

A REASSESSMENT OF PERCHLORATE IN SAMPLES FROM GALE CRATER, MARS. P. E. Martin¹ and K. A. Farley¹, ¹California Institute of Technology, Pasadena, CA 91125 (pmmartin@caltech.edu)

Introduction: Perchlorate anion (ClO_4^-) was discovered in Martian soil by the Phoenix Lander in 2009 [1], with important implications for potential Martian biology, photochemistry, aqueous chemistry, and the chlorine cycle on Mars. Perchlorate is highly soluble, resulting in the potential for the formation of brines via freezing point depression, and it is also highly deliquescent. These combined capabilities have resulted in perchlorate being invoked in a wide range of observations and processes including RSL [2], putative sub-polar cap liquid water [3], and the survivability and detection of organics at the Martian surface [4,5].

Support for the presence of perchlorate on Mars with a distribution beyond the north polar soils where it was originally detected is lent by the detection of perchlorate in Shergottite EETA79001 [6]. Subsequent analyses concluding a more global distribution of perchlorate based on Viking data [7] and orbital spectroscopy [8] have been forcefully challenged [9,10].

The first samples ingested by the SAM instrument on the Curiosity rover yielded temporally correlated releases of O_2 , HCl, and chlorinated hydrocarbons, interpreted as evidence for the presence of perchlorate throughout the rocks in Gale Crater [11]. The large O_2 releases present in many samples subsequently analyzed have also been interpreted as evidence of perchlorate distributed through the Gale stratigraphic sequence [12]. SAM chlorine isotope measurements reveal highly variable chlorine isotopic signatures which indirectly support the presence of perchlorate by analogy to the isotope signatures of perchlorate on Earth [13].

Perchlorate Stability: The stability of perchlorate calls into question whether it could survive for billions of years as a component of ancient bedrock. Although it has a high level of kinetic stability, perchlorate is thermodynamically unstable [14]. Over long time-scales the effect of ionizing radiation from radioactive decay and exposure to cosmic rays is expected to have a dramatic effect on perchlorate survival. Given the range of exposure ages and K contents measured in Gale, and reasonable estimates of U and Th content, we estimate a total fluence of 25-80 MGy over 3.5 Ga. Depending on the valence of the cation in the perchlorate salt, this range would result in the destruction of 75-100% of any ~3.5 Ga perchlorate based on perchlorate radiolysis data from the literature [15] (Figure 1).

These considerations clash with the amounts of putative perchlorate in Gale Crater. Given the measured perchlorate content of 1.19 wt% in a SAM sample

[12], the original perchlorate content of the rock would have to have been >10 wt%; the destruction of such a large fraction of the rock would result in compaction and disruption features, which are not observed in the undisturbed sedimentary layering in Gale.

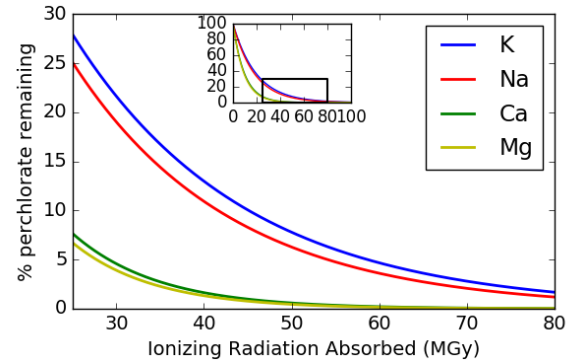


Figure 1: Destruction of 3.5 Ga perchlorate predicted from published radiolysis constants [12].

Geologic Scenario: The putative detection of perchlorate in Hesperian-aged rock is geologically unexpected. The drilled samples analyzed so far include mostly deltaic and lacustrine sediments. Due to perchlorate's extreme solubility, its deposition in a continually wet environment would require extremely high salinity and/or aridity levels in Gale Crater, especially at the ~10 wt% levels required by the radiolysis calculations presented above. However, no evidence for such aridity has been observed. The sedimentary sequence so far explored appears to lack the classic signs of an evaporative setting: abundant mudcracks, tepee structures, bedded evaporites, and displacive evaporite mineral growth are not observed.

Reconsideration of SAM Data: Later work by the SAM team suggests that the breakdown of oxychlorine yields O_2 and chloride salts, which release HCl at higher temperatures due to interactions with water [12, 16]. The release of CH_3Cl has also been given as potential evidence for the presence of perchlorate in SAM data [11], but CH_3Cl release has been demonstrated from chlorides alone [17]. It is therefore impossible to discern whether HCl and/or CH_3Cl has been released from perchlorate or chloride. Given that these gases are fully decoupled, the presence of CH_3Cl , HCl, and O_2 does not necessitate the presence of perchlorate in these samples—if another explanation is found for the large O_2 releases observed, chloride salts could be solely responsible for the release of HCl and CH_3Cl . In other words, the only observation from EGAs that potentially demands perchlorate is the presence of a large O_2 peak.

Alternative Explanations for O₂ Release:

Nitrate. The breakdown of nitrate is known to release both NO and O₂ [18]. The strong temporal and amount correlations between these gases would suggest that nitrate is a strong candidate as an O₂ source. However, the O₂/NO ratio is far too high to result from the breakdown of NO₃, even accounting for their differing ionization efficiencies. We therefore rule out nitrate as a possible source of O₂.

