THE INVESTIGATION OF CHLORATES AS A POSSIBLE SOURCE OF OXYGEN AND CHLORINE DETECTED BY THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT IN GALE CRATER, MARS. B. Sutter¹, P.D. Archer¹-², D.W. Ming³, P.B. Niles³, J.L. Eigenbrode¹, H. Franz², D. P. Glavin³, A.C. McAdam³, P. Mahaffy³, J.C. Stern¹, R. Navarro-Gonzalez², C.P. McKay³, 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 perchlorates has yet to provide an unequivocal temperature match to the SAM O₂ and HCl release data [1,2]. Iron mineralogy found in the Rocknest materials when mixed with Ca-perchlorate does cause O₂ release temperatures to be closer match to the SAM O₂ release data but more work is required in evaluating the catalytic effects of Fe mineralogy on perchlorate decomposition [6]. Chlorates (ClO₃⁻) are relevant Mars materials and potential O₂ and Cl sources [7,8]. The objective of this work is to evaluate the thermal decomposition of select chlorate (ClO₃⁻) salts as possible sources of the O₂ and HCl releases in the Gale Crater materials.

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 10cm apart, horizontally and vertically, respectively [2]. The < 150 um size fraction was examined by SAM. Samples were heated (35 °C min⁻¹) from 35 to ~840°C in a 30 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. Reagent grade (Sigma-Aldrich) NaClO₃•H₂O and KClO₃•H₂O were used for this work. Mg(ClO₄)₂•nH₂O, and Ca(ClO₃)₂•nH₂O were synthesized by combining dissolved reagent BaCl₂•nH₂O in water and with equal molar dissolved reagent MgSO₄ and CaSO₄, respectively. Precipitated BaSO₄ was centrifuged out. The remaining solution was boiled down to ~20 ml and then frozen and subsequently freeze-dried to allow for Ca- and Mg-chlorate precipitation. Chlorate synthesis was verified by X-ray diffraction.

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, 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, while 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 release do not coincide with peak O₂ releases.

The O₂ release peak temperatures for Ca-chlorate and Mg-chlorate are the closest match to the RN and second JK O₂ peaks (Fig. 1). The Mg-chlorate O₂ peak nearly coincides with RN and second JK O₂ peaks while the Ca-chlorate O₂ peak are ~25 to 40°C higher than the RN and JK peaks, respectively. The Na-chlorate and K-chlorate O₂ peaks are higher than all the O₂ peak temperatures for RN, JK, and CB (Fig. 1).

None of the chlorates evaluated here coincide with the CB and first JK O₂ peaks (Fig. 1). Iron-chlorate has yet to be evaluated and may yield O₂ peak temperatures consistent with CB and the first JK O₂ peaks.

The Mg-chlorate HCl peak is closest to the CB HCl peak 1 but does not yield any HCl that could explain the high temperature (>700°C) HCl peaks in RN, JK, or CB (Fig. 2). The HCl evolution is caused by Mg-chlorate decomposition to MgO which liberates Cl₂ that reacts with water to form HCl as indicated by heated stage X-ray diffraction (data not shown). The Mg-chlorate peak HCl release temperature is near (~ within 25°C) to the CB5 peak 1 HCl release. This suggests that Mg-chlorate could be a reasonable candidate for explaining the CB HCl peak 1. The Mg-chlorate O₂ release; however, does not provide an ideal match
Fig. 1. Oxygen release versus temperature from Rocknest-4 (RN4), John Klein-4 (JK4) and Cumberland-5 (CB5) materials as measured by the SAM-QMS and select chlorate salts analyzed by the JSC-SAM testbed. JK4 is multiplied ×5 relative to RN4 and CB5. Arrowed dotted lines indicate Mg- and Ca-chlorate O2 peak positions relative to O2 releases in the Gale Crater materials.

to the CB O2 peak (Fig. 1) suggesting that Mg-chlorate may not be a candidate for CB.

There are two minor HCl releases just above baseline from Ca-chlorate at 70°C and 400°C (Fig. 2). The 400°C release is related to Ca-chlorate decomposition but the low temperature release may be attributed to a temporary HCl baseline rise caused by significant water release associated Ca-chlorate dehydration (data not shown). Much less HCl is produced from Ca-chlorate decomposition because most of the Cl combines with Ca to form CaCl2. No HCl releases were detected for Na- and K-chlorate because all Cl is used to form NaCl and KCl [9]. Above 450°C, the Ca-chlorate HCl baseline levels appear to rise slightly which is similar to the observed HCl baseline rise in RN and JK (Fig. 2). The DSC maximum temperature is 730°C and it is unknown if the baseline would have risen and peaked, similar to what was observed for RN and JK. Nevertheless, the Ca-chlorate HCl baseline rise at high temperature coupled with the close O2 release temperature match to RN and JK suggests that Ca-chlorate may be a candidate oxychlorine species for RN and JK.

No chlorates matched O2 releases for JK peak 1 and CB. Mg-chlorate O2 release temperature is consistent with RN and JK but does not have a matching HCl release. Ca-chlorate O2 and HCl release characteristics are both close with RN and JK (O2 peak 2) which suggests that Ca-chlorate may be a better candidate oxychlorine species than Mg-chlorate. The thermal decomposition of Fe(II)- and Fe(III)-chlorate will be evaluated next to determine if these chlorate species can better explain the O2 and HCl release characteristics of RN, JK and/or CB. Mixing iron phases (e.g., hematite) with chlorates are known to have catalytic effects that cause chlorate O2 and HCl release temperatures to differ from pure chlorate phases [9]. Future work will mix iron phases (e.g., hematite, magnetite, pyrite, fayalite, amorphous Fe material) known to occur in RN, JK, and CB with chlorates to determine if improved O2 and HCl release temperature matches with the Gale materials can be obtained.

References: