

OXIDATION OF CHLORIDE TO PERCHLORATE UNDER AMBIENT MARS CONDITIONS. B. L. Carrier* and S. P. Kounaves, Department of Chemistry, Tufts University, Medford, MA, 02155, USA (*brandi.galotti@tufts.edu).

Introduction: Perchlorate was first detected on the martian surface by the Wet Chemistry Laboratory (WCL) on the Phoenix Lander at a concentration of ~0.5 wt.% [1]. Perchlorate has subsequently been detected at similar levels by the Mars Science Laboratory (MSL) via pyrolysis experiments performed by the Sample Analysis at Mars (SAM) instrument suite [2]. Perchlorate has also been found in martian meteorite EETA79001 with a concentration of 0.6 ± 0.1 ppm by mass [3], and has also been proposed as a possible explanation for the presence of chlorinated hydrocarbons detected at the Viking landing sites [4]. As a whole this data seems to indicate a global distribution of perchlorate on Mars. The presence of perchlorate has wide ranging implications in terms of the oxidizing nature of the soil, the history of water on mars, the planet's current water cycle, formation of liquid brines, and for the preservation of organics on the surface.

Perchlorate on Earth is believed to be formed mainly through oxidation of atmospheric chlorine by ozone or its photochemical products in the stratosphere. A recent photochemical model based on terrestrial reactions that are likely to have been relevant on Mars over the past 3 byr [5] has shown that these reactions are insufficient by several orders of magnitude to explain the large amount of perchlorate measured by the Phoenix WCL [1] and Curiosity [2] on the surface.

Considering that Mars currently has no appreciable atmospheric chlorine source it can be inferred that if perchlorate was formed solely through the reaction of atmospheric chlorine then most of the perchlorate found on Mars would have been produced in the distant past. However, perchlorate has recently been shown to break down over time in the presence of ionizing radiation to form less oxidized intermediates such as hypochlorite (ClO^-) and chlorine dioxide (ClO_2) [6]. This seems to indicate that there is an ongoing mechanism for perchlorate production on Mars. One possible pathway is the heterogeneous reaction of soil chlorides with atmospherically produced oxidants or oxidants generated photochemically at the surface.

An ongoing source of perchlorate formation would indicate the likely presence of other oxychlorine species during the oxidation of chloride to perchlorate, such as ClO^- , ClO_2^- and $\text{ClO}_2(\text{g})$ as well as other possible radicals such as $\bullet\text{OCl}$, $\bullet\text{Cl}$, or $\bullet\text{OH}$. The presence of these intermediates has implications for the survivability of organics on the surface due to their high reduction potentials.

The current research aims to investigate the formation pathway for perchlorate on mineral surfaces under current Mars conditions.

Experimental: Perchlorate formation experiments have been performed in a Mars Simulation Chamber (MSC) which is capable of simulating typical Mars surface conditions such as temperature, pressure, atmospheric composition and UV flux.

The MSC consists of a stainless steel cylindrical chamber with an internal diameter of 60 cm and a depth of 45 cm. A Mars simulant gas mixture (95.3% CO_2 , 2.7% N_2 , 1.6% Ar, 0.13% O_2) is introduced into the chamber at a constant rate (8.25 SCCM) through a mass-flow controller. The pressure in the chamber is controlled via a vacuum pump and pressure transducer and can be regulated to typical Mars atmospheric pressure of $\sim 7.5 \pm 0.1$ mbar.

Temperature is maintained using a stainless steel cold plate coupled to a recirculating water/refrigerant chiller. Temperature for perchlorate formation experiments was maintained at -15°C . UV radiation is delivered via a series of filters through a fused silica window located on top of the MSC by a Newport Oriel 1000W Xe-arc lamp in order to simulate the spectrum of UV radiation incident on the martian surface.



