

OXYCHLORINE DETECTION IN GALE CRATER, MARS AND IMPLICATIONS FOR PAST ENVIRONMENTAL CONDITIONS. P.D. Archer, Jr¹, D.W. Ming², B. Sutter¹, J.V. Hogancamp³, R.V. Morris², B.C. Clark⁴, P.H. Mahaffy⁵, J.J. Wray⁶, A.G. Fairen⁷, R. Gellert⁸, A.S. Yen⁹, D.F. Blake¹⁰, D.T. Vaniman¹⁰, D.P. Glavin⁵, J.L. Eigenbrode⁵, M.G. Trainer⁵, R. Navarro-González¹², C.P. McKay¹⁰, and C. Freissinet¹³, ¹Jacobs, NASA Johnson Space Center, Houston, TX, 77058, doug.archer@nasa.gov, ²NASA Johnson Space Center, Houston, TX, ³Geocontrols Systems – Jacobs JETS Contract, NASA Johnson Space Center, ⁴Space Science Institute, Boulder, CO 80301, ⁵NASA Goddard Space Flight Center, Greenbelt, MD 20771, ⁶Georgia Institute of Technology, Atlanta, GA 30332, ⁷Centro de Astrobiología (INTA-CSIC), Madrid, Spain, ⁸University of Guelph, ON, Canada, ⁹Jet Propulsion Laboratory, Pasadena, CA 91109, ¹⁰NASA Ames Research Center, Moffett Field, CA 94035, ¹¹Planetary Science Institute, Tucson, AZ, ¹²Instituto de Ciencias Nucleares, UNAM, Mexico City, Mexico, ¹³CNRS/LATMOS, France.

Introduction: The Sample Analysis at Mars (SAM) instrument on the Mars Science Laboratory (MSL) rover *Curiosity* has analyzed 3 scooped samples and 15 drilled samples since landing in 2012. Oxychlorine compounds (perchlorate/chlorate) were detected in the first 9 drilled samples but have not been detected in the last 6, starting with the Oudam sample in the Hartmann's Valley member of the Murray formation (Table 1). Scooped samples have all contained detectable oxychlorine. These results suggest that oxychlorine formation and preservation spans the geologic record on Mars but has not been uniform spatially or temporally.

Oxychlorines on Mars: Perchlorate was first discovered on Mars by the Wet Chemistry Lab (WCL) instrument on the Phoenix lander in 2008 [1]. This detection of perchlorate was definitive because it was done using an ion selective electrode (ISE) that was intended to detect nitrates but returned a signal so large it could only be explained by the presence of perchlorate. Subsequently, 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].

The SAM instrument heated samples to ~850 °C and evolved gases were analyzed with a quadrupole mass spectrometer. The identification of oxychlorine compounds in Gale Crater samples by the SAM instrument were based on the following observations:

- Decomposition of oxygen at temperatures consistent with perchlorate/chlorate decomposition [4, 5].
- Release of HCl at high temperatures (>350-400 °C), consistent with laboratory analog runs of oxychlorine/phylosilicate mixtures [5].
- Correlation of nitrate and perchlorate on Mars, which have similar solubility [6].
- Tentative detection of perchlorate-derived gases by the Tunable Laser Spectrometer instrument in SAM.
- No other credible alternative for O₂ release has been discovered (NO₃ and Mn oxides ruled out [6, 7], per-sulfates unlikely).

Table 1 – abundance of Cl₂O₇ inferred from O₂ detected by SAM. Rocknest (first scooped sample) is included for reference to martian soil as well as Gobabeb, a nearly dust free soil.

Sample	Elevation (m)	wt% Cl ₂ O ₇
Rocknest (RN)	-4518	0.4 ± 0.2
Gobabeb (GB)	-4424	0.25 ± 0.06
John Klein (JK)	-4520	0.10 ± 0.04
Cumberland (CB)	-4520	1.15 ± 0.48
Windjana (WJ)	-4479	0.2 ± 0.07
Confidence Hills (CH)	-4461	0.06 ± 0.03
Mojave (MJ)	-4460	0.12 ± 0.05
Telegraph Peak (TP)	-4453	0.09 ± 0.04
Buckskin (BK)	-4447	0.18 ± 0.05
Big Sky (BY)	-4434	0.14 ± 0.04
Greenhorn (GH)	-4434	0.13 ± 0.03
Oudam (OU)	-4436	< 0.02
Marimba (GB)	-4410	< 0.02
Quela	-4379	< 0.02
Duluth	-4192	< 0.02
Stoer	-4170	< 0.02
Highfield	-4147	< 0.02

Perchlorate Formation Mechanisms: Proposed formation mechanisms for perchlorate include oxidation at grain surfaces mediated by a mineral catalyst and UV light [8, 9] and atmospheric formation with production enhanced by OClO produced by radiolysis of surface materials [10].

Evidence for perchlorate formation over time: The highest O₂ signal detected by SAM to date has been in the Cumberland sample in the Sheepbed mudstone in the Yellowknife Bay formation, the lowest stratigraphic location sampled by MSL. The John Klein drill hole was ~2 m away laterally and within ~10 cm vertically and had a low O₂ signal. Drill hole images showed that CB had no veins and JK had abundant sulfate veins indicating post-depositional alteration.

The difference in O₂ content and vein density between these two holes leads to the following conclusion: when the Sheepbed mudstone was formed >3 Ga, oxychlorine formation was active and perchlorate/chlorate was trapped in the rock (CB).

