

**EVOLVED GAS ANALYSIS OF MANGANESE-BEARING PHASES AND IMPLICATIONS FOR THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT ON BOARD THE CURIOSITY ROVER IN GALE CRATER, MARS** J.V. Clark<sup>1</sup>, N. Lanza<sup>2</sup>, E.B. Rampe<sup>3</sup>, P.D. Archer<sup>4</sup>, R.V. Morris<sup>3</sup>, V. Tu<sup>4</sup>, B. Sutter<sup>4</sup>, D.W. Ming<sup>3</sup>, P.R. Mahaffy<sup>5</sup>. <sup>1</sup>Geocontrols Systems – Jacobs JETS Contract, NASA Johnson Space Center, Houston, TX 77058, <sup>2</sup>Los Alamos National Laboratory, Los Alamos, New Mexico 87544, <sup>3</sup>NASA Johnson Space Center, Houston, TX 77058, <sup>4</sup>Jacobs, NASA Johnson Space Center, Houston, TX 77058, <sup>5</sup>NASA Goddard Space Flight Center, Greenbelt, MD 20771.

### Introduction:

Manganese enrichments have been detected in Gale Crater materials throughout its traverse and most recently in a mm-scale dark feature-bearing rock in the Glen Torridon region called “Groken”. It has been suggested that Mn in previously examined rocks could exist as oxides [1,2]. ChemCam reported MnO abundances as high as ~4-6 wt.% in the dark nodules in the rock where Groken was collected, and were elevated compared to the surrounding bedrock [3,4]. The Alpha Particle X-ray Spectrometer (APXS) reported lower MnO abundances (up to 2.4 wt.%) in drill trailings that came from the Groken sample [5]. This discrepancy was attributed to the APXS sample being a mixture of the high-Mn dark features and the low-Mn surrounding bedrock [5]. However, it is not fully understood which phases Mn exists in and its oxidation state. The oxidation state of Mn and the types of Mn-phases present can inform about redox conditions and atmospheric oxygen levels at the time of formation, which has important implications for habitability [1,2]. Groken was analyzed by the Sample Analysis at Mars (SAM) instrument and the Chemistry and Mineralogy (CheMin) X-ray diffraction instrument [6,7]. SAM contains a quadrupole mass spectrometer (QMS) that can detect trace amounts of evolved gases (e.g., O<sub>2</sub>, SO<sub>2</sub>, CO<sub>2</sub>) from substances that thermally decompose below ~900 °C [8]. It is possible that SAM could detect low abundances of Mn-bearing phases if those phases evolve gases upon thermal decomposition.

In these experiments, we characterized the evolved gas profiles of several Mn-bearing phases on SAM-like laboratory instruments. The laboratory evolved gases were compared to SAM evolved gas data from Groken in order to constrain the possible Mn-bearing phases present in Groken.

### Materials and methods:

*Samples:* The samples analyzed included Mn oxides/oxyhydroxides, phosphates, silicates, chlorides, sulfates, and carbonates (Table 1).

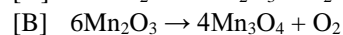
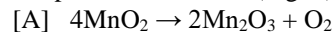
Mineral Name	Chemical Formula
Synthetic MnO <sub>2</sub> (2 brands)	Mn <sup>4+</sup> O <sub>2</sub>
Synthetic KMnO <sub>2</sub>	KMn <sup>3+,4</sup> O <sub>2</sub>
Coronadite	Pb(Mn <sup>4+</sup> Mn <sup>3+</sup> )O <sub>16</sub>
Todorokite	Na <sub>0.2</sub> Ca <sub>0.05</sub> K <sub>0.02</sub> Mn <sup>4+</sup> Mn <sup>3+</sup> O <sub>10</sub> •3H <sub>2</sub> O
Romanichite	Ba <sub>0.7</sub> Mn <sup>3+</sup> <sub>4.8</sub> Si <sub>0.1</sub> O <sub>10</sub> •1.2H <sub>2</sub> O
Manganite	Mn <sup>3+</sup> O(OH)
Synthetic MnO (2 brands)	Mn <sup>2+</sup> O
Purpurite	Mn <sup>3+</sup> PO <sub>4</sub>
Mn oxalate	C <sub>2</sub> H <sub>2</sub> Mn <sup>2+</sup> O <sub>4</sub>
Rhodochrosite	Mn <sup>2+</sup> CO <sub>3</sub>
Mn chloride	Mn <sup>2+</sup> Cl <sub>2</sub>
Mn sulfate monohydrate	Mn <sup>2+</sup> SO <sub>4</sub> •H <sub>2</sub> O
Johannsenite	CaMn <sup>2+</sup> Si <sub>2</sub> O <sub>6</sub>

