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Key Points:
- Perchlorate/chlorate on Mars is produced on chloride-bearing mineral surfaces
- Intermediate radicals during ClO_4^- production can destroy simple organics
- Production mechanism suggests oxychlorines are global and ubiquitous

Supporting Information:
- Text S1, Figures S1–S4, and Tables S1–S3

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The origins of perchlorate in the Martian soil

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Abstract Perchlorate (ClO_4^-) has been detected on Mars, but its production and distribution are unclear. Mechanisms requiring atmospheric chlorine are insufficient for measured concentrations. We conducted studies under Mars conditions using halite (NaCl) alone, soil simulants consisting of silica (SiO_2), Fe_2O_3, Al_2O_3, and TiO_2. After 170 h irradiation, samples analyzed by ion chromatography (IC) showed ClO_4^- and ClO_3^- present in all samples. When SiO_2 was added, yield increased from 2 to 42 nmol and 0.4 to 2.6 nmol, respectively. We attribute this to SiO_2 and metal oxides acting as photocatalysts, generating O_2^- radicals from O_2 which react with chloride. Results show ClO_4^- and ClO_3^- can be produced photochemically on Cl minerals without atmospheric chlorine or aqueous conditions, and explain high concentration of ClO_4^- and ClO_4^-/Cl^- ratios detected by Phoenix. They provide evidence that its distribution on Mars is dictated by distribution of chlorine and provide insight into the oxidizing nature of the soil and its potential effects on organics.

1. Introduction

Perchlorate (ClO_4^-) was first detected in Martian soil by the Wet Chemistry Laboratory (WCL) on board the Phoenix Mars lander at ~0.6 wt % [*Kounaves et al.,* 2010; *Hecht et al.,* 2009]. Perchlorate or another oxychlorine phase has subsequently been indicated at similar levels by the Sample Analysis at Mars instrument on the Mars Science Laboratory (MSL) Curiosity [*Glavin et al.,* 2013]. Perchlorate and chlorate (ClO_3^-) have also been found in Martian meteorite EETA79001 [*Kounaves et al.,* 2014a] and have been proposed as a possible explanation for the presence of chlorinated hydrocarbons detected by Viking as well as MSL [*Navarro-Gonzalez et al.,* 2010; *Freissinet et al.,* 2015; *Ming et al.,* 2014].

The discovery of perchlorate on the Martian surface has had profound implications for both the detection and survivability of organics on Mars. Based solely on organics delivered by meteorites, chondrites and interplanetary dust particles at a postulated rate of 2.4×10^8 g/yr [*Flynn,* 1996; *Pizzarello et al.,* 2006], the organic carbon content of the Martian regolith should be between ~0.2 and 2.9 wt % [*Flynn and McKay*, 1990]. The lack of their definitive detection has been typically ascribed to either an instrumental inability to detect them [*Glavin et al.,* 2013; *Navarro-Gonzalez et al.,* 2010; *Biemann et al.,* 1977] or their indigenous destruction by one or more powerful oxidants [*Yen et al.,* 2000; *Zent and McKay*, 1994]. Several of the oxychlorine intermediates likely to be present during perchlorate production or reduction are known to severely degrade organics on Earth and are in fact often used for remediation of organics in drinking water. Such intermediary oxidants would cause similar degradation of organics on the Martian surface. In addition, the combination of a continuously present source of oxychlorine oxidants and intermediate radicals, in combination with UV and ionizing radiation [*Stalport et al.,* 2009; *ten Kate et al.,* 2005], may be sufficient to fully oxidize most simple low molecular-weight organics at or near the Martian surface to CO_2.

It has been suggested that production pathways for perchlorate on Mars are similar to Earth, primarily photochemically in the upper atmosphere via oxidation of chlorine by ozone (O_3) [*Catling et al.,* 2010]. Studies have shown, however, that atmospheric production of perchlorate on Mars is insufficient by orders of magnitude to explain the amount found [*Smith et al.,* 2014]. A recent study has shown that carbon dioxide (CO_2)-rich chlorine-bearing ices, exposed to 5 keV electrons that mimic the interaction of energetic secondary electrons produced by galactic cosmic rays (GCR), will produce ClO_3- and ClO_2-bearing high-order chlorine oxides [*Kim et al.,* 2013]. On the other hand, it has also been shown that Martian perchlorate is radiolytically degraded and destroyed over time by ionizing radiation [*Quinn et al.,* 2013]. However, other mechanisms may also be responsible for the production of such high levels of perchlorate [*Schuttlefield et al.*, 2011]. Our results show that oxychlorines can be produced globally and continuously on Mars through heterogeneous reactions of chloride-bearing mineral surfaces with oxidants produced either atmospherically

