ACS EARTH AND SPACE CHEMISTRY

Open Access
This article is licensed under CC-BY 4.0

http://pubs.acs.org/journal/aesccq
Article

# Organic Preservation Pathway for UV and Perchlorate-Rich Parts of Mars: Oxidative Polymerization of Organic Compounds on Iron(III)-Rich Goethite

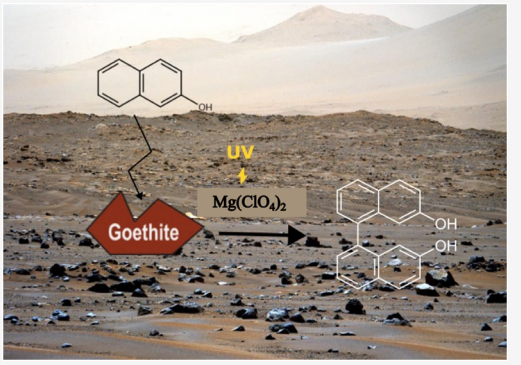
John J. Gumbley,* Jonathan S. Watson, and Mark A. Sephton

Cite This: https://doi.org/10.1021/acsearthspacechem.6c00202

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

**ABSTRACT:** Perchlorate salts are widespread on Mars and are commonly regarded as a potential barrier to organic preservation because ultraviolet (UV) irradiation may activate perchlorate photochemistry and generate destructive oxychlorine species. Despite this, multiple rover missions have identified indigenous organic compounds in Martian sediments, indicating that preservation pathways remain incompletely understood. Previous work showed that Fe(III)-rich minerals such as goethite can promote oxidative coupling of aromatic organic compounds under Mars-analog conditions, producing higher molecular weight products that should be more resistant to degradation. Here, we examine whether UV-irradiated perchlorate suppresses mineral-mediated oxidative polymerization of 2-naphthol adsorbed onto goethite under those same conditions. Across organic loadings of 0.5 to 10 wt %, oxidative coupling proceeded in the presence of magnesium perchlorate, yielding dimers and higher-order oligomers. Yields were not measurably suppressed on experimentally relevant hour time scales. Our results provide experimental constraints on the competition between perchlorate photochemistry and mineral surface oxidative coupling under dry, Mars-analog UV conditions. This may represent a potential preservation mechanism in perchlorate-bearing, iron-rich Martian sediments.




**KEYWORDS:** *goethite, 2-naphthol, BINOL, oxidative coupling, perchlorate photochemistry, UV irradiation, mineral-organic interactions, Mars geochemistry*

## INTRODUCTION

Perchlorate salts were first identified in Martian soils by the Phoenix lander, which detected magnesium and calcium perchlorate at concentrations of approximately 0.4 to 0.6 wt % in the northern plains.[1] Subsequent measurements by landed missions and orbital observations have confirmed that oxychlorine species are widespread components of the Martian regolith rather than localized anomalies.[2−5] Atmospheric modeling and terrestrial analogue studies suggest Martian perchlorates likely form through UV-driven atmospheric oxidation of chlorine-bearing species followed by dry deposition and long-term accumulation under hyperarid conditions.[6]

The recognition of perchlorates has had a profound impact on interpretations of Martian organic chemistry. Pyrolysis experiments conducted by the Viking landers failed to detect indigenous organic compounds, a result long interpreted as evidence for an absence of organics at the Martian surface.[7,8] It has been proposed that perchlorates were present at the Viking landing sites and likely decomposed during thermal analysis, generating reactive chlorine- and oxygen-bearing species capable of oxidizing or chlorinating organic matter during heating.[9,10] Subsequent results from the Sample Analysis at Mars (SAM) instrument suite aboard the Curiosity rover, including the detection of chlorinated hydrocarbons and macromolecular organic carbon, have demonstrated both the complicating influence of perchlorates during analysis and the persistence of indigenous organic matter in Martian sediments.[11−13]

Beyond analytical artifacts, perchlorates have also been implicated as potential agents of organic degradation on the Martian surface.[14] Laboratory studies have shown that perchlorate-bearing materials exposed to simulated Martian ultraviolet (UV) radiation can exhibit enhanced oxidative or bacteriocidal effects under specific irradiation regimes.[15,16] Other work has demonstrated that the effects of UV-irradiated oxychlorine salts depend strongly on molecular structure and local reaction environment rather than the mere presence of

Received: June 15, 2026
Revised: October 7, 2026
Accepted: October 30, 2026

ACS Publications
© XXXX The Authors. Published by American Chemical Society



Downloaded from pubs.acs.org/aesccq/article-pdf/doi/10.1021/acsearthspacechem.6c00202/6908328/acsearthspacechem.6c00202.pdf by guest on 06 November 2026

perchlorates. For example, Liu and Kounaves showed that amino acid degradation under simulated Martian conditions varied according to substrate identity, water availability and the nature of the associated salt.[16] In combination with Mars' thin $CO_2$ atmosphere and limited ozone shielding, these findings have reinforced concerns regarding long-term organic preservation on the surface of Mars.[15,17,18] However, the published studies primarily address bulk oxidative effects and do not explicitly consider rapid mineral-surface reactions that may sequester organic compounds at iron-rich interfaces. Further, the coexistence of widespread perchlorates and preserved indigenous organic matter on Mars presents an apparent paradox.

Mars is not only perchlorate-rich but also iron-rich. Iron oxyhydroxide minerals such as goethite, hematite and ferrihydrite are widespread and form through aqueous alteration processes in environments that were plausibly habitable in early Martian history.[19−21] Iron(III)-bearing mineral surfaces provide chemically active environments capable of adsorbing organic molecules and mediating redox reactions.[20,22,23] On Earth, such minerals have been shown to promote oxidative coupling and polymerization of phenolic and aromatic organic compounds, producing higher-molecular-weight material that may exhibit greater kinetic persistence over geological time.[24−28]

For this study, 2-naphthol was selected as a model aromatic compound because its Fe(III)-mediated oxidative coupling chemistry is well characterized. Oxidative coupling of 2-naphthol to 1,1′-bi-2-naphthol (BINOL) using $FeCl_3$ under solid-state conditions was reported by Toda et al. in 1989.[24] The reaction pathway is shown in Figure 1. Oxidation of 2-naphthol by Fe(III), with concomitant reduction to Fe(II), generates a delocalized radical intermediate that undergoes C−C coupling to form BINOL.[24,29] Previous work demonstrated that Fe(III) in goethite can mediate this transformation under Mars-analogue conditions, producing BINOL and higher-order oligomeric and polymeric products through mineral surface-associated redox processes.[23] What remains unresolved is the extent to which this oxidative coupling pathway persists in the presence of perchlorate under UV irradiation or whether perchlorate photochemistry suppresses mineral surface-mediated organic transformation. The present study, therefore, examines the competition between these processes under dry, Mars-analog UV conditions.

