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

B. A. Parkinson

Department of Chemistry and the School of Energy Resources[3]
University of Wyoming
Laramie, WY 82071

Chemical analysis of Martian soil in the North Polar region by the Phoenix Mars Lander unexpectedly detected high concentrations of perchlorate ion (0.4-0.6 weight %)[1] that accounted for ~60% of the anionic charge and exceeded chloride concentrations by factors of 4 to 8[1]. The atmospheric chemical reaction mechanisms proposed for perchlorate formation on Earth (ozone oxidation of chloride aerosols) has been extended to explain perchlorate production on Mars[2]. This mechanism appears implausible because there is very little ozone-producing oxygen in the Mars atmosphere and there is currently no ocean to produce chloride aerosols. Also, it does not account for the high perchlorate:chloride ratio on Mars because, where perchlorate is found on Earth, chloride exceeds perchlorate by factors of 500-3000:1. Alternative hypotheses for perchlorate formation, such as heterogeneous reactions or the involvement of minerals in the photochemical production of perchlorate, have been suggested[3] but with little evidence to support them. Herein we show that highly oxidizing valence band holes, produced by ultraviolet (UV) illumination of naturally occurring semiconducting minerals, such as the anatase and rutile forms of titanium dioxide, are capable of oxidizing chloride ion to perchlorate in aqueous solutions.

Our results can help explain the presence and accumulation of perchlorate in the polar Martian soil during Martian spring and fall where water is present without any contribution from atmospheric chemistry. In addition, our mechanism predicts that over millenia, even small amounts of semiconducting oxide minerals could eventually convert almost all the chloride to kinetically stable perchlorate, explaining the disparate perchlorate to chloride ratios found on Mars compared to those in naturally occurring perchlorate-containing soils on Earth.

(1) Hecht, M. H. *et al*., *Science*, ***325***, 64-67 (2009).
(2) Catling, D. C. *et al*., *J. Geophys. Res*., ***115***, E00E11 (2010).
(3) Miller, G. C.; Kempley, R.; Awadh, G. & Richman, K., *Abstr. Pap. Amer. Chem. Soc*., ***228***, U92 (2004).