or photochemically under current Martian environmental conditions and without invoking an aqueous phases or GCR. Our results show a mechanism that would be widespread over the entire Martian surface and through cryoturbation and meteoric reworking also at depth. The input by this mechanism, along with input from others, could explain the high concentration of perchlorate detected on Mars, as well as the high ClO_4^-/Cl^- ratios detected at the Phoenix landing site, and provide evidence that the distribution of perchlorate on the Martian surface will be dictated by the geochemical distribution of chlorine-bearing phases. The presence of perchlorate and its oxychlorine precursors and intermediaries on Mars has wide ranging implications in terms of the oxidizing nature of the soil [*Quinn et al.,* 2013], the history of water [*Kounaves et al.,* 2014b], the planet's water cycle, formation of brines [*Hanley et al.,* 2012], and preservation and detection of organics at or near the surface [*Freissinet et al.,* 2015; *Navarro-Gonzalez et al.,* 2010; *Biemann et al.,* 1977], and could serve as an electron acceptor for putative microbes [*Herman and Frankenberger*, 1999; *Zhang et al.,* 2002].

2. Methodology

2.1. Mars Simulation Chamber

The Mars simulation chamber (MSC) consisted of a stainless steel cylindrical chamber with a 25 cm diameter cold plate at the bottom maintained at −15°C, while gases above were at about 0°C. The atmosphere was composed of 95.3% CO_2, 2.8% N_2, 1.8% Ar, and 0.10% O_2 (all ± 2%), delivered at a constant flow rate of 8.25 cm^3/min, and maintained at pressure of 14 mbar. Before the UV lamp was turned on, the MSC was pumped down to remove laboratory ambient gases and water vapor. Relative humidity (RH) in the MSC was measured at < 1% at the start of each experiment. The UV light was provided by a 1000 W xenon-arc lamp through a 22 cm fused silica port on the top of the MSC. The levels of UVC, UVB, and UVA were monitored in situ using a UV spectrophotometer placed on the cold plate next to the samples, and the entire UV spectrum was recorded every 5 min at a resolution of ± 0.10 nm. For each spectrum, irradiance in each wavelength range was integrated and assumed to be constant over that 5 min period. Total dosage of UVA, UVB, and UVC over the entire experiment was determined by summing 5 min intervals, with an uncertainty of ~ 1% for the total UV dosage to account for inconsistencies over each 5 min period.

2.2. Sample Preparation and Irradiation Procedures

The samples exposed in the MSC consisted of (1) halite (NaCl, ≥ 99.0%), (2) halite and ground silica (SiO_2 50–70 mesh), and (3) halite, ground silica, iron (III) oxide (Fe_2O_3, powder < 5 μm, ≥ 99.0%), aluminum oxide (Al_2O_3, powder 10 μm, 99.7%), and titanium dioxide (anatase form, powder, 99.8%). Prior to usage SiO_2, Fe_2O_3, Al_2O3, and TiO_2 were rinsed 5 times with water (Nanopure® 18.2 MΩ-cm) and then dried at ~ 80°C overnight to evaporate the remaining water. Each mineral was weighed out to the nearest 0.1 mg and mixed and homogenized using mortar and pestle. The mixture was spread into a 9 cm diameter Pyrex® dish, resulting in a layer ~ 1.0 mm in thickness. The NaCl was dissolved in 18.2 MΩ-cm water and added to the sample as an aqueous solution. The final sample was then dried overnight at ~ 65°C. Only one sample at a time was exposed in the MSC in order to prevent any cross contamination. Each sample was irradiated for 168 h (7 days) at the end of which the samples were removed and prepared for analysis by ion chromatography (IC).