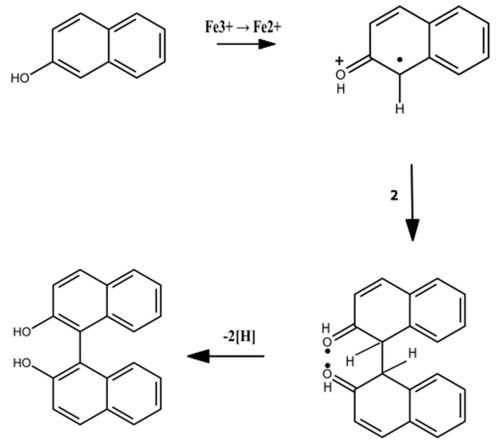



**Figure 1.** Fe(III)-mediated oxidative coupling of 2-naphthol to BINOL, adapted from Toda et al. (1989).

## EXPERIMENTAL SECTION

### Materials and Sample Preparation

2-Naphthol ($C_{10}H_8O$; Acros Organics, 98%), goethite ($\alpha$-FeO(OH); Sigma-Aldrich; ∼35 wt % Fe), and 1,1′-bi-2-naphthol (BINOL; Sigma-Aldrich, 99%) were used as received. Perchlorate was added as magnesium perchlorate ($Mg(ClO_4)_2$; Sigma-Aldrich, ACS reagent grade) to perchlorate-bearing samples at ∼1 wt % relative to the total solid mass. This concentration was selected to reflect reported perchlorate abundances in Martian regolith while maintaining consistency across experiments.[1]

To ensure consistency with previous oxidative polymerization experiments, homogenized bulk mixtures were prepared for all samples. Individual solid components were first ground separately in a clean agate mortar and pestle. For perchlorate experiments, goethite, 2-naphthol and perchlorate were then combined and gently ground together before final homogenization with a clean microspatula. Goethite−2-naphthol mixtures were prepared at 10, 5, 2.5, 1, and 0.5 wt % 2-naphthol, with perchlorate fixed at ∼1 wt % in all perchlorate-bearing samples.

Approximately 30 mg of each homogenized mixture was loaded into clean borosilicate glass tubes (4.0 mm i.d.), including UV-transparent Schott borosilicate 8347 for irradiation experiments. Tubes were cooled in liquid nitrogen and flame-sealed under vacuum (∼1 Pa). For each experimental condition, triplicate tubes were prepared.

Dark procedural controls were prepared by wrapping sealed tubes in aluminum foil and storing them at ambient laboratory temperature for 24 h to account for nonirradiative background reactions. UV irradiation experiments were performed for 3 h using a Ushio Xenon Short Arc Lamp (UXL-306) positioned approximately 20 cm from the samples. A Newport 61945 water filter containing deionized water was placed in the optical path to remove infrared radiation and minimize thermal artifacts while approximating solar irradiation conditions (Supporting Information (SI) Figure S1). The spectral output of the complete irradiation system was measured over the 200−875 nm range (Figure S2). Preliminary monitoring of foil-wrapped control tubes exposed within the irradiation chamber indicated no substantial temperature increase attributable to lamp heating. The 3 h irradiation period was selected as a short-duration Mars analogue consistent with previous xenon lamp simulation studies and designed to represent active irradiation intervals rather than continuous surface exposure.[18,30] Following treatment, all tubes were stored at 4 °C prior to extraction.

### Organic Extraction

Organic compounds from both perchlorate-bearing and nonperchlorate samples used for quantitative analysis were extracted directly with dichloromethane (DCM) which separates the organic fraction from the inorganic mineral and salt residue.[31−33]

After treatment, sealed tubes were cracked open and the contents rinsed three times into clean glass test tubes with dichloromethane (DCM). Each extraction step consisted of vortex mixing (30 s), sonication (3 min), and centrifugation (4 min at 400 relative centrifugal force, hereafter rcf). The solvent was decanted through quartz wool packed Pasteur pipettes to remove mineral particulates.

Combined extracts were evaporated under a gentle stream of dry nitrogen at 40 °C using a block heater. The residue was transferred to a 5 mL measuring cylinder and brought to volume with DCM. Aliquots were transferred to 2 mL autosampler vials and adjusted to a final volume of 0.5 mL, targeting an organic concentration of approximately 80 ng $\mu L^{-1}$ prior to analysis.

Immediately prior to GC-FID analysis, a deuterated internal standard consisting of equal masses of eicosane-$d_{42}$ and naphthalene-$d_8$ was added to each sample vial. Quantification of 2-naphthol loss and oxidative coupling products was achieved by comparison of peak-area ratios between compounds of interest and the internal standard.

Downloaded from pubs.acs.org/aesccq/article-pdf/doi/10.1021/acsearthspacechem.6c00202/6908328/acsearthspacechem.6c00202.pdf by guest on 06 November 2026


https://doi.org/10.1021/acsearthspacechem.6c00202
ACS Earth Space Chem. XXXX, XXX, XXX−XXX

A liquid−liquid extraction procedure was used separately for independently prepared UV-irradiated goethite−2-naphthol−magnesium perchlorate samples to remove soluble perchlorate from mineral residues prior to Py-GC-MS analysis. Mineral residues from 0.5 and 10 wt % samples were prepared using this procedure. This approach addresses analytical challenges previously encountered during Viking and SAM pyrolysis experiments on Mars where oxychlorine-driven oxidation and chlorination reactions can artificially modify detected organic product distributions.[9,12]

After treatment, the sealed tubes were cracked open and the solid contents transferred into large, clean glass test tubes fitted with ground-glass stoppers. To recover any organic material adhering to the inner walls of the original reaction tubes, each cracked tube was rinsed three times with DCM and the rinsates were added to the corresponding stoppered test tube.

Subsequently, 20 mL of deionized (DI) water was added to each stoppered tube. Tubes were gently agitated by hand and allowed to settle, promoting dissolution of perchlorate salts into the aqueous phase. Owing to the low aqueous solubility and hydrophobicity of both 2-naphthol and BINOL relative to magnesium perchlorate, significant partitioning of target organic compounds into the aqueous phase was considered minimal.

Following phase separation, 10 mL of DCM was added to each tube. The mixture was gently agitated by hand and allowed to settle to permit partitioning of organic compounds into the organic solvent. The DCM subnatant was withdrawn using a clean, long glass pipet and transferred to a round-bottom flask (RBF) via a glass syringe packed with DCM-cleaned quartz wool, topped with anhydrous sodium sulfate ($Na_2SO_4$) to remove residual water. This extraction procedure was repeated three times for each sample. Following the final extraction, the aqueous and DCM phases were removed and the washed mineral residue was dried at 25 °C under a gentle stream of nitrogen prior to Py-GC-MS analysis.

