POSSIBLE DETECTION OF PERCHLORATES BY EVOLVED GAS ANALYSIS OF ROCKNEST SOILS: GLOBAL IMPLICATIONS.

P. D. Archer, Jr.[1], B. Sutter[2], D. W. Ming[1], C.P. McKay[3], R. Navarro-Gonzalez[4], H. B. Franz[5,6], A. McAdam[5], P. R. Mahaffy[5], and the MSL Science Team. [1]NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058, doug.archer@gmail.com, [2]Jacobs-ESCG, Houston, TX 77058, [3]NASA Ames Research Center, Moffett Field, CA 94035, [4] Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, [5]NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771, [6]University of Maryland Baltimore County, Baltimore, MD 21228

Introduction: The Sample Analysis at Mars (SAM) instrument suite on board the Mars Science Laboratory (MSL) recently ran four samples from an aeolian bedform named Rocknest. Rocknest was selected as the source of the first samples analyzed because it is representative of both windblown material in Gale crater as well as the globally-distributed dust. The four samples analyzed by SAM were portioned from the fifth scoop at this location. The material delivered to SAM passed through a 150 µm sieve and should have been well mixed during the sample acquisition/preparation/handoff process. Rocknest samples were heated to ~835 °C at a 35 °C/minute ramp rate with a He carrier gas flow rate of ~1.5 standard cubic centimeters per minute and at an oven pressure of ~30 mbar. Evolved gases were detected by a quadrupole mass spectrometer (QMS).

Results: Oxygen (O_2) was one of the most abundant gases released during thermal analysis of Rocknest materials [1] and its release was correlated with the release of chlorinated hydrocarbons [2]. This O_2/Cl correlation makes a strong case for the presence of perchlorate salts in Rocknest soil. Perchlorates were first detected on Mars in the polar region by the Wet Chemistry Laboratory (WCL) on the Phoenix lander in 2008 [3]. This detection of perchlorate was corroborated by an O_2 release observed by the Thermal and Evolved Gas Analyzer (TEGA) instrument during analysis of a soil sample named "Baby Bear", similar to the O_2 released from Rocknest samples (Fig. 1). Although there are other possible sources of oxygen, the presence of perchlorate seems likely based on the temperature of the O_2 release and the simultaneous release of chlorinated hydrocarbons. The detection of perchlorate in Rocknest materials supports the hypothesis that perchlorates are globally distributed on Mars.

Based on WCL results, Phoenix soils were calculated to contain between 0.4-0.6 wt% ClO_4^- (the perchlorate anion) [3]. If all of the oxygen detected by SAM is due to perchlorate decomposition, abundance in Rocknest material would be less than ~2 wt% ClO_4^-. We only report an upper limit for abundance due to current uncertainty in the amount of sample delivered to SAM [1]. Further analysis is currently underway to reduce these uncertainties and give a more accurate abundance estimate. Despite the uncertainty in the exact concentration, the detection of perchlorate at two very different locations on Mars presents a strong argument for the global distribution of perchlorate.

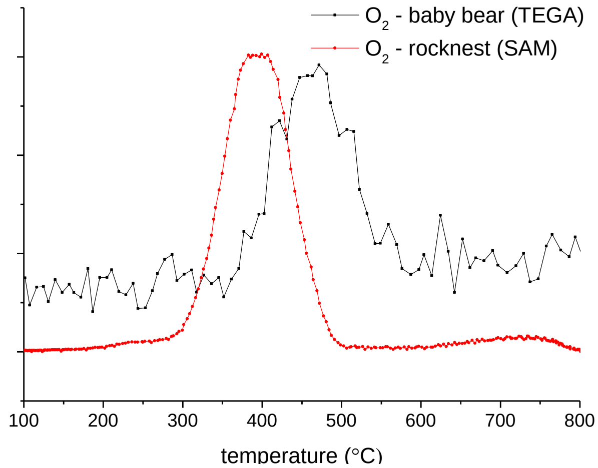

Figure 1 – O_2 abundance vs temperature for TEGA analysis of Baby Bear (black) and SAM analysis of Rocknest (red). Differences in release temperature could be due to factors such as different instrumental design and operational parameters or different cations associated with perchlorate.

Formation Mechanisms. Two mechanisms for perchlorate production on Mars have been hypothesized. The proposed mechanisms are very similar, the primary difference being one proposes atmospheric formation and the other formation on the surface. The first is atmospheric perchlorate production through gas phase oxidation of chlorine to perchloric acid [4]. The second mechanism is formation of perchlorates on the martian surface by UV photoxidation of chlorides aided by mineral catalysts [5, 6]. Both would result in the global distribution of perchlorates and our detection does not distinguish between the two models.

