# IN SITU DETECTION OF CHLORINE DIOXIDE (ClO$_2$) IN THE RADIOLYSIS OF PERCHLORATES AND IMPLICATIONS FOR THE STABILITY OF ORGANICS ON MARS

SÁNDOR GÓBI[1,2], ALEXANDRE BERGANTINI[1,2], AND RALF I. KAISER[1,2]
[1] Department of Chemistry, University of Hawaii at Mānoa, Honolulu, HI 96822, USA; ralfk@hawaii.edu
[2] W.M. Keck Laboratory in Astrochemistry, University of Hawaii at Mānoa, Honolulu, HI 96822, USA

## ABSTRACT

Magnesium perchlorate hexahydrate (Mg(ClO$_4$)$_2$ · 6H$_2$O) samples were exposed to energetic electrons to investigate the products of the decomposition of perchlorates in the Martian soil and to infer their role in the degradation of organics on Mars. The samples were monitored online and in situ via infrared spectroscopy as well as electron impact (EI-QMS) and reflectron time-of-flight mass spectrometry coupled with single photon ionization (PI-ReTOF-MS). Our study reveals that besides chlorates (ClO$_3^-$) and molecular oxygen (O$_2$), the chlorine dioxide radical (ClO$_2$) was observed online and in situ for the first time as a radiolysis product of solid perchlorates. Chlorine dioxide, which is used on Earth as a strong oxidizing agent in water disinfection and bleaching, represents a proficient oxidizer—potentially more powerful than molecular oxygen—to explain the lack of abundant organics in the Martian soil.

*Key words:* astrochemistry – methods: laboratory: solid state – planets and satellites: surfaces – techniques: spectroscopic

## 1. INTRODUCTION

The *Phoenix* spacecraft (Hecht et al. 2009) and the Curiosity rover (Leshin et al. 2013) have revealed the ubiquitous presence of perchlorates—inorganic compounds carrying the tetrahedral perchlorate ion (ClO$_4^-$)—within the Martian soil at levels of 0.5%–1.0% by weight (Davila et al. 2013). These concentrations are comparable to those reported on Earth in the Atacama Desert (Chile) at levels of 0.6% (Ericksen 1981). On Mars, perchlorates are proposed to be formed via heterogeneous photochemistry (Smith et al. 2014), photocatalysis (Carrier & Kounaves 2015), photooxidation (Schuttlefield et al. 2011), or radiation-induced surface chemistry (Kim et al. 2013). Perchlorates (ClO$_4^-$) have been shown to degrade organic molecules indigenous to the Martian surface during pyrolytic experiments (Glavin et al. 2013; Leshin et al. 2013; Ming et al. 2014; Freissinet et al. 2015; Miller et al. 2016). This finding may suggest that they can also oxidize sensitive molecules upon irradiation of energetic particles, which contributes to the lack of organics on the Martian surface. Laboratory experiments have provided compelling evidence that even complex organic molecules such as amino acids like glycine (H$_2$NCH$_2$COOH, Góbi et al. 2016) can be oxidized efficiently in the presence of oxidants such as perchlorates (ClO$_4^-$) exposed to ionizing radiation in the form of ultraviolet (UV) photons and energetic galactic cosmic-ray (GCR) particles in the Martian soil (Pavlov et al. 2012). Although their overall energy flux is four orders of magnitude less than the energy flux of the solar photons (Pavlov et al. 2012), GCRs are the most relevant agent in the destruction of the organics in the deeper layers of the Martian soil since UV photons are effectively absorbed within the first few microns of the soil (Muñoz-Caro et al. 2006). Consequently, a detailed knowledge of the destruction mechanism and kinetics of key organics in the presence of perchlorates (ClO$_4^-$) will shed light on the chemistry and the lifetime of organic molecules in the Martian soil. This, however, requires the identification of the active oxidizing species responsible for the degradation of these organics.

Turner et al. (2016) revealed that the irradiation of magnesium perchlorate hexahydrate (Mg(ClO$_4$)$_2$ · 6H$_2$O) by high-energy electrons, which mimics secondary electrons released by energetic cosmic-ray particles penetrating the Martian soil (Bennett et al. 2005), leads to a gradual degradation of perchlorate (ClO$_4^-$) to the chlorate ion (ClO$_3^-$) plus atomic oxygen (O) with two of the latter recombining to molecular oxygen (O$_2$). These results suggest that energetic oxygen atoms (O) and molecules (O$_2$) provide an efficient oxidizing environment in the radiolyzed samples not only in the laboratory, but also in the Martian soil. However, in our work the online and in situ Fourier-transform infrared spectroscopic (FTIR) analysis suffers from the dominating absorptions of fundamentals associated with the magnesium perchlorate hexahydrate (Mg(ClO$_4$)$_2$ · 6H$_2$O) reactant (Turner et al. 2016), and only chlorate (ClO$_3^-$) could be monitored via FTIR spectroscopy. Likewise, the quadrupole mass spectrometer (QMS), operated in electron impact (EI) ionization mode, identified molecular oxygen (O$_2$) only. Therefore, whereas FTIR and EI-QMS identified solely chlorate (ClO$_3^-$) and molecular oxygen (O$_2$), respectively, novel laboratory experiments exploiting sensitive detection techniques are clearly required to shed light on hitherto unidentified oxidants formed in the radiation exposure of perchlorates (ClO$_4^-$) to comprehensively understand the fundamental mechanism involved in the oxidation of organics in the Martian soil.