**Table 1. Minerals and chemical formulas of Mn-bearing phases analyzed in these experiments.**

*Analysis of Mn-bearing phases:* Powdered Mn-bearing phases (both natural and synthetic) were placed in either a Labsys EVO or Netzsch differential scanning calorimeter (DSC) furnace/thermal gravimeter (TG) connected to quadrupole mass spectrometers (QMS) configured to operate similarly to the SAM oven/QMS system. The DSC furnace was purged with helium gas (30 mbar) and samples were heated to a minimum of 1000 °C at 35 °C/min. The natural samples were analyzed using x-ray diffraction (XRD) to determine crystalline mineralogy.

### Results and Discussion:

Synthetic MnO<sub>2</sub> thermally decomposed in two stages. Reaction [A] produced an oxygen release peak ~519-640 °C and reaction [B] produced an oxygen release peak ~700-800 °C (Fig. 1).



Based on a SAM-QMS O<sub>2</sub> detection limit of 0.01 wt.% and reactions A-B, SAM should be able to detect MnO<sub>2</sub> at abundances as low as 0.11 wt.%. However, other phases present in the sample (e.g., iron-bearing minerals) have been shown to consume O<sub>2</sub> evolved from phases such as oxychlorines [9,10], and may also affect the O<sub>2</sub> releases from Mn oxides.

Manganese oxides evolved oxygen depending on their oxidation state (Fig.1). Mn<sup>4+</sup>O<sub>2</sub> and K<sub>133</sub>Mn<sub>992</sub><sup>3+,4+</sup>O<sub>2</sub> evolved oxygen in 2-3 stages (reactions A-B). Manganite (Mn<sup>3+</sup>) and one of the hausmannite (Mn<sup>2+,3+</sup>) samples also evolved oxygen in two stages, with the first release peaking ~560 °C. Mn<sub>2</sub><sup>3+</sup>O<sub>3</sub> evolved one oxygen release with a peak ~766 °C (reaction B). Coronadite, todorokite, and romanichite also contain higher oxidation states of Mn (3+), and evolved O<sub>2</sub> within the range of SAM (Fig. 1). The Mn<sup>2+</sup>O samples did not produce any oxygen releases.

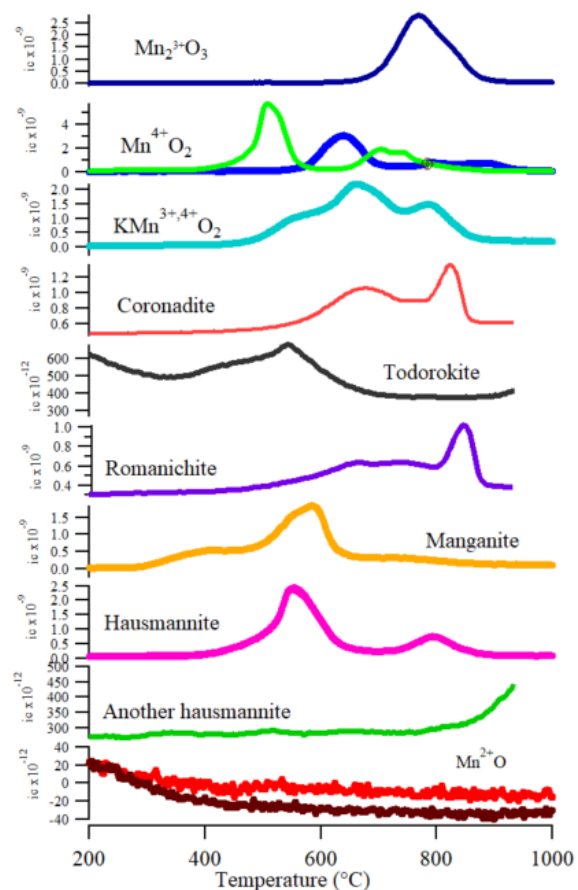
Evolved gas data from these laboratory samples were compared to Groken SAM-EGA data in order to constrain the types of Mn-phases present and their oxidation states. Groken did not evolve O<sub>2</sub> within the range of SAM [11], meaning that if Mn oxides were present, the Mn was likely a lower oxidation state (2+).

