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. Ming3, J.L. Eigenbrode3, H.B. Franz2, D.P. Glavin1, A.C. McAdams3, P.R. Mahaffy3, P.B. Niles4, 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 O2 and 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 (ClO4\(^-\)) by the Mars Phoenix Lander’s Wet Chemistry Laboratory (WCL) [5] suggesting perchlorate is a possible candidate for evolved O2 and chlorine species. Laboratory thermal analysis of individual perchlorates has yet to provide an unequivocal temperature match to the SAM O2 and 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 O2 release temperatures to be closer match to the SAM O2 release data and enhance 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 O2 and HCl have not been evaluated and may provide improved matches to the SAM O2 and 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 O2 and HCl releases from the Gale Crater materials, and 2) evaluate the O2 and HCl releases from the Mg-perchlorate + Fe phase mixtures to determine if Mg-perchlorate mixed with Fe-phases can explain the Gale Crater O2 and 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-μm size fraction was examined by SAM. Samples were heated (35°C min\(^{-1}\)) from 45 to ~860°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°C under flowing He (3 ml/min) at 30 mb total pressure. Experiments consisted of reagent grade (Sigma-Aldrich) Mg(ClO4)\(_2\)•6H2O, and mixtures of Mg(ClO4)\(_2\)•6H2O (~1 mg) plus Mauna Kea palagonite HWMK919 (3.0mg) and Mg(ClO4)\(_2\)•6H2O (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 O2 peak temperatures are ~315 and 385°C for CB and RN, respectively (Fig. 1) suggesting differing O2 producing species for each material. John Klein has two O2 peaks at ~225 and 370°C (Fig. 1), which suggests the presence of two O2 evolving species. The dip between the two JK peaks could be also be attributed to consumption of O2 during organic combustion, or thermal oxidation of a ferrous phase (e.g., magnetite to maghemite transition) [2].

The HCl temperature release characteristics from CB were different than JK and RN. Cumberland was marked by two HCl peaks at ~350 and ~730°C, with what appears to be subtle peak at ~560°C. The RN and JK possessed a gradual HCl release that peaked near ~760°C (Fig. 2). The first HCl phase in CB is coincident with the O2 release indicating that HCl is sourced from an oxychlorine species like perchlorate or chlorate (Figs. 1,2) [2]. The second CB HCl peak and John Klein and RN peak HCl releases do not coincide with peak O2 releases.

The thermal decomposition of Mg-perchlorate is characterized by two O2 release peaks at 456 and 526°C, which occurs at higher temperatures than the Gale Crater O2 peaks (Fig. 1). The mixing of the fayalite/magnetite with Mg-perchlorate had no effect on
No clear HCl contributions.

Reducing the thermal decomposition of Mg-perchlorate (Fig. 1).

Mixing HWMK919 with Mg-perchlorate does reduce the peak O₂ release temperature by 60ºC down to 466ºC (Fig. 1). The HWMK919 also has the effect of reducing the first lower intensity O₂ peak which results in the HWMK919 mixture having a broad O₂ release. While the O₂ peak for the HWMK919 mixture does not coincide with any of the Gale Crater O₂ peaks, the overall O₂ release does overlap with the last half of the Rocknest and 2nd John Klein O₂ releases (Fig. 1). This O₂ overlap suggests that Fe phases mixed with Mg-perchlorate may partly explain the O₂ releases from at least Rocknest and possibly the second John Klein peak. The possibility exists that O₂ could be sourced from reactions of Mg-perchlorate with other Fe phases in Gale Crater materials that have yet to be examined.

The Mg-perchlorate mixtures examined here suggest that some of the CB HCl could be derived from Mg-perchlorate (Fig. 2). No clear HCl contributions from Mg-perchlorate in RN or JK were observed. The HCl release peaks from Mg-perchlorate and Mg-perchlorate-fayalite/magnetite occur at ~530ºC with Mg-perchlorate+HWMK919 peak at ~470ºC (Fig. 2). These peaks are well below the RN and JK peaks but occur between the CB peaks (Fig. 2). The broad nature of the CB O₂ release between the two main peaks along with the subtle peak at ~560ºC indicate that 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, pyrrohotite, 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.