“III Congreso Latinoamericano de Astrobiología (2021)”
Revista Mexicana de Astronomía y Astrofísica Serie de Conferencias (RMxAC), **55**, 77–79 (2023)

https://doi.org/10.22201/ia.14052059p.2023.55.21

III Latin American Congress of Astrobiology (3CLA)(Virtual-Modality, August 3-6, 2021)
Editors: Leticia Carigi, Sandra I. Ramírez Jiménez, Miguel Chávez Dagostino, and Millarca Valenzuela - DOI: https://doi.org/10.22201/ia.14052059p.2023.55.21

PRODUCTION OF PERCHLORATES AND NITRATES BY ELECTRIC DISCHARGES IN DUST DEVILS ON MARS

P. U. Martínez-Pabello[1] and X. Walls[2]

RESUMEN

La presencia de nitratos y percloratos en Marte ha sido ampliamente estudiada. Los percloratos debido a su capacidad para oxidar materia orgánica, mientras que los nitratos por la posibilidad de formar un ciclo del nitrógeno en Marte. En este trabajo demostramos experimentalmente el mecanismo de formación de estas sales por descargas triboeléctricas en torbellinos de arena. Se irradió un suelo análogo a Marte (HW) dentro de una atmósfera simulada marciana y, simulando descargas eléctricas, se logró producir nitratos y percloratos en el reactor. Esto fue determinado mediante Espectroscopía de Fotoelectrones emitida por Rayos X (XPS) y Espectroscopía Raman (RS).

ABSTRACT

The presence of nitrates and perchlorates on Mars has been extensively studied. Perchlorates for their ability to oxidize organic matter while Nitrates for the possibility of forming a nitrogen cycle on Mars. In this work we experimentally demonstrate the mechanism of formation of these salts by triboelectric discharges in dust devils. A Mars-like soil (HW) was irradiated within a simulated Martian atmosphere and, by simulating electrical discharges, it was possible to produce nitrates and perchlorates in the reactor. This was determined by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy (RS).

Key Words: Mars

1. INTRODUCTION

The search for organics by the Viking mission in 1976 concluded that there was no organic matter in the Martian soil (Biemann, 1977). It was later determined that the presence of a strong oxidant was responsible for these negative results (Navarro-González et al., 2010). In 2009, the Phoenix mission landed at the north pole of Mars, the presence of a strong oxidant was determined: perchlorate (ClO_4^-) (Hetch et al., 2009). Perchlorates would also be detected from orbit by the Curiosity rover in 2013 and by the Mars Reconnaissance Orbiter (MRO) in 2015 (Glavin et al., 2013; Ojha et al., 2015), indicating a global distribution in the planet (Clark and Kounaves, 2016). Nitrogen is considered an essential element for life since it is part of amino acids and proteins. It is believed to be found on Mars in the form of nitrates and was first observed in 2014 by the Curiosity rover (Archer et al., 2014; Ming et al., 2014). Since the discovery of perchlorates and nitrates on Mars, different research groups have made proposals for reaction mechanisms for the formation of both salts (Atreya et al., 2006; Smith et al., 2014; Tennakone, 2016). The photodissociation of HCl and N_2 by gamma and ultraviolet rays in the Martian atmosphere have been some of the most accepted theories. Recently, a new theoretical proposal has been developed in this respect, the formation of these oxidizing compounds by electrical discharges in dust devils and sandstorms (Tennakone, 2016). The presence of dust devils and sandstorms on Mars has been detected by different orbiters and rovers (Thomas and Gierasch, 1985; Schofield et al., 1997; Fisher et al., 2005; Stanzel et al., 2006; Reiss et al., 2014; Guzewich et al., 2017). Within them there may be triboelectricity (electrical discharges due to friction between small dust particles), and they can volatilize and oxidize salts associated with chlorine and nitrogen (Kok and Rennó, 2008; Zhai et al., 2006). Some studies have been carried out on the subject, where simulated electrical discharges were applied to sodium chloride crystals inside of a simulated martian atmosphere (Wu et al., 2018; Martínez-Pabello et. al., 2019). In the present work we demonstrated, for the first time, that perchlorates and nitrates can be formed inside of an experimental system that simulates the existent conditions of dust devils and sandstorms by using a Mars analog soil (Hawaiian basalt). The results were confirmed

[1]Instituto de Geología, UNAM, Ciudad Universitaria, C.P. 04510, CDMX,México (pavelm@geologia.unam.mx).
[2]Department of Mechanical and Aerospace Engineering, Carleton University, Ottawa, Canada (xalls16@gmail.com).