Here, by probing the radiolysis products of magnesium perchlorate hexahydrate (Mg(ClO$_4$)$_2$ · 6H$_2$O) via soft photoionization reflectron time-of-flight mass spectrometry (PI-ReTOF-MS, Kaiser et al. 2010; Zhang et al. 2011; Golan et al. 2013; Jones & Kaiser 2013; Abplanalp et al. 2016), we demonstrate the very first in situ detection of the chlorine dioxide radical (ClO$_2$). Although there have been earlier works investigating the radiolytic decomposition of perchlorates (ClO$_4^-$), these studies exploited only offline and ex situ detection methods (Cole 1960; Prince & Johnson 1965; Quinn et al. 2013). This may allow the sample to be chemically altered between irradiation and measurement by oxidation of

**Table 1**
Summary of Magnesium Perchlorate Hexahydrate (Mg(ClO$_4$)$_2$ · 6 H$_2$O) Sample Preparation Details and CASINO Simulation Results on the Radiolysis Experiments

| | Experiment I (10.49 eV) | Experiment II (10.20 eV) |
|---|---|---|
| Mass weighed (g) | 0.0389 ± 0.0001 | 0.0400 ± 0.0001 |
| Mass of solvent H$_2$O (g) | 28.26 ± 0.01 | 25.72 ± 0.01 |
| Volume of solution used (mL) | 0.280 ± 0.005 | 0.250 ± 0.005 |
| Average thickness of the sample (nm) | 1950 ± 50 | 1970 ± 50 |
| Average density of the film (g cm$^{-3}$) | 1.98 ± 0.03 | 1.98 ± 0.03 |
| Molar masses of molecules in the film (g mol$^{-1}$) | 331.3 | 331.3 |
| Number of molecules in the sample ($\times 10^{17}$) | 7.02 ± 0.22 | 7.08 ± 0.23 |
| Angle of incidence (°) | 20 | 20 |
| Irradiated area (cm$^2$) | 1.0 ± 0.1 | 1.0 ± 0.1 |
| Irradiation time (s) | 3600 ± 2 | 3600 ± 2 |
| Applied electron current (nA) | 30.7 ± 0.8 | 29.2 ± 1.1 |
| Number of electrons generated ($\times 10^{14}$) | 6.89 ± 0.18 | 6.56 ± 0.25 |
| Initial energy of the electrons (keV) | 5.00 | 5.00 |
| Average backscattered energy of the electrons (keV) | 3.51 ± 0.09 | 3.51 ± 0.09 |
| Average transmitted energy of the electrons (keV) | 0.00 ± 0.00 | 0.00 ± 0.00 |
| Fraction of backscattered electrons (%) | 41.6 ± 2.9 | 41.6 ± 2.9 |
| Fraction of transmitted electrons (%) | 0.0 ± 0.0 | 0.0 ± 0.0 |
| Simulated average penetration depth (nm) | 165 ± 7 | 165 ± 7 |
| Number of exposed molecules ($\times 10^{16}$) | 5.93 ± 0.64 | 5.93 ± 0.64 |
| Dose per molecule (eV) | 41.2 ± 1.3 | 39.7 ± 1.2 |

the chlorine oxide radicals initially formed. Although this might lead to chlorine dioxide (ClO$_2$), the result makes a compromise from an astrophysical point of view because the irradiated sample is exposed to atmospheric gases and/or dissolved in a solvent for offline studies (for more details, see Section 3.2). Therefore, only the explicit detection of chlorine dioxide (ClO$_2$) in a solid magnesium perchlorate hexahydrate (Mg(ClO$_4$)$_2$ · 6H$_2$O) sample can demonstrate without any doubt that the radiolysis of Martian perchlorates (Cl$_x$O$_y$-) does not lead exclusively to chlorine oxide anions (ClO$_n^-$) along with atomic (O) and molecular (O$_2$) oxygen in the condensed phase. The chlorine dioxide radical (ClO$_2$) is used on Earth as an agent in water treatment, disinfection (Block 2001), and bleaching (Suess 2010). As a consequence, it represents a proficient oxidizer—potentially more powerful than molecular oxygen (O$_2$), whose reactions with organics are often kinetically blocked due to high-energy barriers—to efficiently degrade organic compounds on the Martian surface.

