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SEARCH OF PHOSPHINE IN THE EVOLVED GASES FROM HYPOPHOSPHITE/PHOSPHITE MINERALS IN LACUSTRINE SEDIMENTARY ROCKS AT GALE CRATER BY THE SAMPLE ANALYSIS AT MARS. R. Navarro-González[1], P. Coll[2], C. Szopa[3], C. Freissinet[3], A. Buch[4], C.P. McKay[5], O. McIntosh[3], M. Millan[6], P.D. Archer[7], J.L. Eigenbrode[8], B. Sutter[7], B.D. Prats[9], A.J. Williams[10], A.C. McAdam[8], H.B. Franz[8], A. Steele[11], S. Atreya[12], G.M. Wong[13], J.C. Stern[8], D.W. Ming[14], D. Coscia[15], S. Teinturier[8], J.-Y. Bonnet[15], J.V. Clark[7], C.H. House[13], D.P. Glavin[8], F. Raulin[2], M. Cabane[3], C.A. Malespin[8], P. Mahaffy[8], F.J. Martín-Torres[16], M.-P. Zorzano-Mier[16], P.-Y. Meslin[17], J.A. Rodriguez-Manfredi[18], A. Fraeman[19], and A.R. Vasavada[20], [1]Universidad Nacional Autónoma de México (navarro@nucleares.unam.mx), [2]Université Paris-Est Créteil, [3]Université Versailles Saint-Quentin, [4]Ecole Centrale Paris, [5]NASA Ames Research Center, [6]Georgetown University, [7]Jacobs, NASA Johnson Space Center, [8]NASA Goddard Space Flight Center, [9]NASA GSFC/eINFORMe, Inc., [10]University of Florida at Gainesville, [11]Carnegie Institution of Washington, [12]University of Michigan at Ann Arbor, [13]Pennsylvania State University at University Park, [14]NASA Johnson Space Center, [15]Université Paris-Saclay, [16]University of Aberdeen, [17]Université de Toulouse, [18]Centro de Astrobiología, [19]NASA Jet Propulsion Laboratory, and [20]California Institute of Technology.

Introduction: Phosphorous (P) is a fundamental element for life that is utilized as phosphate (PO_4^{3-}), phosphate esters (R_3PO_4) and anhydrides ($P_2O_7^{4-}$), and is encountered in structural (*e.g.,* phosphoproteins, phospholipids), catalytic (*e.g.,* ribozymes), energy carrier (*e.g.,* ATP, glucose-6-phosphate) and encoding/decoding (RNA and DNA) biomolecules [1]. P in the form of phosphorus pentoxide (P_2O_5) has been detected on soils and rocks on the surface of Mars using APXS instruments on the MER [2,3] and Curiosity [4] rovers. The occurrence of fluoroapatite ($Ca_5(PO_4)_3F$) has been identified in the LIBS spectra collected by ChemCam [5] and on powders of drill rocks by CheMin [6] by Curiosity at Gale crater. Based on APXS abundances of P, $Ca_5(PO_4)_3F$ is expected to be present in both amorphous and crystalline phases, and other P phases could be present below CheMin detection limits [6]. Phosphates are not directly detected by the Sample Analysis at Mars (SAM) Instrument because they do not release volatile phosphorous oxides upon heating and instead polymerize to polyphosphates or metaphosphates. Hydrated and hydroxylated phosphates release water at characteristic temperature regimes [7] but the emission overlaps with those released by other minerals that are present at higher abundances in the martian fines [8] and rocks [9,10]. Therefore, their detection by SAM is extremely challenging.

The presence of other mineral phases of P on the martian surface is likely based on their detection in martian meteorites, such as merrillite ($Ca_9NaMg(PO_4)_7$ [11]. Less oxidized states of P, such as in hypophosphites ($H_2PO_2^-$) and phosphites ($H_2PO_3^-$) are possible on the martian surface from the accretion of interplanetary dust particles [12], asteroid impacts [13] and the corrosion of schreibersite $(Fe,Ni)_3P$ delivered by iron meteorites [14]. These reduced forms of P would be detectable in the SAM instrument because they thermally decompose releasing inorganic gases according to two reaction channels [15]. Reaction 1 is the interaction with absorbed water forming molecular hydrogen (H_2):

$$H_2PO_2^- + H_2O \rightarrow H_2 + H_2PO_3^- \quad (1a)$$

$$H_2PO_3^- + H_2O \rightarrow H_2 + H_2PO_4^- \quad (1b)$$

And reaction 2 is the disproportionation forming phosphine (PH_3) and HPO_2^- or HPO_3^-:

$$3\,H_2PO_2^- \rightarrow PH_3 + H_2PO_3^- + HPO_3^{2-} \quad (2a)$$

$$4\,H_2PO_3^- \rightarrow PH_3 + 2\,H_2PO_4^- + HPO_4^{2-} \quad (2b)$$

Here we report a thorough analysis to search for the release of PH_3 in the evolved gas analyses (EGA) of the drill rock samples by SAM using fragmentation patterns of the ion mass ratios: P^+/PH_2^+~1, P^+/PH_3^+~0.3, and PH_2^+/PH_3^+~0.3.

