THE DETECTION OF EVOLVED OXYGEN FROM THE ROCKNEST EOLIAN BEDFORM MATERIAL BY THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT AT THE MARS CURIOSITY LANDING SITE.

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Introduction: The Sample Analysis at Mars (SAM) instrument onboard the Curiosity rover detected an O_2 gas release from the Rocknest eolain bedform (Fig. 1). The detection of perchlorate (ClO_4^-) by the Mars Phoenix Lander's Wet Chemisty Laboratory (WCL) [1] suggests that perchlorate is a possible candidate for evolved O_2 release detected by SAM. The perchlorate would also serve as a source of chlorine in the chlorinated hydrocarbons detected by the SAM quadrupole mass spectrometer (QMS) and gas chromatography/mass spectrometer (GCMS) [2,3]. Chlorates (ClO_3^-) [4,5] and/or superoxides [6] may also be sources of evolved O_2 from the Rocknest materials. The work objectives are to 1) evaluate the O_2 release temperatures from Rocknest materials, 2) compare these O_2 release temperatures with a series of perchlorates and chlorates, and 3) evaluate superoxide O_2^- sources and possible perchlorate interactions with other Rocknest phases during QMS analysis.

Materials and Methods: The Rocknest bedform material examined by SAM consists mostly of unconsolidated sand and dusty material [6]. The < 150 µm size fraction (~15-40 mg) was examined by SAM. Four replicate Rocknest samples were heated (35 ˚C min^{-1}) from 35 to ~840 ˚C in a 30 mb He purge at 1 sccm. Evolved gases were analyzed by the SAM-QMS over the entire temperature range and at select temperatures by the SAM-GCMS [2,3].

A laboratory Setaram Sensys-Evo differential scanning calorimeter coupled to a Stanford Research Systems Universal Gas Analyzer at Johnson Space Center have been configured to operate similar to the SAM oven/QMS system. This JSC SAM-testbed operates at 30 mb He with a 3 ml/min flow rate. Reagent grade $NaClO_4{\bullet}H_2O$, $KClO_4{\bullet}H_2O$, $Mg(ClO_4)_2{\bullet}6H_2O$, $Ca(ClO_4)_2{\bullet}4H_2O$, $Fe(II)(ClO_4)_2{\bullet}6H_2O$, $Fe(III)(ClO_4)_2{\bullet}6H_2O$ and $NaClO_3$ and $KClO_3$ were evaluated by the JSC-SAM-testbed for comparison to O_2 release temperatures determined by the SAM-QMS on Mars.

Results: The SAM-QMS detected a major O_2 release (300-500 ˚C) from the Rocknest bedform materials, which coupled with the contemperanous release of chlorinated hydrocarbons [2,3], suggests the presence of perchlorate (Fig. 1). A minor O_2 release was detected at a lower temperature (Fig. 1) and may be another another gas species. This report will focus on the main O_2 release between (300-500 ˚C)

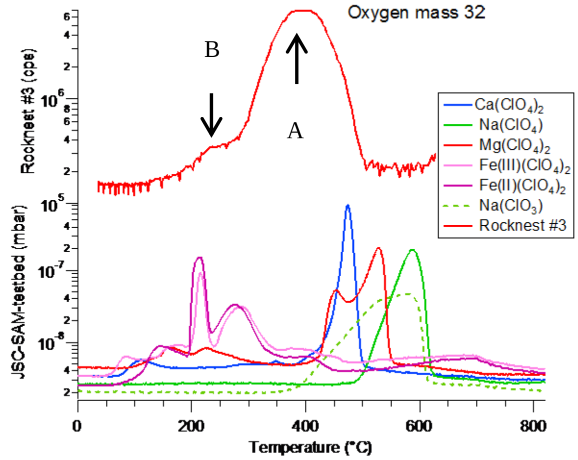

Fig. 1. Oxygen release versus temperature from the third EGA analysis of Rocknest eolian bedform material as measured by SAM and select perchlorate/chlorate salts analyzed by the JSC-SAM-testbed. Main release and minor O_2 releases are labelded A and B, respectively.

Fe and Mg-perchlorates are not likely candidate perchlorates for the Rocknest material. JSC-SAM testbed studies demonstrate that Mg- and Fe-perchlorates release Cl, (Fig. 2), Cl_2, and HCl (data not shown) along with O_2 upon decomposition. These species were not detected indicating that Fe and Mg-perchlorates are not likely in the Rocknest material. Furthermore, Fe and Mg-perchlorates possess distinct multiple O_2 release peaks while the Rocknest O_2 appears to consist mostly of a single peak.

Na- and K-perchlorate release O_2 and decompose to NaCl and KCl, respectively, at temperatures higher than the O_2 release for Rocknest (Fig. 1). These perchlorates do not release chlorinated species. The presences of Na- and K-perchlorates is therefore unlikey in Rocknest.

Ca-perchlorate is currently the best perchlorate candidate for evolved O_2 in the Rocknest samples. The Ca-perchlorate O_2 release temperature (400-500 ˚C) overlaps with the Rocknest O_2 release but does occur on the high end of the O_2 termperature release.

