

FORMATION OF PERCHLORATE FROM CHLORINE SPECIES UNDER SIMULATED MARS CONDITIONS. B. L. Carrier* and S. P. Kounaves, Department of Chemistry, Tufts University, Medford, MA, 02155, USA. (brandi.galotti@tufts.edu).

Introduction:

Perchlorate (ClO_4^-) was first discovered on Mars at the Phoenix landing site in 2008 at concentrations of 0.4 to 0.6 wt % [1]. More recently results from Mars Science Laboratory (MSL) pyrolysis experiments performed by the Sample Analysis at Mars (SAM) instrument suite indicate the presence of an oxychlorine species in samples collected at Rocknest, Cumberland and John Klein sites, with calcium perchlorate being the most likely candidate [2,3]. Perchlorate has also been identified in martian meteorite EETA79001 [4] and has been proposed as a possible explanation for the detection of chlorinated hydrocarbons at the Viking landing sites [5]. Taken together this seems to indicate a global distribution of perchlorate on the martian surface. 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 and detection of organics on the surface.

On Earth perchlorate is formed primarily through the oxidation of atmospheric chlorine by ozone and/or oxygen containing radicals found in the stratosphere. Since Mars currently lacks a source of atmospheric chlorine this type of mechanism would only allow for formation of perchlorate in the distant past and would not support ongoing perchlorate formation. A recent photochemical model based on terrestrial reactions thought to be relevant on Mars over the past 3 byr suggests that this atmospheric formation mechanism would be insufficient by several orders of magnitude to explain the amount of perchlorate found by Phoenix and Curiosity [6]. It has also recently been shown that perchlorate is broken down over time by ionizing radiation to form less oxidized chlorine species such as hypochlorite (OCl^-) and chlorine dioxide (ClO_2) [7]. This seems to indicate that there must be an ongoing mechanism for perchlorate production on Mars to explain the high concentrations present on the surface.

One possible pathway is the heterogeneous reaction of soil chlorides with atmospherically produced oxidants or oxidants generated photochemically at the surface. Our current research shows that perchlorate, as well as chlorate (ClO_3^-), can in fact be formed through UV-irradiation of chloride salts on mineral surfaces under simulated Mars conditions. Further research has shown that oxychlorine ions such as chlorite (ClO_2^-) and chlorate (ClO_3^-) can also be oxidized to perchlorate under the same conditions. This suggests

an ongoing mechanism for perchlorate formation from chloride, and likely indicates the probable presence of other oxychlorine intermediates and radicals such as OCl^- , ClO_2^- , $\text{ClO}_2(\text{g})$, $\bullet\text{OCl}$, $\bullet\text{Cl}$ and others. The presence of these intermediates has serious implications for the survival and detection of organics as most of these intermediates, unlike perchlorate, are strong oxidizing agents at Mars ambient conditions. All of this seems to indicate the presence of a complex chlorine cycle on the martian surface.

Our current research aims to investigate factors that may influence the rate of perchlorate formation such as UV dosage, exposure time, relative humidity, concentration of atmospheric oxidants and effects of direct exposure to UV photons vs. exposure to atmospherically formed oxidants only.

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. UV dosage is measured over the course of the experiment using a Stellarnet UV spectrophotometer.

All samples were analyzed for perchlorate, chlorite and chlorate using a Dionex ICS-2000 ion chromatography system. Perchlorate analysis was performed using a Dionex AS-16 analytical column. Chlorite and chlorate analysis were performed using a Dionex AS-18 analytical column.

Results and Discussion:

Perchlorate formation from chlorite and chlorate

Our results show that perchlorate can be formed on mineral surfaces under Mars conditions from chloride, chlorite and chlorate starting materials. Figure 1 describes the percentage of Cl converted from ClO_2^- to ClO_4^- as a function of exposure time while Figure 2 shows the percentage of Cl converted from ClO_3^- starting material under the same conditions. As expected the amount of conversion to perchlorate increases with increasing exposure time. The amount of perchlorate formed from chlorite was about an order of magnitude of higher than the amount of perchlorate formed from chlorate at the same exposure times.

Experiments were conducted with and without the presence of water vapor in the MSC and no significant difference was found, suggesting that water vapor and hydroxyl radicals formed in situ do not play an important role in the oxidation of chlorite and chlorate to perchlorate.

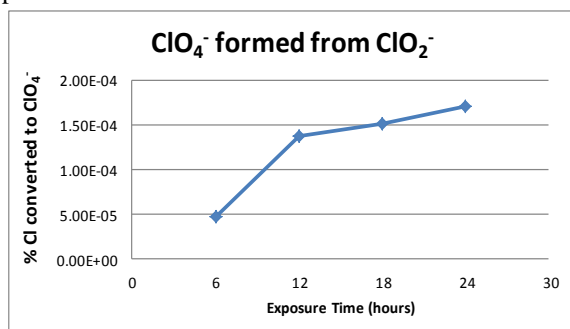


Figure 1. % of Cl (as ClO_2^-) converted to ClO_4^- as a function of time in the MSC.

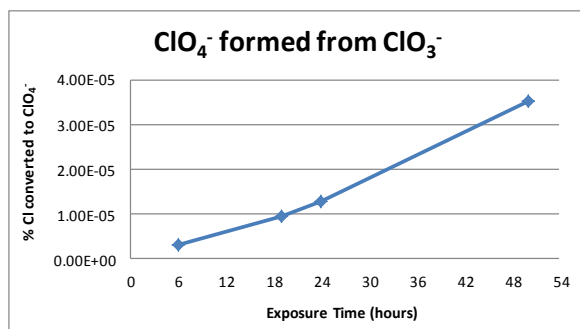


Figure 2. % of Cl (as ClO_3^-) converted to ClO_4^- as a function of time in the MSC.

Formation of perchlorate from chloride

All chloride containing samples were irradiated in the MSC for a period of 7 days (168 hours). Total sample mass was ~10 g and consisted of ground SiO_2 (50-70 mesh) coated with 0.4% Cl^- . Samples were then analyzed for ClO_2^- , ClO_3^- and ClO_4^- formation.

All samples were found to contain both ClO_3^- and ClO_4^- but not ClO_2^- . This may indicate that ClO_2^- is not an intermediate in the oxidation of Cl^- to ClO_4^- under typical Mars conditions. The amounts of chlorate and perchlorate formed in these experiments were found to increase with increasing UVC radiation dosage, as one might expect. The amount of chlorate formed was several orders of magnitude higher than the amount of perchlorate formed in all cases (see Table 1).

One sample was run consisting of only 0.4 g NaCl in a pyrex dish, and the amount of perchlorate formed was below the LOQ of the IC, but was approximately 5x lower than the amount formed when Cl^- was deposited on a SiO_2 substrate. This indicates that a mineral substrate increases the rate of perchlorate formation, most likely by allowing for adsorption of atmospherically formed oxidants on the surface and increasing their interaction with chloride.

Initial Cl^- (g)	ClO_3^- formed (ug)	ClO_4^- formed (ng)	UVC (J)
0.398	3.16	0.137	80
0.400	3.21	0.217	84
0.398	3.50	0.257	96

Table 1. Formation of ClO_3^- and ClO_4^- from simulants consisting of SiO_2 and Cl^- at appx 0.4 %.

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 formed more quickly from chlorite or chlorate starting materials suggesting an initial slow step in the oxidation of chloride to perchlorate.

All of this points to a potentially much more complex chlorine chemistry at the martian surface than as is currently understood. This has implications for the formation of liquid brines on Mars, as well as for the survival and detection of organics on the surface.

References:

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