### Gas Chromatography Analysis

Quantitative analysis was performed using gas chromatography−flame ionization detection (GC-FID) on an Agilent 6890N GC system. Samples were injected splitless (1 μL) at an injector temperature of 270 °C. Separation was achieved using a ZB-5 capillary column (30 m × 0.25 mm × 0.25 μm). The GC oven temperature program was: 40 °C (2 min), ramp at 5 °C $min^{-1}$ to 310 °C, hold for 14 min.

To assess the presence of higher-molecular-weight products (trimers or polymers), selected samples were analyzed using a high-temperature GC-FID method. A DB-5HT column (15 m × 0.25 mm × 0.10 μm) was used with splitless injection at 280 °C. The oven temperature program was: 40 °C (2 min), ramp at 10 °C $min^{-1}$ to 330 °C, hold for 11 min.

The shorter column length and elevated maximum temperature enabled elution of less volatile macromolecular products that may not elute under standard GC conditions.

Compound identification was confirmed by gas chromatography−mass spectrometry (GC-MS) using an Agilent 7890 GC coupled to a 5975 MSD operating in electron ionization mode (70 eV). Injection was splitless at 270 °C, using a DB-5MS ultrainert column (30 m × 0.25 mm × 0.25 μm). The oven temperature program matched that used for standard GC-FID analyses.

Mass spectra were compared against the NIST mass spectral library with peak identities confirmed by comparison with 1,1′-bi-2-naphthol (BINOL) authentic standard (Sigma-Aldrich ≥ 99% purity).

Control experiments lacking either goethite or perchlorate, together with nonirradiated controls, were performed under identical experimental conditions. Additional control experiments and chromatographic data are presented in the SI.

## RESULTS

Under Mars-analogue UV irradiation, mixtures of goethite and 2-naphthol exhibit transformation of the parent compound to higher-molecular-weight products. Gas chromatographic analyses show a decrease in the 2-naphthol monomer signal accompanied by the appearance of peaks corresponding to the 2-naphthol dimer following UV exposure. GC-FID quantitative monomer recovery and dimer yields for all experimental conditions are summarized in Table 1. The GC-FID measurements quantify the extractable 2-naphthol recovered and BINOL produced relative to the initial 2-naphthol loading. Higher-order products may not be quantitatively represented where they remain associated with the mineral residue or do not elute under the GC-FID conditions used.

**Table 1. Comparison of Oxidative Polymerization of 2-Naphthol on Goethite under Mars-Analog UV Irradiation in the Absence and Presence of Magnesium Perchlorate[a]**

| | no perchlorate | | perchlorate added | |
|---|---|---|---|---|
| 2-naphthol (wt %) | 2-naphthol recovered (%) | BINOL produced (%) | 2-naphthol recovered (%) | BINOL produced (%) |
| 10 | 30 | 5 | 33 | 6 |
| 5 | 52 | 13 | 35 | 10 |
| 2.5 | 21 | 28 | 13 | 25 |
| 1 | 3 | 31 | 25 | 32 |
| 0.5 | 1 | 20 | 0.2 | 36 |

[a]Values are taken after GC-FID analysis using an internal standard and represent the percentage of 2-naphthol recovered after irradiation and the percentage converted to the BINOL dimer.

Across the range of organic loadings investigated (0.5 to 10 wt %), goethite−2-naphthol systems irradiated in the presence of magnesium perchlorate yield monomer recoveries and dimer signals comparable to those observed in perchlorate-free systems. Figures 2 and S5 present GC-MS chromatograms for direct comparison of perchlorate-bearing and perchlorate-free samples subjected to identical conditions. Table 1 shows no systematic difference in monomer recovery or dimer yield attributable to perchlorate addition across the experimental conditions investigated.

In perchlorate−2-naphthol mixtures lacking goethite, no BINOL dimer peak or higher-order oxidative coupling products were detected following UV irradiation at any loading investigated (Figure S3). The chromatograms are dominated by the parent 2-naphthol peak and no new peaks attributable to oxidative coupling products are observed under these conditions.

Recovery of 2-naphthol was below 100% across the experimental conditions and the combined quantities of recovered 2-naphthol and BINOL therefore do not constitute a complete organic mass balance. Pyrolysis-GC-MS analysis of postextraction goethite residues identified aromatic degradation products (Figure S6). We do not identify specific intact higher-molecular-weight structures but these products provide qualitative evidence for retained nonextractable organic material.

Control experiments showed that UV irradiation of 2-naphthol alone produced no detectable BINOL. UV irradiation of 2-naphthol in the presence of magnesium perchlorate but without goethite similarly produced no detectable BINOL, with 2-naphthol remaining substantially recovered. Nonirradiated goethite−2-naphthol−perchlorate controls produced detectable BINOL. Results from the nonirradiated controls are presented in Figure S4.

Downloaded from pubs.acs.org/aesccq/article-pdf/doi/10.1021/acsearthspacechem.6c00202/6908328/acsearthspacechem.6c00202.pdf by guest on 06 November 2026


https://doi.org/10.1021/acsearthspacechem.6c00202
ACS Earth Space Chem. XXXX, XXX, XXX−XXX

