THE RADIOLYTIC DECOMPOSITION OF SOIL PERCHLORATES ON MARS. R. C. Quinn[1] and P. J. Grunthaner[2], C. L. Taylor[1], C. E. Bryson[3], F. J. Grunthaner[2], [1]Carl Sagan Center, SETI Institute, NASA Ames Research Center, Moffett Field, CA 94035, Richard.C.Quinn@nasa.gov, [2]NASA Jet Propulsion Laboratory, Pasadena, CA 91109, [3]Apparati Inc., Mountain View CA, 94041

Introduction: We have reevaluated the results of the Viking biology experiments in the context of the discovery of the presence of soil perchlorate at 0.4 to 0.6 wt % at the Mars Phoenix landing site [1]. Primary observations made in the Viking biology experiments include: the release of O_2 from the soil when humidified or wetted with an aqueous solution in the Gas Exchange (GEx) experiment and the release of CO_2 resulting from the decomposition of one or more organic components of an aqueous solution added to the soil in the Labeled Release (LR) experiment [2].

Historically, interpretations of the results of the GEx and LR experiments have primarily focused on the possible presence of superoxide and hydrogen peroxide in the Viking soils and hypotheses of formation mechanisms for these species in the martian environment [3]. However, to date, no direct measurement of these species in martian soil has been made and neither H_2O_2 nor superoxide have been shown to reproduce all aspects (e.g., temperature stabilities) of the GEx and LR results in laboratory experiments. Complicating the interpretations of photochemically produced peroxide, superoxide, or other reactive oxygen species as the basis of the Viking results is the positive LR and GEx responses observed from soil collected at a depth of 10-20 cm. Transport mechanisms across grain boundaries in the soil or long duration stabilization mechanisms are required to explain the presence and persistence of these reactive species in soils shielded from UV light (at depth and under rocks).

Perchlorate Stability on Mars: The Mars Radiation Environment Experiment (MARIE) has measured ionizing radiation dose rates of 76 mGy/a at a 400km Mars orbit[4]. Ionizing radiation in the form of Galactic Cosmic Rays (GCR) and Solar Energetic Particles (SEP) is only slightly attenuated before reaching the martian surface and the penetration depth of the more energetic GCR radiation, with an estimated Pfotzer maximum up to 40 cm [5], exceeds the Viking sampling depth. Results of the Viking GCMS soil analyses indicate the presence of perchlorate in all tested samples [6]. Although perchlorate salts are strong oxidants, their stability under the aqueous conditions of the GEx and LR preclude them from being a direct explanation for the measured responses in these experiments. However, we expect that on Mars, perchlorate salts decompose in the surface and near subsurface ionizing radiation environment to form more reactive oxychlorine and oxygen species.

Experimental/Results: Figures 1 and 2 show the transformation of magnesium perchlorate into lower oxidation state chlorine species by 1.487 keV X-rays as measured by X-ray photoelectron spectroscopy (XPS). We have identified the formation of at least four chlorine species including chlorate, chlorite, hypochlorite, and chloride resulting from the radiolytic decomposition of perchlorate. Additionally, the formation of small amounts of chloride dioxide appears to be possible, although unambiguous identification has not yet been made.

In the Viking GEx experiment, the release of O_2 gas was observed when soil samples were either exposed to water vapor or wetted with an dilute solution of aqueous organics. We have measured the loss of chemically bond oxygen from the perchlorate samples during radiation exposure using XPS in combination with mass spectroscopic measurement of evolved gases. After radiolysis, consistent with the Viking GEx experiment, humidified samples are found release O_2 gas. Likewise, we have measured the production of $^{13}CO_2$ (g) after the addition of ^{13}C-labeled aqueous formate (one of the LR organics) to radiation exposed perchlorate samples. The quantities of O_2 (g) and CO_2 (g) produced in our experiments is variable and depends on an number of parameters including sample preparation methods and, as expected, the extent of perchlorate decomposition.

