OXYCHLORINE SPECIES ON MARS: IMPLICATIONS FROM GALE CRATER SAMPLES. P.D. Archer, Jr[1], D.W. Ming[2], B. Sutter[1], R.V. Morris[2], B.C. Clark[3], P.H. Mahaffy[4], J.J. Wray[5], A.G. Fairen[6], R. Gellert[7], A.S. Yen[8], D.F. Blake[9], D.T. Vaniman[10], D.P. Glavin[4], J.L. Eigenbrode[4], M.G. Trainer[4], R. Navarro-González[11], C.P. McKay[9], and C. Freissinet[4], [1]Jacobs, NASA Johnson Space Center, Houston, TX 77058, doug.archer@gmail.com, [2]NASA Johnson Space Center, Houston, TX, [3]Space Science Institute, Boulder, CO 80301, [4]NASA Goddard Space Flight Center, Greenbelt, MD 20771,[5]Georgia Institute of Technology, Atlanta, GA 30332, [6]Centro de Astrobiologia (INTA-CSIC), Madrid, Spain, [7]University of Guelph, ON, Canada , [8]Jet Propulsion Laboratory, Pasadena, CA 91109, [9]NASA Ames Research Center, Moffett Field, CA 94035, [10]Planetary Science Institute, Tucson, AZ, [11]Instituto de Ciencias Nucleares, UNAM, Mexico City, Mexico.

Introduction: The Sample Analysis at Mars (SAM) instrument on the Mars Science Laboratory (MSL) rover has analyzed one scooped sample and nine different drilled samples since landing over three years ago. Every sample analyzed has had a release of oxygen somewhere between 100 and 600 °C (*Figure 1*). This oxygen release is consistent with the decomposition of an oxychlorine species such as perchlorate (ClO_4^-) or chlorate (ClO_3^-). The samples analyzed have come from different geologic units, representing different periods of martian history. The detection of oxychlorine species at Gale Crater in samples spanning a large history of the planet, coupled with detections elsewhere on Mars, indicate that oxychlorine species are globally distributed on Mars and the production of perchlorate has occurred throughout the last 3 Ga.

Perchlorate was discovered on Mars by the Wet Chemistry Lab (WCL) instrument on the Phoenix lander in 2008 [1]. Although not definitive, it has been suggested that perchlorate was detected at both Viking landing sites, inferred from the detection of chlorinated hydrocarbons by the Gas Chromatograph/Mass Spectrometer (GCMS) instruments and the response of some of the life detection instruments [2, 3]. Recently, hydrated perchlorate salts have been detected from orbit and suggested as the cause of the Recurring Slope Lineae (RSL) [4].

Gale Crater Samples: The SAM instrument has detected O_2 released from each of the ten samples analyzed to date. After drilled or scooped material has been delivered to SAM, the sample is heated to ~850 °C and the evolved gas is measured directly with a quadrupole mass spectrometer. The simultaneous release of O_2 and chlorinated hydrocarbons such as chloromethane between temperatures of 100-600 °C. along with the release of HCl starting around 400 °C is consistent with the decomposition of oxychlorine species. The lowest temperatures releases (100-200 °C) are likely from the decomposition of chlorate salts, the higher temperatures (450-600 °C) are likely from the decomposition of perchlorates, and the intermediate temperatures could be a mixture of the two or depression of the perchlorate decomposition temperature by catalytic material present in the samples [5]

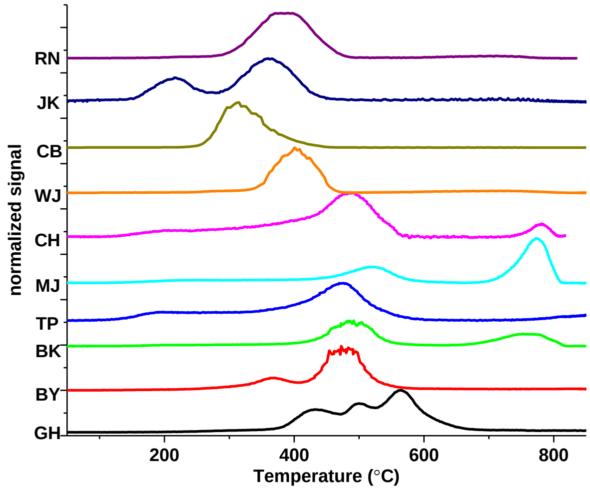

Figure 1 – O_2 releases measured by SAM. The releases from 100-600 °C are consistent with the decomposition of an oxychlorine species. The different peak temperatures indicate the presence of chlorate in addition to perchlorate as well as different cations (with the most likely Ca^{2+}, Mg^{2+}, and Na^+).

Oxygen and Chlorine: After analyzing the first six samples on Mars, we reported a strong linear correlation between evolved O_2 detected by SAM and total wt% Cl detected by the Alpha Particle X-ray Spectrometer (APXS) instrument on MSL. When new samples are included, the linear correlation disappears, with an R^2 value <0.3 if the Cumberland sample is excluded from the fit. Similarly, there is no longer a relationship between the fraction of Cl that can be accounted for by SAM O_2/total Cl from APXS vs. APXS Cl (Figures 2 and 3) [6].