2.3. Ion Chromatographic Analysis

Each irradiated sample was leached in 25 mL of 18.2 MΩ-cm water for 1 h and filtered through a 0.2 μm sterile filter to prevent any particulates from being introduced into the IC. Excess chloride was removed using a Dionex Ag/H Onguard™ pretreatment cartridge. Extensive tests were performed with these cartridges prior to analysis using the same chloride background as was present in the samples in order to ensure 100% recovery of the chlorate and perchlorate. Once the chloride was removed, the leachate was then injected into the IC for ClO_4^- analysis using a 100 μL sample loop, a Dionex Ionpac™ AS16 analytical column, and an AG16 guard column. The eluent consisted of 35 mM potassium hydroxide and runs at a flow rate of 1.25 mL/min with a suppression current of 175 mA. For the ClO_3^-/ClO_2^- analysis, a 25 μL sample loop, a Dionex Ionpac™ AS18 analytical column, and an AG18 guard column were used. The eluent consisted of 23 mM potassium hydroxide and runs at a flow rate of 1.00 mL/min with a suppression current of 59 mA. The method detection limit for ClO_4^- was ~ 1 ppb in leachate, while the LOQ for ClO_4^- was 2.5 ppb in leachate or 6.25 ppb in the original sample. The method detection limits for ClO_3^- and ClO_2^- were 5 ppb

Table 1. Initial Composition of Samples and Resulting Production of Oxychlorine After Irradiation at Indicated UVC (200–280 nm) Wavelength Range and Total Dosage[a]

	Total Mass(g)	NaCl(g)	SiO_2(g)	Fe_2O_3(g)	Al_2O_3(g)	TiO_2(g)	Total Chloride (mmol)	ClO_3^- Produced (nmol)	ClO_4^- Produced (nmol)	UVC Dosage (J)
1	0.6568 ± 0.0001	0.6568 ± 0.0001	-	-	-	-	11.24 ± 0.01	1.8 ± 0.9	0.4 ± 0.2	108 ± 1%
2	10.0076 ± 0.0001	0.6560 ± 0.0001	9.3516 ± 0.0001	-	-	-	11.22 ± 0.01	41.99 ± 0.03	2.58 ± 0.07	96 ± 1%
3	10.0076 ± 0.0001	0.6560 ± 0.0001	9.3516 ± 0.0001	-	-	-	11.22 ± 0.01	37.90 ± 0.09	1.38 ± 0.07	80 ± 1%
4	9.9972 ± 0.0002	0.6591 ± 0.0001	6.6797 ± 0.0001	1.7953 ± 0.0001	0.7601 ± 0.0001	0.1030 ± 0.0001	11.28 ± 0.01	38.44 ± 1.32	2.18 ± 0.15	84 ± 1%
5	9.9956 ± 0.0002	0.6592 ± 0.0001	6.6784 ± 0.0001	1.7942 ± 0.0001	0.7602 ± 0.0001	0.1036 ± 0.0001	11.28 ± 0.01	30.72 ± 3.42	1.80 ± 0.19	76 ± 1%

[a]All samples were irradiated in a Martian gas mixture that included 0.10% O_2.

in leachate, while the LOQ was 50 ppb in leachate or 125 ppb in the original sample. A calibration curve was run immediately before each sample was analyzed, and peaks were identified based on their retention times.

3. Results and Discussion

Our study was formulated to specifically test the hypothesis that perchlorate can be produced on chloride-bearing mineral surfaces interacting with photochemically generated oxidants under ambient Mars conditions. The Mars simulation chamber (MSC) used for these experiments was configured and calibrated to provide Martian temperatures, pressures, atmospheric composition, and appropriate Mars surface UVA, UVB, and UVC fluxes (Tables S1 and S2, supporting information). Soil simulants consisted of either pure halite (NaCl), halite, and ground silica (SiO_2) or in two cases Fe_2O_3, Al_2O_3, and TiO_2 added at levels consistent with those found in Martian surface fines [*Clark et al.,* 1982] in order to determine if these components enhanced the oxidation of the chloride. After ~170 h of irradiation under Mars conditions, the samples were leached in Nanopure® water to remove any product, and the leachate was then analyzed by ion chromatography (IC) to determine the amounts of chlorite (ClO_2^-), chlorate (ClO_3^-), and perchlorate (ClO_4^-) present in the irradiated samples.

