

**THE INVESTIGATION OF CHLORATE/IRON-PHASE MIXTURES AS A POSSIBLE SOURCE OF OXYGEN AND CHLORINE DETECTED BY THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT IN GALE CRATER, MARS.** J. Clark<sup>1,2</sup>, B. Sutter<sup>1,2</sup>, R.V. Morris<sup>2</sup>, P.D. Archer<sup>1,2</sup>, D.W. Ming<sup>2</sup>, P. Niles<sup>2</sup>, P. Mahaffy<sup>3</sup>, R. Navarro-Gonzalez<sup>4</sup>. <sup>1</sup>Jacobs, Houston, TX 77058, <sup>2</sup>NASA/JSC, Houston, TX 77058, <sup>3</sup>NASA Goddard Space Flight Center, Greenbelt, MD 20771, <sup>4</sup>Universidad Nacional Autonoma de Mexico, Mexico.

**Introduction:** The Sample Analysis at Mars (SAM) instrument on board the Curiosity Rover has detected oxygen and HCl gas releases from all analyzed Gale Crater sediments. The presence of perchlorate ( $\text{ClO}_4^-$ ) and/or chlorates ( $\text{ClO}_3^-$ ) are potential sources of the aforementioned  $\text{O}_2$  releases. The detections of  $\text{O}_2$  and HCl gas releases and chlorinated hydrocarbons by SAM [1,2,3] coupled with the detection of perchlorates by Phoenix Lander's 2008 Wet Chemistry Laboratory [4] all suggest that perchlorates, and possibly chlorates, may be present in the Gale Crater sediments.

Previous laboratory studies have attempted to replicate these  $\text{O}_2$  releases by heating perchlorates and chlorates in instruments operated similarly to those in the SAM instrument. Early studies found that pure perchlorates release  $\text{O}_2$  at temperatures higher than those observed in SAM data [5]. Subsequently, studies were done to test the effects of mixing iron-phase minerals, analogous to those detected on Mars by ChemMin, with perchlorates [5,6]. The iron in these minerals acts as a catalyst and causes  $\text{O}_2$  to be released from the perchlorate at a lower temperature. These studies found that perchlorate solutions mixed with either Hawaii palagonite or ferrihydrite produce  $\text{O}_2$  releases at temperatures similar to the Rocknest (RN) windblown deposit and the John Klein (JK) drill sample from the Sheepbed mudstone. The study also determined that perchlorate mixtures with magnetite, hematite, fayalite-magnetite, ilmenite, and pyrrhotite produce  $\text{O}_2$  releases at temperatures similar to the Confidence Hills (CH) drill sample from the Murray mudstone. Oxygen releases from pure chlorates were recently compared with the SAM data. Laboratory analyses determined that Ca-chlorate produces  $\text{O}_2$  and HCl peaks that are similar to those detected in RN and JK materials [7]. Currently, no perchlorate/chlorate mixture with iron-phase minerals can explain the  $\text{O}_2$  releases from either the Cumberland (CB) drill sample from the Sheepbed mudstone or Windjana (WJ) drill sample from the Kimberly sandstone. Mixtures of chlorate solutions with iron-phase minerals may produce  $\text{O}_2$  peaks at temperatures that match those from CB and WJ materials. The goal of this work is to determine if heating chlorate solutions mixed with iron-phase minerals will

produce  $\text{O}_2$  and HCl peak temperatures similar to  $\text{O}_2$  and HCl peak temperatures of sediments analyzed by SAM, particularly the WJ and CB materials.

**Materials and methods:** Samples were prepared for analysis by mixing Mg-, Ca-, K-, or Na-chlorate solutions with 100  $\mu\text{mol}$  of hematite, magnetite, ferrihydrite, or Hawaii palagonite (20 mg) ( $<50 \mu\text{m}$ ). These mineral powders were placed in an alumina crucible and saturated with 24  $\mu\text{mol}$  of a chlorate solution and then placed in a vacuumed desiccator overnight to dry.

The sample crucible and an identical empty crucible were placed in a Setaram Sensys Evo differential scanning calorimeter (DSC) furnace connected to a Stanford Research Systems Universal Gas Analyzer configured to operate similarly to the SAM oven/QMS system. The DSC furnace was purged with helium gas and set to a pressure of approximately 30 mbar He. The crucibles were heated to 730  $^\circ\text{C}$  at a heating rate of 35  $^\circ\text{C}/\text{min}$  and at a flow rate of 3 ml He/min.

**Results and Discussion:** The SAM instrument detected peak  $\text{O}_2$  releases at 380  $^\circ\text{C}$  (RN), 218  $^\circ\text{C}$  and 370  $^\circ\text{C}$  (JK), 310  $^\circ\text{C}$  (CB), 401  $^\circ\text{C}$  (WJ), and 429  $^\circ\text{C}$  (CH) (Fig. 1). These releases may be attributed to perchlorates and/or chlorates mixed with different iron-phase minerals.

K-chlorate only produces a broad  $\text{O}_2$  release starting at 392  $^\circ\text{C}$ , peaking at 489  $^\circ\text{C}$ , and ending at 569  $^\circ\text{C}$ . This release is broader and peaks at a higher temperature than any of the Gale Crater materials (Fig. 1). Mixtures of the K-chlorate with iron-phase minerals substantially decreases the  $\text{O}_2$  release temperatures. The mixtures of magnetite or Hawaii palagonite with K-chlorate produce  $\text{O}_2$  releases peaking at approximately 370  $^\circ\text{C}$ , which is similar to the second JK  $\text{O}_2$  release (370  $^\circ\text{C}$ ; Fig. 1). The mixture of ferrihydrite and K-chlorate produces an  $\text{O}_2$  release that approaches that of CB (Fig. 1). No significant HCl peaks were detected (data not shown).

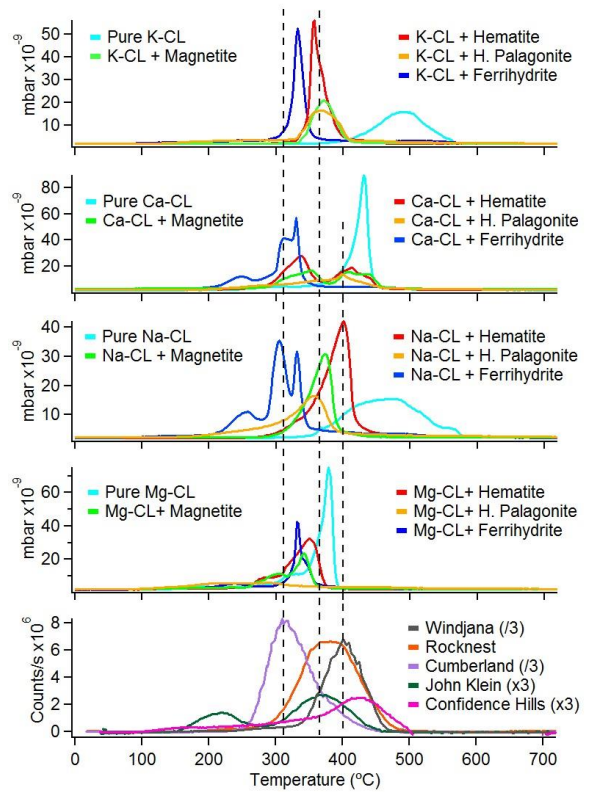
Laboratory analyses determined that Na-chlorate only has a broad  $\text{O}_2$  release starting at 349  $^\circ\text{C}$ , peaking at 474  $^\circ\text{C}$ , and ending at 578  $^\circ\text{C}$  (Fig. 1). This release occurs at a higher temperature and is much broader than any of the materials analyzed by SAM. Mixtures of Na-chlorate with iron-phase minerals generate  $\text{O}_2$  releases at lower temperatures than Na-chlorate only

(Fig 1). The mixture of ferrihydrite with Na-chlorate produces an O<sub>2</sub> release at a very similar temperature to that of the CB material (310 °C; Fig. 1). Although ferrihydrite has not been detected by ChemMin in CB, it may exist in the XRD amorphous components. A mixture of magnetite and Na-chlorate produces an O<sub>2</sub> release similar to the second JK peak (370 °C; Fig. 1). Additionally, a mixture of Na-chlorate with hematite produces an O<sub>2</sub> release at the same temperature as the WJ materials (401 °C; Fig. 1). Hematite was not detected by ChemMin in WJ, but it may exist in the XRD amorphous components. No significant HCl releases were detected with these mixtures (data not shown).