Methods: SAM-Like EGA-Mass Spectrometry (MS) of H_3PO_2 and H_3PO_3 were done using a Netzsch STA 449 F1 Jupiter thermobalance with a silicon carbide furnace coupled to a Netzsch QMS 403 C Aëolos. The evolved gases were transferred out of the thermobalance at 35 mbar under a stream of N_2 at 2 cm^3/min. SAM EGA-MS analyses of drilled rock powders were conducted from 40°C to ~860°C with a ramp rate of 35°C/min under reduced pressure (~25 mbar) using a He flow of ~0.8 cm^3/min, and the evolved gases were analyzed by electron impact MS.

Results and Discussion: Figure 1a shows the thermal decomposition of H_3PO_2 under SAM like conditions that occurred in two steps: First, formation of H_2, PH_3 and H_3PO_3 from 150°C to 240°C according to reactions 1a and 2a; and then the production of PH_3 and H_3PO_4 from 250°C to 380°C according to reaction 2b. Figure 1b shows the thermal decomposition of H_3PO_3 which took place in one step: The formation of H_2, PH_3 and H_3PO_4 in the temperature range from ~250°C to 380°C according to reactions 1b and 2b. PH_3 breaks down by electron impact MS into P^+

(~32%, m/z 31), PH^+ (~13%, m/z 32), PH_2^+ (~33%, m/z 33), and PH_3^+ (100%, m/z 34). A number of chemical species can potentially interfere with these mass ion fragments during identification; however, the ratios of 31/33, 31/34 and 33/34 provide a pattern that together with the evolution peak temperature can be used for identification purposes. Figure 2 compares 15 possible gases that that could be released during SAM EGA and none of them overlap with PH_3.

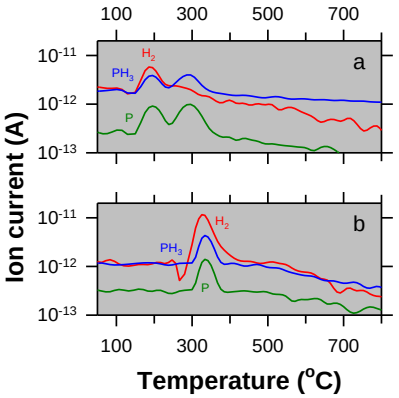


Fig. 1. Evolution profiles for H_3PO_2 (a) and H_3PO_3 (b) under SAM-Like EGA-MS .

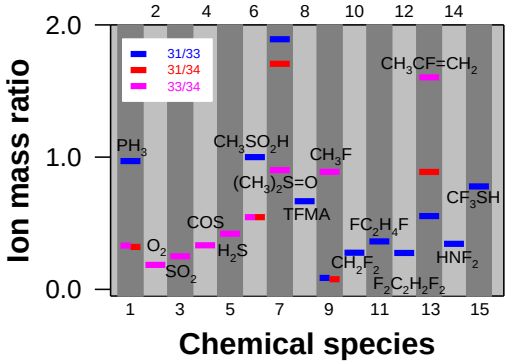


Fig.2. Fragmentation patterns of several inorganic and organic molecules.

All rocks examined by Curiosity from John Klein to Mary Anning show the evolution of mass ions 31, 33 and 34 in these temperature regimes that could appear to track to PH_3 at first glance. However, a comprehensive analysis is required to exclude possible interfering mass ions, and confirm the identity of PH_3. Here we focus on the Oudam (OU) sample to show the approach to search for PH_3 in the EGA data. Figure 3a shows the unprocessed signals for m/z 2, 31, 32, 33 and 34 for OU. The intensity of the peak (m/z 31, 33, and 34) at 150±3°C is ~7 times higher than the baseline levels from 50 to 80°C. Figure 3b shows the reconstructed signals for possible interferences on m/z 31 and 32, and figure 3c on m/z 33 and 34. $^{13}CH_2O$ originated from MTBSTFA, ^{15}NO from martian nitrates, CF from trifluoro-N-methyl-acetamide (TFMA) and CHF_3, CHF and CH_2F from TFMA, ^{32}S, ^{33}S and ^{34}S from SO_2 from martian sulfates, $^{17}O^{16}O$ and $^{18}O^{16}O$ from martian oxychlorine species releasing $^{16}O_2$, and HS and H_2S from martian sulfides. Figure 3d shows the corrected signals after subtraction of interfering mass fragments. The evolution profiles of m/z 2, 31, 33, and 34 seem to be consistent with the presence of $H_2PO_2^-$ and $H_2PO_3^-$. Further work is underway to exclude any other possible interfering fragments, to extend the search in the EGA and GC-MS analyses of all rocks so far investigated, and to optimize the GC conditions for better separation of PH_3 from other low molecular weight volatiles in future runs.

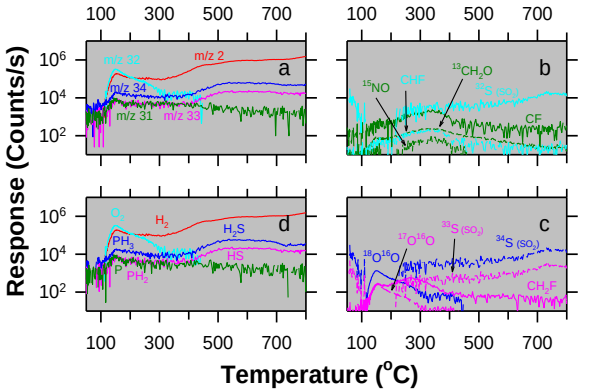


Fig. 3. Evolution profiles for raw EGA signals (a), reconstructed interfering fragments (b and c), and corrected signals (d) showing the resultant suggested gases for OU.

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