much research has been carried out into the burial history of this unit (e.g., Borlina et al., 2015; Caswell & Milliken, 2017; Nachon et al., 2014).

Indigenous fossil chlorohydrocarbons in the Sheepbed mudstone would therefore be 3.8–3.6 Ga old (dating from the Noachian-Hesperian boundary; Thomson et al., 2011); have been rapidly and deeply buried down to 1–3 km and then exhumed again (Caswell & Milliken, 2017); have been subjected to numerous phases, both early and late stages, of persistent (nonacidic) aqueous activity; and would have experienced temperatures around 50 °C (Léveillé et al., 2014; Nachon et al., 2014).

Nonindigenous chlorohydrocarbons, including contaminants and those formed from indigenous organic molecules during analysis by thermal decomposition with perchlorate, in comparison, would have been on the Martian surface for no longer than the life span of the mission—a few years at most and would have experienced no diagenetic history.

This study attempted to investigate the survivability of simple chlorohydrocarbons under Martian diagenetic conditions with the aim to determine a means of distinguishing between organic material which has been chlorinated prior to, or during, analysis.
Hydrous pyrolysis was utilized to simulate diagenesis. It has been shown that high-temperature, short-duration experiments are capable of replicating the low-temperature, long-duration diagenetic process as the underlying chemical reactions may be suitably described by a pseudo-first-order Arrhenius equation (Lewan et al., 1979). Previous hydrous pyrolysis experiments, both on whole source rocks (e.g., Koopmans et al., 1995; Lewan et al., 1985; Spigolon et al., 2015) or specific biomass (e.g., Watson et al., 2012) and isolated organic compounds (e.g., Li et al., 2017), have found similarities between the pyrolysates and the organic compounds produced by natural oil generation. Thus, the present work utilized hydrous pyrolysis to artificially mature chlorohydrocarbons to examine the effects of diagenesis.

2. Methods

2.1. Hydrous Pyrolysis

1-Chloronaphthalene (technical grade, ≥90% 1-chloronaphthalene, ~10% 2-chloronaphthalene; Figure 2) was obtained from Sigma-Aldrich as a representative of the types of chlorohydrocarbons that could be expected to form on the Martian surface. Chlorobenzene itself was not deemed suitable as a starting molecule for the experiment as it is unlikely to be present in the Martian regolith due to its high vapor pressure and volatility (Guzman et al., 2018). Thus, in the hypothesized case that chlorohydrocarbons are present in the regolith prior to analysis, the detection of chlorobenzene, along with the other volatile chlorohydrocarbons, is likely to be due to the pyrolytic breakdown of a larger chlorinated parent molecule during thermal decomposition. Simple aromatic compounds such as naphthalene have been detected in numerous meteorites and are believed to be indigenous to the samples (Sephton, 2002; Sephton et al., 2002), and these are suggested to be the main sources of organic matter on the Martian surface (Flynn et al., 2004); naphthalene is also one of the molecules that have been detected by MSL and was suggested to be indicative of complex macromolecular organic material present in the Martian sediments (Eigenbrode et al., 2018).

Hydrous pyrolysis was carried out following the method of Sephton et al. (1998). Briefly, 2 μL samples of 1-chloronaphthalene along with 0.4 mL degassed, deionized water were pyrolyzed in duplicate in 1.8-mL (internal volume) bomblets, assembled from T316 stainless steel and sealed with Swagelock SS-600-C end caps, under varying experimental conditions. Samples were pyrolyzed under an inert atmosphere by loading and sealing the bomblets in a gas bag under nitrogen.

Experimental conditions were varied to test how combinations of variables altered the survivability of 1-chloronaphthalene and any products generated. Samples were subjected to temperatures of 240, 270, 300, or 330 °C for durations of 24 or 72 hr. A procedural blank of deionized water was run at 240 °C for 24 hr to assess the introduction of analytical artifacts.

After the duration of the experiment, the pyrolysis equipment was allowed to cool and the contents of the bomblet were extracted and prepared for analysis via liquid-liquid extraction. The pyrolysate was pipetted from the bomblet to a clean test tube, any remaining pyrolysate was removed from the bomblet by extracting once with 1 mL methanol and 3 times with 1 mL hexane, and these fractions were added to the test tube. 2 mL deionized water and 1 mL excess hexane were added to the test tube containing the extracted pyrolysate; it was shaken to mix and was allowed to separate. The hexane fraction was pipetted off to another clean test tube. This process was completed twice more, and then an aliquot of this hexane solution was transferred to a clean sample vial.