Table 1 shows the amounts of chlorate and perchlorate produced in each sample, as well as the total UVC (200–280 nm) dosage in joules delivered over the course of irradiation. The amounts of perchlorate and chlorate produced by irradiation substantially increased when silica was added to the halite samples, with chlorate increasing about 20 times in concentration (from ~2 to 42 nmol) and perchlorate about 6 times (from ~0.4 to 2.6 nmol). We believe that this is most likely due to the SiO_2 acting as a semiconducting photocatalyst, generating free O_2^- radicals from the O_2 [*Yen et al.,* 2000], which then react with the chloride in the sample. The interaction of UV radiation with the O_2 produces ozone (O_3) as well as O_2^- radicals, both of which may oxidize the chloride. In all cases, the O_2 was delivered to the system via a Mars gas mixture which contained 0.10% O_2 (Table S1 supporting information). The Mars gas mixture did not contain water vapor, but since the relative humidity in the MSC was measured with a limit of detection of $<1\%$, thin films of water on the sample or trace water molecules cannot be ruled out. Water vapor in the presence of UV radiation could be a source for hydroxyl radicals, which could then also play a role in the oxidation process. This would also support proposed mechanisms regarding the oxidation of chloride by oxide minerals in the presence of water, as well as providing evidence that SiO_2 is sufficient as a substrate to promote the reaction despite the fact it has a much larger band gap than TiO_2 [*Schuttlefield et al.,* 2011; *Yen et al.,* 2000]. This may be due to the release of interstitial oxygen from the SiO_2 matrix under the influence of UV radiation [*Salh,* 2011]. Other oxide minerals also tend to contain trapped oxygen that could be released under these conditions. Adding the other oxides, which are possible constituents of Martian surface materials, did not appear to cause any significant difference in production of chlorate or perchlorate. This may be a result of their low concentrations relative to the bulk SiO_2, resulting in limited interaction between them and the chloride particles, but the lack of any decrease in production indicates that they also support the same heterogeneous reactions.

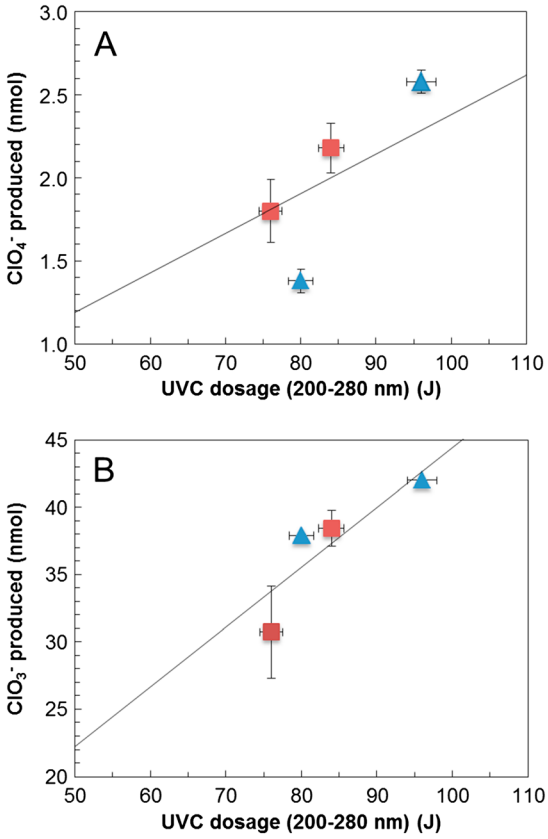

Figure 1. (a) Plot of perchlorate production versus UVC dosage for each sample. (b) Plot of chlorate production versus UVC dosage for each sample. There is a general trend of increasing perchlorate/chlorate production with increasing UVC dosage for each sample. NaCl is not shown due to extremely low production of ClO_3^- and ClO_4^- (see Table 1). The line has been force fitted to zero intercepts. (▲, SiO_2 + NaCl; ■, $SiO_2 + Fe_2O_3 + Al_2O_3 + TiO_2$ + NaCl).