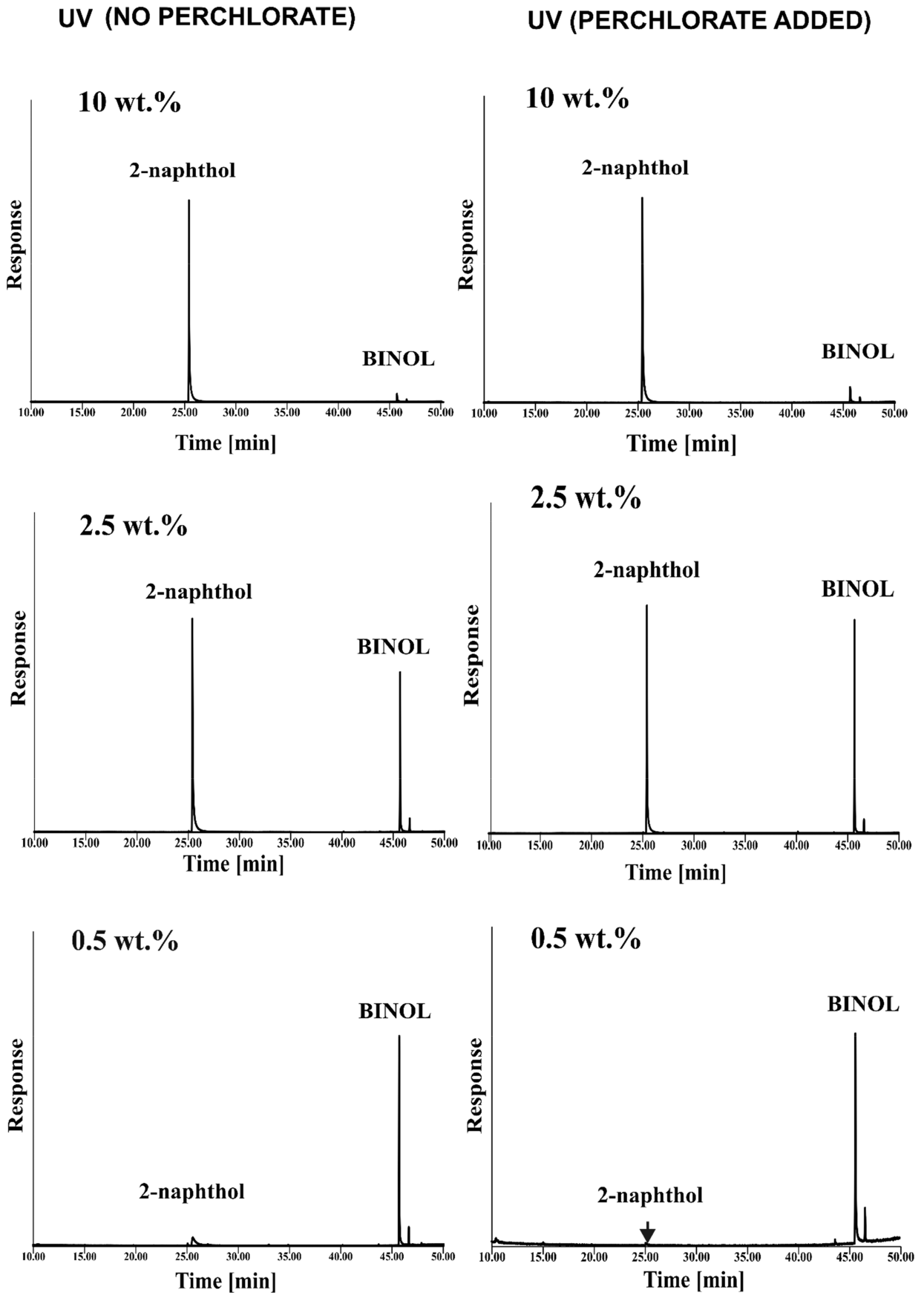



**Figure 2.** Representative GC-MS total ion chromatograms of mixtures of goethite and 2-naphthol at 10, 2.5, and 0.5 wt % following UV irradiation (3 h) in the absence (left column) and presence (right column) of magnesium perchlorate. Chromatograms show the parent 2-naphthol peak and

Downloaded from pubs.acs.org/aesccq/article-pdf/doi/10.1021/acsearthspacechem.6c00202/6908328/acsearthspacechem.6c00202.pdf by guest on 06 November 2026


https://doi.org/10.1021/acsearthspacechem.6c00202
ACS Earth Space Chem. XXXX, XXX, XXX−XXX

**Figure** 2. continued

formation of the 1,1′-bi-2-naphthol (BINOL) dimer under both conditions. These plots illustrate product identity and qualitative similarity between systems; quantitative comparisons of 2-naphthol recovery and BINOL yield are provided in Table 1.

## DISCUSSION

The assumption that perchlorate photochemistry may control the fate of organic compounds on the Martian surface arises from the widespread detection of oxychlorine salts, the intense ultraviolet (UV) radiation environment of the red planet and laboratory demonstrations of enhanced oxidative or bactericidal effects in perchlorate-bearing materials exposed to UV irradiation.[1,15,16,34,35] The results presented here do not contradict these observations. Rather they place quantitative constraints on the conditions and time scales under which perchlorate-derived pathways dominate aromatic organic transformation under UV Martian conditions.

Under the dry, vacuum-sealed configuration investigated here perchlorate alone does not produce detectable transformation of 2-naphthol on hour time scales under Mars-analogue UV irradiation. In contrast, oxidative polymerization of 2-naphthol proceeds readily when the organic compound is associated with iron-rich goethite. The presence of perchlorate does not measurably alter monomer recovery or BINOL dimer yield across the experimental conditions investigated.

However, extractable BINOL abundance (Table 1) likely represents only a partial measure of total organic transformation. Higher-molecular-weight products may resist solvent extraction and remain strongly mineral-associated. As well, larger oligomeric or macromolecular products may be retained within the chromatographic column and therefore fail to elute during the analytical runtime employed here. Pyrolysis−GC−MS analysis of DCM-exhausted mineral residues further supports the presence of retained higher molecular weight organic material within the goethite matrix (Figure S6). Incomplete recovery reflects the use of nominal starting loadings and losses during sample handling, transfer and extraction. The experiments were not designed to provide a complete organic mass balance and GC-FID quantifies the solvent-extractable compounds recovered by the analytical procedure rather than the total organic carbon present in each sample.

We employ 2-naphthol as a model compound rather than as a proxy for the behavior of all aromatic organics. 2-naphthol is particularly amenable to Fe(III)-mediated oxidative coupling and forms the readily identifiable BINOL product.[24] Reactivity depends on molecular structure and reaction conditions, and other aromatic compounds may therefore undergo coupling at different rates. Magnesium perchlorate is also hygroscopic and perchlorate deliquescence has been proposed as a plausible mechanism for transient brine formation on Mars.[36] Although the samples investigated here were nominally dry, some uptake of ambient moisture cannot be excluded. Importantly, oxidative coupling persisted in the presence of magnesium perchlorate under these conditions. The behavior of other organic substrates and more extensively hydrated or brine-forming systems remains an area for future investigation.

The control experiments further constrain the origin of the observed transformation. UV irradiation of 2-naphthol alone produced no detectable BINOL while irradiation of 2-naphthol with magnesium perchlorate in the absence of goethite produced no detectable transformation of the organic compound. In contrast, oxidative coupling occurred when goethite was present and was not discernibly suppressed by the addition of perchlorate. Thus, whatever photochemical transformation of perchlorate may occur under these irradiation conditions, its effects are insufficient over the 3 h experimental period either to produce detectable transformation of 2-naphthol in the absence of goethite or to measurably inhibit its goethite-mediated oxidative coupling.

