RADIOLYTIC ALTERATION OF BIOSIGNATURES ON MARS. R. C. Quinn[1], [1]Carl Sagan Center, SETI Institute (NASA Ames Research Center, M/S 239-4 Moffett Field, CA 94035, Richard.C.Quinn@nasa.gov)

Introduction: A major objective of the Mars 2020 mission will be to "explore an astrobiologically relevant ancient environment on Mars to decipher its geological processes and history, including the assessment of past habitability and potential preservation of possible biosignatures" [1]. This exploration strategy follows on the success of the remarkable geological discoveries made with the Mars Science Laboratory (MSL) and Mars Exploration Rovers (MER), including evidence of ancient environments, which based on evaluation of geological context, may have once been habitable. For example, a habitable fluvio-lacustrine environment at Yellowknife Bay in Gale Crater has been explored by MSL [2]. The discovery of clay minerals in Esperance by the Opportunity rover on the rim of Endeavour Crater, suggests that the area was once a habitable aqueous environment with a circum-neutral pH [3]. Much earlier in the MER mission, the Sprit rover uncovered ample evidence for the presence of potentially habitable environments in the form of sedimentary outcrops including sulfates and carbonates [e.g., 4]. These are just a few examples and with each successive Mars mission the geological evidence for, and distributions of, ancient habitable environments increases.

However, while contextual information derived from in situ observations has lead to the identification of numerous preserved geological formations that were likely habitable on early Mars, examination of some of these materials on a molecular scale indicate that extensive chemical alteration has occurred. The results of the biological and chemical analyses performed at the Viking, Phoenix, and MSL landing sites highlights the current knowledge gaps in our understanding of the alteration of ancient habitable environments and potential impacts on chemical and biosignature preservation. It appears that chemical alteration mechanisms on Mars, driven by surface and subsurface radiation environments, is remarkably different from environments on Earth, and calls into question the current state knowledge about the chemical state of martian geological formations and preservation state of biosignatures on Mars.

Experimental: Spatially and temporally evolved alterations in synthetic and natural Mars analogs materials are experimentally probed using X-ray Photoelectron Spectroscopy (XPS). The technique allows the characterization of localized chemical alteration induced in situ in the XPS system using X-ray, e-beam, and ion-gun ionizing radiation sources.

Figure 1 shows an example of the transformation of calcium perchlorate into lower oxidation state chlorine species by ionizing radiation (1.487 keV X-rays) as measured by XPS in the lab.

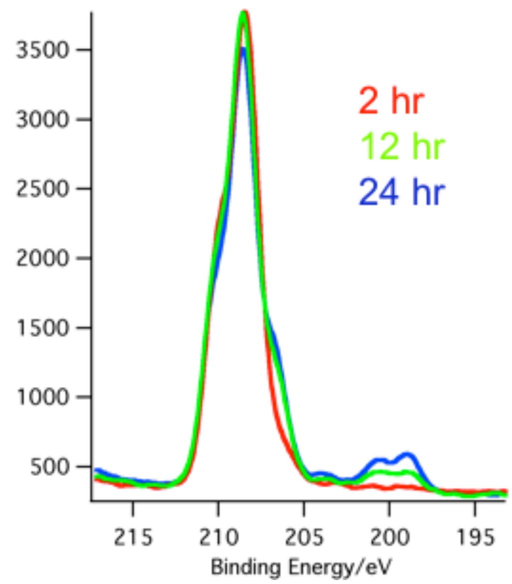

Fig. 1. Calcium perchlorate XPS spectra of the chlorine 2p region ($2p_{3/2}$ $2p_{1/2}$ doublet). Formation of peaks at binding energies 204-198 eV over time indicate the formation of chlorine dioxide, hypochlorite and chloride upon sample to exposure to ionizing radiation.

Our results show a that, when exposed to ionizing radiation, a complex distribution of redox states and reactive intermediates form in both perchlorate and nitrate salts. These reactive species, in turn act to alter associated organic biosignatures in situ. These results will be discussed in the context of organic biosignature alteration mechanisms and forms organic biosignatures that may be preserved on Mars.

References:

[1] NASA Mars 2020 Announcement of Opportunity. [2] Grotzinger et al. (2013) *Science*, 341(6153), 1475–1475. [3] Arvidson et al. (2014) *Science* 343(6169). [4] Morris et al. (2010) *Science*, 329(5990), 421–424.

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