Post-lithification, the mudstone was aqueously altered along fractures/veins and oxychlorines, which are very soluble, were removed (JK).

Oxychlorines were also detected in northern plains soils (Phoenix) and the three scooped samples analyzed by MSL, all of which are interpreted as much younger samples, indicating more recent oxychlorine formation.

These data suggest that oxychlorine formation has occurred throughout Mars' history, but that formation/preservation rates have not been uniform over time.

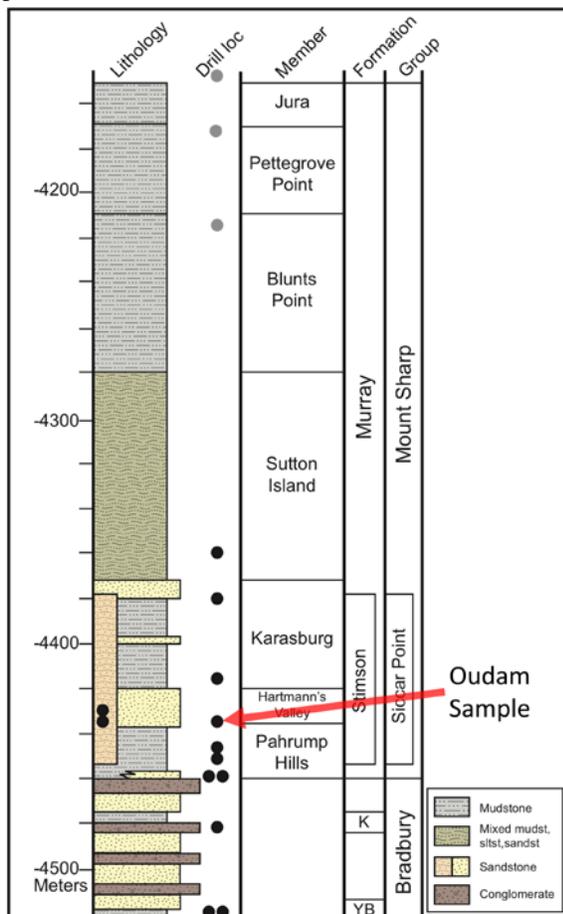


Figure 1 - Stratigraphic column for Gale Crater sediments encountered by MSL. The disappearance of oxychlorine compounds begins with the Oudam sample. Courtesy of the MSL sedimentology/stratigraphy group.

Oxychlorine detections in Gale Crater: Oxychlorine was detected in all samples up to Oudam, and has not been detected in drilled samples since. This change corresponded to a facies change from mudstone to sandstone, but later mudstone samples also contained no detectable oxychlorine (Figure 1). Due to issues with the drill, we do not know if oxychlorines were present between the Quela and Duluth samples (~190 m in elevation). Oxychlorine abundance (in terms of wt % Cl_2O_7 assuming all the evolved O_2 came

from perchlorate decomposition) varied between a low of 0.06 ± 0.03 wt % in the Confidence Hills sample and 1.15 ± 0.48 in the Cumberland sample (Table 1). Samples with no O_2 release have <0.02 wt % Cl_2O_7 based on SAM detection limits for oxygen.

Potential explanations for oxychlorine variation.

Oxychlorine variability can be caused by the variation in formation and/or preservation rates, which depend on environmental conditions. The following table lists possible explanations for this variability:

Explanation	Mechanism
More rapid lithification	Chlorine from volcanic sources deposited on the surface was lithified before reacting to form oxychlorines.
Higher atmospheric pressure	Higher atmospheric pressure increased atmospheric O_3 , decreasing the UV flux at the surface and oxychlorine formation rates.
Increased precipitation	Increased precipitation washed soluble chlorine into basins. These more concentrated deposits had less surface area exposed to UV. Oxidation of chlorine in a lake/ocean was also significantly reduced.
Change in mineralogy	O_2 evolved from a sample during SAM pyrolysis reacted with other minerals such as magnetite or pyrrhotite. However, the mineralogy of Oudam upwards is not significantly different from previous samples with respect to O_2 absorbers.
Aqueous alteration	Highly soluble oxychlorines were removed by post-depositional aqueous alteration leaving less soluble species. Difficult to explain given similar Cl content.

Conclusions: Based on the variability in detection of oxychlorine compounds in Gale Crater samples, oxychlorine formation has been occurring throughout martian history. However, the rate of formation and/or preservation varies throughout time, dependent on environmental conditions such as increased lithification rates (decreased formation) or increased rock porosity (decreased preservation). Further work will investigate how parameters such as mineralogy, grain size, and distribution of other soluble species can be used in conjunction with oxychlorine detection to constrain past environmental conditions on Mars.

References: [1] Hecht, M.H., et al., (2009) *Science*, 325, 5936. Author A. B. and Author C. D. (1997) *JGR*, 90, 1151–1154. [2] Navarro-González, R., et al., (2006) *PNAS*, 103, 44. [3] Quinn, R.C., et al., (2013) *Astrobiology*, 13, 6. [4] Sutter, B. et al., (2017) *JGR*, 122. [5] Hogancamp, J.V., et al., (2018) *JGR*, 123. [6] Stern, J.C. et al., (2017) *GRL*, 44. [7] Hogancamp, J.V. et al., (2018), *XLIX LPSC*, 2482. [8] Schuttlefield, J.D., et al., (2011) *JACS*, 133, 44. [9] Carrier, B.L. and S.P. Kounaves, (2015) *GRL*, 42, 10. [10] Wilson, E.H., et al., (2016) *JGR*, 121.