

THE INVESTIGATION OF PERCHLORATE/IRON PHASE MIXTURES AS A POSSIBLE SOURCE OF OXYGEN DETECTED BY THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT IN GALE CRATER, MARS. B. Sutter^{1,2}, E. Heil^{1,2}, R.V. Morris², P.D. Archer^{1,2}, D.W. Ming², P.B. Niles², J.L. Eigenbrode³, H. Franz³, C. Freissinet^{3,4}, D. P. Glavin³, A.C. McAdam³, P. Mahaffy³, F. Javier Martin-Torres⁵, R. Navarro-González⁶, María Paz-Zorzano⁷, J.C. Stern³, C.P. McKay⁸. ¹Jacobs, Houston, TX 77058, ²NASA/JSC, Houston TX 77058, ³NASA Goddard Space Flight Center, Greenbelt, MD 20771, ⁴Oak Ridge Associated Universities, TN, ⁵Inst. Andaluz de Ciencias de la Tierra, Granada, Spain, ⁶Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, ⁷Centro de Astrobiología (INTA-CSIC), Madrid, ⁸NASA 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), Cumberland (CB), Windjana (WJ), and Confidence Hills (CH) drill hole materials in Gale Crater (Fig. 1) [1,2,3]. Chlorinated hydrocarbons have also been detected by the SAM quadrupole mass spectrometer (QMS) and gas chromatography/mass spectrometer [1,2,4]. These detections along with the detection of perchlorate (ClO₄) by the Mars Phoenix Lander's Wet Chemistry Laboratory [5] suggested perchlorate is a possible candidate for evolved O₂ and chlorine species. Laboratory thermal analysis of pure perchlorates has yet to provide an unequivocal temperature match to the SAM O₂ and HCl release data [1,2]. Analog laboratory analysis of iron mineralogy detected in Gale materials that was physically mixed with Ca- and Mg-perchlorate has been shown to catalyze lower O₂ release temperatures and approach some SAM O₂ release data [6,7]. Instead of physical mixtures used in previous work, the work presented here utilized perchlorate solutions added to Fe phases. This technique allowed for perchlorate to come in closer contact with the Fe-phase and may more closely mimic Mars conditions where humidity can increase enough to cause deliquescence of the highly hygroscopic perchlorate phases [8]. The objective of this work is to 1) Utilize a laboratory SAM analog instrument to evaluate the O₂ release temperatures from Mg- and Ca-perchlorates solutions applied to Fe-phases detected in Gale Crater and 2) Determine if perchlorate solutions can provide improved matches with the SAM O₂ temperature release profiles.

Materials and Methods: The RN material examined by SAM consists of unconsolidated sand and dust [1]. John Klein (mudstone), CB (mudstone), WJ (sandstone), and CH (sandstone) are drill hole samples (~6 cm deep) [2, 3]. The < 150 μm size fraction was examined by SAM. Samples were heated (35 °C min⁻¹) from 35 to ~860°C (RN, JK, CB) or 965°C (WJ, CH) in a 25 mb He purge at ~0.8 sccm. Evolved gases were analyzed by the SAM-QMS. A laboratory Setaram Sensys-Evo differential scanning calorimeter coupled to a Stanord Research Systems Universal Gas Analyzer at

Johnson Space Center 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 Mg(ClO₄)₂•6H₂O (Sigma-Aldrich) and Ca(ClO₄)₂•4H₂O (Acros Organics) were mixed with different synthetic Fe phases that included goethite, and ferrihydrite. Natural phases that were used include hematite, magnetite, fayalite/magnetite mixture, ilmenite, pyrrhotite, and Mauna Kea palagonite (HWMK919). All mixtures consisted of dissolving 12 μmole of a perchlorate in water and adding it to 100 μmoles of the Fe phases except for the for the HWMK919 palagonite and Fayalite+magnetite materials where 20 mg was used.

Results and Discussion: The five samples evaluated by SAM had varying O₂ release peak temperatures that occurred at 380°C (RN), 225 and 374°C (JK), 318°C (CB), 328°C (WJ) and 461°C (CH) (Fig. 1). Confidence Hills has two additional higher temperature peaks that are, at this time, attributed to sulfate decomposition (Fig. 1). The presence of varying O₂ release temperatures could be attributed to the presence of differing perchlorate (PCL) or chlorate species in the Gale materials. The same perchlorate or chlorate phase may be present in all samples but variation in the Fe mineralogy between samples could catalyze a variation in O₂ peak release temperatures.

Laboratory analog analysis demonstrated that O₂ peak temperature for pure Ca-PCL (486°C) and Mg-PCL (533°C) were higher than what was detected in the Gale Crater materials (Fig. 1). The perchlorate/Fe phases mixtures cause the O₂ peak release temperatures to drop from 16 to 152°C relative to the pure perchlorates depending on the Fe phase that was present.

The perchlorate mixtures with the Mauna Kea palagonite (HWMK919) and ferrihydrite provide O₂ peak release temperatures that coincide with the RN and JK peak 2 O₂ releases (Fig. 1). The Mauna Kea palagonite possesses plagioclase feldspar, magnetite, minor pyroxene and hematite, basaltic glass, allophane, and nanophase ferric oxide [9]. The hematite and magnetite mixtures cause higher O₂ release temperatures (Fig. 1),

which suggests that hematite and magnetite are not responsible for affecting the O₂ release temperature in the perchlorate-palagonite mixture. Ferrihydrite, a nanophase iron oxide, when mixed with the perchlorate does provide coinciding O₂ release temperatures with RN and JK peak 2 (Fig.1). This suggests the nanophase Fe-oxides present in palagonite may be responsible for lowering the O₂ release temperatures in the palagonite mixture. The presence of 27 -28 wt.% amorphous material [10] that is dominated by Fe, Si, and S [11] suggests that nanophase Fe-oxides are possibly interacting with perchlorates in O₂ evolution in the RN and JK materials.

