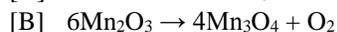
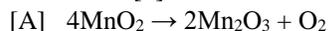


DETECTABILITY OF MANGANESE-BEARING PHASES BY THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT ON BOARD THE CURIOSITY ROVER IN GALE CRATER, MARS. J.V. Hougancamp¹, P.D. Archer², R.V. Morris³, V. Tu², N. Lanza⁴, B. Sutter², D.W. Ming³, P.R. Mahaffy⁵. ¹Geocontrols Systems – Jacobs JETS Contract, NASA Johnson Space Center, Houston, TX 77058, ²Jacobs, NASA Johnson Space Center, Houston, TX 77058, ³NASA Johnson Space Center, Houston, TX 77058, ⁴Los Alamos National Laboratory, Los Alamos, New Mexico 87544, ⁵NASA Goddard Space Flight Center, Greenbelt, MD 20771.

Introduction:

Manganese has been detected in Gale Crater materials throughout its traverse, but it is not fully understood which phases it exists in and its oxidation state [1,2]. Understanding the oxidation state of Mn and the Mn-phases present can elucidate the level of atmospheric oxygen at formation, which has important implications for habitability [1,2]. ChemCam has tracked the abundance of Mn in rocks and soils throughout Curiosity's traverse [1,2]. Mn was detected as high as 25 wt % in fracture filling materials in sandstones in the Kimberley region of Gale Crater, and it has been suggested that the Mn in these fractures exist as oxides [1,2]. However, in post-sieved dump piles analyzed by the Sample Analysis at Mars (SAM) instrument, APXS has detected Mn abundances from 0.09 to 0.56 wt% MnO [4-8]. The SAM instrument on board the Curiosity Rover contains a quadrupole mass spectrometer (QMS) which detects the presence of volatiles in the Martian soil, rock, and atmosphere. The SAM instrument can detect trace amounts of oxygen from substances that thermally decompose below ~900 °C [3]. It is possible that SAM could detect low abundances of manganese if it exists in phases that release oxygen upon thermal decomposition.

Synthetic MnO₂ thermally decomposes in two stages. Reaction [A] produces an oxygen release peak at 483 °C and reaction [B] produces an oxygen release peak at 799 °C [9].



The temperatures of these oxygen release peaks are within the temperature range of SAM, therefore MnO₂ could be detectable by SAM if present in amounts surpassing the detection limit.

In these experiments, we tested the detection limit of MnO₂ mixed with silica in a commercial SAM-like instrument. We also characterized the oxygen release temperatures and patterns from synthetic and natural Mn-bearing phases, including oxides and silicates, and compared to oxygen release data from SAM samples.

Materials and methods:

Detection limit of MnO₂: Synthetic MnO₂ (Baker Chemical) was mixed with silica gel in different ratios ranging from 0 wt % (pure SiO₂) to 100 wt % (pure

MnO₂). ~45 mg of the MnO₂/SiO₂ mixture was used in order to be consistent with the amount of material analyzed by the SAM instrument. The mixture was stirred gently with a dental tool. The sample crucible and an identical empty crucible were placed in a Labsys EVO differential scanning calorimeter (DSC) furnace/thermal gravimeter (TG) connected to a ThermoStar quadrupole mass spectrometer (QMS) configured to operate similarly to the SAM oven/QMS system. The DSC furnace was purged with helium gas (30 mbar and 10 sccm He) and samples were heated to 1200 °C at 35 °C/min. The mass 32 releases evolved from mixtures of MnO₂ and SiO₂ were compared to the control (SiO₂), blanks, and the standard (pure MnO₂) to estimate the lowest MnO₂:SiO₂ ratio detectable by the SAM-like instrument.

Analysis of Mn-bearing phases: Mn-bearing phases (both natural and synthetic) were analyzed using the same instrumental methods. Laboratory samples were analyzed for mass 32 releases and compared to mass 32 releases from SAM samples (RN, JK, CB, WJ, CH, MJ, TP, BK, BS, GH, and GB). The natural samples were analyzed using x-ray diffraction (XRD) to determine crystalline mineralogy. Natural samples included 100% potassium manganese oxide, 58.5 % johannsenite mixed with calcite, 100 % manganite, 99.4 % hausmannite mixed with cristobalite, and a rock containing black and pink rhodonite mixed with quartz.

Results and Discussion:

MnO₂ in silica is detectable by our commercial SAM-like instrument down to 0.177 wt % (and possibly lower). The detector in SAM's QMS is far more sensitive than the detector on our commercial instrument, therefore SAM can likely detect lower weight percentages of MnO₂. More studies will be done to determine the detection limit of MnO₂ in a basaltic matrix. If the Mn-phases present in Gale Crater produce oxygen within the SAM temperature range, our results demonstrate that they may be detectable at low abundances comparable to those in SAM samples (0.09 to 0.56 wt% MnO [4-8]).

Manganese oxides evolved oxygen depending on their oxidation state (Fig.1). Mn⁴⁺O₂ and K_{1.33}Mn_{0.992}^{3+,4+}O₂ evolved oxygen in 2-3 stages. The two synthetic MnO₂ samples evolved oxygen releases with peaks at different temperatures. These samples

will be further analyzed using XRD in order to characterize their crystal structure and understand their different oxygen evolution patterns. Manganite (Mn^{3+}) and hausmannite ($\text{Mn}^{2+,3+}$) also evolved oxygen in two stages, with the first release peaking ~ 560 °C. $\text{Mn}_2^{3+}\text{O}_3$ evolved one oxygen release with a peak ~ 766 °C. The Mn^{2+}O samples did not produce any oxygen releases.