## 2. EXPERIMENTAL

The experiments were conducted in a contamination-free ultra-high vacuum stainless steel chamber, which can be evacuated to a base pressure of a few $10^{-11}$ mbar exploiting oil-free magnetically suspended turbomolecular pumps and dry scroll backing pumps. A polished silver mirror acts as a sample holder and is mounted on a cold finger assembled from oxygen-free high-conductivity copper and interfaced with indium foil to ensure thermal conductivity. This system is subsequently cooled with a closed-cycle helium refrigerator (Sumitomo Heavy Industries, RDK-415E) down to 5.5 ± 0.1 K. We are aware that the low temperature does not represent the Martian environment of 160–240 K. However, these experiments are designed as a proof of concept to provide evidence of the formation of chlorine dioxide (ClO$_2$) upon exposure to energetic electrons; follow-up studies are planned to elucidate the temperature-dependent formation of chlorine

dioxide (ClO$_2$) and hence to provide actual rate constants for the planetary science community, which then can be incorporated into models. Films of 2000 nm magnesium perchlorate hexahydrate (Mg(ClO$_4$)$_2$ · 6H$_2$O, Sigma Aldrich, 99.0+%) were prepared on the silver substrate. The low-temperature samples were then exposed to 5 keV electrons for 1 hr at a current of 25 nA scanned over an area of 1.0 ± 0.1 cm$^2$ and an angle of incidence of 70° relative to the surface normal. The average dose per magnesium perchlorate hexahydrate (Mg (ClO$_4$)$_2$ · 6H$_2$O) deposited into the sample was determined from simulations based both on Monte Carlo (CASINO) simulations (Drouin et al. 2007) to be 40–41 eV (Table 1) and experimental parameters (e.g., electron current, estimated number of sample molecules). The irradiation-induced chemical processing was monitored online and in situ via an FTIR spectrometer (Nicolet 6700) over a range of 6000–650 cm$^{-1}$ at a resolution of 4 cm$^{-1}$. Also, a QMS (Extrel Model 5221) operating in residual gas analyzer mode in the mass range of 1–500 $m/z$ was employed during the experiment to detect the species in the gas phase via EI ionization (70 eV) exploiting a 1.2 MHz oscillator. After the irradiation, the sample was kept at 5.5 ± 0.1 K for 1 hr; then the temperature programmed desorption (TPD) program was initiated by heating the irradiated samples at a rate of 1.0 K minute$^{-1}$ to 300 K then kept at 300 K for additional 3 hr to allow any potential product to diffuse out of the sample into the gas phase. The TPD profiles of product molecules were collected via PI-ReTOF-MS using photoionization energies of 10.49 and 10.20 eV in separate experiments (Table 1); soft photoionization exploiting coherent single VUV photons prepared via four-wave mixing has been demonstrated to lead essentially to a fragment-free ionization of the neutral products (Jones & Kaiser 2013; Maity et al. 2014). Blank experiments were also performed by conducting the same experimental sequence, but without irradiating the sample.
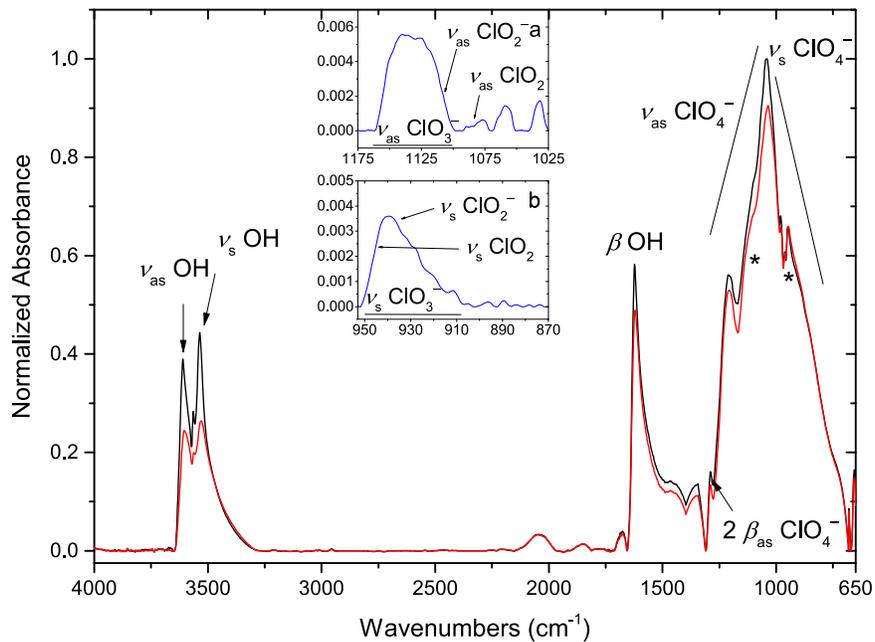
**Figure 1.** FTIR spectra of magnesium perchlorate hexahydrate (Mg(ClO$_4$)$_2$ · 6H$_2$O) before (black) and after (red) the exposure to energetic electrons. The asterisks define the position of the newly formed chlorate (ClO$_3^-$) and chlorite (ClO$_2^-$) ions along with the chlorine dioxide molecule (ClO$_2$). The inserts show the difference spectra of the marked regions from (a) 1175–1125 cm$^{-1}$ and (b) 970–870 cm$^{-1}$ with a tentative assignment of the signals also given.