III Latin American Congress of Astrobiology (3CLA)(Virtual-Modality, August 3-6, 2021)
Editors: Leticia Carigi, Sandra I. Ramírez Jiménez, Miguel Chávez Dagostino, and Millarca Valenzuela - DOI: https://doi.org/10.22201/ia.14052059p.2023.55.21

by analyzing the samples with two analytical techniques.

2. METHODS

Volcanic soil samples (HW), collected from the Ka'u desert in Hawaii, were used. This site is considered one of the best analogues to the Martian basalt. The sample was introduced into a vacuumed glass reactor at $2X10^{-3}$ mbar and filled with the present-day Martian atmosphere: 96% CO2, 2% N_2 and 2% Ar. All the Praxair gases used were of high purity (CO_2 = 99.99%, N_2 = 99.999% and Ar = 99.99%). The simulated atmosphere gas mixture was prepared using a gas blender (Linde FM-4660), the gases were dosed with electronic channels that measure the mass flow of the gas by thermal conductivity (Omega DP-80). The simulation of electric discharges was performed by focusing a 6mm diameter beam from a pulsed Nd: YAG laser source (Surelite II-10 Continuum), which was operated at 10 Hz for 7 ns and a pulse of 300 mJ. The reactor was irradiated four times for 45 min until obtaining dust from the HW sample as a product of laser ablation. The collected dust was analyzed with X-ray Photoelectron Spectroscopy (XPS) and Raman Spectroscopy (RS).

3. RESULTS

With both analytical techniques used, the presence of various oxidized salts of chlorine and nitrogen was found.

3.1. *X-Ray Photoelectron Spectroscopy (XPS)*

Irradiated and unirradiated HW sample spectra are shown in Figure 1. Figure 1a, shows the amplification of the region from 411 to 395 eV which corresponds to nitrogen. The sample that was not irradiated shows a less abundant peak (400.33 eV) compared to the irradiated sample. This implies that the nitrogen abundance increased after the ablation. On the other hand, Figure 1b, shows an amplification of the region from 212 to 204 eV which corresponds to chlorine abundance. The irradiated HW sample shows an abundant peak, which might be the result of the sum of several oxidized species of chlorine (2p bonds of Cl-O: $NaClO_4$ = 208.5 eV, 2p for $NaClO_3$ = 206.4 eV and 2p for $NaClO_2$ = 203.4 eV). In unirradiated HW, no significant abundances of chlorine-associated species are observed.

3.2. *Raman Spectroscopy (XPS)*

Figure 2 shows the Raman spectra of two pure standards of sodium nitrate ($NaNO_3$) and sodium

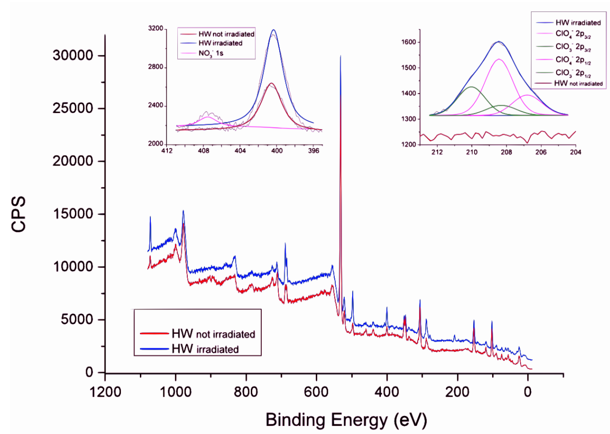

Fig. 1. Comparison of unirradiated and irradiated HW XPS spectra. The signal corresponding to nitrate is at 407.3 eV (a), while for perchlorate (b) it is at 208.5eV with a contribution of 1/2 (purple) and chlorate at 206.4 eV also with its contribution 1/2 (green).

perchlorate ($NaClO_4$• H2O), an unirradiated sample of hawaiian basalt HW and the ablation products of HW. Irradiated HW signals (red) in the peaks at 941 cm^{-1} and 1044 cm^{-1} fit with the main signals of the perchlorate (952 cm^{-1}) and nitrate (1052 cm-1) standards respectively (Gu et al., 2004); the perchlorate standard peak is slightly shifted to the left, probably due to the presence of water molecules in its structure. Basalt is rich in silicates (Si-O) and this compound has a main band around 1100 cm^{-1} that could be increasing the observed signal; however, it also has characteristic signals at 570 and 460 cm^{-1} (White and Minser, 1984) that are not observed in the spectrum, which suggests that there is the presence of nitrate and perchlorate formed after laser ablation. The unirradiated HW sample (blue), has a characteristic behavior to that of obsidian, which is an amorphous glass; this indicates that there was no previous contribution of any oxidized salt of chlorine or nitrogen.