In principle, Mars-relevant UV photons are energetically capable of driving perchlorate photochemistry.[15,37] However, transmission of UV to the Martian surface is selective. $CO_2$ absorbs strongly below ∼200 nm, with attenuation extending into the 200−250 nm range even in Mars' thin atmosphere, whereas longer wavelength near-UV radiation (≥250 nm) is transmitted more efficiently and constitutes a substantial fraction of surface UV flux.[38−40]

Order-of-magnitude calculations and justification of UV flux assumptions are provided in Section S1. As discussed there, perchlorate is a weak chromophore at longer wavelengths and exhibits low single-photon quantum yields above ∼200−250 nm. Even under conservative upper-bound assumptions, radical production is therefore expected to remain kinetically constrained on hour time scales.[41] These constraints are amplified further in regolith-like materials where UV penetration is limited by grain size, mineralogy and packing geometry. Estimated clear-sky Martian surface UV fluxes across the 200−400 nm range are approximately ∼50 W $m^{-2}$ (∼5 mW $cm^{-2}$) but effective attenuation occurs over micrometer- to millimeter-scale depths in granular materials.[18,30,42] Only a small fraction of perchlorate present in bulk regolith is directly exposed to incident UV flux at any given time.

In terrestrial hyperarid analogues such as the Atacama Desert, natural perchlorate accumulations occur through analogous atmospheric processes. These coexist with mineral refuges and preserved organic material despite prolonged UV exposure.[6,43,44] These systems demonstrate that perchlorate presence alone does not inevitably preclude long-term preservation in dry surface environments. The present experiments represent a short-time scale snapshot. They demonstrate that oxidative coupling proceeds in the presence of perchlorate during the 3 h irradiation period. The behavior of the system during prolonged Martian surface exposure was beyond the scope of the present study.

Iron(III)-bearing minerals such as goethite may also provide localized chemical environments that strongly favor mineral-surface reactions.[22] Aromatic compounds readily adsorb to Fe-oxyhydroxide surfaces, forming strong mineral−organic associations at redox-active surface sites.[22,45] Previous experimental work has shown that phenolic compounds adsorb directly to Fe oxide surfaces, where oxidation rates increase with surface area and proceed via surface-controlled electron transfer pathways.[46,47] Under irradiation, surface-associated Fe(III)/Fe(II) cycling may further accelerate oxidative coupling.[23] UV irradiation in these systems likely acts primarily as an energetic trigger that facilitates electron transfer within preorganized mineral−organic complexes rather than generating large fluxes of oxidizing radicals.[41,47]

Downloaded from pubs.acs.org/aesccq/article-pdf/doi/10.1021/acsearthspacechem.6c00202/6981328/acsearthspacechem.6c00202.pdf by guest on 06 November 2026



https://doi.org/10.1021/acsearthspacechem.6c00202
ACS Earth Space Chem. XXXX, XXX, XXX−XXX

Concern over the influence of perchlorates on Martian organic detection arose during thermal extraction experiments performed by instruments such as the Viking lander's GC-MS and the Sample Analysis at Mars (SAM) suite aboard the Curiosity rover where perchlorate decomposition generated reactive chlorine species that were capable of chlorinating and fragmenting organic molecules.[9,11,12] These high-temperature analytical effects should not be conflated with near-ambient surface processes. Instead, the present experiments isolate a nonthermal regime in which UV irradiation and mineral-surface chemistry govern the fate of organic compounds. Previous studies have demonstrated that the effects of UV-irradiated oxychlorine salts depend strongly on the nature of the organic substrate and local reaction environment. For example, UV irradiation of amino acids in perchlorate-bearing systems can produce markedly different degradation outcomes depending on molecular structure and matrix composition.[16] The present study extends this concept to Fe(III)-mediated oxidative coupling at mineral surfaces, where mineral−organic interactions may favor preservation pathways over detectable perchlorate-driven degradation on hour time scales. Previous studies also suggest that chlorate may represent an important oxychlorine oxidant on Mars,[2,3] although chlorate was not directly examined here and warrants future investigation.

Organic compounds found on Mars may derive from multiple sources including exogenous infall, endogenous geochemical synthesis and ancient sedimentary environments like those identified in Gale and Jezero craters.[13,48,49] Interplanetary dust particles (IDPs) and micrometeorites are estimated to deliver ∼200−300 tonnes $yr^{-1}$ of organic carbon to the Martian surface.[50−52] A large proportion of this infall material already exists as insoluble macromolecular organic matter, although smaller soluble fractions composed of aromatic and functionalized compounds are also present and remain susceptible to mineral-surface transformation.[53−55] The oxidative coupling pathways examined here are therefore most relevant to lower-molecular-weight fractions and may contribute to the gradual accumulation of kerogen-like, mineral-associated macromolecular carbon within iron-rich Martian sediments.[22,25,56]

This study builds on previous experimental work demonstrating iron(III)-mediated oxidative polymerization of aromatic compounds under Mars-relevant conditions.[23] The results presented here demonstrate a plausible pathway by which aromatic material could be transformed into more kinetically persistent macromolecular material upon contact with iron(III)-rich minerals even in the presence of perchlorate salts on the UV irradiated surface of Mars. Preserved organic assemblages recovered from iron-rich, perchlorate-bearing environments may, therefore, contain signatures of dimeric, oligomeric or otherwise mineral-associated aromatic products. The present work provides a testable hypothesis for future in situ investigations and returned-sample analyses.

## CONCLUSION

The characterization of perchlorates as either chemically "inert" or universally destructive oversimplifies the complexity of Martian surface organic chemistry. Instead, this study indicates the behavior of perchlorate under Mars-relevant UV radiation must be considered within the context of activation pathways, reaction kinetics, mineralogical environment and competing organic transformation processes. Our findings challenge simplified models of a uniformly "self-sterilizing" Martian surface in which photochemistry dominates the fate of organic compounds.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspacechem.6c00202.

Additional experimental details, energetic calculations, GC-FID and GC-MS chromatograms, pyrolysis-GC-MS data, and supporting figures (PDF)

## AUTHOR INFORMATION


### Corresponding Author

**John J. Gumbley** − *Department of Earth Science and Engineering, Imperial College London, London SW7 2AZ, U.K.*; orcid.org/0009-0002-7367-6354; Email: j.gumbley23@imperial.ac.uk

### Authors

**Jonathan S. Watson** − *Department of Earth Science and Engineering, Imperial College London, London SW7 2AZ, U.K.*

**Mark A. Sephton** − *Department of Earth Science and Engineering, Imperial College London, London SW7 2AZ, U.K.*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsearthspacechem.6c00202


### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

M.A.S.'s work was supported by UK Space Agency grants ST/V002732/1, ST/V006134/1, and ST/Y006194/1. For the purpose of open access, the author has applied a Creative Commons Attribution (CC BY) licence to any Author-Accepted Manuscript version arising.