2.2. Gas Chromatography-Mass Spectrometry Analysis

Analyses of the extracted samples were carried out on an Agilent 7890A gas chromatograph interfaced to an Agilent 5975C inert mass selective detector. Separation was performed on a 27 m × 250 μm × 0.25-μm J&W Scientific 122–5532 column. The oven temperature program comprised a start temperature of 40 °C, held for 2 min, followed by a ramp of 5 °C/min to 310 °C where the temperature was held for 14 min. Helium
Table 1
Data Used to Calculate the Kinetics of the Dechlorination of 1-Chloronapthalene

| Sample Name | C0/Cf | k | T (°C) | T/K | 1/T |
|-------------|-------|---|--------|-----|-----|
| 1           | 1.099225651 | 0.001314 | -6.6347 | 240 | 513 | 0.001949 |
| 2           | 1.091816158 | 0.00122 | -6.70888 | 240 | 513 | 0.001949 |
| 7           | 1.290090702 | 0.003538 | -5.64428 | 270 | 543 | 0.001841 |
| 8           | 1.177750243 | 0.002272 | -6.08696 | 270 | 543 | 0.001841 |
| 3           | 2.886992141 | 0.032594 | -3.42364 | 300 | 573 | 0.001745 |
| 4           | 2.525397568 | 0.005079 | -5.28259 | 300 | 573 | 0.001745 |
| 5           | 55.82620032 | 0.055864 | -2.88483 | 330 | 603 | 0.001658 |
| 6           | 53.32437999 | 0.055228 | -2.89629 | 330 | 603 | 0.001658 |

Note: C0/Cf is the ratio of the initial and final concentration of 1-chloronapthalene; k is the reaction rate constant calculated from C0/Cf, assuming a pseudo-first-order reaction; Ln(k) is the natural logarithm of k; and T is the temperature. It is assumed that all 1-chloronapthalene dechlorinates to naphthalene, and that there is a negligible amount of naphthalene present in the initial 1-chloronapthalene spike.

2.3. Kinetics
Hydrous pyrolysis is a useful technique to study the effects of diagenesis on organic compounds as studies have shown that the hydrous pyrolysis of organic-rich source rocks generates products similar to crude oils (Lewan et al., 1979), and it is reasonable to extrapolate the kinetic parameters applied into the conditions experienced in natural systems (Hunt, 1991). Replicating diagenesis of organic compounds in the laboratory via hydrous pyrolysis means that the long reaction periods and slow reaction rates of geological processes must be replaced by short-duration experiments increasing reaction rates by using higher temperatures—a method used by several authors to study the evolution of organic compounds with increasing thermal maturity (e.g., Eglinton & Douglas, 1988; Jaeschke et al., 2008; Koopmans et al., 1996; Peters et al., 1990; Rush et al., 2014). Previous work has shown that the diagenetic and catagenetic breakdown of organic compounds in natural oil generation can be described by simple pseudo-first-order reaction kinetics controlled by initiating free radicals (Lewan, 1997; Lewan et al., 1985). The chemical kinetic parameters derived from the hydrous pyrolysis can be extrapolated to low-temperature geological systems using the Arrhenius equation (Ruble et al., 2001).

\[ \kappa = Ae^{-E/RT} \]

This equation expresses the relationship between k, the reaction rate constant (units/s), and T, the absolute temperature (in K); R is the gas constant (J·mol⁻¹·K⁻¹), E is the activation energy (J/mol), and A is the frequency factor (s⁻¹).

Similar to the precursor organic matter involved in oil generation, chlorohydrocarbons should also thermally dissociate according to specific kinetic parameters which control the degradation reaction, and should result in the increased relative abundance of the degradation products compared to the original chlorohydrocarbon (relative abundances shown in Table 1). For reactions in which a single product (e.g., naphthalene) is derived from the dechlorination of a single starting material (e.g., 1-chloronaphthalene), it is possible to estimate the progress of the equilibrated dechlorination reaction (Düppenbecker & Horsfield, 1990; Landais et al., 1994), and thus derive the reaction rate constant at a specific temperature (Hunt, 1991; Lewan et al., 1985). The kinetic parameters of the aforementioned reaction could thus be derived by rearranging the Arrhenius equation to its linear form to return the Arrhenius constant or frequency factor, A, as well as the activation energy of the reaction, Eₐ.