Global distribution. The discovery of perchlorate in Rocknest soil lends credence to the idea of the global distribution of perchlorate. Elemental chlorine has been detected at similar levels in every soil analyzed on Mars (Table 1) and orbital measurements by the Gamma Ray Spectrometer (GRS) on the Mars Odyssey spacecraft show that chlorine is globally distributed at similar levels (Fig. 2). Whatever the formation model, these measurements lead to the conclusion that perchlorates are globally distributed on Mars. Though we expect perchlorates to be globally distributed, the amount of chlorine in Rocknest soil as inferred from the amount of O_2 evolved cannot account for all of the chlorine detected by APXS, allowing for the presence of other chlorine-bearing species as well.

Table 1 – Chlorine abundance in martian soils.

Soil (detection method)	Chlorine (wt%)
Portage (scuffed soil) (APXS) [7]	0.61
Phoenix (wet chemistry) [3]	0.18-0.25
Gusev Basaltic Soils (APXS) [8]	0.54-0.94
Meridiani Basaltic Soils (APXS) [8]	0.41-0.59
Meridiani Hematitic Soils (APXS) [8]	0.65-0.77
Pathfinder mean soil (APXS) [9]	0.55
Viking Lander 1 (XRF) [10]	0.7-0.9
Viking Lander 2 (XRF) [10]	0.6

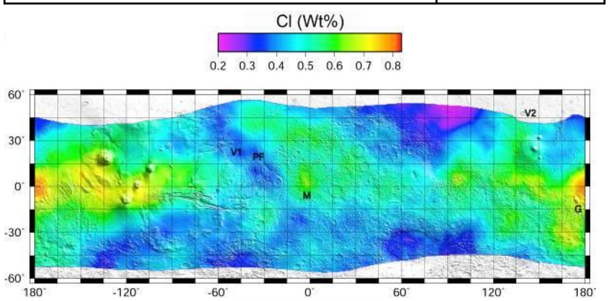

Figure 2 – Chlorine distribution on Mars as measured by the GRS on Mars Odyssey [11].

Viking. The discovery of perchlorates in Rocknest material adds weight to the argument that both Viking landers measured signatures of perchlorates, in the form of chlorinated hydrocarbons, detected by the Gas Chromatograph/Mass Spectrometer (GC/MS) instruments [12]. This is true even if the source of the organic carbon detected was terrestrial contamination because the chlorine source was likely martian. Furthermore, chlorates and chlorites, which can be produced by the radiolytic decay of perchlorates, might be the reactive species inferred from the results of the Viking life detection experiments. When exposed to similar experimental conditions, chlorates and chlorites produce results very similar to those seen by the Viking labeled release and gas exchange instruments [13].

Climate. The presence and abundance of globally distributed perchlorate on Mars is also a climate indicator. Perchlorate is very soluble in water and only accumulates in extremely arid environments (such as the Atacama desert [14] and the Anarctic Dry Valleys [15] on Earth). As more work is done on perchlorate formation mechanisms and the rates of those mechanisms, measurements of perchlorate abundance and distribution on Mars will lead to better constraints on the history of liquid water at a given location on Mars.

Habitability. Perchlorate has important implications for habitability. Although perchlorate is a strong oxidant, it is very stable and will not react readily with organic matter in the soil [3]. Furthermore, perchlorate can be a source of chemical energy for life and is used as such by some organisms on Earth [e.g. 16].

Aqeuous processes. Many perchlorate salts are extremely deliquescent and can form eutectic brines down temperatures as low as -34 to -74 °C [17]. These low temperature brines could exist under current martian conditions and have important implications for aqueous processes on present-day Mars.

Implications for organic or life detection instruments. Although perchlorate is highly stable under martian conditions, heating perchlorates above their decomposition temperature releases oxygen which can combust organic material present. This oxygen release has important implications for the design and operations of current and future organic or life detection instruments on Mars that involve thermal analysis.

Conclusion: The detection of a well-defined oxygen release correlated with the detection of chlorinated hydrocarbons is strong evidence for the presence of perchlorates in Rocknest soil. Rocknest was sampled to be representative of typical aeolian material in Gale crater and because it also likely contains a component of global dust. The detection of perchlorate in this material strongly supports the hypothesis that perchlorates are globally distributed on Mars. The presence of perchlorates is important because they can be a sensitive marker of past climate, an energy source for any martian biota, can lead to liquid brines under current martian conditions, and must be accounted for by future attempts at organic or life detection on Mars.

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