

Photoelectrochemical generation of perchlorate and chlorate: Semiconducting minerals and Mars

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The discovery of abundant perchlorate (ClO_4^-) on Mars has resulted in many studies of photochemical ClO_4^- generation [1,2]. Some have concluded that it is impossible to explain the abundance of ClO_4^- on Mars using generation mechanisms akin to atmospheric gas-phase photochemical processes on Earth [3]. Here, we expand our study of the role of semiconducting minerals [4] either on the surface or in atmospheric suspension. Perchlorate can be generated via the action of simulated sunlight on anatase and rutile polymorphs of titanium dioxide (TiO_2), both with single crystals and with nanocrystalline films of particles. Chlorate (ClO_3^-) can be a major reaction product, however – in some experiments, no ClO_3^- is detected and in other experiments very little ClO_4^- is detected and ClO_3^- is the major product. The chloride (Cl^-) concentration is a key variable such that low Cl^- results in ClO_4^- , and high Cl^- results in ClO_3^- . Chlorate is not subject to rapid degradation in experiments with deliberately high starting ClO_3^- concentration, so we think that ClO_3^- is a key reaction endpoint under higher-chloride conditions. We also detect a Cl-deficit in detailed Cl mass balance calculations, and we suspect that a volatile reaction product, probably chlorine dioxide (ClO_2) gas, is escaping the aqueous phase.

As reported previously, under Earth conditions, ClO_4^- generation using TiO_2 polymorphs reaches a photostationary state akin to a photoequilibrium in which some of the reaction free energy is provided by photons.

We have conducted a series of experiments in a Mars Simulation Chamber (MSC) under Mars-like temperature, pressure, and atmospheric composition. Perchlorate is detected as a reaction product for illuminated semiconducting minerals when there is more oxygen in the atmosphere than is the case for Mars at present. This is true for different semiconducting minerals, probably reflecting the fact that Cl oxidation must be accompanied by a reduction reaction, and that under frozen conditions, metal reduction is not easily accompanied by reductive dissolution or photochemical water splitting. We have not detected abundant ClO_3^- in the MSC experiments. Perchlorate is not detected in the presence of silicon dioxide (SiO_2) solids – consistent with the hypothesis that the UV light absorption by semiconducting minerals produces oxidizing conditions, and we suggest that previous observation of ClO_4^- production with SiO_2 solids reflects an ozonation process, not a process of valence-band holes oxidizing Cl⁻.

[1] Hecht et al. (2009) *Science*. **325**, 64–67. [2] Carrier & Kounaves (2015) *Geophys. Res. Lett.*, **42**, 3739-3745. [3] Smith et al. (2014) *Icarus* 231, 51-64. [4] Schuttlefield et al. (2011) *J. Am. Chem. Soc.*, **133**, 17,521–17,523.