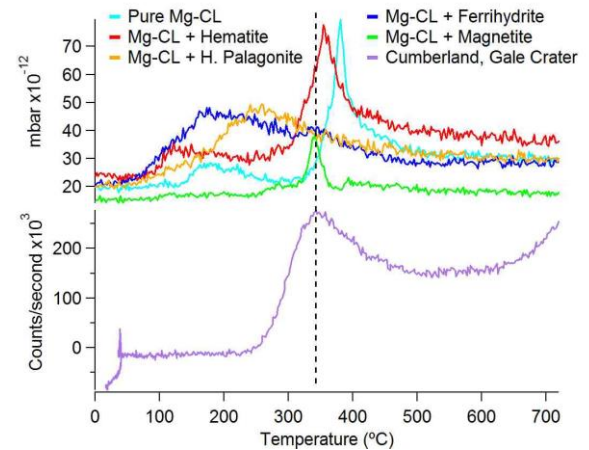
Ca-chlorate only produces an O<sub>2</sub> release starting at 353 °C, peaking at 430 °C, and ending at 448 °C. This release occurs at approximately the same temperature as CH but occurs over a narrower temperature range. When Ca-chlorate is mixed with iron-phase minerals, the O<sub>2</sub> release temperatures decrease. Ca-chlorate mixed with hematite produces an O<sub>2</sub> release (411 °C) at a similar temperature to that of WJ material (401 °C; Fig. 1). The mixture with ferrihydrite produces an O<sub>2</sub> release at approximately 312 °C, which is similar to the CB peak (310 °C; Fig. 1). HCl peaks were not detected unlike in previous work [7].

Mg-chlorate only produces a sharp O<sub>2</sub> release starting at 279 °C, peaking at 379 °C, and ending at 397 °C. This release peaks at approximately the same temperature as RN but occurs over a narrower temperature range. Mixtures of Mg-chlorate and iron-phase minerals decrease the O<sub>2</sub> release temperatures, but none of these mixtures provide exact matches with Gale Crater materials (Fig. 1). However, Mg-chlorate mixtures are the only chlorate mixtures to produce significant HCl releases (Fig. 2). The magnetite/Mg-chlorate mixture produces an HCl peak at the same temperature as the CB mudstone (Fig. 2) but does not reproduce the entire CB HCl release pattern. Additionally, the hematite/Mg-chlorate mixture produces an HCl peak similar to CB (Fig. 2).

**Conclusion:** Laboratory analyses demonstrate that mixtures of chlorates and iron-phase minerals decrease the oxygen release temperatures and provide many close matches to Gale Crater materials. Thus, the oxygen and HCl from these materials may be caused in part by chlorates. Ferrihydrite/chlorate mixtures produce O<sub>2</sub> releases at similar temperatures as the CB mudstone, although ferrihydrite was not detected in those materials. Furthermore, the HCl release from CB can be explained by Mg-chlorate/magnetite or Mg-chlorate/hematite, or a combination of both. Future work will include investigating other chlorate/mineral mixtures to obtain a closer match to the CB HCl peak.



**Fig. 1.** O<sub>2</sub> release versus temperature from mixtures of 100 μmols iron-phase mineral with 24 μmol dried chlorate solution. Dashed lines indicate locations of O<sub>2</sub> release peaks of JK, CB, and WJ (CL = chlorate).



**Fig. 2.** HCl releases versus temperature from CB material and mixtures of 100 μmols iron-phase mineral with 24 μmol magnesium chlorate solution. Dashed line represents the CB HCl peak (CL = chlorate).

- [1] Leshin et al. (2013) *Science*, 341 DOI: 10.1126/science.1238937 [2] Ming et al. (2013) *Sci. Exp.* 10.1126/science. 1245267. [3] Rampe et al. (2014), AGU Fall. [4] Hecht et al. (2009) *Science*, 325, 64-47. [5] Sutter et al. (2013) *LPS XLIV* #2046. [6] Sutter et al. (2015) *LPS XLVI* #2137 Sutter et al. (2014) 8<sup>th</sup> Mars Conf. [7] Sutter et al. (2014) *LPS XLV* #2136.