3. Results
3.1. Breakdown Products
Total ion chromatograms of 1-chloronaphthalene starting material and products from all hydrous pyrolysis experiments are shown in Figures 3 and 4, respectively. Analysis of the 1-chloronaphthalene starting material confirmed its composition as 99.7% 1-chloronaphthalene. Other products found include naphthalene and 1,4-dichloronaphthalene, but were considered to have a negligible contribution to the breakdown products. The only compounds detected in the deionized water blank (pyrolyzed at 240 °C for 24 hr) were siloxanes (from column-bleed) and C₈ to C₁₁ alkanes. The alkanes were observed as low responses in all analyses, suggesting that they are products of minor background contamination.

Hydrous pyrolysis of 1-chloronaphthalene in all cases caused some dechlorination with the major product detected being naphthalene (Figure 5).
3.2. Dechlorination Kinetics of 1-Chloronapthalene

It was seen that there were differences in the products detected following different hydrous pyrolysis experiments with varying temperatures and pressures. The reduced 1-chloronapthalene abundance in the 72-hr experiments compared to the 24-hr experiments indicated that the organic compounds do not reach equilibrium at $T = 24$ hr (full data in Table S1 in the supporting information). In contrast, previous work has shown that the 72-hr experiments had either reached equilibrium, or were at least approximating steady state conditions (Düppenbecker & Horsfield, 1990; Landais et al., 1994). Several studies involving the use of hydrous pyrolysis to study the effects of diagenesis on organic compounds have found that 72-hr experiments adequately mimic the processes that occur during natural maturation (e.g., Eglinton & Douglas,

Figure 4. Representative total ion chromatograms from the hydrous pyrolysis of 1-chloronaphthalene under all conditions: 1-CINap = 1-chloronaphthalene and nap = naphthalene.
Figure 5. Dechlorination of 1-chloronaphthalene to naphthalene and a chlorine ion.

Figure 6. Calculation of kinetic parameters for the dechlorination of 1-chloronaphthalene using the average values from Table 1. A linear relationship between lnk and 1/T suggests that the assumption that reaction kinetics can be approximated by a first-order reaction is valid ($R^2 = 0.9714$), where $\ln A = 18.715$ and $E_a/R = -13155.68$.

4. Discussion

The Sheepbed mudstone is the apparent source of the widest range of “indigenous” chlorinated organic compounds so far detected on Mars (Freissinet et al., 2015). This unit was deposited as part of the Yellowknife Bay Formation, part of the Bradbury Group, in the Late Noachian/Hesperian, 3.8–3.6 Ga (Grotzinger et al., 2015; Thomson et al., 2011). Thus, assuming they were detected in situ and have not migrated from a younger overlying unit, any indigenous organic compounds detected in the Sheepbed mudstone must be at least of this age.

4.1. Sources of Organic Compounds

Organic molecules are expected to be present on Mars from exogenous sources via continual infall of meteorites, comets, or interplanetary dust particles (Flynn, 1996; Gibson, 1992; Sephton, 2012) or formed from indigenous igneous, hydrothermal, or atmospheric processes (Chyba & Sagan, 1992; Konn et al., 2015; Steele et al., 2012; ten Kate, 2010). Additionally there may be products of extant or extinct life, with aqueously deposited Noachian sediments such as the Sheepbed mudstone being an obvious target in the search for the latter.

Based on the delivery of micrometeorite carbon, organic carbon in the Martian regolith has been estimated to be around 60 ppm (Steininger et al., 2012). However, the 60-ppm value was calculated using a large number of uncertainties, including the assumption that no degradation of organic material over time (caused by radiation or atmospheric oxidants) has occurred and so the suggested value is likely an overestimation due to deleterious effects of radiation and oxidants (Benner et al., 2000; Pavlov et al., 2012).

4.2. Noachian Perchlorate Production

Studies on Martian meteorites, with ages up to 4 Ga, suggest that perchlorate formation has been ongoing for most of Martian history on a global scale (Bellucci et al., 2017). Conditions on Mars have been relatively
constant for the Amazonian period and so oxychlorine, and subsequent chlorohydrocarbon, production levels should have been similar to today for at least the last 3 Ga.