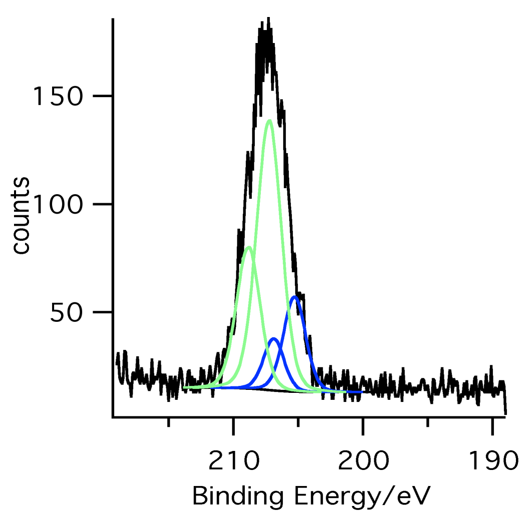

Figure 1: X-ray (1.48 keV) decomposition of 99% magnesium perchlorate. XPS spectra of chlorine 2p region ($2p_{3/2}$ $2p_{1/2}$ doublet). 2 hour exposure; 76% perchlorate (green) and 24% chlorate (blue).

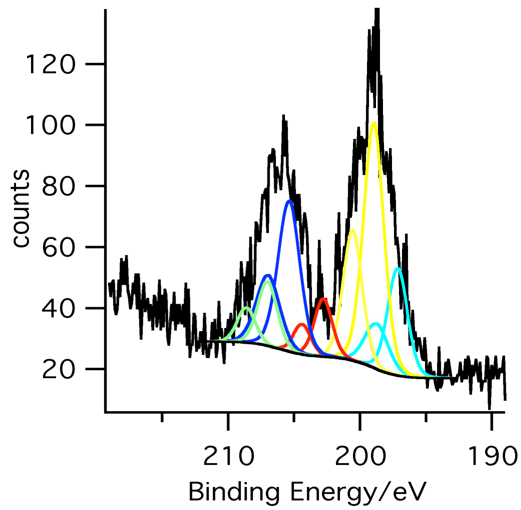

Figure 2: X-ray (1.48 keV) decomposition of 99% magnesium perchlorate. XPS spectra of chlorine 2p region ($2p_{3/2}$ and $2p_{1/2}$ doublet). 64 hour exposure; 17% perchlorate (green), 39% chlorate (blue), 8% chlorite (red), 26% chloride (yellow; tentative), 10% hypochlorite (cyan; tentative).

Discussion: In the absence of secondary soil reactions or transport driven ion segregation, the measured ClO_4^- to Cl^- ratios (~10:1 average) at the Phoenix site [6] indicate that extensive radiolytic decomposition of perchlorate on Mars has not occurred. This is consistent with recent atmospheric formation as the origin of soil perchlorates on Mars [7] and the relatively small amounts gases produced in the GEx and LR experiments. On Mars, perchlorate decomposition rates and products should be influenced by a number of factors including ionizing radiation particle distributions and the generation of secondary particles in the regolith, as well as chemical reaction of radiolysis intermediates. During the radiolysis of perchlorate, the formation of reactive oxygen intermediate species including superoxide radicals is likely. However, the observed formation and release of O_2 (g) from irradiated perchlorate suggests that trapped molecular oxygen maybe responsible for the release of oxygen in the Viking GEx experiments. The presence of trapped oxygen is also consistent the high thermal (145 C) and temporal stability of the species responsible for the GEx O_2 release.

Conclusions: Our experiments indicate that on Mars ionizing radiation will decompose soil perchlorates to form reactive oxyhalide and oxygen species. These species likely play a role in the alteration of soil organics *in situ* and are likely responsible for the release of O_2 in the Viking GEx experiment and the decomposition of organics in the Viking LR experiment. The surface penetration depth of ionizing radiation on Mars exceeds the sampling depth of the Viking Lander and, in combination with soil perchlorate, can explain both the presence and persistence of reactive species in Martian soils that are shielded from UV light.

References: [1] Hecht M. H., et al. (2009) *Science*, 325, 64-76. [2] Klein H. P., et al. (1976) *Science*, 194, 99-105. [3] ten Kate I. L. (2010) *Astrobiology*, 10, 589-603. [4] Zeitlin C., et al. (2004) *Adv. Space Res.* 33, 2204-2210. [5] Morthekai P., et al. (2007) *Nuc. Ins. Met. Phys. Res.* 580, 667-670. [6] Navarro-Gonzalez R., et al. (2010) *JGR*, 115, E12010. [7] Kounaves S. P., et al. (2009) *JGR*, 114, E00A19. [8] Catling D. C. et al. (2010) JGR, 115 E00E11.

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