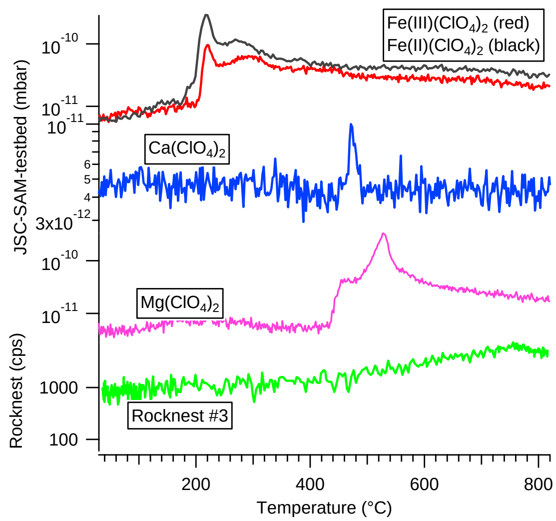

Fig. 2. Chlorine (mass 35) release versus temperature from the third EGA analysis of Rocknest material as measured by SAM and select perchlorate species as measured by the JSC-SAM-testbed.

The proximity of the O_2 releases suggests that Ca-perchlorate is possible for Rocknest.

Ca-perchlorate mostly decomposes to $CaCl_2$, but a small amount of evolved Cl was detectable in JSC-SAM testbed experiments (Fig. 2). This could be the source of the Cl in the chlorinated-hydrocarbons species that were detected by the QMS and GCMS. The small amount of Cl that is released by Ca-perchlorate could have been complexed by organic material in SAM, which prevented direct Cl (m/z 35) detection by the QMS.

The amount of the chlorinated hydrocarbon detected by the GCMS above 200°C only accounts for ~ 0.2 % of the total Cl in the proposed perchlorate [2,7]. This small amount of chlorine species in organics could not account for the expected amount of Cl released by Fe- or Mg-perchlorates. This further supports that Ca-perchlorate with its limited Cl release as the source of Cl for the chlorinated hydrocarbon phases detected by the GCMS and QMS.

Chlorate (ClO_3^-) is another possible O_2 source. Chlorate is a stable intermediate oxidation species between Cl and perchlorate (ClO_4^-) and is a possible species in Martian soil [4,5]. Na-chlorate has a decomposition onset temperature of 460 ˚C which is 90 ˚C lower than the decomposition onset temperature of Na-perchlorate. The decomposition onset temperature of Na-chlorate is still higher than the Rocknest O_2 onset temperature (300 ˚C). Although Ca-chlorate has to be evaluated in our testbeds, the decomposition and O_2 release temperature may be lower than Ca-perchlorate and could better match the Rocknest O_2 release temperature. This will be evaluated in future work.

Superoxide radical ions are not a likely source of the Rocknest O_2 detected by SAM-QMS. Superoxide radical ions (e.g, O_2^-) are a proposed source of the reactive nature of the Martian soil and absence of organic material as determined by Viking gas exchange and GCMS experiments [6]. Superoxide radicals are not stable in the presence of water [6] and the large release of water from the Rocknest soil that peaks at ~250 ˚C (data not shown) does not correspond with Rocknest O_2 release that peaks at 390 ˚C. While superoxide radicals may be present, they are unlikely the source of O_2 detected by SAM.

Catalytic reactions of other phases in the Rocknest material with perchlorates or chlorates can potentially reduce the decomposition temperatures of these otherwise pure perchlorate/chlorate phases [e.g., 8,9]. Potassium perchlorate reactions with Fe(II) containing oxides reduces the $KClO_4$ decomposition temperature by 125 ˚C [8]. The reduction of Cl^{7+} to Cl^{5+} or Cl^- in the ClO_4^- by Fe(II) promotes perchlorate instability, which reduces the perchlorate decomposition temperature [9]. Fe(II) containing phases (e.g., olivine, pyroxene) detected in the Rocknest material by CheMin [10] are potential electron donors and could reduce the decomposition temperature of any perchlorates/chlorates in the Rocknest material.

The detection of oxygen and chlorinated hydrocarbons by the SAM instrument suggests that a perchlorate and/or chlorate phase is present in the Rocknest material. Testbed evaluation of individual perchlorates and select chlorates have not identified an unequivocal match to the SAM data, but at this time Ca-perchlorate is the leading candidate. Additional chlorate phases have not yet been evaluated (e.g., Ca-, Mg-chlorates) and may yield results consistent with those detected by SAM. More importantly, testbed analyses involving mixtures of perchlorates and chlorates with other potential catalytic phases may reveal effects on decomposition temperatures, which may provide a more comprehensive explanation for the O_2 release characteristics observed by SAM.

References:

[1] Hecht et al. (2009) *Science, 325*, 64. [2] Glavin et al. (2013), *LPS XLIV*. [3] Eigenbrode et al. (2013), *LPS XLIV*. [4] Quinn et al. (2011) *LPS XLIII*. [5] Hanely et al. (2012), GRL, 39, L08201. [6] Yen, A.S. et al. (2000) Science, 289,1909. [7] Archer et al. (2012), *LPS XLIV*. [8] Markowitz, M.M. and Boryta, D.A. (1965) *J. Phys. Chem. 69*, 1114. [9] Furuichi R. et al. (1974) *J. Therm Anal. 6*,305. [10] Blake, D.F. et al. (2013), *LPS XLIV*.