Prior to the onset of modern conditions in the late Noachian, despite the luminosity of the young Sun being lower than present-day levels, its short-wavelength fluxes (UV, extreme UV, X-ray, and gamma-ray) were greatly enhanced owing to a much higher level of magnetic activity as a consequence of its faster rotation (Güdel & Kasting, 2011).

The decreased luminosity of the young Sun means that an efficient greenhouse effect is required to explain the relatively mild climate on Noachian Mars and so a thicker atmosphere is hypothesized for this period before the increased extreme UV and X-ray flux stripped it away (Güdel & Kasting, 2011).

On Earth the major atmospheric screen against UV transmission to the surface is ozone (Lacis et al., 1974). On present-day Mars, ozone is only detectable in the atmosphere at mid to high latitudes and is higher during the autumn and winter (Barth & Dick, 1974), although it is still 2 orders of magnitude lower in concentration than on present-day Earth (Barth et al., 1973; Hansen et al., 1997; Perrier et al., 2006). Ozone is not suggested to have ever been a major constituent of the Martian atmosphere with the majority of UV shielding being provided by SO2 and dust, and this would have been highly spatially and temporally variable owing to its volcanic origin (Córdoba-Jabonero et al., 2003).

This increased solar radiation flux is thus suggested to have offset the thicker Noachian atmosphere and allowed the formation of at least atmospheric, if not surface, oxychlorines during the Noachian.

4.3. Survivability of Noachian Chlorohydrocarbons to the Present Day

With a continual meteoritic infall (along with other potential indigenous processes) providing a constant source of new organic molecules, and the continual meteoritic impact gardening, cryoturbation, and past aqueous processes, would have ensured that any produced Noachian chlorohydrocarbons would have likely been preserved in the subsurface.

If chlorohydrocarbons were produced on the surface/shallow subsurface of Mars during this period as hypothesized, then it is possible to model the likelihood of the survival of these chlorinated molecules in the Sheepbed mudstone throughout its diagenetic history using the calculated properties of the reaction and some environmental constraints on the burial conditions. This can be achieved by modeling the percent loss of chlorinated molecules as a result of the dechlorination process by using the integrated form of the first-order rate equation in conjunction with the Arrhenius equation in the following manner:

\[
\frac{[C_t]}{[C_0]} = \exp\left(-\frac{t \cdot A \cdot e^{\frac{E_a}{R} \cdot \frac{1}{T}}}{T}\right)
\]

where \([C_t]\) is the amount of reactant at time \(t\), \([C_0]\) is the amount of reactant at time \(0\), \(A\) is the frequency factor, \(E_a\) is the activation energy as derived from the hydrous pyrolysis results, \(R\) is the gas constant, and \(T\) is the temperature in kelvin.

The model calculates the percent loss of chlorinated molecules at any time \(t\) by iterating over a given time step over a specified length of time to determine the amount of reactant lost in that step, given parameters that dictate the temperature during that time step. It is well understood that the temperature at which the reaction takes place is dependent on the burial and exhumation history of the sediment within which it is hosted. Factors that would affect the temperature of the reaction include the burial and exhumation rates, the geothermal gradient, the surface temperature of the environment, and the time at which the sediment is uplifted. By inferring or estimating the values of the above parameters, it is possible to model the evolution of 1-chloronaphthalene degradation over the course of Martian history, and thus determine the conditions under which chlorinated organic compounds from any specified period of Martian history would have survived to the present day.

There are several notable constraints of the model—the first is that it assumes constant geothermal gradients, surface temperatures, and burial and exhumation rates for the duration of the modeled period. It also assumes that the reaction kinetics derived from the hydrous pyrolysis experiment are fully applicable to the Martian sedimentary environment—most notably, the experiment was conducted with pure 1-chloronaphthalene and in the absence of a solid substrate; different mixtures of chlorinated organic
compounds will almost certainly be controlled by different kinetic parameters, as will the effect of organic-
mineral interactions. In addition, the model assumes a closed system, where no chlorohydrocarbons are
lost by aqueous transport or similar processes.

