Perchlorate on Mars: Hematite and ilmenite as photocatalysts

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The discovery of abundant perchlorate (ClO_4^-) on Mars has prompted many studies of photochemical ClO_4^- generation [1,2]. The abundance of ClO_4^- on Mars cannot be explained using generation mechanisms thought to operate on Earth [3]. Here, we expand our study of semiconducting mineral photocatalysts [4] to include ClO_4^- generation by illumination of hematite and ilmenite in Cl^- solutions.

Experiments were conducted at -6°C and 4°C in a controlled-atmosphere Mars Simulation Chamber to maintain Mars-like temperature (experiments at lower temperatures are ongoing), pressure, gas composition, and illumination. The MSC was connected to a residual gas analyzer (RGA). Specially mixed "Mars atmosphere" compressed gas with variable O_2 concentration was used. Cl^--containing solutions were aspirated into a mineral particle-containing cup by the low chamber pressure, just enough to cover the mineral particles. The system was illuminated with a custom-built array of UV LEDs emitting at 340, 365, 375, 385, 395 and 405 nm with a total output between 100 and 240 W m^{-2}.

A subset of samples were cleaned with oxygen plasma to avoid complicating effects of organic impurities. ClO_4^- was not detected during illumination up to 6 days for all experiments with hematite and no plasma cleaning. ClO_4^- was detected in plasma cleaned samples – including hematite samples with no added chloride. The oxygen plasma provides oxidizing power that generates perchlorate. Some Cl^- may be embedded (absorbed into) the hematite particles.

For ilmenite, little or no perchlorate was detected for low gas-phase O_2 concentrations. For higher O_2 concentrations, photochemical ClO_4^- generation occurred. Similar results were found for hematite. Following [5], this implies OH radical production via an O_2-reduction pathway rather than by photogenerated holes in the semiconductor valence band. Another possibility is ozone production, but no volatile ClO_2, Cl_2, or O_3 species was detected by RGA.

[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. [5] Xu et al. (2013) EPSL 363, 156-167.