

Reply to Comment by F. Kenig, L. Chou, and D. J. Wardrop on “Evaluation of the Tenax Trap in the Sample Analysis at Mars Instrument Suite on the Curiosity Rover as a Potential Hydrocarbon Source for Chlorinated Organics Detected in Gale Crater” by Miller et al., 2015

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Roger Summons, Kristen Miller, Benjamin Kotrc, Imene Belmahadi, Arnaud Buch, et al.. Reply to Comment by F. Kenig, L. Chou, and D. J. Wardrop on “Evaluation of the Tenax Trap in the Sample Analysis at Mars Instrument Suite on the Curiosity Rover as a Potential Hydrocarbon Source for Chlorinated Organics Detected in Gale Crater” by Miller et al., 2015. *Journal of Geophysical Research. Planets*, Wiley-Blackwell, 2019, 124 (2), pp.648-650. 10.1029/2018JE005641 . insu-02083375

HAL Id: insu-02083375

<https://hal-insu.archives-ouvertes.fr/insu-02083375>

Submitted on 26 Apr 2019

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JGR Planets

REPLY

10.1029/2018JE005641

This article is a reply to comment by Kenig et al. (2019), <https://doi.org/10.1029/2018JE005606>.

Key Points:

- Kenig et al. (2019) speculate on the chemical structures and subsequent fate of two unknown compounds produced during repetitive laboratory testing of the Tenax TA polymer used in the SAM instrument on board the Curiosity Rover
- They further speculate that Tenax TA decomposition products are the source of chlorobenzene detected by SAM in experiments on Mars
- Multiple lines of evidence show that chlorobenzene identified by SAM in Cumberland samples comes from an indigenous carbon source including Evolved Gas Analysis experiments that do not involve any sample contact with Tenax TA

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Citation:

Summons, R. E., Miller, K. E., Kotrc, B., Belmahadi, I., Buch, A., Eigenbrode, J. L., et al (2019). Reply to Comment by F. Kenig, L. Chou, and D. J. Wardrop on “Evaluation of the Tenax trap in the Sample Analysis at Mars instrument suite on the Curiosity rover as a potential hydrocarbon source for chlorinated organics detected in Gale Crater” by Miller et al., 2015. *Journal of Geophysical Research: Planets*, 124, 648–650. <https://doi.org/10.1029/2018JE005641>

Received 16 APR 2018

Accepted 11 JAN 2019

Accepted article online 28 JAN 2019

Published online 14 FEB 2019






Author Contributions:

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(continued)

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Abstract Kenig et al. comment on our 2015 reporting of laboratory analog experiments aimed at testing the stability of the hydrocarbon trap material used in the Sample Analysis on Mars (SAM) instrument on board the Curiosity Rover operating in Gale Crater on Mars. They propose chemical structures for some decomposition products of the Tenax TA polymer when it is exposed at high temperatures to the Cl₂ and O₂ gases formed by the thermal decomposition of perchlorate. Further, Kenig et al. propose that these decomposition products accumulate and then react further in cooler downstream sections of the SAM analytical pipeline to produce the chlorobenzene that was detected in the Cumberland mudstone of Gale Crater. However, numerous experiments conducted in the laboratory show that Tenax TA decomposition products only appear after repeated exposure to much higher levels of Cl₂ and O₂ than those seen by the flight instrument. Moreover, the sequence of chlorobenzene detections during gas chromatography-mass spectrometry experiments conducted on Mars cannot be explained by Tenax TA decomposition, nor can the detection of chlorobenzene in Evolved Gas Analysis experiments that involve pathways devoid of Tenax TA. Kenig et al. are incorrect in their assertion that Tenax TA decomposition products can account for the chlorobenzene detected on Mars by SAM.

Plain Language Summary Calcium and magnesium salts of chlorate and perchlorate have been detected in surface sediments on Mars. The presence of these compounds, which emit corrosive gases when heated to high temperatures, can potentially compromise experiments aimed at detecting organic carbon compounds in Mars sediments. Perchlorate decomposition products also have the potential to damage components, namely the hydrocarbon trap, used in the construction of the Sample Analysis on Mars on instrument the Curiosity rover. In earlier work, we evaluated this possibility and provided evidence that the hydrocarbon trap was stable unless exposed to high concentrations of corrosive gases far beyond those that would be seen by the instrument operating on Mars. Experiments conducted by the SAM instrument have detected several organic compounds, including chlorobenzene, which cannot be explained by decomposition of organic materials carried on flight instrument. In particular, chlorobenzene was detected in the Cumberland mudstone in experiments that used pathways that did not include exposure to a hydrocarbon trap.

The discovery of highly oxidizing oxychlorine compounds in the Mars regolith (Hecht et al., 2009) evoked many questions concerning the consequences of heating sediment samples to high temperatures during efforts to detect in situ organic matter with equipment on board the Viking and Curiosity landed missions to Mars. Although chlorates and perchlorates and their hydrates are relatively stable under Mars ambient temperatures, oxygen and chlorine along with water are produced when these compounds are heated to decomposition. At temperatures in the pyrolysis ovens of the Viking landers and the Curiosity rover, the oxygen and chlorine have the potential to combust or chlorinate coproduced small, volatile organic compounds and otherwise interact with other materials present in the analytical system downstream from

Writing – review & editing: Roger E. Summons

the ovens. Miller et al. (2015) used laboratory simulations to study the impact of perchlorate pyrolysis products on Tenax TA, an aromatic polymer that is a component of the hydrocarbon trap used in gas chromatography-mass spectrometry (GC-MS) experiments of the Sample Analysis on Mars (SAM) instrument on board the Curiosity Rover. The aim of these simulations was to determine to what extent the trap material was stable after repeated use and whether or not any of the organics detected by SAM could be formed from the trap material rather than be derived from any organic that may be present in the samples.