As shown in Figure 1, there is a clear correlation between increasing UVC dosage and increasing perchlorate and chlorate production. This relationship does not exist for UVA, UVB, or total UV dosage (Table S3, supporting information). There is no evidence that visible or infrared radiation result in oxidation of chloride to perchlorate, even in the oxygen-rich environment of Earth, so these wavelengths were not considered. This is expected since, from an energetic point of view, shorter wavelength UVC radiation is of higher energy and results in formation of ozone from O_2. This might also explain why this surface production mechanism has not been observed on Earth, where UVC radiation does not reach the surface, though the observation that the varying isotopic signatures of terrestrial perchlorate may indicate that it may be possible [*Jackson et al.,* 2010]. It is likely that some UVB and/or UVA wavelengths play a role in the oxidation of some intermediate oxychlorine species based on previous experimental work [*Kang et al.,* 2009], but based on the limited data set presented here, it appears that UVC plays a larger role in the overall oxidation of Cl^- to ClO_4^-. In addition, the dependence of perchlorate formation on UVC radiation dosage suggests that perchlorate concentrations will increase over time while chloride concentrations will decrease, explaining perchlorate/chloride ratios found at the Phoenix landing site. These results point to the need for further experiments to better understand the effects of various wavelengths on different steps in the formation process and to determine if the production rate continues at a linear rate or decreases as relative concentrations change.

Higher levels of ClO_3^- versus ClO_4^- were also reported in the EETA79001 Mars meteorite [*Kounaves et al.,* 2014a]. However, there have been no direct measurements made of ClO_3^- in Martian soil. The Phoenix WCL was not able to measure definitive amounts of species such as ClO_3^- or NO_3^- with the Hofmeister sensor because of its 10^3 selectivity of ClO_4^- over all other anions. The WCL measured ~2.5 mM ClO_4^- in solution; however, there could have been as much as 3–6 mM ClO_3^- in solution (being limited by total conductivity and ion balance), but WCL would not have detected it [*Kounaves et al.,* 2010]. There may also have been very little or no ClO_3^- in the Phoenix soil since some of the excess anions were most likely nitrate. So it is possible that, as on Earth, $ClO_4^- \approx ClO_3^-$ or $ClO_3^- > ClO_4^-$ [*Rao et al.,* 2010]. If true, then this would then be similar to ratios produced by O_3 oxidation of adsorbed Cl as reported for laboratory experiments on Earth [*Kang et al.,* 2008].

The detection of perchlorate and chlorate in all irradiated samples, while chlorite was not identified above the LOQ of the IC in any, indicates that chlorite is most likely not a significant intermediate product in the oxidation of the chloride to perchlorate under the simulated Martian conditions used in this study, although it may be present transiently or below the limits of detection. Other possible intermediates even more highly oxidizing than perchlorate itself produced during the oxidation of chloride, such as hypochlorite (ClO^-), chlorine dioxide (ClO_2(g)), and radicals such as $^{\bullet}OCl$, $^{\bullet}Cl$, and $^{\bullet}OH$, were not analyzed but would necessarily be present during the oxidation process as shown for gas and aqueous phase reactions [*Catling et al.,* 2010; *Schuttlefield et al.,* 2011; *Kang et al.,* 2006, 2008; *Dasgupta et al.,* 2005].

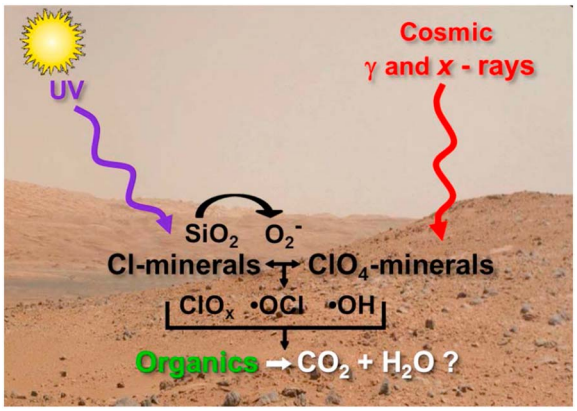

Figure 2. Highly reactive oxychlorines and radicals can be produced both from oxidation of mineral chlorides to perchlorate by the action of UV irradiation as shown by our results and from the radiolysis of perchlorates by the action of cosmic gamma and X-rays [*Quinn et al.,* 2013]. The highly reactive intermediates produced from these pathways are capable of attacking organics by oxidizing and/or chlorinating them.

