

PYROLYSIS OF ATACAMA SOILS WITH ADDED PERCHLORATES: IMPLICATIONS FOR THE VIKING RESULTS. R. Navarro-González¹, E. Vargas¹, J. de la Rosa¹, and C.P. McKay², ¹Laboratorio de Química de Plasmas y Estudios Planetarios, Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Apartado Postal 70-543, México D.F. 04510, MEXICO (navarro@nucleares.unam.mx), ²Space Science Division, NASA Ames Research Center, Moffett Field, CA 94035-1000, USA (chris.mckay@nasa.gov).

Introduction: The abundance of chlorine in the martian soil has been measured *in situ* by the Viking Landers [1-3], the Mars Pathfinder Rover [4-6], and the twin Mars Exploration Rovers [7-9] with the use of x-ray fluorescence spectrometry. In addition, it has been determined by remote sensing using the gamma ray spectrometer onboard the Mars Odyssey [10]. Chlorine has been recognized as an important chemical component of the Martian surface with a chemical abundance that varies from 0.2 to 2.6 wt% from the equator to mid latitudes ($\pm 50^\circ$). However, these instruments detected the element itself but provided no information on its chemical form. Because chlorine on Earth is generally found as chloride, it was logically believed to be in this form in the martian soil [11]. The only chemical analysis of soluble salts in soils on Mars has been recently carried out by the Phoenix Lander [12] in the arctic ($+68.3^\circ$). Surprisingly, chlorine was present as perchlorate at 0.4 to 0.6 wt% and chloride was only a minor constituent: 0.01 to 0.04 wt%. Additional support for the identification of perchlorate came from the thermally evolved gas analysis [12, 13], which detected the release of molecular oxygen when the soil was heated from 325 to 625°C. No inorganic chlorine species were observed during this analysis presumably because chlorine atoms reacted with the Ni ovens of the instrument and therefore were not evolved to MS. Based on the abundances of dissolved cations present in the martian soil [12], it is expected that perchlorate is in the form of magnesium perchlorate or calcium perchlorate. The discovery of perchlorate at an arctic site does by itself demonstrate perchlorate at the equatorial sites.

In perchlorate, the chlorine atom is in a high oxidation state (+7) and is surrounded by four oxygen atoms in a tetrahedral (T_d) symmetry. Thermodynamically speaking, perchlorate is a very strong oxidant. The standard oxidation potential for perchlorate is $E^\circ = 1.20\text{V}$ ($\text{ClO}_4^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{ClO}_3^- + \text{H}_2\text{O}$); however, due to its symmetry, it has tremendous kinetic stability unless it is present in a highly acidic medium or subjected to heat [14]. Naturally occurring perchlorates have been found in the Atacama Desert [15], one of the driest places on Earth with Mars-like soils [16], where its soil abundance is only about 0.03 wt% in contrast to 4.6 wt% for chloride.

We report here results from the characterization of major gases and volatiles released by thermal volatilization (TV) of Mars-like soils from the Atacama Desert which have been enriched with 1 wt% magnesium perchlorate, and processed using the Viking lander heating protocol [17, 18] but with an extended temperature range: 200°-1,000°C. In these experiments, soil was subjected to TV-GC-MS; this assay consisted of a rapid heating of the soil to vaporize small molecules and break down larger ones into smaller organic molecules, and the resultant fragments were swept away from the oven into the GC, where they were separated and then analyzed by MS. The resultant gases and volatiles were separated by GC and analyzed by MS. Soil samples were collected from the arid core region of the Atacama Desert in Yungay, Chile, which contains Mars-like soils in the surface [16]. These soils have extremely low levels of culturable bacteria, low organic concentrations, and the presence of a non-chirally specific oxidant. Search for organics in this soil sample has been thoroughly investigated using the Viking [19] and Phoenix [20] Landers protocols.

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