The Mn-bearing silicates also evolved oxygen depending on their oxidation state (Fig. 1). Johannsenite (Mn^{2+}) produced an oxygen release that co-occurred with a water release, caused by fractionation of water in the mass spectrometer. Pink rhodonite (Mn^{2+}) did not evolve oxygen. Black oxidized rhodonite ($\text{Mn}^{3+,4+}$) produced oxygen in two stages, with the first release peaking at 570 °C.

Phases containing higher oxidation states of Mn (3+ and 4+) evolved oxygen release peaks ranging from 504 °C to ~ 875 °C. One of the Mn^{4+}O_2 samples evolved two oxygen releases, one of which peaked at a similar temperature to GH and GB1 [3]. However, GH and GB1 did not evolve the higher temperature oxygen release characteristic of Mn (IV) oxides. Mn^{3+} bearing silicates and oxides evolved oxygen releases not similar to those observed in SAM data. Therefore, if Mn oxides and/or silicates are present in the samples analyzed by SAM, they are likely Mn^{2+} because Mn^{2+} oxide and silicates do not evolve oxygen within the SAM temperature range, and would not be detected. In order to provide more evidence for this interpretation, more Mn phases will be analyzed to characterize their oxygen evolution.

Recently, ChemCam detected Mn abundances as high as >10 wt % in dark nodules and laminae in targets analyzed in Vera Rubin Ridge (VRR) [2,10]. These high-Mn nodules and laminae may be interesting potential drill, and SAM, targets before departing VRR. As we have demonstrated, evolved gas data from SAM could potentially constrain the oxidation state of these high-Mn features. This is valuable information when assessing past oxidative conditions and thus, habitability [1,2].

Conclusion: In this study, we investigated the detectability of Mn oxides and silicates by a laboratory SAM-like instrument. ChemCam has detected high Mn abundances in the Kimberley area as well as in VRR [1,2,10]. Although APXS analyses of post-sieved dump piles analyzed by SAM report low Mn abundances, results here demonstrate that SAM could have detected O_2 evolved from Mn(III) or Mn(IV) oxides or silicates if they were present. Evolved O_2 consistent with the presence of Mn(III) and Mn(IV) oxides and silicates were not detected by SAM and are therefore not likely present in samples analyzed by SAM. Mn(II) oxide does not evolve oxygen and may be present, though not

detectable, in SAM samples. Furthermore, high-Mn surface features such as dark nodules and laminae [10] may be interesting samples to drill and analyze with SAM before departing VRR. Analyzing these targets with SAM may constrain the oxidation state of Mn and further elucidate oxidative conditions and habitability at the time of formation.

■ Ranges of SAM O_2 release peaks (RN-GB)

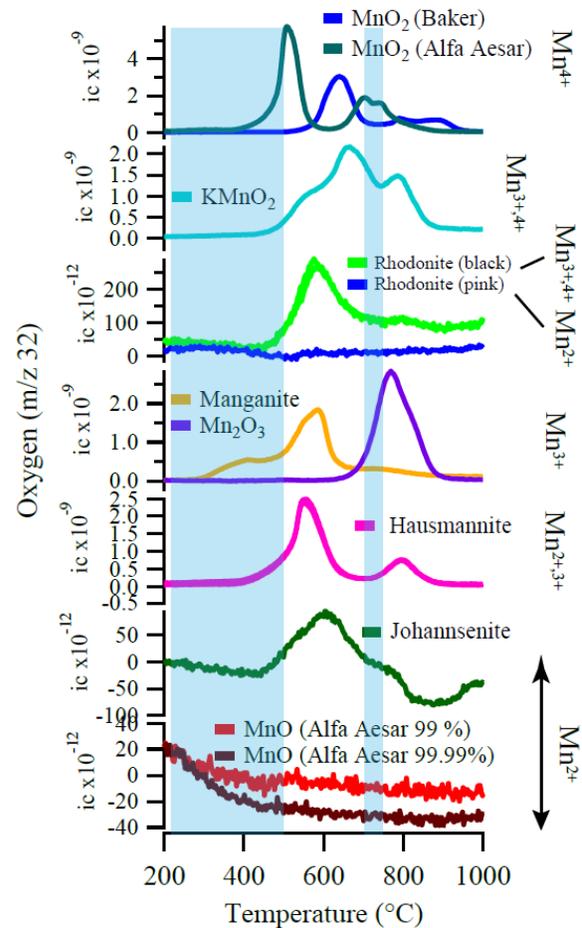


Fig. 1. Oxygen (mass 32) releases from natural and synthetic manganese bearing samples compared to oxygen release peak temperatures from SAM samples (RN-GB).

[1] Lanza et al. (2016) *GRL*, 43. [2] Lamm et al. (2018) *this LPSC* [3] Sutter et al. (2017) *JGR Planets* DOI: 10.1002/2016JE005225. [4] Rampe et al. (2017) *EPSL*, 471. [5] Yen et al. (2017) *EPSL*, 471. [6] Achilles et al. (2017) *JGR Planets*, 122. [7] Vaniman et al. (2013) *Science Express*, 343. [8] Treiman et al. (2016) *JGR Planets*, 121. [9] Terayama and Ikeda. (1983), *Transactions of the Japan Institute of Metals*, 24. [10] Wiens et al. (2017) *AGU*.