Photoelectrochemical generation of perchlorate on Mars: A photostationary state

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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. We show that ClO_4^- can be generated via the action of simulated sunlight on anatase and rutile polymorphs of TiO_2, both with single crystals and with nanocrystalline films of particles. Rutile, unlike anatase, results in relatively abundant chlorate intermediate, suggesting that the two polymorphs take different reaction pathways. Most importantly, ClO_4^- generation from chloride (Cl^-) levels out over time; in experiments with high starting ClO_4^-, the concentration decreases to a similar level as when ClO_4^- is generated from a zero starting concentration (Fig. 1).

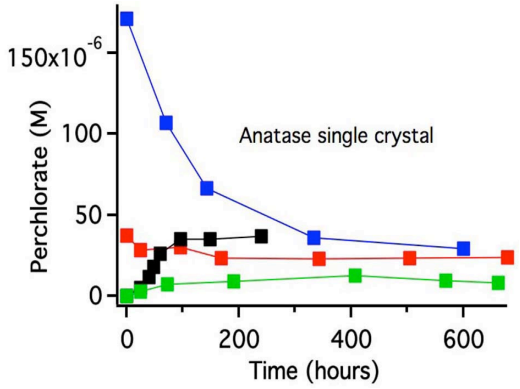

Fig. 1: Production/loss of aqueous ClO_4^- as a function of starting ClO_4^- concentration. Final [ClO_4^-] is similar despite variable initial [ClO_4^-]. Black = results from ref. 4, 0.5M Cl^-; Blue, Red, Green = 1.5, 0.7, 2.8 mM starting Cl-, respectively. Analytical error is smaller than symbol size.

The results suggest a photostationary state for perchlorate production; as [ClO_4^-] increases the rate of photochemical back-reaction increases until a "steady state" is reached. We have investigated heterogeneous ClO_4^- production using hematite as well, and in more Mars-like conditions. If the [ClO_4^-] that can be attained photochemically is thus limited, other concentration mechanisms may be required to explain how [ClO_4^-] on Mars are similar to those of 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.