Based on hydraulic fracture properties, the minimum inferred burial depth of the Sheepbed mudstone is
1 km but most likely around 3 km (Caswell & Milliken, 2017). Assuming equal periods of net deposition
and net erosion, burial and exhumation rates in Gale crater have been estimated as 5 to 35 m and 5 to
29 m per million years, respectively (Borlina et al., 2015). Mars’ Late Noachian/Hesperian geothermal
gradient has been estimated at around 15–20 °C/km (Hahn et al., 2011), with a Late Noachian/Hesperian surface
temperature of around 0 °C (Borlina et al., 2015) giving a burial temperature of 45 to 60 °C; mineralogical observa-
tions suggest a maximum temperature of no more than 75 °C (Bristow et al., 2015; Vaniman et al., 2014).
Based on the assumption of an average sediment density of 2.5 \times 10^{3} \text{ kg/m}^3 (Grotzinger et al., 2015) and
using a value of 3.711 \text{ ms}^2 for Mars’ gravitational acceleration the lithostatic pressure subjected to would
be 27.8 MPa (at 3-km depth).

As these early Mars conditions are poorly constrained it is also reasonable to use modern Martian conditions
with a –50 °C surface temperature (average annual equatorial temperature) and an 8 °C/km geothermal gra-
dient (Hoffman, 2001) for minimum burial temperature constraints.

Figure 7 shows the results of modeling the survivability of 1-chloronaphthalene in the Sheepbed mudstone
under a range of these burial history scenarios.

All panels in Figure 8 have a total burial period of 400 Ma and assume that periods of net deposition/burial
and erosion/exhumation were equal in both duration and rate. The top 3 panels have a Noachian geothermal
gradient of 20 °C/km while the bottom 3 panels have an Amazonian (modern) geothermal gradient of
8 °C/km. Left to right burial rate (and therefore maximum burial depth and subsequent exhumation rate)
are increased between the panels. Each panel plots the effects of various surface temperatures (from the
maximum 0 °C of the Noachian to the –50 °C of average modern-day Mars). We have attempted to model
the change in temperature across Martian geological time by linearly reducing surface temperatures for all
modeled parameters to Amazonian levels (–50 °C) within 1,500 Ma of deposition. This corresponds to

Figure 7. Survivability of 1-chloronaphthalene in the Sheepbed mudstone from deposition to the present day under a range of possible surface temperature (ST), burial and uplift rate (BR), and geothermal gradient (GG) conditions. This simulation assumes that the chloronaphthalene compounds were buried for a total of 400 Ma, including exhumation time, and were modeled over 3.8 Ga with a time step of 1 Ma. Note that the periods of net deposition and net erosion (i.e., burial and uplift) in Gale crater have been modeled as equal in length and rate.
temperatures reaching present-day levels 2.5 Ga ago, an assumption we believe is valid given the uncertainty of Martian temperature variations.

Model data (Figure 7) suggest that the survivability of 1-chloronaphthalene is strongly dependent on the conditions it is subjected to, especially with regards to surface temperature. For example, all 1-chloronaphthalene is lost when modeled with a (Noachian) surface temperature of 0 °C in all scenarios except for one with an extremely low burial rate and geothermal gradient. While there are scenarios that result in the survival of chloronaphthalene through to the present day (Figure 7), many of these are highly

Figure 8. Survival of 1-chloronaphthalene under Noachian or Amazonian environmental conditions. 1-Chloronaphthalene is shown to be far more survivable under Amazonian conditions compared to Noachian conditions, with approximately 80% of chlorinated compounds retained after 400 Ma even in the harshest conditions.
unlikely given our knowledge of Martian environmental conditions. For example, good survivability (>50% 1-chloronaphthalene survival) occurs with Noachian surface temperatures less than −30 °C (243 K) at all but the highest burial rates and even with the high Noachian geothermal gradient. However, Noachian surface temperatures below 0 °C (273 K) would be unrealistic under the oft proposed warm and wet climate of Noachian Mars (Davis et al., 2016; Squyres & Kasting, 1994).

Figure 8 compares realistic condition sets for both the Noachian and Amazonian while varying the burial/exhumation rates. It is clear that under Noachian conditions (0 °C surface temperature and 20 °C/km geothermal gradient), 1-chloronaphthalene is rapidly destroyed during the initial stages of burial and diagenesis and would not survive to the present day for detection. In contrast, under Amazonian conditions (−25 °C surface temperature and 8 °C/km geothermal gradient), 1-chloronaphthalene survivability is good, even at the highest burial rates/depths proposed for the Sheepbed mudstone.

