

EOLIAN MATERIALS ON MARS AS A RECORD OF SURFACE - ATMOSPHERE PROCESSES. J. C. Stern¹, B. Sutter², P. D. Archer², H. B. Franz¹, A. C. McAdam¹, C. R. Webster³, R. Navarro-González⁴, J. L. Eigenbrode¹, C. McKay⁵, C. Manning⁵, D. W. Ming⁶, P. Martin⁷, A. Pavlov¹, C. Malespin¹, P. R. Mahaffy¹
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Introduction: While many of the analyses made by the Curiosity Rover focus on the question of habitability of Mars at 3.5 Ga, eolian samples reflect contributions representing both ancient and modern Mars environmental conditions. For example, surface materials may serve as a repository for products of photochemical processes operating over long timescales. These could include nitrate, perchlorate, small organic molecules, and other species that are too dilute to directly measure in the atmosphere. In addition, materials exposed at the surface for long periods of time accumulate cosmogenic nuclides which can be measured to better understand both geomorphology and preservation of organic molecules. We seek to examine the extent to which eolian samples analyzed thus far on the Sample Analysis at Mars (SAM) instrument on the Curiosity Rover contain a record of ancient and modern atmosphere and surface processes on Mars.

Sample Description: We present evolved gas data from the SAM quadrupole mass spectrometer (QMS) and tunable laser spectrometer (TLS) for four eolian samples: Rocknest (RN), Gobabeb1 (GB1), Gobabeb2 (GB2), and Ogonquit Beach (OG3). RN (<150 μm) was sampled early in the mission in the wind shadow of a rock and contains a fine-grained component (~40-60% < 100 μm) thought to represent global dust [1,2]. GB1 (<150 μm) and GB2 (150 μm -1 mm) are from the first set of samples at Bagnold Dunes, an active dune field, and represent different size fractions of the same material. OG3 (<150 μm) is Bagnold Dune material sampled downwind of a dune and expected to have low contribution from the surrounding bedrock. The RN sample was a single portion (45 mg \pm 18 mg), while GB1 and OG3 represent triple portions (135 \pm 31 mg). We were unable to estimate the volume of sample that was delivered to SAM for GB2, so results are not quantitative.

Bulk mineralogy of RN and GB1/GB2 are similar overall with the major crystalline phases being Na,Ca feldspar, olivine, augite, and pigeonite [3,4]. GB materials have an amorphous component consisting of Si-enriched H₂O or OH-bearing phases (alteration products or glasses) [4]. These materials were distinct from the fine, dust fraction found in RN, which was enriched in Fe, S, Cl, and H₂O [4]. H₂O evolutions

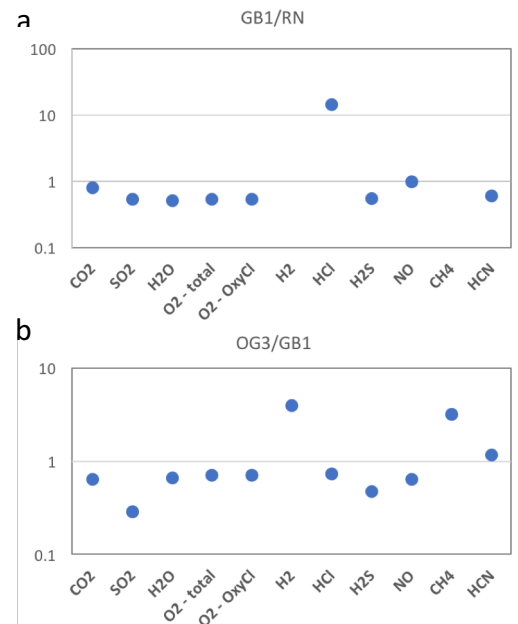


Figure 1. a) GB1 materials are depleted in volatiles with respect to RN, while b) OG3 materials are even more volatile depleted, particularly in sulfur bearing species.

from Rocknest are consistent with adsorbed H₂O in addition to H₂O or OH in alteration products and/or glasses. The larger amount of fine grains in Rocknest likely provide a larger surface area for adsorbed H₂O.

Results: Figure 1a compares abundances of major volatiles in GB1 and RN measured by SAM QMS. GB1 is slightly depleted in most volatiles with respect to RN, except in the case of HCl. A lack of coincident O₂ evolution suggests that more chlorine present as chloride than in O₂ evolving oxychlorine species in Bagnold Dune materials. OG3 is similar to GB1, but is further depleted in most volatiles with respect to GB1, particularly sulfur bearing species SO₂ and H₂S. Reduced species H₂ and CH₄, however, are enriched in OG3 materials.

Major volatile evolutions during EGA-QMS analysis of OG3 are similar to GB1/GB2, and both of these Bagnold Dune materials have thermal decomposition patterns distinct from RN (Figure 2a). Bagnold Dune materials release CO₂ between 450°-650° C, consistent with thermal decomposition of carbonate. The large CO₂ releases at these temperatures distinguish the GB

and OG3 samples from the majority of sedimentary rock samples analyzed by Curiosity, which release most of their CO₂ below 450° C [e.g., 5]. RN also releases CO₂ above 450° C, although a significant amount of CO₂ is released below 450° C. In Bagnold Dune materials, NO is released between 350°-650° C, while the Rocknest NO release is between 200°-500° C, likely representing a combination of Fe and Mg nitrate phases (Figure 2b). Similarities also exist between the water release at GB1 and OG3, consistent with hydrated phases or mineral/glass inclusions.

