RAPID DEGRADATION OF THE ORGANIC MOLECULES IN MARTIAN SURFACE ROCKS DUE TO EXPOSURE TO COSMIC RAYS. SEVERE IMPLICATIONS TO THE SEARCH OF THE "EXTINCT" LIFE ON MARS. A. A. Pavlov[1], J. Eigenbrode[1], D. Glavin[1], M. Floyd[1], [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771 (alexander.pavlov@nasa.gov)

Introduction: Until recently, long-term exposure to cosmic rays (CRs) has not been recognized as a major environmental factor, which can alter and destroy organic molecules in the Martian surface rocks. This topic is critical because the entire strategy of the Mars Exploration Program's search for the extinct life on Mars is based on the assumption that some original complex organic molecules would be able to survive for hundreds of millions - billions of years in the ancient Martian outcrops. Moreover, current MSL, future Mars2020 will sample only the top few cm of the surface Martian rocks. Organic molecules at those depths are essentially unprotected against cosmic ray radiation.

Recent modeling studies [e.g. 1] suggested that organic molecules with masses >100 amu would be effectively destroyed in less than 1 billion years in the top 5 cm of the Martian rocks. However, Pavlov et al calculated the fraction of the survived organic molecules using conservative radiolysis constants derived from the gamma irradiation experiments on pure dry amino acid mixtures [2]. Cosmic rays can produce oxidative radicals in the immediate vicinity of the organic molecules within the rocks and increase the rate of organic degradation.

Methods: To evaluate the rate of organic degradation by cosmic rays in Martian rocks we exposed aminoacids (AAs) and carboxylic acids (CAs) mixed with SiO_2 powder to gamma ray ionizing radiation (an analogue of CRs). For the analysis of AAs abundance and distribution in SiO_2 powder we used the extraction procedure and liquid chromatography time of flight mass spectrometry techniques from [3]. Analysis of CAs abundance and distribution in SiO_2 powder were conducted using a modified thermochemolysis gas chromatography mass spectrometry (i.e., a reactive pyrolysis) method [4]. The effects of accumulated dosage of up to 2 MGy were investigated by comparing the amount of organic compounds in control (non-irradiated) samples relative to irradiated materials.

New radiolysis constants for aminoacids and carboxylic acids were derived. Radiation accumulation rates in the Martian rocks were derived with the state-of-the-art GEANT4 code. Newly derived radiolysis constants were then combined with the radiation accumulation rates to determine the rate of organic destruction and alteration by Galactic Cosmic Rays (GCRs) and Solar Cosmic Rays (SCRs) on Mars.

Results: 1) Aminoacids. The destruction rate of aminoacids (AAs) in silicate powder mixtures is dramatically higher than in pure dry amino acid mixtures (Fig 1). Therefore, all aminoacid molecules, which were either produced (by biosphere) or deposited (by meteorites) on Mars earlier than 100 million years ago would have very little chance of survival in the surface Martian rocks.

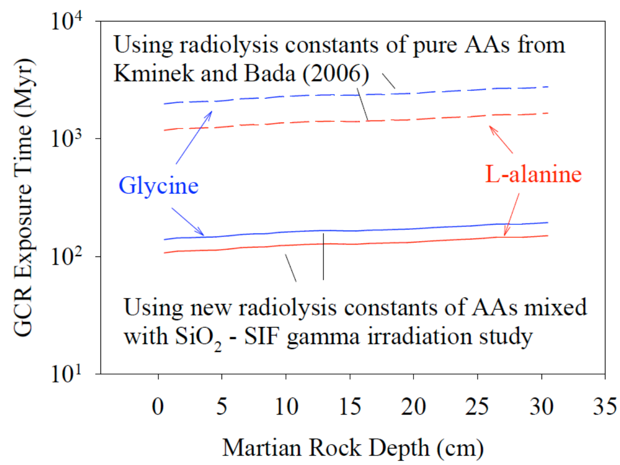

Fig 1 *GCR exposure time for a 1000-fold decrease in AAs abundance in Martian rocks. Here we compare changes in the degradation rates of pure aminoacids (dashed lines) vs. amino-acids mixed with SiO_2 (solid lines). Addition of silica powder makes degradation much more effective.*

2) Carboxylic acids. Large polycyclic aromatic hydrocarbons (PAHs) having a single carboxylic acid group are regarded as stable and refractory to geological processing by terrestrial standards. Therefore, PAHs should have displayed the least amount of loss when exposed to radiation in pure from. However, once added to silicate (with or without the presence of water), nearly the entire standard had degraded by 0.2 MGy dosage. It is particularly surprising that PAHs, generally thought of as more refractory organic molecules in sedimentary conditions, are lost at the fastest rate. This suggests that PAHs in silicates on Mars will not survive long after surface exposure, unless there is another, yet unknown, mechanism that aids their resilience in an ionizing radiative environment.

3) AAs and CAs. The destruction rate of both carboxylic acid or aminoacids increases dramatically even

further if several percents of H_2O are added to the SiO_2 mixture. Hydrated minerals may be the worst place to look for the intact ancient organic molecules on Mars.

Discussion: Rapid degradation of the original organic molecules in the Martian rocks by CRs does not necessarily mean that the organic matter in the irradiated rocks is destroyed completely. It is very plausible that during CRs' irradiation the complex organic molecules would be broken only partially. It is also likely that the survived small organic molecules would have incorporated O, OH, Cl radicals in their structure during irradiation. However, for the search of the "extinct" ancient life on Mars the detection of transformed, partially oxidized or chlorinated organic matter may not be definitive. Our results strongly imply that in order to have a chance to detect the intact complex organic molecules in the surface rocks on Mars, MSL and future missions should seek rocks with <10 Myr (million years) exposure ages. Therefore, if the future missions maintain the focus on the "extinct" life then they should have the capability to drill below 2 meters or their landing location should be in the vicinity of the freshly exposed rock (e.g. recent crater or highly erodible rock).

References: [1] Pavlov A. A. et al. (2012) GRL doi:10.1029/2012GL052166. [2] Kminek, G., and J. Bada (2006), Earth Planet. Sci. Lett. 245, 1-5. [3] Glavin D & Dworkin J (2009) P Natl Acad Sci USA 106(14):5487-5492. [4] Blokker P. et al. (2002) Journal of Chromotography A, 959 (2002), pp. 191-201.