## 3. RESULTS AND DISCUSSION

### 3.1. Infrared Spectrum of Magnesium Perchlorate Hexahydrate Samples

The response of the perchlorate (ClO$_4^-$) samples by the energetic electrons can be visualized in the IR spectra (Figure 1). A gradual decrease of all fundamentals can be clearly seen in the mid-infrared region implying the decomposition of magnesium perchlorate hexahydrate (Mg(ClO$_4$)$_2$ · 6H$_2$O). In detail, the higher frequency regions are dominated by the antisymmetric and symmetric stretching modes of the crystal water ($\nu_{as}$ H$_2$O, $\nu_s$ H$_2$O) around 3600 cm$^{-1}$ (Miller & Wilkins 1952; Bishop et al. 2014; Hanley et al. 2015; Turner et al. 2016), while the bending mode of water is also detectable at 1623 cm$^{-1}$. Considering the perchlorate ion (ClO$_4^-$), the stretching vibrations can be found at lower wavenumbers as a broad absorption feature between 1300 and 700 cm$^{-1}$ consisting of the antisymmetric ($\nu_{as}$ ClO$_4^-$) and the symmetric ($\nu_s$ ClO$_4^-$) modes along with the overtone of the antisymmetric bending mode ($2\beta_{as}$ ClO$_4^-$). Unfortunately, the vibration modes of the potential radiation products such as of the chlorate ion (ClO$_3^-$) reside close to the perchlorate parent in this region (Hanley et al. 2015; Turner et al. 2016). In other words, limited resolution of the method and overlapping with the broad and intense band of the parent molecule do not allow the explicit assignment of the peaks of the radiolysis products. Nevertheless, the shoulder at 935 cm$^{-1}$ is attributable to the symmetric stretching mode of the chlorate ion ($\nu_s$ ClO$_3^-$). A subtraction of the spectra before and after the irradiation reveals that this band could also have contributions from the symmetric stretching mode of chlorites ($\nu_s$ ClO$_2^-$) monitored in previous studies between 935 and 950 cm$^{-1}$ (Hanley et al. 2015). More importantly, according to the review (and references therein) of Kopitzky et al. (2002) on this topic, the symmetric stretching mode of monomeric chlorine dioxide ($\nu_s$ ClO$_2$) can also be found at approximately 950 cm$^{-1}$

(Figure 1(b)). The asymmetric stretching of chlorates at approximately 1125 cm$^{-1}$ ($\nu_{as}$ ClO$_3^-$) may be seen in the raw data as a shoulder overlaid on the diminishing antisymmetric stretch of the parent molecule ($\nu_{as}$ ClO$_4^-$) and as a clear absorption in the IR difference spectrum as well; this signal may also consist of antisymmetric stretching of chlorite ($\nu_{as}$ ClO$_2^-$) and likely ClO$_2$ ($\nu_{as}$ ClO$_2$, Figure 1(a), Gane et al. 1997; Kopitzky et al. 2002; Turner et al. 2016). A tentative assignment of the irradiation products is shown in Figures 1(a) and (b). Besides the main radiolytic product chlorate (ClO$_3^-$) IR signal positions of the other species formed elements during irradiation—i.e., chlorite (ClO$_2^-$) and chlorine dioxide (ClO$_2$)—are also marked.