The production of all the ClO_x species by the mechanism proposed here would only occur at UV-exposed mineral surfaces; however, there are several short- and long-term physical and aqueous processes that would redistribute the ClO_x to depths ranging from meters to hundreds of meters, and perhaps even deeper. These include cryoturbation [*Levy et al.,* 2010; *Mellon et al.,* 2008], meteoric impact reworking [*Knauth et al.,* 2005; *Zent*, 1998], diffusion, and transport by aqueous films or liquid runoff or infiltration [*Crumpler et al.,* 2015; *Amundson et al.,* 2008; *Davila et al.,* 2008]. Assuming that ClO_x production has been ongoing for billions of years, these processes would by now have resulted in widespread redistribution of all the ClO_x species both laterally and vertically. Such processes would account for the perchlorate detected by Curiosity in the dark drill material at Yellowknife Bay [*Ming et al.,* 2014]. The perchlorate in these sediments, considered to be ~3.5 Gyr old and deeply buried until ~70 Myr ago, was also accompanied by the release of reduced species (H_2S). This may initially seem contradictory since it would imply the coexistence of both a reducing and oxidizing environment. The presence of the perchlorate could be due to either the production or deposition of perchlorate on early Mars by processes similar to those currently operating on Earth, or it is just as likely that it may be due to later aqueous transport processes as described above.

The fact that perchlorate is likely being continuously and globally produced on Mars indicates that several, if not all, of these intermediates are most likely also continuously present on or near the Martian surface. This is in addition to the perchlorate degradation products that are produced by radiolysis of already present perchlorate [*Quinn et al.,* 2013]. Taken together, the evidence points to the global presence of strong oxidants throughout the Martian regolith and a complex ongoing chlorine production and destruction cycle (Figure 2).

4. Conclusions

The current research indicates that perchlorate formation is most likely an ongoing process and is occurring globally on a continuous basis wherever chloride-bearing mineral phases exist. Thus, the implications of our results are relevant for both the survivability and detection of organic compounds on the surface of Mars. Previous studies of the effects of UV radiation on amino acids under Martian conditions have shown that alanine and glycine would have half-lives on the order of days on the Martian surface, and this did not even take into account the effects of other strong oxidants in the soil [*ten Kate et al.,* 2005]. Though studies of several carboxylic acids have yielded similar results [*Stalport et al.,* 2010], others have been found to produce higher molecular-weight compounds when irradiated under simulated Mars conditions, often containing carbonyl, hydroxyl, and alkenyl functional groups [*Hintze et al.,* 2010]. Nonvolatile salts of benzene carboxylic acids (e.g., mellitic acid and its derivatives), and possibly of oxalic and acetic acids, may be metastable intermediates produced by oxidation of organics of meteoritic origin [*Stalport et al.,* 2009; *Benner et al.,* 2000]. Such organics, depending on their initial abundance and the type of sedimentary matrix and chemistry they are associated with, might be able to survive in the subsurface where UV radiation is not able to penetrate or in sedimentary rocks representing earlier eras on Mars during which oxychlorines and UV radiation may not have been as dominant as today.

This further evidence for the global production and presence of perchlorate also has implications for our understanding of the Martian water cycle and history of water on the Martian surface. The identity of the parent salts of perchlorate in a given location can help to determine if it has been severely arid since it

was deposited or if aqueous transportation or alteration has occurred subsequent to its deposition. For example, the presence of highly soluble calcium perchlorate ($Ca(ClO_4)_2$) salt would tend to indicate that the site has not been in contact with liquid water, since on dissolution the Ca^{2+} would tend to precipitate as a sulfate mineral such as anhydrite or gypsum [*Kounaves et al.,* 2014b].

Perchlorate can not only help identify whether a location on Mars has been wet or dry subsequent to perchlorate deposition but also allows for transient liquid water reservoirs in the form of brines. Perchlorate, as well as chlorate, may play an active role in the Martian water cycle, allowing for the formation of metastable liquid brines at or near the Martian surface. Perchlorate can depress the freezing point of water to between 206 and 273 K, depending on salt concentration and relative humidity [*Gough et al.,* 2011; *Hanley et al.,* 2012; *Chevrier et al.,* 2009]. Deliquescence of atmospheric water vapor may lead to formation of metastable supersaturated solutions which would allow for the presence of aqueous solutions on the Martian surface for up to several hours a day [*Fischer et al.,* 2014] and facilitate the production of midlatitude gullies and recurring slope lineae [*Ojha et al.,* 2014]. The evidence that perchlorate and chlorate are both likely ubiquitous on Mars suggests that if pockets of liquid brine are present in the subsurface, and are thus protected from the effects of the UV and oxychlorines, they could serve as transient subterranean habitats for chemotrophic microbes.

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