In essence, these experiments, which were conducted on laboratory instruments at the Massachusetts Institute of Technology customized for SAM-like operations, examined how pyrolysis products of Mars analogue soils composed of olivine sand that was spiked with calcium perchlorate, magnesium perchlorate, or ferric iron chloride differed when operated with and without a hydrocarbon trap. When the trap was in place, the principal organic products comprised benzene, toluene, benzoic acid, phthalic anhydride, and small amounts of chlorobenzene. Moreover, the abundances of these decomposition products, together with HCl, varied in direct proportion to the amounts of chlorine-containing salt used in each SAM simulation experiment.

When tested almost to destruction through repeated exposures to high concentrations of perchlorate decomposition products, some unidentified higher molecular weight Tenax decomposition products, denoted A1 and A2, were detected. No additional work was conducted to determine the identity of these compounds because they only appeared in significant abundance after hundreds of experiments (Figures 3 and 6 of Miller et al., 2015). Further, if formed during experiments on Mars, A1 and A2 would have condensed in cooler regions of the SAM manifold and never have been detected by the SAM GC-MS experiment due to their low volatility. Accordingly, it was determined that the chlorobenzene and other chlorinated hydrocarbons detected by SAM in numerous analyses of the Cumberland mudstone in Gale Crater on Mars were not related to the hydrocarbon trap and must have originated from the Cumberland sample (Freissinet et al., 2015).

In their comment on the work of Miller et al. (2015) Kenig et al. (2019) tentatively identified A1 and A2 as a rearranged monomer and a chlorinated monomer, respectively, of Tenax TA. These assignments were largely based on similarities in the published mass spectra of A1 and 4-phenyldibenzofuran and on the presence of chlorine-containing fragment ions in the spectrum of A2. Kenig et al. went on to speculate that further decomposition of these products might have led to high chlorobenzene backgrounds in SAMs GC-MS experiments. While it is true that the mass spectrum of phenyldibenzofuran in the National Institute of Standards and Technology library is similar to A1, the structural assignment of A2 is tentative but logical. We agree that A2 is a chlorine-containing species and that this chlorine likely resides on the same phenyl moiety at the position previously occupied by an ether oxygen, that is, the ether bond through which Tenax TA monomers were polymerized. This rationalization is consistent with results of a second study by Miller and coauthors that showed high temperature chlorination reactions taking place when perchlorate is copolyolyzed with simple aromatic precursors and affording products where chlorine substitutes at sites that were originally functionalized (Miller et al., 2016).

Although we do not disagree with the structural assignments of A1 and A2, there are numerous reasons why the remainder of the Kenig et al. comment is incorrect in its claim that Tenax TA decomposition products A1 and A2 contribute to the SAM background during experiments on Mars. In the first instance, and as noted above, individual simulation experiments showed that the amounts of Tenax TA degradation products A1 and A2 are directly related to the amount of HCl produced from the decomposing salt. The data supporting this are presented as cross-plots of HCl abundance versus product abundance where HCl is a proxy for the amount of Cl₂ produced by the sample (Figure 5 of Miller et al., 2015). In contrast, in SAM's analysis of Cumberland samples, there was no relationship between the abundances of chlorobenzene and either O₂ or HCl produced. Second, Kenig et al. offer no evidence for the claim that chlorobenzene observed at Cumberland could come from the pyrolysis of A1 and A2 produced from the trap decomposition and subsequently accumulated in the gas lines. A1 and A2 only became evident over time and after hundreds of experiments on the same trap and with perchlorate concentrations far above those present in Mars samples (Figures 3 and 6 of Miller et al., 2015). Third, chlorination of aromatic compounds takes place via electrophilic substitution, which typically requires catalysis by a Lewis acid (Vollhardt & Schore, 2009). However, either or both electrophilic substitution or radical chain mechanisms could operate in the vapor phase

and at high (>500 °C) temperatures (Procaccini et al., 2003; Vollhardt & Schore, 2009) such as those present in the pyrolysis oven. Accordingly, chlorination of any condensed (i.e., liquid or solid) Tenax TA decomposition products would be imperceptibly slow in the absence of a Lewis acid catalyst and at transfer line temperatures that are in the vicinity of 135 °C. Fourth, in SAM experiments on Mars, rather than observe an increase in chlorobenzene following analyses of Cumberland samples, chlorobenzene reverted to background levels.

Finally, should there be any doubt concerning chlorobenzene originating from in situ organic matter present in the Cumberland samples, we refer Kenig et al. to the detection of chlorobenzene when SAM was operated in evolved gas analysis mode (Freissinet et al., 2015). While the path to the GC column used for the Cumberland analysis experiments goes via the hydrocarbon trap with Tenax TA, there is no hydrocarbon trap on the pathway to evolved gas analysis (Glavin et al., 2013) and, hence, no opportunity for Cl₂ or HCl to interact with Tenax TA.

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