### 3.2. TPD Profiles of Magnesium Perchlorate Hexahydrate Samples

Having identified chlorate ions (ClO$_3^-$) along with potentially chlorite (ClO$_2^-$) and chlorine dioxide (ClO$_2$) via FTIR spectroscopy, we are correlating now these observations with data obtained by EI-QMS and PI-ReTOF-MS (in different experiments using 10.49 eV and 10.2 eV photons, respectively) of the species released into the gas phase during the TPD process (Figure 2). Three ion currents were observed at $m/z = 32$ (O$_2^+$), 67 ($^{35}$ClO$_2^+$), and 69 ($^{37}$ClO$_2^+$) in the range of 100–300 K. It should be stressed that none of these species were observed in the blank experiments. The PI-ReTOF-MS data at $m/z = 65$ and 67 can be attributed to the chlorine dioxide radical (ClO$_2$), namely $^{35}$ClO$_2$ and $^{37}$ClO$_2$. The ionization energy of chlorine dioxide (ClO$_2$) is 10.33 eV (Flesch et al. 1993), which is—unlike for other chlorine oxides—lower than the energy of the 10.49 eV photons to ionize the subliming molecules (Table 2); however, the ionization energy is higher than the 10.2 eV photon exploited, and hence, the signal at $m/z = 65$ and 67 is absent on those experiments as predicted since the ionization energy of chlorine dioxide (ClO$_2$) is above the 10.2 eV VUV photon. This interpretation is also confirmed by evaluating the ratio of the
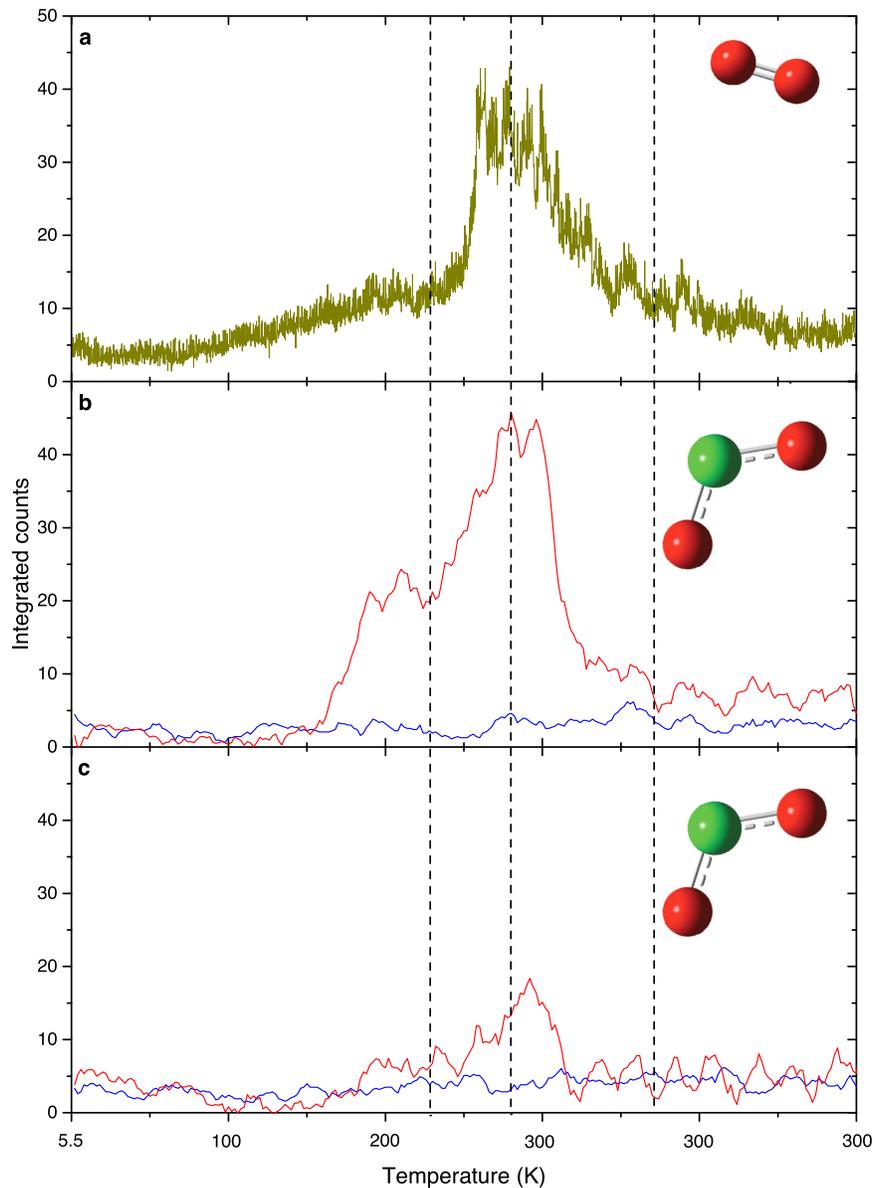
**Figure 2.** TPD profiles of irradiated magnesium perchlorate hexahydrate (Mg(ClO$_4$)$_2$ · 6H$_2$O) samples for (a) molecular oxygen (O$_2$) recorded via EI-QMS, (b) PI-ReTOF-MS data of chlorine dioxide (ClO$_2$) at $m/z = 67$ ($^{35}$ClO$_2^+$), and (c) at $m/z = 69$ ($^{37}$ClO$_2^+$). The lines on panels (b) and (c) with different colors represent the data taken at photon energies of 10.49 eV (red) and 10.20 eV (blue), respectively.

baseline corrected integrated peak areas of $m/z = 67$ and 65 of $A[^{37}$ClO$_2]/A[^{35}$ClO$_2] = 0.306 \pm 0.027$, which agrees exceptionally well with the natural isotopic abundance ratio of $^{37}$Cl versus $^{35}$Cl of $^{37}$Cl/$^{35}$Cl $= 0.3198$.

A close inspection of the TPD profiles reveals the bimodal structure depicting two sublimation events from 150 K to about 230 K and a second one from 230 K extending to 300 K. The second sublimation event correlates well with the emerging EI-QMS ion profile of $m/z = 32$, which originates from molecular oxygen (O$_2$). It is important to point out that upon EI ionization at 70 eV, chlorine dioxide (ClO$_2$) does not undergo dissociative EI ionization to $m/z = 32$ (O$_2^+$, Cordes & Smith 1970). The co-release of molecular oxygen (O$_2$) is hardly noticeable during the first sublimation event from 150 to 230 K. Therefore, we can conclude that most likely two distinct formation mechanisms contribute to the formation of chlorine dioxide (ClO$_2$). The first sublimation event can be attributed to

the chlorine dioxide (ClO$_2$) sample, which also results in a tentative detection of chlorine dioxide (ClO$_2$) in the IR data (Figure 1) and possible formation mechanisms might involve the radiolysis of perchlorate (ClO$_4^-$) and/or chlorate (ClO$_3^-$) to chlorite (ClO$_2^-$) followed by electron detachment of the latter (Turner et al. 2016).

