THE INVESTIGATION OF MAGNESIUM PERCHLORATE/IRON PHASE-MINERAL MIXTURES AS A POSSIBLE SOURCE OF OXYGEN AND CHLORINE DETECTED BY THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT IN GALE CRATER, MARS. B. Sutter1,2, E. Heil1,2, P.D. Archer1,2, D.W. Ming2, J.L. Eigenbrode3, H.B. Franz3, D.P. Glavin3, A.C. McAdam3, P.R. Mahaffy3, P.B. Niles3, J.C. Stern3, R. Navarro-Gonzalez4, C.P. McKay5 and the MSL Science Team. 1Jacobs, Houston,TX 77058, 2NASA Johnson Space Center, Houston TX 77058, 3NASA Goddard Space Flight Center, Greenbelt, MD 20771, 4Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, 5NASA Ames Research Center, Moffett Field, CA 94035.

Introduction: The Sample Analysis at Mars (SAM) instrument onboard the Curiosity rover detected \( \text{O}_2 \) and \( \text{HCl} \) gas releases from the Rocknest (RN) eolian bedform and the John Klein (JK) and Cumberland (CB) drill hole materials in Gale Crater (Fig. 1) [1,2]. Chlorinated hydrocarbons have also been detected by the SAM quadrupole mass spectrometer (QMS) and gas chromatography/mass spectrometer (GCMS) [1,2,3,4]. These detections along with the detection of perchlorate (\( \text{ClO}_4^- \)) by the Mars Phoenix Lander’s Wet Chemistry Laboratory (WCL) [5] suggesting perchlorate is a possible candidate for evolved \( \text{O}_2 \) and chlorine species. Laboratory thermal analysis of individual perchlorates has yet to provide an unequivocal temperature match to the SAM \( \text{O}_2 \) and \( \text{HCl} \) release data [1,2]. Catalytic reactions of Fe phases in the Gale Crater material with perchlorates can potentially reduce the decomposition temperatures of these otherwise pure perchlorate/chlorate phases [e.g., 6,7]. Iron mineralogy found in the Rocknest materials when mixed with Ca-perchlorate was found to cause \( \text{O}_2 \) release temperatures to be closer match to the SAM \( \text{O}_2 \) release data and enhance \( \text{HCl} \) gas releases. Exact matches to the SAM data has unfortunately not been achieved with Ca-perchlorate-Fe-phase mixtures [8]. The effects of Fe-phases on magnesium perchlorate thermal decomposition release of \( \text{O}_2 \) and \( \text{HCl} \) have not been evaluated and may provide improved matches to the SAM \( \text{O}_2 \) and \( \text{HCl} \) release data. This work will evaluate the thermal decomposition of magnesium perchlorate mixed with fayalite/magnetite phase and a Mauna Kea palagonite (HWMK 919). The objectives are to 1) summarize \( \text{O}_2 \) and \( \text{HCl} \) releases from the Gale Crater materials, and 2) evaluate the \( \text{O}_2 \) and \( \text{HCl} \) releases from the Mg-perchlorate + Fe phase mixtures to determine if Mg-perchlorate mixed with Fe-phases can explain the Gale Crater \( \text{O}_2 \) and \( \text{HCl} \) releases.

Materials and Methods: The Rocknest material examined by SAM consists of unconsolidated sand and dusty material [1]. John Klein and CB are drill hole samples (\(~6\) cm deep) derived from the Sheepbed mudstone and are \( 3 \) m and \( 10 \) cm apart, horizontally and vertically, respectively [2]. The \(< 150\)-\( \mu \)m size fraction was examined by SAM. Samples were heated (\( 35^\circ\text{C min}^{-1} \)) from \( 45 \) to \(~860^\circ\text{C} \) in a \( 25 \) mb He purge at \(~0.8 \) sccm. Evolved gases were analyzed by the SAM-QMS over the entire temperature range.

A laboratory Setaram Sensys-Evo differential scanning calorimeter (DSC) coupled to a Stanford Research Systems Universal Gas Analyzer at Johnson Space Center (JSC) were configured to operate similarly to the SAM oven/QMS system. Samples are heated from \( 25 \) to \( 730^\circ\text{C} \) under flowing He (3 ml/min) at 30 mb total pressure. Experiments consisted of reagent grade (Sigma-Aldrich) \( \text{Mg(ClO}_4\text{)}_2\cdot6\text{H}_2\text{O} \), and mixtures of \( \text{Mg(ClO}_4\text{)}_2\cdot6\text{H}_2\text{O} \) (1 mg) plus Mauna Kea palagonite HWMK919 (3.0 mg) and \( \text{Mg(ClO}_4\text{)}_2\cdot6\text{H}_2\text{O} \) (0.7 mg) plus fayalite/magnetite (Wards, Quebec) (0.7 mg) were evaluated in this work. The HWMK919 material consists plagioclase feldspar, minor pyroxene, magnetite, minor hematite, basaltic glass, allophane, and nanophase ferric oxide [9].

Results and Discussion: The \( \text{O}_2 \) peak temperatures are \(~315 \) and \(~385^\circ\text{C} \) for CB and RN, respectively (Fig. 1) suggesting differing \( \text{O}_2 \) producing species for each material. John Klein has two \( \text{O}_2 \) peaks at \(~225 \) and \(~370^\circ\text{C} \) (Fig. 1), which suggests the presence of two \( \text{O}_2 \) evolving species. The dip between the two JK peaks could be also be attributed to consumption of \( \text{O}_2 \) during organic combustion, or thermal oxidation of a ferrous phase (e.g., magnetite to maghemite transition) [2].

The \( \text{HCl} \) temperature release characteristics from CB were different than JK and RN. Cumberland was marked by two \( \text{HCl} \) peaks at \(~350 \) and \(~730^\circ\text{C} \), with what appears to be subtle peak at \(~560^\circ\text{C} \). The RN and JK possessed a gradual \( \text{HCl} \) release that peaked near \(~760^\circ\text{C} \) (Fig. 2). The first \( \text{HCl} \) phase in CB is coincident with the \( \text{O}_2 \) release indicating that \( \text{HCl} \) is sourced from an oxychlorine species like perchlorate or chlorate (Figs. 1,2) [2]. The second CB \( \text{HCl} \) peak and John Klein and RN peak \( \text{HCl} \) releases do not coincide with peak \( \text{O}_2 \) releases.

The thermal decomposition of Mg-perchlorate is characterized by two \( \text{O}_2 \) releases peaks at 456 and 526\(^\circ\text{C} \), which occur at higher temperatures than the Gale Crater \( \text{O}_2 \) peaks (Fig. 1). The mixing of the fayalite/magnetite with Mg-perchlorate had no effect on
No clear HCl contributions (Fig. 2). Multiple HCl releases may be possible in CB suggesting that Mg-perchlorate may contribute to some of the HCl released from CB.

Mg-perchlorate may provide some O₂ and HCl due to overlapping temperatures of O₂ and HCl releases between the Gale Crater materials and the Mg-perchlorate+Fe-phases mixtures. The Mg-perchlorate and corresponding Fe-phase mixtures examined here; however, did not appear to provide ideal matches to the O₂ and HCl releases from the Gale Crater materials. Additional Fe-phases that occur in the Gale Crater materials (e.g., ilmenite, pyrite, pyrrhotite, hematite, magnetite) that have yet to be mixed with Mg-perchlorate will be analyzed to determine if improved matches of O₂ and HCl release temperatures with Gale Crater materials can be obtained.