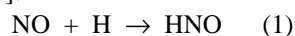


DETECTION OF NITRITES BY THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT. IMPLICATIONS FOR THE OXIDATION STATE OF THE ATMOSPHERE. R. Navarro-González¹, P. Coll², B. Sutter³, J.C. Stern⁴, C.P. McKay⁵, F.J. Martín-Torres^{6,7}, M.-P. Zorzano-Mier^{6,8}, P.D. Archer³, A. Buch⁹, M. Cabane¹⁰, D. Coscia¹¹, D. Glavin⁴, H.B. Franz⁴, C. Freissinet¹⁰, A.C. McAdam⁴, D.W. Ming¹¹, B.D. Prats⁴, F. Raulin², C. Szopa¹⁰, S. Teinturier⁴, P. Mahaffy⁴, C.A. Malespin⁴, and A.R. Vasavada¹², ¹Universidad Nacional Autónoma de México, Mexico City 04510, Mexico, navarro@nucleares.unam.mx, ²LISA, Univ. Paris-Est Créteil, Univ. Denis Diderot & CNRS, 94000 Créteil, France, ³Jacobs, NASA Johnson Space Center, Houston, TX 77058, ⁴NASA Goddard Space Flight Center, Greenbelt, MD 20771, ⁵NASA Ames Research Center, Moffett Field, CA 94035, ⁶Luleå University of Technology, Luleå, Sweden, ⁷Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Armilla, Granada, Spain, ⁸Centro de Astrobiología, Torrejón de Ardoz, Spain, ⁹Ecole Centrale Paris, Grande Voie des Vignes, 92290 Châtenay-Malabry, France, ¹⁰Laboratoire Atmosphère, Milieux, Observations Spatiales, Université Versailles Saint-Quentin en Yvelines, UPMC Univ. Paris 06, 78280 Guyancourt, France, ¹¹NASA Johnson Space Center, Houston, TX 77058, ¹²Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109.

Introduction: Nitrates (NO_3^-) have been detected in lacustrine sediments and eolian samples at Gale crater examined by the SAM instrument onboard the NASA Curiosity rover [1-5]. NO_3^- thermally decomposes in the SAM oven releasing nitric oxide (NO) at characteristic temperatures which is then transferred with a helium flow into the quadrupole mass spectrometer where it is detected and quantified [6-7]. Curiosity has drilled fifteen sedimentary rocks during its 17.9 km traverse up until Sol 1905 (December 15, 2017). Twelve of these rocks have been investigated by SAM from the lowest stratigraphic unit Sheepbed mudstone encountered in Yellowknife Bay to the Murray and Stimson formations located at the base of Aeolis Mons. The highest concentration of NO_3^- is found at Yellowknife bay and decreases with elevation gain in the stratigraphic record of Aeolis Mons [8]. Several energy sources could have contributed to the production of NO_3^- found at Gale crater, such as ultraviolet light, cosmic rays, lightning, volcanic lightning, and bolide impacts, among others [9]. However, a hydrogen (H_2) rich atmosphere arising from volcanic emissions is required to yield sufficient NO by bolide impacts to explain the high levels of NO_3^- detected in the mudstone sediments encountered in Yellowknife Bay [8].

NO in the Martian atmosphere was converted into nitroxyl (HNO) by its reaction with hydrogen atoms arising from the photolysis of water or H_2 according to reaction 1 [10]:



Because HNO is readily soluble in water, it was efficiently carried by rainout onto the Martian surface where it dissociated and formed N_xO_x^- species that rapidly decayed into NO_3^- , nitrites (NO_2^-), and nitrous oxide (N_2O) [11-12]. N_2O escaped to the atmosphere where it was subsequently destroyed back to N_2 and O_2 [13]. Consequently, it is expected that both NO_3^- and NO_2^- were deposited at Gale crater in the presence of a H_2 -rich atmosphere. The purpose of this work is to determine the thermal properties of both NO_2^- and

NO_3^- in the absence and presence of chlorates and perchlorates in order to identify these species in the rocks that have been investigated by SAM during the Curiosity rover's traverse from Yellowknife Bay to the Murray and Stimson formations.