Considering the sublimation temperatures, chlorine dioxide (ClO$_2$) released in the second sublimation event cannot originate from the radiolytically generated molecules since at 230–300 K, they should have sublimed already (Kim et al. 2013). However, higher chlorine oxides could still be present at 230 K. These results suggest that at least one additional chlorine oxide with a higher oxidation state of chlorine is formed upon radiolysis, which is in the sample at 230 K, but decomposes to chlorine dioxide (ClO$_2$) and molecular oxygen (O$_2$) upon heating the sample to 300 K. What can be the nature of the(se) chlorine oxide(s)? Chlorine

**Table 2**
Adiabatic Ionization Energies (*IE* in eV) of Chlorine ($Cl_2$) and Various Chlorine Oxides with the General Formula of $Cl_xO_y$ ($x = 1, 2, y = 1$–7)

| Formula | Structure | $m/z$ ($^{35}Cl$, $^{37}Cl$) | *IE*, eV | References |
|---|---|---|---|---|
| $Cl_2$ | Cl–Cl | 70, 72 | $11.48 \pm 0.01$ | Dibeler et al. (1971) |
| ClO | Cl–O | 51, 53 | $10.885 \pm 0.016$ | Thorn et al. (1996) |
| $ClO_2$[a] | O=Cl–O | 67, 69 | $10.33 \pm 0.02$ | Flesch et al. (1993) |
| $ClO_3$ | O=Cl(=O)=O | 83, 85 | $11.4 \pm 0.1$ | Alekseev et al. (1989) |
| $Cl_2O$ | Cl–O–Cl | 86, 88 | $10.88 \pm 0.02$ | Rühl et al. (1999) |
| $Cl_2O_2$ | Cl–O–O–Cl | 102, 104 | $11.05 \pm 0.05$ | Schwell et al. (1996) |
| $Cl_2O_3$[b] | Cl–O–Cl–$O_2$ | 118, 120 | $11.11 \pm 0.02$ | Li et al. (2000) |
| $Cl_2O_4$ | Cl–O–Cl–$O_3$ | 134, 136 | $11.23 \pm 0.05$ | Rühl et al. (1999) |
| $Cl_2O_5$[b] | Cl–O–O–Cl–$O_3$ | 150, 152 | 10.88?[c] | Li et al. (2000) |
| $Cl_2O_6$ | $O_2$–Cl–O–Cl–$O_3$ | 166, 168 | $12.66 \pm 0.05$ | Rühl et al. (1999) |
| $Cl_2O_7$ | $O_3$–Cl–O–Cl–$O_3$ | 182, 184 | $12.15 \pm 0.05$ | Rühl et al. (1999) |

**Notes.**
[a] *IE* lower than the VUV photon energy used (10.49 eV).
[b] No experimental values; only theoretical data (for the remaining $Cl_2O_x$ molecules, computed data agreed well with the experimental ones).
[c] No convergence.

monoxide (ClO), dichloromonoxide ($Cl_2O$), dichlorodioxide ($Cl_2O_2$), and dichlorotrioxide ($Cl_2O_3$) do not produce molecular oxygen ($O_2$) in their decomposition. Chlorine trioxide ($ClO_3$), chlorine tetraoxide ($ClO_4$), and dichlorine pentaoxide ($Cl_2O_5$) could produce molecular oxygen ($O_2$) upon annealing, but not chlorine dioxide ($ClO_2$); this suggests that dichlorine tetraoxide ($Cl_2O_4$, Schack & Pilipovich 1970), dichlorine hexaoxide ($Cl_2O_6$), and/or dichlorine heptaoxide ($Cl_2O_7$) represent the decomposing chlorine oxides leading to molecular oxygen ($O_2$) and chlorine dioxide ($ClO_2$, Witt & Hammaker 1973; Jansen et al. 1988; Greenwood & Earnshaw 1997; Kopitzky et al. 2002).

These results—unlike earlier studies—provide compelling evidence on the formation of chlorine dioxide ($ClO_2$) during the irradiation and warming up of perchlorates ($ClO_4^-$). More precisely, former studies in the literature have used solution-phase UV-VIS spectrophotometry after the irradiation of the samples. Furthermore, samples in some of these past works were extensively altered in order to be analyzed. Prince (1964) determined chlorine dioxide ($ClO_2$) altogether with hypochlorite ($OCl^-$) and chlorite ($ClO_2^-$) from the absorbance of the triiodide ($I_3^-$) aqueous solution at two different pHs exploiting that these species can oxidize iodide ($I^-$). This indirect method was used because the sensitivity of UV-VIS spectrometers did not allow the explicit detection of chlorine dioxide ($ClO_2$) at that time, owing to its very weak absorption. It is important to point out that the measured compound (triiodide, $I_3^-$) was the sum of these chlorate species and the contribution of the particular ones could be estimated on the stoichiometry of their reactions with iodide ($I^-$) only. Furthermore, partial escape of chlorine dioxide ($ClO_2$) from the sample between irradiation and ex situ detection methods cannot be ruled out completely. The other methods used in this study (i.e., X-ray diffraction and FTIR spectroscopy) could not evidently identify the structures of the decomposition products (Prince & Johnson 1965).