Figure 1. Mars Simulation Chamber (MSC)

Sample preparation:

All mineral components are weighed and mixed using an agate mortar and pestle. Sodium salts are dissolved in 18.2 megohm-cm water and added to each sample. The sample is then dried, homogenized with a mortar and pestle, and distributed as a thin layer in a pyrex

dish. The samples are placed in the MSC, which is then allowed to reach optimal temperature, pressure and atmospheric composition before the sample is irradiated. After irradiation samples are leached in 18.2 megohm-cm water, typically at a 5:1 ratio, filtered through a 0.2 μm sterile filter and analyzed for perchlorate using a Dionex ICS-2000 ion chromatography system. For investigating the production of:

(a) ClO_4^- from Cl^- :

Samples consist of ground silica (SiO_2 50-70 mesh), iron(III) oxide (Fe_2O_3 , powder <5 μm , $\geq 99.0\%$), aluminum oxide (Al_2O_3 , powder 10 μm , 99.7%), titanium(IV) oxide, anatase (TiO_2 , powder, 99.8%) and sodium chloride (NaCl , $\geq 99.0\%$).

(b) ClO_4^- from ClO_2^- :

Samples consist of ground silica (SiO_2 50-70 mesh) and sodium chlorite (NaClO_2 , 80%)

(c) ClO_4^- from ClO_3^- :

Samples consist of ground silica (SiO_2 50-70 mesh) and sodium chlorate (NaClO_3 , $\geq 99.0\%$)

Results and Discussion: Preliminary experiments with ClO_2^- and ClO_3^- have shown that perchlorate forms relatively quickly from these species under MSC conditions without requiring the introduction of mineral oxidants to the soil simulant. Perchlorate has been detected in all samples of ClO_2^- and ClO_3^- which were irradiated for at least 6 hours. The amount of perchlorate formed from ClO_2^- was found to be an order of magnitude higher than the amount of perchlorate formed from ClO_3^- . This indicates that ClO_2^- may be a more likely intermediate for perchlorate formation on Mars, and that any reaction involving the oxidation of ClO_2^- to ClO_4^- does not appear to take place through a ClO_3^- intermediate.

The formation of perchlorate from Cl^- has proven to be more difficult, with no detection of perchlorate above the detection limit of the IC instrument using a simple SiO_2/NaCl soil simulant after exposure times of up to 4 weeks. For this reason several oxidized minerals known to be present on Mars have been added to the samples in an attempt to speed up the reaction. Concentrations of minerals were chosen based on analysis of martian surface fines in order to match martian surface conditions as closely as possible [7]. Samples consisting of ground silica, iron(III) oxide, aluminum oxide, titanium(IV) oxide and sodium chloride were found to contain perchlorate following 15 days of irradiation in the MSC. The amount of starting chlorine converted to perchlorate was found to be similar between these Cl^- samples and samples of ClO_2^- which were irradiated for 12 hours, indicating a rate up to 30x

slower for the initial oxidation of Cl^- to ClO_2^- than for the oxidation of ClO_2^- to ClO_4^- .

Conclusion: Our preliminary experiments have shown that perchlorate can be formed from chloride on mineral surfaces under current Mars conditions, which may explain the abundance of perchlorate found on the martian surface by Phoenix and MSL. Perchlorate is also formed easily from chlorite or chlorate starting materials under Mars conditions suggesting an initial slow step in the oxidation of chloride to perchlorate. Further research into the precise reaction mechanisms and pathways is warranted in order to fully understand martian oxychlorine chemistry as well as the oxidizing nature of the martian surface.

References:

- [1] Hecht M. H. et al. (2009) *Science*, 325, 64–67.
- [2] Leshin L. A. et al. (2013) *Science*, 341, DOI: 10.1126/science.1238937.
- [3] Kounaves S. P. et al. (2014) *Icarus*, 229, 206–213.
- [4] Navarro-Gonzalez R. et al. (2010) *J. Geophys. Res.*, 115, E12010.
- [5] Smith M. L. et al. (2014) *Icarus*, 231, 51-64.
- [6] Quinn R. C. et al. (2013) *Astrobiology*, 13(6), 515-520.
- [7] Clark B. C. et al. (1982) *J. Geophys. Res.*, 87, 10059-10067.