Certain phases analyzed in these experiments, including purpurite and johannsenite (Table 1), did not evolve gases within the temperature range of SAM. Because of the possible detection of Mn-phosphates in Groken with CheMin [6] and APXS [5], other phosphates will be analyzed for their evolved gases in order to determine if they are detectable by SAM (e.g., through dehydroxylation).

Groken also evolved HCl with a peak at ~780 °C, SO<sub>2</sub> with a peak ~540 °C, and CO<sub>2</sub> with a peak ~410 °C [11]. MnCl<sub>2</sub> evolved an HCl release (peak = 758 °C) at a similar temperature as Groken, although if it were present in Groken it would have to be in the amorphous component or lower than the detection limit of CheMin (~1 wt.%). APXS detected a Cl abundance of ~0.5 wt.% [5] in Groken drill tailings, indicating that if all the Cl was in MnCl<sub>2</sub>, it would likely be detectable by CheMin. Therefore, either a small component of the detected Cl is in MnCl<sub>2</sub> or MnCl<sub>2</sub> is not present in Groken. The SO<sub>2</sub> release from Mn sulfate (peak = 830 °C) occurred at too high of a temperature to explain the major SO<sub>2</sub> releases observed in Groken. Rhodochrosite evolved CO<sub>2</sub> (peak = 520 °C) at too high a temperature to explain the CO<sub>2</sub> release in Groken. Mn oxalate evolved a CO<sub>2</sub> release (peak = 420 °C) that was similar to the CO<sub>2</sub> release observed in Groken, however Mn oxalate was deemed unlikely due to the CO<sub>2</sub>/CO ratio detected in Groken [12].

**Conclusion:** In this study, Mn-bearing phases were analyzed for their evolved gases under SAM-like

conditions and compared to data from Groken. The results from this study demonstrate that SAM can generally detect O<sub>2</sub> evolved from Mn(III) or Mn(IV) oxides if present in Gale Crater samples. Evolved O<sub>2</sub> consistent with the presence of Mn(III) and Mn(IV) oxides were not detected by SAM in the Groken sample and are likely not present. Mn(II) oxide does not evolve oxygen and may be present in Groken, though not detectable. MnCl<sub>2</sub> is another candidate Mn-bearing phase in Groken, however, if present it would only account for a small portion of the Cl detected by APXS. Overall, constraining the phase and oxidation state of Mn can help elucidate oxidative conditions and habitability at the time of formation.



**Fig. 1. Oxygen (mass 32) releases from natural and synthetic manganese-bearing samples.**

[1] Lanza et al. (2016) *GRL*, 43. [2] Lamm et al. (2018) *LPSC*. [3] Lanza et al. (2021) *this LPSC*. [4] Gasda, P.D., et al. (2021) *this LPSC* [5] Berger et al. (2021) *this LPSC*. [6] Thorpe et al. (2021) *this LPSC* [7] Treiman et al. (2021) *this LPSC* [8] Sutter et al. (2017) *JGR Planets*, 122. [9] Sutter et al. (2015) *LPSC* [10] Hogancamp et al. (2018) *JGR: Planets*, 123. [11] McAdam et al. (2021) *this LPSC*. [12] Galwey & Brown. (1999) *Elsevier*.