Later, direct UV-VIS spectroscopy of irradiation products became available, however, this still required the radiolysis sample to be solved in a slightly basic aqueous borax solution (Quinn et al. 2013). This could have lead to a conversion of other chlorine oxides to chlorine dioxide ($ClO_2$), therefore, contaminating the irradiated sample. Although the samples were kept at low temperatures between irradiation and

measurement, undesirable side-reactions could have still occurred in the solution phase. There was also an Electron Magnetic Resonance study, in which the samples were irradiated at room temperature and exposed to atmospheric gases; the oxygen content of the atmosphere may have altered the reaction mechanism of the experiment (Cole 1960). This also applies to the solution-phase UV-VIS measurements mentioned above, questioning whether the species detected in these works were present in the sample during radiolysis. Therefore, because of the exposure of the irradiated samples to solutions and atmospheric oxygen—which might have caused chlorine dioxide ($ClO_2$) to be present in the sample as an artifact—these results make a bigger compromise regarding astrophysical processes such as the ones occurring on the Martian surface.

## 4. ASTROPHYSICAL IMPLICATIONS

In conclusion, we have provided compelling evidence on the formation of the chlorine dioxide radical ($ClO_2$) in the radiolysis of magnesium perchlorate hexahydrate ($Mg(ClO_4)_2 \cdot 6H_2O$) samples with energetic electrons mimicking secondary electrons formed in the track of GCR particles penetrating the Martian soil exploiting PI-ReTOF-MS. The low-temperature radiolysis experiments provide the proof-of-concept and the very first in situ detection of chlorine dioxide ($ClO_2$) as a radiolysis product of solid perchlorates ($ClO_4^-$) following the identification of chlorate ($ClO_3^-$) and tentatively chlorite ($ClO_2^-$) anions via FTIR spectroscopy and molecular oxygen ($O_2$) via EI-QMS. Perchlorates ($ClO_4^-$) can be easily degraded by secondary electrons generated in the track of energetic GCRs penetrating the Martian soil up to a few meters deep. The Radiation Assessment Detector on board NASA's Curiosity Rover analyzed the radiation levels confirming that energetic GCRs can easily penetrate the tenuous atmosphere of Mars lacking a magnetic field (Guo et al. 2015). At Mars-relevant temperatures from 165 to 300 K, chlorine dioxide ($ClO_2$) is released into the gas phase to become actively involved in the atmospheric chlorine–oxygen chemistry. Considering that perchlorates ($ClO_4^-$) are presumably formed at least partially via atmospheric chlorine oxides such as chlorine monoxide (ClO) and chlorine dioxide ($ClO_2$), our work also suggests that perchlorates ($ClO_4^-$) can be cycled back to their corresponding gas-phase precursors upon

interaction with ionizing radiation. Finally, molecular oxygen $(O_2)$ has been thought for the last decades to be the principle radiation product of perchlorate $(ClO_4^-)$ decomposition, which in turn oxidizes organics in the Martian soil. However, molecular oxygen $(O_2)$ holds a $^3\Sigma_g^-$ electronic ground state. Compared to singlet dioxygen, triplet dioxygen is relatively unreactive toward organics at Mars-relevant temperatures (Mayer & Schieler 1968). This is quite different compared to reactions of the chlorine dioxide radical $(ClO_2)$, which is exploited on Earth as a powerful oxidizer to actually destroy (oxidize) organics and bacteria in drinking water (Block 2001). Consequently, the chlorine dioxide $(ClO_2)$ radical radiolysis product of solid perchlorates $(ClO_4^-)$ may represent a more powerful oxidizer in the Martian soil than molecular oxygen $(O_2)$, possibly explaining the lack of abundant organics on the Martian surface. Quantitative determination of the perchlorate $(ClO_4^-)$ to chlorine dioxide $(ClO_2)$ conversion rate and comparison of this reaction pathway to radiolysis to chlorate $(ClO_3^-)$ was out of the scope of present work. However, future experiments are planned to quantify these reaction rates and also the temperature-dependent branching ratios of molecular oxygen $(O_2)$ versus chlorine dioxide $(ClO_2)$ produced in the radiolysis of perchlorates $(ClO_4^-)$. Extension of the present low-temperature study to the Martian temperature regime from 160 to 300 K will also be the focus of future work. Combined with planetary surface modeling, these data will ultimately untangle the decay products of perchlorates $(ClO_4^-)$ and the fate of organics on the Martian surface.