Materials and Methods:

Laboratory experiments. A thermal analyzer (Netzsch STA 449 F1 Jupiter Simultaneous TG/DSC) coupled to a mass spectrometer (Netzsch QMS 403 C Aëolos) was used in the laboratory to heat samples up to 850°C at a rate of 35°C/min under a N_2 carrier gas flow rate of 2 cm^3/min and at an oven pressure of 35 mbar. Several mixtures of chlorates, perchlorates, nitrates, and nitrites salts were analyzed and the results were used to assist in SAM data interpretation.

SAM measurements. The details of the SAM instrument suite have been previously described [14]. A sieved (<150 μm) rock powder was delivered in single (~76 mm^3) or triple portions into one of SAM's quartz-glass cups, which was preconditioned before the experiment by heating to >800°C under a flow of He and active pumping by SAM's wide-range pumps. After the sample was received, the quartz cup was sealed inside a SAM pyrolysis oven. During the nominal solid-sample analysis mode, evolved gas analysis was performed, in which the quadrupole mass spectrometer continuously analyzes the gases released from samples heated from Mars ambient to ~870 °C at 35 °C/min under a ~0.8 cm^3 He flow and a pressure of ~25 mbar in the pyrolysis oven.

Results and Discussion: We investigated the thermal stability of Na-, K-, Mg-, Ca-, Fe^{2+} -nitrates, and Na-nitrite in the absence or presence of Na-, K-, Mg-, Ca-, Fe^{2+} and Fe^{3+} -perchlorates and Mg-, and Ca-chlorates by monitoring the NO released during thermal analysis coupled to mass spectrometry (Figure 1). Both NO_2^- and NO_3^- decompose releasing NO at lower and higher temperatures, respectively that are characteristic depending on the cation present. The occurrence of perchlorate / chlorates results in a reduction in the

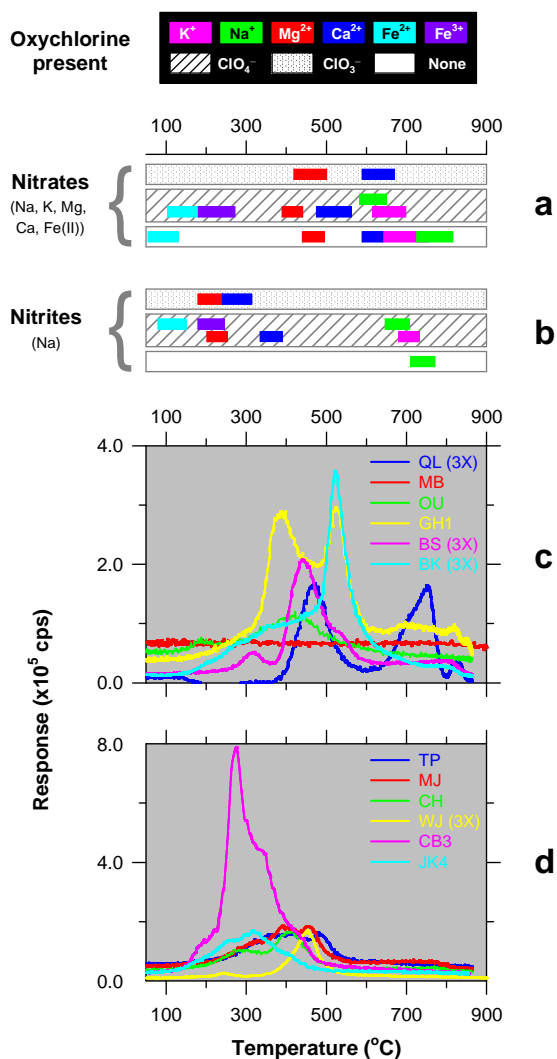
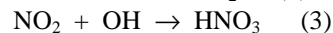
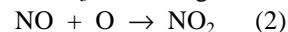