Discussion: The speciation of carbon and nitrogen in these surface samples is of great interest for understanding the movement of these elements between reservoirs. Evidence for both organic and inorganic carbon on Mars suggests that multiple carbon fixation processes were or are active in the martian atmosphere. For example, Oxidation of organics to CO₂ by thermal decomposition of oxychlorine during SAM analysis could explain low temperature (<450° C) CO₂ releases seen in many sedimentary rocks [6] as well as in RN [7,8] and to some degree in GB1 and OG3 [5]. Carbon-oxygen bearing organics such as acetate and oxalate (products of photochemical reactions in the Mars atmosphere) could also contribute to CO₂ detections. One line of evidence for multiple carbon inventories in a single sample are the SAM TLS measurements of $\delta^{13}\text{C}$ of CO₂ evolved at RN. While our TLS

measurements cannot completely isolate different C sources, CO₂ evolved between 234°-425° C had $\delta^{13}\text{C} = -2 \pm 5\text{‰}$, while CO₂ evolved between 350°-443° had $\delta^{13}\text{C} = +16 \pm 4\text{‰}$ and CO₂ evolved between 440-601° had $\delta^{13}\text{C} = +17 \pm 6\text{‰}$. These isotope values represent different carbon species. Organic products of photochemistry should show depletion in ¹³C with respect to atmospheric CO₂ [9]; this could explain the depleted $\delta^{13}\text{C}$ for lower temperature CO₂ at RN. Carbonate formed from atmospheric CO₂ is actually slightly enriched over atmosphere (but within analytical error of TLS measurements) and should basically reflect atmospheric CO₂ at the time of formation; this value should be given by the higher temperature CO₂ evolution. Because all $\delta^{13}\text{C}$ values at RN are significantly (~30‰) depleted with respect to modern atmospheric CO₂, formation of both organic and inorganic carbon at RN likely took place prior to establishment of modern atmospheric $\delta^{13}\text{C}$ values, under a thicker atmosphere.

Other products of photochemistry potentially accumulating in eolian soils include nitrate and oxychlorine species. We note that eolian samples have some of the highest abundances of both nitrate and perchlorate [10] measured at Gale. It is possible that production of these species by photochemistry is ongoing. $\delta^{15}\text{N}$ of NO from decomposition of nitrate in eolian samples could help confirm whether or not this is occurring.

Conclusions: Bagnold Dune materials represent a different, more localized inventory of volatiles than the highly dusty materials at RN. GB was previously reported to be depleted in S, Cl, and H₂O with respect to RN and Gale sedimentary rocks [3]. OG3 materials are similar to GB1 and further support this finding. The dust/silt size fraction in RN is a major volatile inventory on Mars that likely contains globally mixed carbon and nitrate bearing dust [3,5]. Even if Bagnold Dune materials lack a dust fraction representing this globally mixed carbon and nitrate, they likely accumulate these species as products of atmospheric photochemistry (as well as meteoritic/IDP infall). Therefore, measurements of surface materials may yield information relevant to atmospheric processes over a range of time-scales on Mars.

References:[1] Minitti et al. (2013) *JGR Planets*, 118, 2338-2360. [2] Morris et al. (2006) *JGR Planets*, 111, E12S15. [3] Ehlman et al. (2017) *JGR Planets*, 122. [4] Achilles et al. (2017) *JGR Planets* 122. [5] Sutter et al. (2017) *JGR Planets*. [6] Ming et al. (2013) *Science*, 342. [7] Eigenbrode et al. 2014, *LPSC XLV* [8] Leshin et al. (2013) *Science*, 341. [9] Schmidt et al. (2013) *PNAS* 110. [10] Stern et al. (2017) *GRL* 44 (6), 2643-2651.

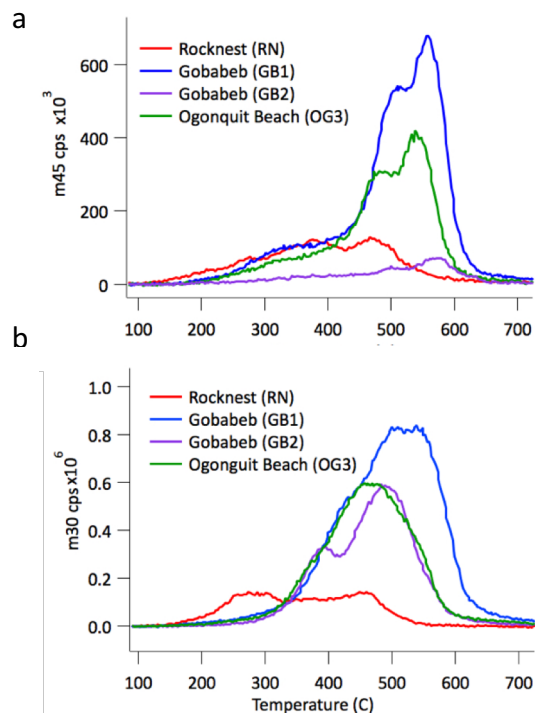


Figure 2. a) CO₂ (m45) and b) NO (m30) releases from eolian materials. (RN was a single portion, GB and OG were triple portions).