## REFERENCES


(1) Hecht, M. H.; Kounaves, S. P.; Quinn, R. C.; West, S. J.; Young, S. M. M.; Ming, D. W.; Catling, D. C.; Clark, B. C.; Boynton, W. V.; Hoffman, J.; DeFlores, L. P.; Gospodinova, K.; Kapit, J.; Smith, P. H. Detection of Perchlorate and the Soluble Chemistry of Martian Soil at the Phoenix Lander Site. *Science* **2009**, *325* (5936), 64−67.

(2) Kounaves, S. P.; Carrier, B. L.; O'Neil, G. D.; Stroble, S. T.; Claire, M. W. Evidence of Martian Perchlorate, Chlorate, and Nitrate in Mars Meteorite EETA79001: Implications for Oxidants and Organics. *Icarus* **2014**, *229*, 206−213.

(3) Kounaves, S. P.; Chaniotakis, N. A.; Chevrier, V. F.; Carrier, B. L.; Folds, K. E.; Hansen, V. M.; McElhoney, K. M.; O'Neil, G. D.; Weber, A. W. Identification of the Perchlorate Parent Salts at the Phoenix Mars Landing Site and Possible Implications. *Icarus* **2014**, *232*, 226−231.

(4) Ojha, L.; Wilhelm, M. B.; Murchie, S. L.; McEwen, A. S.; Wray, J. J.; Hanley, J.; Massé, M.; Chojnacki, M. Spectral Evidence for Hydrated Salts in Recurring Slope Lineae on Mars. *Nat. Geosci.* **2015**, *8* (11), 829−832.

(5) Sutter, B.; Quinn, R. C.; Archer, P. D.; Glavin, D. P.; Glotch, T. D.; Kounaves, S. P.; Osterloo, M. M.; Rampe, E. B.; Ming, D. W. Measurements of Oxychlorine Species on Mars. *Int. J. Astrobiol.* **2017**, *16* (3), 203−217.


Downloaded from pubs.acs.org/aesccq/article-pdf/doi/10.1021/acsearthspacechem.6c00202/6908328/acsearthspacechem.6c00202.pdf by guest on 06 November 2026