Figure 1. Nitric oxide (NO) evolution for the thermal treatment of nitrates (a), and nitrites (b) under SAM-like conditions, and sedimentary facies (c and d) measured by SAM along the stratigraphic column from the Yellowknife Bay to the Stimson formations. The characteristic temperatures for the evolution of NO are shown for pure nitrate (a) or nitrite (b) standards, as well as for the mixtures of nitrates (10%) or nitrites (10%) in the presence of different oxychlorine species (90%) in the form perchlorates and chlorates (a,b). The temperature range shown in these panels corresponds to the average peak widths of the NO signals at 75% peak height for the different nitrates/nitrites studied in the presence of a given perchlorate/chlorate salt. The sedimentary facies analyzed were delivered to SAM in single (~76 mm³) or triple (3X) portions from the lower to the upper stratigraphic column: John Klein (JK), Cumberland (CB), Windjana (WJ), Confidence Hills (CH), Mojave (MJ), Telegraph Peak (TP), Buckskin (BK), Big Sky (BS), Greenhorn (GH), Oudam (OU), Marimba (MB), and Quela (QL). The SAM data shown in panels c and d has been normalized to single portions. The Quela sample remained inside SAM for over 250 Sols before analysis, and had HCHO from MTBSTFA. Therefore the intensity of NO was corrected to remove this interference by a factor 0.58.

temperature of decomposition of NO_3^- and NO_2^- , and the characteristic temperature of evolution of NO is determined by the cation present in the oxychlorine species, and not in the nitrate. Both NO_2^- and NO_3^- are extremely labile in the presence of iron(II) or (III) perchlorates decomposing at temperatures below 270°C. However, in the presence of magnesium and calcium chlorates or perchlorates, NO_2^- decomposes below 400°C while NO_3^- decomposes above this temperature. Figure 1 also shows the NO releases of the different sedimentary facies analyzed by SAM from the lower to the upper stratigraphic column (panels c and d). Interestingly the samples from lowest stratigraphic sections (JK and CB) showed NO releases below 400°C but at higher layers the NO release gradually shifted to higher temperatures. All these samples showed the release of oxygen that is consistent with the presence of Mg- and Ca-chlorates and/or perchlorates [5]. Consequently the NO release below 400°C suggests the presence of NO_2^- or both NO_2^- and NO_3^- in the lowest stratigraphic column and above 400°C the presence of NO_3^- in the highest layers. There are other phases that could affect the nitrate/nitrite decomposition. These results provide clues into the shift of the atmosphere from reducing, when NO was converted into NO_2^- and NO_3^- (reaction 1), to oxidizing, when NO was converted to NO_3^- according to reaction 2 and 3:



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References: [1] Archer P.D. et al (2014) JGR, 119, 237-254. [2] Ming D.W. et al (2014) Science, 343,1245267. [3] Stern, J.C. et al (2015) PNAS USA, 112, 4245-4250. [4] Stern J.C. et al (2017) GRL 44, 2643-2651. [5] Sutter B. et al , (2017) JGR, 122, doi:10.1002/2016JE005225. [6] Navarro-González R. et al. (2013) XLIV, 2648. [7] Navarro-González R. et al. (2013) XLV, 2909. [8] Navarro-González R. et al. (2017) submitted to JGR. [9] Navarro-González R. et al. (1998) GRL 25, 3123-3126. [10] Mancinelli R.L. and McKay C.P. (1988) Orig Life Evol Biosph 18, 311-325. [11] Mancinelli R. L. and Banin A. (2003) Int J Astrobiol 2, 27-561. [12] Summers D. P. and Khare, B. (2007) Astrobio 7, 333-341. [13] McEwan, M. J. et al (1974) J Chem Phys 61, 2857-2859. [14] Mahaffy P. R. et al (2012) Space Sci Rev, 170, 401-478.