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Photooxidation of Chloride by Oxide Minerals: Implications for Perchlorate on Mars

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S *Supporting Information*

ABSTRACT: We show that highly oxidizing valence band holes, produced by ultraviolet (UV) illumination of naturally occurring semiconducting minerals, are capable of oxidizing chloride ion to perchlorate in aqueous solutions at higher rates than other known natural perchlorate production processes. Our results support an alternative to atmospheric reactions leading to the formation of high concentrations of perchlorate on Mars.

Chemical analysis of Martian soil in the North Polar Region by the Phoenix Mars Lander provided evidence for the presence of high concentrations of perchlorate ion (0.4−0.6 wt %).[1] This ion accounted for approximately 25% of the anionic charge and exceeded chloride concentrations in different samples by factors of 4 to 8.[1,2] The atmospheric chemical reaction mechanisms proposed for Martian perchlorate formation[3] have difficulty explaining both the high perchlorate concentrations and perchlorate/chloride ratio. On Earth, levels of naturally occurring perchlorate found in many arid regions,[4] such as in nitrate ore deposits in the Atacama Desert, have concentrations ranging from 0.03 to 0.6 wt %[3,5] with chloride/perchlorate ratios of ~500:1. Recent results also indicate that naturally occurring perchlorate is present in the Antarctic Dry Valleys (ADV), a terrestrial environment considered to be the most like Mars, at levels of up to 1 ppm with a chloride/perchlorate ratio of ~1500−3000:1.[4f] The origin of such large concentrations of perchlorate on Mars is difficult to explain given its very high oxidation potential and the low concentrations of ozone and chlorine precursors in the Martian atmosphere compared to those on Earth.[5] The mechanism of terrestrial perchlorate production is still being debated,[3,4f] but current hypotheses invoke atmospheric chemical reactions of chlorine containing species with photochemically produced ozone as the primary oxidant[3,5b,6] Alternative hypotheses for perchlorate formation, such as heterogeneous reactions or the involvement of minerals in the photochemical production of perchlorate, have been suggested[3,5b,7] but with little supporting evidence. The thin Martian atmosphere, with low ozone levels, allows more solar UV radiation to impinge on the surface of Mars than on Earth, making heterogeneous reactions on mineral surfaces particularly relevant during carbon dioxide ice-free periods in Martian polar regions when condensed liquid water eutectics containing chloride and other salts could undergo photochemical reactions. The periodic wetting of the soil during Martian seasonal ice cap thawing and melting cycles, where initially a chloride containing eutectic electrolyte was present, could eventually oxidize nearly all available chloride ion especially as the freezing point of the eutectic was lowered[8] by the accumulation of perchlorate. Recent studies have also provided an explanation for the locally high concentrations of perchlorate resulting from translocation and concentration of perchlorate on the Martian surface.[9] Unspecified heterogeneous photochemical reactions on Mars have been invoked to explain the production of oxidants that could explain the Viking Lander observation of rapid initial oxidation of added organic material by the Martian soil[10] including Yen et al. who demonstrated the production of highly oxidizing superoxide ion from 254 nm illumination of feldspars.[11] However, there is little solar flux at this and shorter wavelengths and there are no reports of superoxide reacting with chloride ion to produce perchlorate. Therefore we explore whether UV illumination of naturally occurring semiconducting minerals could result in significant rates for the photochemical oxidation of chloride to perchlorate.

In a typical experiment, naturally occurring anatase or rutile crystals were mounted as a photoelectrode, immersed in a 0.5 M NaCl solution (adjusted to pH 9.7 with NaOH), connected to a graphite counter electrode in a quartz cell and irradiated with the unfiltered output of a 100 W Xenon lamp. The spectral distribution of UV photons in a Xenon arc resembles that of sunlight in space. Anatase and rutile are two polytypes of TiO_2 and have band gaps of 3.2 and 3.0 eV respectively allowing them to produce reactive electron hole pairs under illumination from any light with wavelengths shorter than about 400 nm where there is significant solar flux. The short circuit (no applied bias) photocurrent density and total charge passed between the anatase or rutile working electrode and the graphite rod counter electrode were monitored by a digital coulometer. Since the solution was exposed to atmosphere the reduction reaction at the counter electrode is assumed to be oxygen reduction. A perchlorate ion selective electrode (ISE)[12] was used to measure the photoelectrochemical production of perchlorate.