Implications for Formation Mechanisms: On Earth, there is also no strong correlation between ClO_4^- and Cl^-, which implies a different source for each anion [7]. Based on the oxygen isotopes of terrestrial perchlorate, almost all natural perchlorate is formed in the stratosphere. On Mars, the lack of correlation between SAM O_2 (a proxy for perchlorate/chlorate) and total Cl could also indicate different sources for the Cl/ClO_4^-. However, atmospheric production of perchlorate on Mars is not efficient enough to explain the abundance of perchlorate detected at the surface [8]. Other formation mechanisms that have been proposed include oxidation at grain surfaces mediated by a mineral catalyst [9], radiolysis by ionizing radiation [10], or UV irradiation [11]. The efficiency of these processes would be affected by local chemistry/mineralogy and could explain why the Cl/ClO4 ratio varies at different sites.

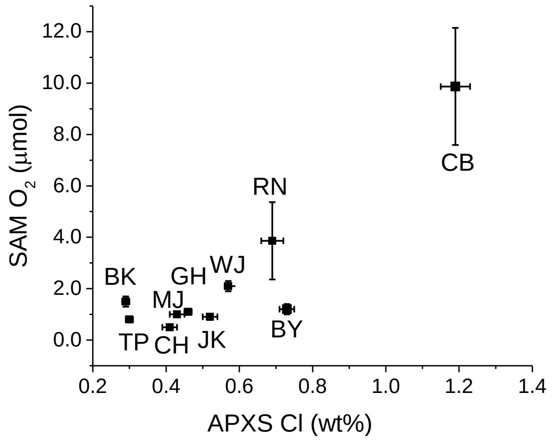

Figure 2 – Total O_2 detected by SAM vs. the wt% Cl of the same sample as measured by APXS. There is no strong correlation between the two values.

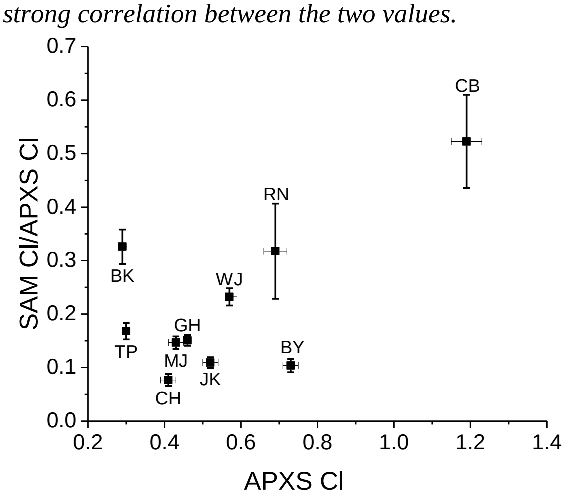

Figure 3 – SAM O_2 is converted to Cl, assuming the O_2 was all evolved from a chlorate (which has a higher Cl/O ratio and gives an upper limit to Cl from SAM) and ratiod with APXS Cl. This shows the fraction of Cl that can be accounted for by the evolved O_2.

Formation Over Time: The amount of O_2 released from two samples of the Sheepbed mudstone imply that perchlorate formation has been ongoing throughout Mars' history. The John Klein (JK) and Cumberland (CB) samples are both from the Sheepbed mudstone, which is billions of years old [12], and were only separated by a few meters of lateral distance and a few centimeters vertically. Despite their proximity, the Cumberland sample contained 1.15 ± 0.48 wt% Cl_2O_7 whereas John Klein contained only 0.10 ± 0.04 wt% Cl_2O_7 (both based on O_2 released). These are the highest and among the lowest amount of O_2 released during analysis. The difference can be best explained by the perchlorate being emplaced at the time the mudstone was formed, then subsequent fracturing of the rock and fluid flow through the fractures removed perchlorate in JK but not CB. This is consistent with the drill hole imagery which shows fractures throughout the JK material but almost none in CB.

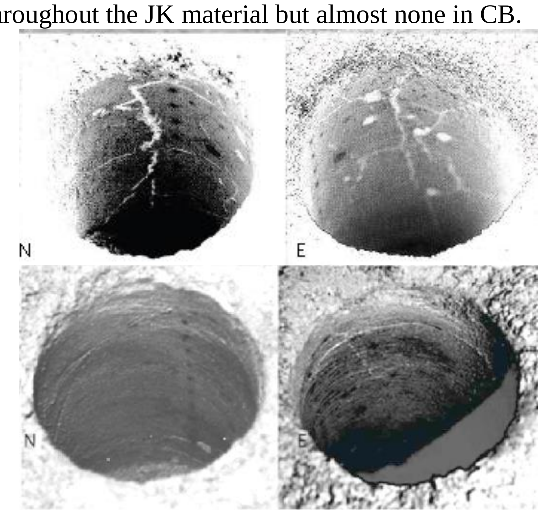

Figure 4 – drill hole imagery of John Klein (top) and Cumberland (bottom), showing the extensive veins in JK that are not present in CB [13], image credit: NASA/JPL-Caltech/MSSS.

Conclusions: The presence of O_2 evolved from every sample analyzed by SAM to date implies that perchlorate formation has occurred throughout martian history and, coupled with results from other missions, is globally distributed. Perchlorate on Mars is important because it can be a window to local chemistry, which can affect perchlorate formation rates, it is a potential chemical energy source for microbes [14], it has implications for organic detection, and has potential utility for In-Situ Resource Utilization enabling future human missions to Mars.

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