4. DISCUSSION

The formation of perchlorates and nitrates by simulating electrical discharges on Mars had only been a theoretical proposal (Tennakone, 2016) and had been only experimentally demonstrated on sodium chloride (Martínez-Pabello et al., 2019). The present work demonstrated the formation of these salts directly in a soil analogous to Mars, which implies that this formation mechanism is feasible for it to happen in dust devils and sandstorms on Mars, since they are very common and global phenomena. It is also feasible that a two step process is involved

III Latin American Congress of Astrobiology (3CLA)(Virtual-Modality, August 3-6, 2021)
Editors: Leticia Carigi, Sandra I. Ramírez Jiménez, Miguel Chávez Dagostino, and Millarca Valenzuela - DOI: https://doi.org/10.22201/ia.14052059p.2023.55.21

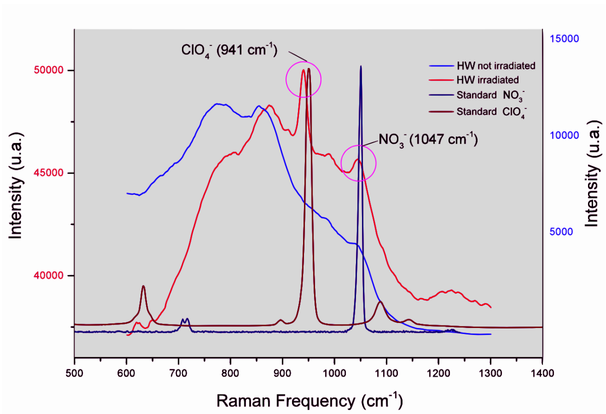

Fig. 2. Raman spectra of unirradiated HW (blue), HW with ablation (red), nitrate standard (dark blue) and perchlorate standard (cherry). The bands at 941 and 1047cm^{-1} of HW fit with the main signals of the reference compounds (perchlorate and nitrate, respectively).

in the formation of these salts. Chlorides on the martian surface would be affected by triboelectricity, volatilizing them. The suspended particles would be irradiated by cosmic, gamma, ultraviolet rays and also by the same electric discharges within them, transforming atmospheric N_2 and surface chlorides into nitrates, chlorates and perchlorates respectively. After the geological phenomenon they would be deposited, fixed and accumulated on the surface of the red planet. These experiments are a first approach to a more complex formation mechanism; gas evolution, low pressures and temperatures should be considered in future works.

5. CONCLUSION

The presence of chlorates, perchlorates and nitrates was determined by XPS and RS in an irradi-

6. CONCLUSION

ated basalt sample from Hawaii inside a simulated Martian atmosphere. This demonstrates that atmospheric N_2 and chlorides on the surface of Mars can be volatilized into the atmosphere by triboelectricity within dust devils and sandstorms and subsequently be fixed as nitrates, chlorates and perchlorates on the surface of Mars.

REFERENCES

Archer Jr, P. D., et al. 2014, JGRE, 119, 237
Atreya, S. K. et al. 2006, Asbio, 6, 439
Biemann, K., et al. 1977, JGRE, 82, 4641
Clark, B. C., and Kounaves, S. P. 2016, IJAsB, 15, 311
Fisher, J. et al. 2005, JGRE, 110, 1
Guzewich, S.D., et al. 2017, 6th Int Worksh Mars Atmos, Spain
Glavin, D. P., et al. 2013, JGRE 118, 1955
Gu, B., Tio, J., Wang, W., Ku, Y. K., & Dai, S. 2004, ApSpe 58, 741
Hecht, M. H., et al. 2009, Sci, 325, 64
Kok, J. F., and Nilton O. R., 2009, GeoRL, 36, 2
Martínez-Pabello, P. U., et al. 2019, LSSR, 22, 125
Ming, D. W., et al. 2014, Sci, 343, 6169
Navarro-González, R., et al. 2006, PNAS, 103, 16089
Ojha, L., et al. 2015, NatGe, 8, 829
Reiss, D., Hoekzema, N., and Stenzel, O., 2014, P&SS 93, 54
Schofield, J. T. et al. 1997, Sci, 278, 1752
Smith, M. L., et al. 2014, Icar, 231, 51
Stanzel, C. et al. 2006, GeoRL, 33, L11202
Tennakone, K., 2016. Astrobio, 16, 811
Thomas, P. and Gierasch, P.J., 1985, Sci, 230, 175
White, W. B., and Minser D. G., 1984, JNCS 67, 45
Wu, Z., et al. 2018, EPSL, 504, 94
Zhai, Y., Cummer, S.A., and Farrell, W. M., 2006, JGRE 111, 1