Figure 1a shows the photoelectrochemical production of perchlorate as a function of total charge passed during UV illumination of natural anatase (101) (black) and synthetic rutile (110) (red) crystals. The error bars were calculated from repeated measurements taken with the ISE during multiple perchlorate analyses. Multiple control experiments were performed in which
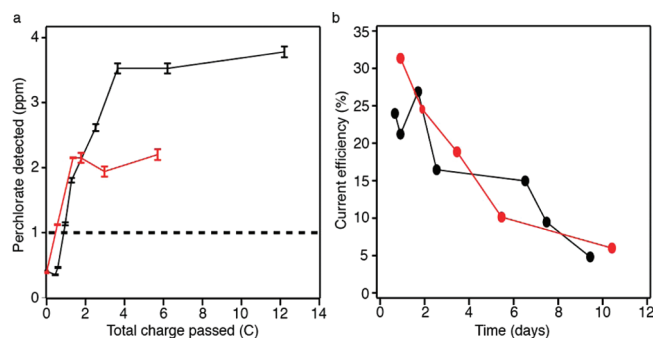
Figure 1. Photoelectrochemical production of perchlorate in chloride solutions. (a) The total amount of perchlorate detected as a function of total charge passed during UV illumination of natural anatase (101) (black) and synthetic rutile (110) (red) TiO_2 crystals over ~10 days. The dashed line represents the calculated ion selective electrode response from the maximum concentration from interfering ions (nitrate, bromide, iodide, and chlorate), and error bars represent the standard error in the electrode based on multiple perchlorate measurements. (b) The current efficiency of perchlorate production versus time is shown for the anatase (101)(black) and rutile (110) (red) crystals.

chloride solutions without a TiO_2 electrode present were illuminated or TiO_2 electrodes immersed in chloride solutions without illumination showed <1 ppm of perchlorate. Illuminated TiO_2 electrodes initially produced increasing perchlorate concentrations with time (or charged passed), but production eventually slowed as shown in Figure 1a. The initial photocurrent density of approximately 100 $\mu A/cm^2$ (anatase) and 140 $\mu A/cm^2$ (rutile) decayed to 10 $\mu A/cm^2$ and 14 $\mu A/cm^2$ (rutile) after about 18 h. The final concentration of perchlorate produced during the experiments was 3.8 and 2.2 ppm for the anatase and rutile electrodes respectively.

To exclude the possibility that interfering intermediate anions could account for the perchlorate ion selective electrode response, aliquots of the electrolyte removed from the sample cell at different times were analyzed with ion chromatography via EPA Method 314 by an independent laboratory[13] which confirmed the presence of perchlorate at concentrations comparable to our ISE measurements.

Using the total amount of perchlorate produced and the total charge passed during UV illumination of the TiO_2, the current efficiency of the 8 hole oxidation of chloride to perchlorate on both anatase and rutile was calculated (Figure 1b). The initial current efficiency for the oxidation process exceeds 20% and subsequently decays with time. We assume that the photooxidation of water to oxygen or chloride to chlorine accounts for the majority of the photocurrent on anatase and rutile photoelectrodes. On Mars, where there is only 0.13% oxygen in the atmosphere, the reaction cycle could proceed by a local electrochemical cell reducing oxygen from water oxidation or from the atmosphere to balance the chloride photooxidation. For example, the photoactive semiconducting particles in Martian soil could have highly doped conductive regions that are not illuminated where oxygen reduction could occur resulting in local photocatalytic cells. It is also possible that chlorine is produced as an intermediate product or byproduct and is easily reduced by photogenerated electrons, whereas any perchlorate production is a kinetic dead end due to its inertness to reduction. The half reactions for the 8 photogenerated valence band hole oxidation of chloride to perchlorate at the photoelectrode is

$$Cl^- + 4H_2O + 8h^+ \rightarrow ClO_4^- + 8H^+ \quad E° = 1.39 \text{ V} \tag{1}$$
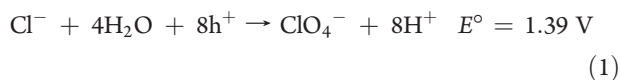
Other oxidation reactions that could compete with perchlorate production include the oxidation of water to oxygen and chloride to chlorine:

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \quad E° = 1.23 \text{ V} \tag{2a}$$
$$2Cl^- + 2h^+ \rightarrow Cl_2 \quad E° = 1.35 \text{ V} \tag{2b}$$
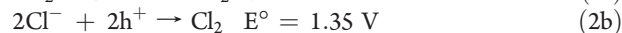
The reduction reactions from conduction band electrons at the counter electrode are the reduction of chlorine and/or oxygen.