Our data suggest that any chlorohydrocarbons detected in the Sheepbed mudstone, or any other Noachian units with a similar burial history, cannot be indigenous to the unit in its current molecular architecture. The 0-m/Ma burial rate is unrealistic as the Sheepbed mudstone has a minimum burial depth of 1 km. The low stability of chlorinated hydrocarbons under Noachian conditions thus supports the hypothesis that these molecules are a product of sample analysis on Mars.

A more in-depth model of burial under Noachian conditions supports this hypothesis of modern chlorohydrocarbon formation during analysis. Figure 9 shows that under Noachian environmental conditions and a burial history relevant to Gale crater (10-m/Ma burial rate), all codeposited 1-chloronaphthalene buried greater than 2 km would have been lost within 2 Ga. As the likely burial depth of Gale crater sediments is 3 km, this would suggest that MSL cannot expect to detect indigenous chlorinated molecules within the current sediment sequence in Gale crater, especially at 150–300-ppb levels at which chlorobenzene has been detected (Freissinet et al., 2015). However, the models also suggest that chloronaphthalene buried less than 1 km can survive to the present day—although 99.41% of 1-chloronaphthalenes buried at 1 km are lost by the Amazonian, this number decreases to 94.86% when buried to a maximum depth of 500 m. Assuming a chloronaphthalene detection limit of 10 ppb, only 1.7 ppm of indigenous Noachian 1-chloronaphthalene is required to be detectable if buried to a depth of 1 km. Thus, as Curiosity continues its transect upward through the sedimentary sequence in Gale crater, mudstones in the Murray formation and elsewhere in lower Mount Sharp that are younger and may have been less deeply buried than those of the Sheepbed mudstone (Caswell & Milliken, 2017) may contain detectable indigenous chlorinated organic compounds.
Units from the current Amazonian period are also likely to contain less diagenetically altered organic molecules, and organic compounds found in these units could potentially have surviving chlorine bonds; this is due to present-day environmental and diagenetic conditions that are more favorable to their survival.

Despite the preservation of chlorinated organic molecules being theoretically possible in Amazonian sediments, other factors make the survival of such compounds more unlikely than the models suggest. Organic molecules need to be buried rapidly and deeply enough to be protected from radiation. While a few millimeters of coverage is enough to protect from UV and X-ray radiation (Cockell & Raven, 2004), galactic and cosmic rays (GCRs and SCRs) can penetrate down to 1–2 m below the surface to destroy organic compounds down to this depth (Pavlov et al., 2012). Irradiation will drastically decrease the abundance of organic molecules in the shallow subsurface both preburial and postexposure. For the aforementioned potential survival and detection of chlorinated hydrocarbons at ≤1-km burial depth, at least 3% of the 60 ppm organic carbon estimated to be in the Martian regolith (Steininger et al., 2012) would have to be chlorinated and survive irradiation and oxidation both prior and subsequent to chlorination.

It has now been shown that nonchlorinated organic molecules were able to survive the diagenetic (and radiative) history of Gale crater through the detection of macromolecular organic matter indigenous to the lower Murray mudstone (Eigenbrode et al., 2018). Lower levels of perchlorate in these sediments, around 10X less than those of the Sheepbed Mudstone (Sutter et al., 2017), have likely aided both the nonoxidation and nonchlorination (only minor chlorobenzene was detected) of these organic molecules during thermal decomposition analysis methods (Royle et al., 2018).

5. Conclusions

Any attempts to understand organic compounds detected in the Sheepbed mudstone through geologic time must take into account their burial by several kilometers and the associated increased temperature and pressure to which they have been subjected to because of this.

Due to the likelihood of increased surface temperatures and geothermal gradient on ancient Mars, the chances of indigenous Late Noachian/Hesperian chlorinated organic compounds surviving to the present day, given the deep burial history of the Sheepbed mudstone, are very low.

Chlorinated organic molecules detected in the Sheepbed mudstone almost certainly must have derived from chlorination during pyrolysis as previously hypothesized. However, we do not propose a source for the organic carbon, and our data neither support nor disprove the idea of an indigenous Martian source of the organic carbon.

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