## REFERENCES

Abplanalp, M. J., Förstel, M., & Kaiser, R. I. 2016, CPL, 644, 79
Alekseev, V. I., Zyubina, T. S., Zyubin, A. S., & Baluev, A. V. 1989, Bull. Acad. Sci. USSR Div. Chem. Sci., 38, 2092
Bennett, C. J., Jamieson, C. S., Osamura, Y., & Kaiser, R. I. 2005, ApJ, 624, 1097
Bishop, J. L., Quinn, R., & Dyar, M. D. 2014, AmMin, 99, 1580
Block, S. S. 2001, Disinfection, Sterilization, and Preservation (5th ed.; Philadelphia, PA: Lippincott Williams & Wilkins)
Carrier, B. L., & Kounaves, S. P. 2015, GeoRL, 42, 3739
Cole, T. 1960, PNAS, 46, 506
Cordes, H. F., & Smith, S. R. 1970, J. Chem. Eng. Data, 15, 158
Davila, A. F., Willson, D., Coates, J. D., & McKay, C. P. 2013, IJAsB, 12, 321
Dibeler, V. H., Walker, J. A., McCulloh, K. E., & Rosenstock, H. M. 1971, IJMIP, 7, 209
Drouin, D., Couture, A. R., Joly, D., et al. 2007, Scanning, 29, 92
Ericksen, G. E. 1981, Geology and the Origin of the Chilean Nitrate Deposits, Geological Survey Professional Paper 1188 (Washington, DC: US Govt Printing Office)
Flesch, R., Rühl, E., Hottmann, K., & Baumgärtel, H. 1993, JPhCh, 97, 837
Freissinet, C., Glavin, D. P., Mahaffy, P. R., et al. 2015, JGRE, 120, 495
Gane, M. P., Williams, N. A., & Sodeau, J. R. 1997, FaTr, 93, 2747
Glavin, D. P., Freissinet, C., Miller, K. E., et al. 2013, JGRE, 118, 1955
Góbi, S., Abplanalp, M. J., & Kaiser, R. I. 2016, ApJ, 822, 8
Golan, A., Ahmed, M., Mebel, A. M., & Kaiser, R. I. 2013, PCCP, 15, 341
Greenwood, N. N., & Earnshaw, A. 1997, Chemistry of the Elements (2nd ed.; London: Butterworth-Heinemann)
Guo, J., Zeitlin, C., Wimmer-Schweingruber, R. F., et al. 2015, ApJ, 810, 24
Hanley, J., Chevrier, V. F., Barrows, R. S., Swaffer, C., & Altheide, T. S. 2015, JGRE, 120, 1415
Hecht, M. H., Kounaves, S. P., Quinn, R. C., et al. 2009, Sci, 325, 64
Jansen, M., Schatte, G., Tobias, K. M., & Willner, H. 1988, InCh, 27, 1703
Jones, B. M., & Kaiser, R. I. 2013, JPhCh, 4, 1965
Kaiser, R. I., Maksyutenko, P., Ennis, C., et al. 2010, FaDi, 147, 429
Kim, Y. S., Wo, K. P., Maity, S., Atreya, S. K., & Kaiser, R. I. 2013, JAChS, 135, 4910
Kopitzky, R., Grothe, H., & Willner, H. 2002, CEJ, 8, 5601
Leshin, L. A., Mahaffy, P. R., Webster, C. R., et al. 2013, Sci, 34, 1238937
Li, W.-K., Lau, K.-C., Ng, C. Y., Baumgärtel, H., & Weitzel, K. M. 2000, JPCA, 104, 3197
Maity, S., Kaiser, R. I., & Jones, B. M. 2014, FaDi, 168, 485
Mayer, S. W., & Schieler, L. 1968, JPhCh, 72, 2628
Miller, F. A., & Wilkins, C. H. 1952, AnaCh, 24, 1253
Miller, K. E., Eigenbrode, J. L., Freissinet, C., et al. 2016, JGRE, 121, 296
Ming, D. W., Archer, P. D., Glavin, D. P., et al. 2014, Sci, 343, 1245267
Muñoz-Caro, G. M., Mateo-Martí, E., & Martínez-Frías, J. 2006, Sensors, 6, 688
Pavlov, A. A., Vasilyev, G., Ostryakov, V. M., Pavlov, A. K., & Mahaffy, P. 2012, GeoRL, 39, L13202
Prince, L. A. 1964, AnaCh, 36, 613
Prince, L. A., & Johnson, E. R. 1965, JPhCh, 69, 359
Quinn, R. C., Martucci, H. F. H., Miller, S. R., et al. 2013, AsBio, 13, 515
Rühl, E., Rockland, U., Baumgärtel, H., et al. 1999, IJMSp, 185–187, 545
Schack, C. J., & Pilipovich, D. 1970, InCh, 9, 1387
Schuttlefield, J. D., Sambur, J. B., Gelwicks, M., Eggleston, C. M., & Parkinson, B. A. 2011, JAChS, 133, 17521
Schwell, M., Jochims, H.-W., Wassermann, B., et al. 1996, JPhCh, 100, 10070
Smith, M. L., Claire, M. W., Catling, D. C., & Zahnle, K. J. 2014, Icar, 231, 51
Suess, H. U. 2010, Pulp Bleaching Today (Berlin: De Gruyter)
Thorn, R. P., Stief, L. J., Kuo, S.-C., & Klemm, R. B. 1996, JPhCh, 100, 14178
Turner, A. M., Abplanalp, M. J., & Kaiser, R. I. 2016, ApJ, 820, 127
Witt, J. D., & Hammaker, R. M. 1973, JChPh, 58, 303
Zhang, F., Kaiser, R. I., Kislov, V. V., et al. 2011, JPhCh, 2, 1731