Hydrogen Peroxide. Hydrogen peroxide has historically been a candidate cause of oxidation on Mars. As it forms via gas reactions, diffusion of a few cm into the surface where it would be sampled by SAM is plausible. However, upon heating, H₂O₂ releases oxygen at temperatures well below those observed in EGAs [19]. We therefore conclude that hydrogen peroxide is highly unlikely to be the dominant source of O₂.

Metal Oxides. In the high temperature/low *f*O₂ conditions within SAM, metal oxides such as hematite and manganese oxides, both of which have been observed in Gale Crater, become unstable. Depending on the temperature of spontaneous reduction, these metals could serve as a source of O₂. Typical hematite and MnO₂ oxygen release occurs >600°C [20], too high to match the observed O₂ releases in SAM. However, grain size appears to play a large role in the release temperature of O₂ for these solids. Nanophase Mn-oxides have much lower release onset temperatures of around 350°C (Figure 1), which fits well with the SAM EGA data. As natural Mn-oxides tend to exist in poorly crystalline, mixed oxidation states, the presence of Mn-oxides with individual crystallite sizes of <50 nm in drilled samples is plausible, with variations in grain size (and potentially mineralogy) among these crystallites being responsible for the variations in release temperature in SAM data and the second-order variations in peak shape. We conclude that Mn-oxides could be responsible for the release of O₂ in EGAs.

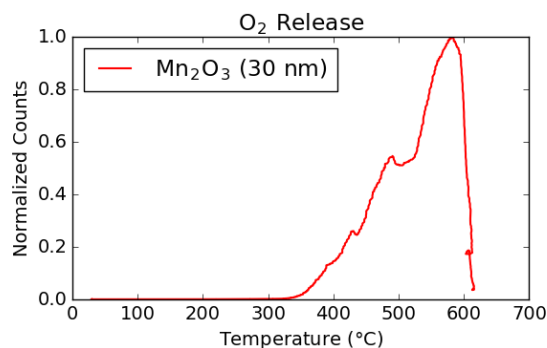


Figure 2: Release of Oxygen from nanophase Mn₂O₃.

Given the amount of O₂ released, nearly all of the Mn in the SAM samples would have to be Mn-oxides.

As Mn is mostly held in olivine as a primary phase and most of the olivine appears to have weathered away in Gale Crater, control of the Mn budget by Mn-oxides is a strong possibility. However, there are several samples where there is insufficient Mn to account for the O₂ released, even assuming all Mn is in its most oxidized form (MnO₂). There is also no correlation between O₂ and Mn measured by APXS. Overall, Mn-oxide is a strong candidate as the source of observed O₂ in EGAs, but the discrepancies in stoichiometry need further evaluation to confirm or rule out the plausibility of this O₂ source.

Perchlorate. While there is no evidence that requires the presence of perchlorate to explain the observed data, there is no evidence directly contradicting its presence. Based on the geologic and stability considerations discussed above, if perchlorate is the source of EGA O₂, *it must be geologically young*. There are two possibilities which could result in the presence of fresh perchlorate in drilled bedrock samples: 1. As a deliquescent salt, it could form thin films of water which permeate downwards into the rock, depositing atmospherically produced perchlorate in these ancient rocks; 2. Small amounts of dust with high concentrations of perchlorate have been included in samples delivered to SAM.

Conclusions: Of these four options, given the temperatures of O₂ release and highly variable chlorine isotope signatures in Gale, perchlorate is likely the strongest candidate for O₂ release in SAM. However, other possibilities should necessarily be entertained when analyzing this data. If perchlorate is determined to be the most likely O₂ source, the requirement that it be geologically young places useful restrictions on conjecture regarding perchlorate as a potential energy source for putative life on ancient Mars, barriers to the preservation of organic biosignatures, and the ancient geochemical environment of Mars.

References: [1] Hecht et al. (2009) *Science*, 325, 64-67. [2] McEwen et al. (2011) *Science*, 333, 740-743. [3] Orosei et al. (2018) *Science*, 361, 490-493. [4] Quinn et al. (2013) *Astrobiology*, 13, 515-520 [5] ten Kate et al. (2010) *Astrobiology*, 10, 589-603 [6] Kounaves et al. (2014) *Icarus*, 229, 206-213 [7] Navarro-Gonzalez et al. (2010) *JGR: Planets*, 115, E12 [8] Ojha et al. 2015 *Nat. Geoscience*, 11, 829-832 [9] Biemann and Bada (2011) *JGR: Planets*, 116, E12 [10] Leask et al. (2018) *GRL*, in press [11] Glavin et al. (2013) *JGR: Planets*, 118, 1955-1973 [12] Sutter et al. (2017) *JGR: Planets*, 112, 2574-2609 [13] Farley et al. (2016) *EPSL*, 438, 14-24. [14] Urbansky (2002) *Env. Sci. Pollut. R.*, 9, 087-192. [15] Prince and Johnson (1965) *J. Phys. Chem.*, 69, 359-377. [16] Hogancamp et al. (2017) *AGU, P51H-09* [17] Keppler et al. (2014) *Science Reports*, 4, 7010 [18] Stern et al. (2015) *PNAS*, 201420932 [19] Yen et al. (2000) *Science*, 289, 1909-1912 [20] Hogancamp et al. (2018) *LPSC*, 2482.