The Mg-PCL-goethite mixture possessed multiple O₂ peaks while Ca-PCL-goethite mixture yielded two O₂ peaks (Fig. 1) that spanned the RN and JK peak 2 O₂ release (Fig. 1b). This suggests that perchlorate-goethite mixtures could be considered consistent with O₂ release from Ca- or Mg-PCL mixed with goethite in RN and JK. However, no goethite was detected in the RN or JK materials by CheMin [10] and the Gale O₂ releases were mostly characterized by broad single peaks not multiple peaks, as in RN and JK peak 2.

The perchlorate mixtures with magnetite, hematite, fayalite-magnetite, ilmenite, and pyrrhotite yield O₂ release temperatures consistent with CH O₂ release temperature. The CH material consists of 8 wt. % hematite with minor magnetite, olivine, and ilmenite. Initial mineralogical analysis suggests that the CH amorphous (~31 wt.%) [11] component is more silica rich with less Fe less than the RN, CB, and JK amorphous materials. This presence of greater hematite and lack of nanophase Fe-oxides may be responsible for the relatively higher O₂ release temperature from perchlorate in CH.

No Mg- or Ca- perchlorate-Fe phase mixture can explain the much lower O₂ release temperatures detected in the JK-peak 1, CB and WJ materials. Chlorates are candidate phases for the source of O₂ in CB and WJ [12]. Fe(III)-perchlorate has two O₂ release peaks at low temperature near O₂ peak temperatures detected in CB, WJ, and JK-peak1. Laboratory analog work evaluating Fe-phase mixtures with Fe(III)-perchlorate and chlorates will be conducted to determine if O₂ release temperatures consistent with those in JK-peak1 and CB and WJ can be achieved.

The amount of evolved O₂ from 12 μmol perchlorate was reduced in the presence of 100 μmol of the Fe-phases (100 μmol) relative to pure perchlorate. The Fe-oxide containing phases caused up to a 2 to 3X reduction of evolved O₂. The use of pyrrhotite (FeS) caused a 3 to 7X reduction in evolved O₂. Iron phases (e.g., hematite, magnetite, pyrite, pyrrhotite) in the Gale materials can reduced the amount of detected O₂ resulting in an underestimation of the amount of perchlorate or chlorate present.

Mg-, Ca-, or Na-perchlorate (data not shown) when mixed with nanophase-Fe-oxides may explain the O₂ releases from RN and JK-peak 2. Mg- or Ca-perchlorate mixed with hematite produces O₂ releases consistent with the CH O₂ releases. Future work with chlorate-Fe phase mixtures should provide insight into evolved O₂ from CB and WJ materials.

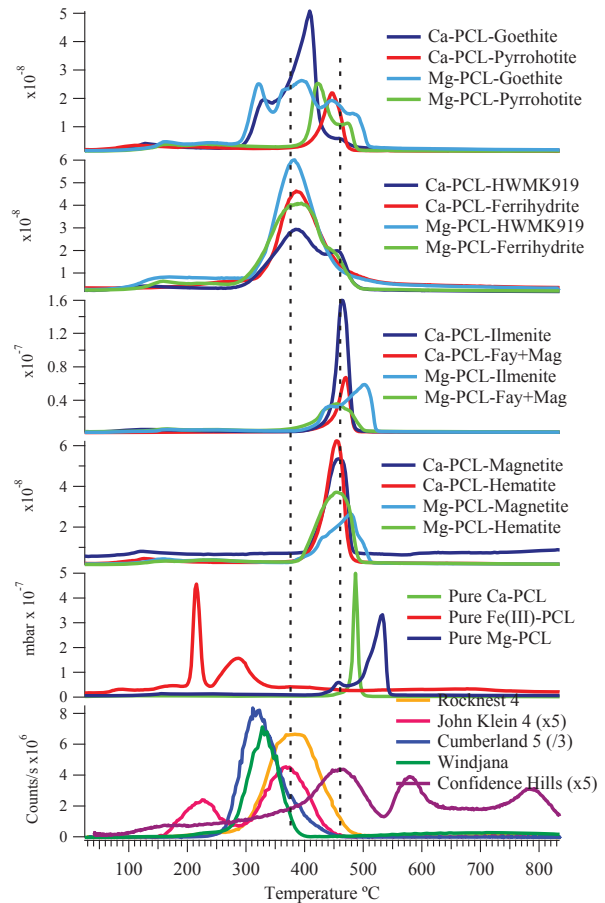


Fig. 1. O₂ release versus temperature as detected by SAM for five Gale Crater materials along with pure Ca-perchlorate (PCL), Mg-PCL, Fe(III)-PCL, and iron phases mixed with Ca-PCL and Mg-PCL. Vertical dashed lines marks O₂ peak locations for RN, JK peak 2 and CH.

[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]Glavin et al. (2013) *JGR*, 118,1955. [5]Hecht et al. (2009) *Science*, 325, 64. [6] Bruck et al. (2014) *LPS XLV* #2057. [7]Sutter et al., (2014) 8th Mars Conf. [8]Nuding et al. (2014) *Icarus*, 243,420. [9] Morris et al. (2001), *JGR*, 106, 5057. [10]Vaninen et al. (2014) *Science Express* 10.1126/science.1243480. [11]Cavanagh et al.(2015) *LPS XLVI This Conf.* [12]Sutter et al. (2014) *LPS XLV* #2136