(6) Catling, D. C.; Claire, M. W.; Zahnle, K. J.; Quinn, R. C.; Clark, B. C.; Hecht, M. H.; Kounaves, S. Atmospheric Origins of Perchlorate on Mars and in the Atacama *J. Geophys. Res. Planets* 2010; Vol. *115* E1 DOI: 10.1029/2009JE003425.
(7) Biemann, K.; Oro, J.; Toulmin, P., III; Orgel, L. E.; Nier, A. O.; Anderson, D. M.; Simmonds, P. G.; Flory, D.; Diaz, A. V.; Rushneck, D. R.; Biller, J. E.; Lafleur, A. L. The Search for Organic Substances and Inorganic Volatile Compounds in the Surface of Mars. *J. Geophys. Res. 1896–1977* **1977**, *82* (28), 4641–4658.
(8) Royle, S. H.; Oberlin, E.; Watson, J. S.; Montgomery, W.; Kounaves, S. P.; Sephton, M. A. Perchlorate-Driven Combustion of Organic Matter During Pyrolysis-Gas Chromatography-Mass Spectrometry: Implications for Organic Matter Detection on Earth and Mars. *J. Geophys. Res. Planets* **2018**, *123* (7), 1901–1909.
(9) Navarro-González, R.; Vargas, E.; de la Rosa, J.; Raga, A. C.; McKay, C. P. Reanalysis of the Viking Results Suggests Perchlorate and Organics at Midlatitudes on Mars *J. Geophys. Res. Planets* 2010; Vol. *115* E12 DOI: 10.1029/2010JE003599.
(10) Biemann, K.; Bada, J. L. Comment on "Reanalysis of the Viking Results Suggests Perchlorate and Organics at Midlatitudes on Mars" by Rafael Navarro-González et Al. *J. Geophys. Res. Planets* 2011; Vol. *116* E12 DOI: 10.1029/2011JE003869.
(11) Glavin, D. P.; Freissinet, C.; Miller, K. E.; Eigenbrode, J. L.; Brunner, A. E.; Buch, A.; Sutter, B.; Archer, P. D., Jr.; Atreya, S. K.; Brinckerhoff, W. B.; Cabane, M.; Coll, P.; Conrad, P. G.; Coscia, D.; Dworkin, J. P.; Franz, H. B.; Grotzinger, J. P.; Leshin, L. A.; Martin, M. G.; McKay, C.; Ming, D. W.; Navarro-González, R.; Pavlov, A.; Steele, A.; Summons, R. E.; Szopa, C.; Teinturier, S.; Mahaffy, P. R. Evidence for Perchlorates and the Origin of Chlorinated Hydrocarbons Detected by SAM at the Rocknest Aeolian Deposit in Gale Crater. *J. Geophys. Res. Planets* **2013**, *118* (10), 1955–1973.
(12) Freissinet, C.; Glavin, D. P.; Mahaffy, P. R.; Miller, K. E.; Eigenbrode, J. L.; Summons, R. E.; Brunner, A. E.; Buch, A.; Szopa, C.; Archer, P. D., Jr.; Franz, H. B.; Atreya, S. K.; Brinckerhoff, W. B.; Cabane, M.; Coll, P.; Conrad, P. G.; Des Marais, D. J.; Dworkin, J. P.; Fairén, A. G.; François, P.; Grotzinger, J. P.; Kashyap, S.; ten Kate, I. L.; Leshin, L. A.; Malespin, C. A.; Martin, M. G.; Martin-Torres, F. J.; McAdam, A. C.; Ming, D. W.; Navarro-González, R.; Pavlov, A. A.; Prats, B. D.; Squyres, S. W.; Steele, A.; Stern, J. C.; Sumner, D. Y.; Sutter, B.; Zorzano, M.-P.; MSL Science Team. Organic Molecules in the Sheepbed Mudstone, Gale Crater, Mars. *J. Geophys. Res. Planets* **2015**, *120* (3), 495–514.
(13) Eigenbrode, J. L.; Summons, R. E.; Steele, A.; Freissinet, C.; Millan, M.; Navarro-González, R.; Sutter, B.; McAdam, A. C.; Franz, H. B.; Glavin, D. P.; Archer, P. D.; Mahaffy, P. R.; Conrad, P. G.; Hurowitz, J. A.; Grotzinger, J. P.; Gupta, S.; Ming, D. W.; Sumner, D. Y.; Szopa, C.; Malespin, C.; Buch, A.; Coll, P. Organic Matter Preserved in 3-Billion-Year-Old Mudstones at Gale Crater, Mars. *Science* **2018**, *360* (6393), 1096–1101.
(14) Rzymski, P.; Losiak, A.; Heinz, J.; Szukalska, M.; Florek, E.; Poniedziałek, B.; Kaczmarek, Ł.; Schulze-Makuch, D. Perchlorates on Mars: Occurrence and Implications for Putative Life on the Red Planet. *Icarus* **2024**, *421*, No. 116246.
(15) Wadsworth, J.; Cockell, C. S. Perchlorates on Mars Enhance the Bacteriocidal Effects of UV Light. *Sci. Rep.* **2017**, *7* (1), No. 4662.
(16) Liu, D.; Kounaves, S. P. Degradation of Amino Acids on Mars by UV Irradiation in the Presence of Chloride and Oxychlorine Salts. *Astrobiology* **2021**, *21*, 793 DOI: 10.1089/ast.2020.2328.
(17) Kminek, G.; Bada, J. L. The Effect of Ionizing Radiation on the Preservation of Amino Acids on Mars. *Earth Planet. Sci. Lett.* **2006**, *245* (1), 1–5.
(18) Dartnell, L. R. Ionizing Radiation and Life. *Astrobiology* **2011**, *11* (6), 551–582.
(19) Ehlmann, B. L.; Mustard, J. F.; Murchie, S. L. Geologic Setting of Serpentine Deposits on Mars *Geophys. Res. Lett.* 2010; Vol. *37* 6 DOI: 10.1029/2010GL042596.
(20) Ehlmann, B. L.; Edwards, C. S. Mineralogy of the Martian Surface. *Annu. Rev. Earth Planet. Sci.* **2014**, *42*, 291–315.
(21) Carter, J.; Loizeau, D.; Mangold, N.; Poulet, F.; Bibring, J.-P. Widespread Surface Weathering on Early Mars: A Case for a Warmer and Wetter Climate. *Icarus* **2015**, *248*, 373–382.
(22) Watson, J. S.; Sephton, M. A. Heat, Aromatic Units, and Iron-Rich Phyllosilicates: A Mechanism for Making Macromolecules in the Early Solar System. *Astrobiology* **2015**, *15*, 787–792.
(23) Gumbley, J. J.; Lau, N.; Watson, J. S.; Sephton, M. A. Oxidative Polymerization of Organic Compounds in the Presence of Iron-Bearing Minerals: Implications for Organic Preservation on Mars. *ACS Earth Space Chem.* **2026**, *10*, 1493.
(24) Toda, F.; Tanaka, K.; Iwata, S. Oxidative Coupling Reactions of Phenols with iron (III) chloride in the Solid State. *J. Org. Chem.* **1989**, *54* (13), 3007–3009.
(25) Lalonde, K.; Mucci, A.; Ouellet, A.; Gélinas, Y. Preservation of Organic Matter in Sediments Promoted by Iron. *Nature* **2012**, *483* (7388), 198–200.
(26) Moore, O. W.; Curti, L.; Woulds, C.; Bradley, J. A.; Babakhani, P.; Mills, B. J. W.; Homoky, W. B.; Xiao, K.-Q.; Bray, A. W.; Fisher, B. J.; Kazemian, M.; Kaulich, B.; Dale, A. W.; Peacock, C. L. Long-Term Organic Carbon Preservation Enhanced by Iron and Manganese. *Nature* **2023**, *621* (7978), 312–317.
(27) Wallis, P. J.; Booth, K. J.; Patti, A. F.; Scott, J. L. Oxidative Coupling Revisited: Solvent-Free, Heterogeneous and in Water. *Green Chem.* **2006**, *8* (4), 333.
(28) Kleber, M.; Bourg, I. C.; Coward, E. K.; Hansel, C. M.; Myneni, S. C. B.; Nunan, N. Dynamic Interactions at the Mineral–Organic Matter Interface. *Nat. Rev. Earth Environ.* **2021**, *2* (6), 402–421.
(29) Choi, H.; Suh, S.; Kang, H. Advances in Exploring Mechanisms of Oxidative Phenolic Coupling Reactions. *Adv. Synth. Catal.* **2024**, *366* (21), 4347–4384.
(30) Carrier, B. L.; Abbey, W. J.; Beegle, L. W.; Bhartia, R.; Liu, Y. Attenuation of Ultraviolet Radiation in Rocks and Minerals: Implications for Mars Science. *J. Geophys. Res. Planets* **2019**, *124* (10), 2599–2612.
(31) Gran, U.; Wennerström, O.; Westman, G. Stereoselective Reductions with Macrocyclic NADH Models. *Tetrahedron:Asymmetry* **2000**, *11* (14), 3027–3040.
(32) Badocco, D.; Di Marco, V.; Venzo, A.; Frasconi, M.; Frezzato, D.; Pastore, P. Ion Pair Formation between Tertiary Aliphatic Amines and Perchlorate in the Biphasic Water/Dichloromethane System. *J. Phys. Chem. B* **2017**, *121* (40), 9403–9410.
(33) Vázquez, J.; Šindelář, V. Phase-Transfer Extraction for the Fast Quantification of Perchlorate Anions in Water. *RSC Adv.* **2019**, *9* (61), 35452–35455.
(34) Cockell, C. S.; Bush, T.; Bryce, C.; Direito, S.; Fox-Powell, M.; Harrison, J. P.; Lammer, H.; Landenmark, H.; Martin-Torres, J.; Nicholson, N.; Noack, L.; O'Malley-James, J.; Payler, S. J.; Rushby, A.; Samuels, T.; Schwendner, P.; Wadsworth, J.; Zorzano, M. P. Habitability: A Review. *Astrobiology* **2016**, *16* (1), 89–117.
(35) Zhang, X.; Berkinsky, D.; Markus, C. R.; Chitturi, S. R.; Grieman, F. J.; Okumura, M.; Luo, Y.; Yung, Y. L.; Sander, S. P. Reaction of Methane and UV-Activated Perchlorate: Relevance to Heterogeneous Loss of Methane in the Atmosphere of Mars. *Icarus* **2022**, *376*, No. 114832.
(36) Gough, R. V.; Chevrier, V. F.; Baustian, K. J.; Wise, M. E.; Tolbert, M. A. Laboratory Studies of Perchlorate Phase Transitions: Support for Metastable Aqueous Perchlorate Solutions on Mars. *Earth Planet. Sci. Lett.* **2011**, *312* (3), 371–377.
(37) Quinn, R. C.; Martucci, H. F. H.; Miller, S. R.; Bryson, C. E.; Grunthaner, F. J.; Grunthaner, P. J. Perchlorate Radiolysis on Mars and the Origin of Martian Soil Reactivity. *Astrobiology* **2013**, *13* (6), 515–520.
(38) Cockell, C. S.; Raven, J. A. Zones of Photosynthetic Potential on Mars and the Early Earth. *Icarus* **2004**, *169* (2), 300–310.
(39) Patel, M. R.; Zarnecki, J. C.; Catling, D. C. Ultraviolet Radiation on the Surface of Mars and the Beagle 2 UV Sensor. *Planet. Space Sci.* **2002**, *50* (9), 915–927.
(40) Hu, R.; Cahoy, K.; Zuber, M. T. Mars Atmospheric CO2 Condensation above the North and South Poles as Revealed by Radio

Downloaded from pubs.acs.org/aesccq/article-pdf/doi/10.1021/acsearthspacechem.6c00202/6908328/acsearthspacechem.6c00202.pdf by guest on 06 November 2026

Occultation, Climate Sounder, and Laser Ranging Observations *J. Geophys. Res. Planets* 2012; Vol. *117* E7 DOI: 10.1029/2012JE004087.
(41) Sauer, M. C.; Shkrob, I. A.; Lian, R.; Crowell, R. A.; Bartels, D. M.; Chen, X.; Suffern, D.; Bradforth, S. E. Electron Photodetachment from Aqueous Anions. 2. Ionic Strength Effect on Geminate Recombination Dynamics and Quantum Yield for Hydrated Electron. *J. Phys. Chem. A* **2004**, *108* (47), 10414−10425.
(42) Schuerger, A. C.; Mancinelli, R. L.; Kern, R. G.; Rothschild, L. J.; McKay, C. P. Survival of Endospores of *Bacillus Subtilis* on Spacecraft Surfaces under Simulated Martian Environments: *Icarus* **2003**, *165* (2), 253−276.
(43) Thomas, D. J.; Boling, J.; Boston, P. J.; Campbell, K. A.; McSpadden, T.; McWilliams, L.; Todd, P. Extremophiles for Ecopoiesis: Desirable Traits for and Survivability of Pioneer Martian Organisms. *Gravitational Space Biol.* **2006**, *19*, 91−104.
(44) Azua-Bustos, A.; González-Silva, C.; Fairén, A. G. The Atacama Desert in Northern Chile as an Analog Model of Mars. *Front. Astron. Space Sci.* **2022**, *8*. DOI: 10.3389/fspas.2021.810426.
(45) Parikh, S. J.; Chorover, J. FTIR Spectroscopic Study of Biogenic Mn-Oxide Formation by Pseudomonas Putida GB-1. *Geomicrobiol. J.* **2005**, *22* (5), 207−218.
(46) McBride, M. B. Adsorption and Oxidation of Phenolic Compounds by Iron and Manganese Oxides. *Soil Sci. Soc. Am. J.* **1987**, *51* (6), 1466−1472.
(47) Kung, K.-H.; McBride, M. B. Electron Transfer Processes Between Hydroquinone and Iron Oxides. *Clays Clay Miner.* **1988**, *36* (4), 303−309.
(48) Stern, J. C.; Malespin, C. A.; Eigenbrode, J. L.; Webster, C. R.; Flesch, G.; Franz, H. B.; Graham, H. V.; House, C. H.; Sutter, B.; Archer, P. D.; Hofmann, A. E.; McAdam, A. C.; Ming, D. W.; Navarro-Gonzalez, R.; Steele, A.; Freissinet, C.; Mahaffy, P. R. Organic Carbon Concentrations in 3.5-Billion-Year-Old Lacustrine Mudstones of Mars. *Proc. Natl. Acad. Sci. U.S.A.* **2022**, *119* (27), No. e2201139119.
(49) Sharma, S.; Roppel, R. D.; Murphy, A. E.; Beegle, L. W.; Bhartia, R.; Steele, A.; Hollis, J. R.; Siljeström, S.; McCubbin, F. M.; Asher, S. A.; Abbey, W. J.; Allwood, A. C.; Berger, E. L.; Bleefeld, B. L.; Burton, A. S.; Bykov, S. V.; Cardarelli, E. L.; Conrad, P. G.; Corpolongo, A.; Czaja, A. D.; DeFlores, L. P.; Edgett, K.; Farley, K. A.; Fornaro, T.; Fox, A. C.; Fries, M. D.; Harker, D.; Hickman-Lewis, K.; Huggett, J.; Imbeah, S.; Jakubek, R. S.; Kah, L. C.; Lee, C.; Liu, Y.; Magee, A.; Minitti, M.; Moore, K. R.; Pascuzzo, A.; Rodriguez Sanchez-Vahamonde, C.; Scheller, E. L.; Shkolyar, S.; Stack, K. M.; Steadman, K.; Tuite, M.; Uckert, K.; Werynski, A.; Wiens, R. C.; Williams, A. J.; Winchell, K.; Kennedy, M. R.; Yanchilina, A. Diverse Organic-Mineral Associations in Jezero Crater, Mars. *Nature* **2023**, *619* (7971), 724−732.
(50) Carrillo-Sánchez, J. D.; Gómez-Martín, J. C.; Bones, D. L.; Nesvorný, D.; Pokorný, P.; Benna, M.; Flynn, G. J.; Plane, J. M. C. Cosmic Dust Fluxes in the Atmospheres of Earth, Mars, and Venus. *Icarus* **2020**, *335*, No. 113395.
(51) Flynn, G. J. The Delivery of Organic Matter from Asteroids and Comets to the Early Surface of Mars. *Earth Moon Planets* **1996**, *72* (1), 469−474.
(52) Bland, P. A.; Smith, T. B. Meteorite Accumulations on Mars. *Icarus* **2000**, *144* (1), 21−26.
(53) Sephton, M. A.; Wright, I. P.; Gilmour, I.; de Leeuw, J. W.; Grady, M. M.; Pillinger, C. T. High Molecular Weight Organic Matter in Martian Meteorites. *Planet. Space Sci.* **2002**, *50* (7), 711−716.
(54) Fox, A. C.; Eigenbrode, J. L.; Freeman, K. H. Radiolysis of Macromolecular Organic Material in Mars-Relevant Mineral Matrices. *J. Geophys. Res. Planets* **2019**, *124* (12), 3257−3266.
(55) Pizzarello, S. The Chemistry of Life's Origin: A Carbonaceous Meteorite Perspective. *Acc. Chem. Res.* **2006**, *39* (4), 231−237.
(56) Hedges, J. I.; Keil, R. G. Sedimentary Organic Matter Preservation: An Assessment and Speculative Synthesis. *Mar. Chem.* **1995**, *49* (2), 81−115.

Downloaded from pubs.acs.org/aesccq/article-pdf/doi/10.1021/acsearthspacechem.6c00202/6908328/acsearthspacechem.6c00202.pdf by guest on 06 November 2026