We can then sum reaction 1 and the reverse of reaction 2a to obtain the overall perchlorate production reaction:

$$Cl^- + 2O_2 \rightarrow ClO_4^- \tag{3}$$

Reaction 3 is thermodynamically uphill with a $\Delta G°$ of 122.8 kJ/mol (1.28 eV/molecule) with the energy coming from UV light of greater energy than the TiO_2 band gap. However, the reaction pathway and the involvement or buildup of possible intermediates in the solution, such as chlorine, hypochlorite (ClO^-), chlorite (ClO_2^-), or chlorate (ClO_3^-), were not investigated.

It is clear that the experiments described herein using bulk aqueous conditions were not conducted under Mars-like conditions where temperatures between −20 and −98 °C were measured at the Phoenix lander site. However, there are several facts that we believe make these experiments relevant to the production of perchlorate in this environment. Photochemical reactions do not require thermal activation and so occur at low temperatures. The water needed for the photoelectrochemical reactions could be in the form of thin liquid water films that can exist and persist for long periods of time on mineral surfaces under Mars conditions as described by Mohlmann in a series of publications.[14] Aqueous freezing points are also significantly depressed by perchlorate, which has one of the largest freezing point depression constants of any anion, being as low as −70 °C with 30−50% perchlorate solutions. Liquid electrolyte phases are still present in equilibrium with water ice in solutions containing ions known to be present on the surface of Mars at temperatures as low as −50 °C. Liquid droplets, inferred to be salt eutectics, were observed on the Phoenix Lander.[15] The presence of the droplets, to temperatures as low as −48 °C, could be explained by the deliquesence of sodium perchlorate even under Mars-like conditions of low temperature, pressure, and relative humidity.[16] In addition, Mars experiences periodic climate oscillations on the 10 000 to several million year time scale that influence polar temperatures and water transport between the poles and lower latitudes[17] meaning larger quantities of ice and liquid water eutectics could have been present at this site during Mars' recent history.

Although there is no evidence for large concentrations of rutile or anatase on the Martian surface, there is clear evidence for titanium in Mars rocks and soils. Analyses of Martian soils have revealed up to 1.4% TiO_2 reported as oxide, but possibly existing within magnetite, ilmenite, and sphene.[18] Additionally, a micro-Raman survey of probable Mars-origin SNC meteorite SaU 060 revealed clear evidence of anatase.[19] The potential of the oxygen p-band in most semiconducting oxides is very oxidizing suggesting that other oxides such as hematite (α-Fe_2O_3) and ilmenite ($FeTiO_3$) could also accomplish this photocatalytic reaction. As a result, even small amounts of these minerals in the Martian soil could, over millennia, produce high concentrations of perchlorate, since once formed the highly oxidizing perchlorate ion is very kinetically stable in the absence of organic reductants, high temperatures, and microbial activity. The considerably higher perchlorate

to chloride ratios on Mars, as compared to the Atacama Desert of Chile and the Antarctic dry valleys, probably reflect the mechanisms of perchlorate loss that operate on Earth more quickly than on the colder and more arid surface of Mars. For hundreds of millions of years Mars has had no ocean and little volcanic activity resulting in an extremely slow chloride deposition rate. Slow deposition from atmospheric processes, coupled with slow loss, will probably not change the steady-state concentrations of both chloride and perchlorate by several orders of magnitude between the two planets. In contrast, even the lowest perchlorate production rates reported here, if active on less than 0.1% of the Mars near surface, could produce perchlorate at a rate 2000 times faster than the current atmospheric deposition rate at the Atacama Desert on Earth.[3]

In conclusion we have shown that perchlorate can be produced from chloride solutions by highly oxidizing valence band holes produced from UV irradiation of naturally occurring semiconducting oxide minerals. These results can explain the presence and accumulation of perchlorate in Martian soil. In addition, our mechanism, which is the most efficient natural perchlorate production process yet observed, predicts that, given enough time, chloride will eventually be mostly converted to perchlorate. This is one explanation for the disparate perchlorate to chloride ratios found on Mars compared to those in naturally occurring perchlorate deposits on Earth.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Complete refs 15 and 18a. This material is available free of charge via the Internet at http://pubs.acs.org.

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