

The nitrate/(per)chlorate relationship on Mars

Authors

- Jennifer C. Stern,
- Brad Sutter,
- W. Andrew Jackson,
- Rafael Navarro-González,
- Christopher P. McKay,
- Douglas W. Ming,
- P. Douglas Archer,
- Paul R. Mahaffy

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Abstract

Nitrate was recently detected in Gale Crater sediments on Mars at abundances up to ~600 mg/kg, confirming predictions of its presence at abundances consistent with models based on impact-generated nitrate and other sources of fixed nitrogen. Terrestrial Mars analogs, Mars meteorites, and other solar system materials help establish a context for interpreting in situ nitrate measurements on Mars, particularly in relation to other cooccurring salts. We compare the relative abundance of nitrates to oxychlorine (chlorate and/or perchlorate, hereafter (per)chlorate) salts on Mars and Earth. The nitrate/(per)chlorate ratio on Mars is < 1 , significantly lower than on Earth (nitrate/(per)chlorate $> 10^3$), suggesting not only the absence of biological activity but also different (per)chlorate formation mechanisms on Mars than on Earth.

1 Introduction

Recent detections of nitrate on Mars [*Stern et al.*, [2015](#)] indicate that nitrogen fixation mechanisms existed early in Martian history. This fixed nitrogen may indicate the development of a primitive nitrogen cycle on the surface of ancient Mars and would have provided a biochemically accessible source of nitrogen. Life as we know it requires a fixed form of nitrogen for incorporation into biomolecules such as nucleobases and amino acids that serve as building blocks for DNA, ribonucleic acid, and proteins. The Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) Curiosity rover has detected nitrate in unconsolidated windblown deposits that likely contain a component of modern global dust as well as in drilled sedimentary rocks. The presence of nitrate in drilled sedimentary rock samples in the Gale Crater basin suggests that atmospheric nitrogen fixation was active at the time of the lithification of these sediments in the early Hesperian. Impact and lightning have long been invoked as mechanisms to fix atmospheric N_2 on early Mars [*Mancinelli*, [1996](#); *Manning et al.*, [2008](#); *Manning et al.*, [2009](#); *Segura and Navarro-González*, [2005](#)] and likely produced the nitrate we detect at Gale Crater. Nitrate formation from thermospheric NO [*Fox*, [2015](#)] has been modeled for modern Mars [*Krasnopolsky*, [1993](#)], although products of these photochemical reactions have not been detected in the lower atmosphere. Nitrate on Earth is produced by both photochemistry and biology, and in most places, biological processes dominate the production and consumption of nitrate. However, dry deposition of nitrate from HNO_3 derived from oxidation of stratospheric NO occurs today in

hyperarid environments on Earth, such as the Atacama Desert [Böhlke *et al.*, 1997] and the McMurdo Dry Valleys (MDV) of Antarctica [Michalski *et al.*, 2005], where it accumulates in soils with little postdepositional alteration by water or biology [Jackson *et al.*, 2010, 2016, 2015b; Michalski *et al.*, 2004]. Like Mars, these terrestrial environments have experienced long periods of landscape stability and aridity, allowing nitrate and other soluble salts such as perchlorate to accumulate in upper soil layers [Lybrand *et al.*, 2016]. Furthermore, nitrate in the Atacama and MDV retains a significant atmospheric component unaltered by biological processing, based on stable isotopic composition [Michalski *et al.*, 2004; Michalski *et al.*, 2005]. Therefore, these places may serve as appropriate analogs on Earth for understanding nitrogen fixation and preservation on Mars.

(Per)chlorate has been detected at three separate locations on Mars and in both drilled and unconsolidated surface materials [Hecht *et al.*, 2009; Leshin *et al.*, 2013; Ming *et al.*, 2014; Navarro-Gonzalez *et al.*, 2010]. (Per)chlorate was first detected on Mars (as ClO_4^-) by the Mars Phoenix Lander's Wet Chemistry Laboratory [Hecht *et al.*, 2009]. This detection prompted reanalysis of original Viking data [Navarro-Gonzalez *et al.*, 2010; Sutter *et al.*, 2016] suggesting that (per)chlorates were present at the Viking landing site. A combination of observations by the MSL's SAM instrument including the detection of chlorinated hydrocarbons in Gale Crater sediments [Freissinet *et al.*, 2015; Glavin *et al.*, 2013] has led to the detection of a significant O_2 release concurrent with HCl release during pyrolysis of Mars surface material, suggesting the existence of oxychlorine phases [Archer *et al.*, 2014; Ming *et al.*, 2014]. While chlorate cannot be distinguished from perchlorate based on SAM evolved gas analysis (EGA) due to the presence of iron phases which alter the O_2 evolution temperatures of oxychlorine species [Sutter *et al.*, 2016], we recognize that chlorate is a likely constituent of the Martian regolith based on Mars meteorite data [Kounaves *et al.*, 2014] and terrestrial Mars analogs [Jackson *et al.*, 2016], and thus, use of the term (per)chlorate encompasses the likely cooccurrence of chlorate and perchlorate.

While natural (per)chlorate production on Earth occurs through atmospheric photochemistry involving chlorine oxidation by ozone or its products [Catling *et al.*, 2010], it is thought that additional mechanisms control its formation on Mars. For example, (per)chlorate abundance given by in situ measurements from two different latitudes on Mars is a factor of 10^6 – 10^7 greater than model predictions based on atmospheric chemistry of volcanic chlorine alone [Smith *et al.*, 2014]. Accordingly, several mechanisms to accelerate (per)chlorate production on Mars have been proposed. For example, UV-induced oxidation of chloride-bearing mineral surfaces in the absence of aqueous conditions was shown to readily produce both chlorate and perchlorate [Carrier and Kounaves, 2015]. Other mechanisms currently being explored include production of chlorinated oxidants by electrostatic discharge on dust [Wu and Wang, 2016]. Injection of chlorine oxides into the atmosphere by radiolysis of Mars surface materials by galactic cosmic rays and the subsequent formation of perchloric acid has also been proposed to explain the (per)chlorate abundance on Mars [Wilson *et al.*, 2016].

The relationship between nitrate and (per)chlorate has been the focus of recent attention in terrestrial Mars analog studies [Jackson *et al.*, 2010, 2016, 2015b; Lybrand *et al.*, 2013; Lybrand *et al.*, 2016]. In arid and hyperarid environments, the

nitrate/(per)chlorate ratio ($\text{NO}_3^-/\text{ClO}_4^-$ hereafter) can be indicative of the degree of biological and redox processing of atmospherically derived nitrate. Additionally, it can highlight alternative mechanisms for input or preservation of these salts. For example, the low $\text{NO}_3^-/\text{ClO}_4^-$ in the Atacama coupled with the unique isotopic composition of Atacama (per)chlorate suggests either an unknown (per)chlorate production mechanism or preservation of relic atmospheric (per)chlorate [Jackson *et al.*, 2015b].

The $\text{NO}_3^-/\text{ClO}_4^-$ ratio on Earth can reflect the mechanism of formation and degree of preservation of these species, and $\text{NO}_3^-/\text{ClO}_4^-$ ratios on Mars should preserve similar information. Our approach is to evaluate Martian nitrate and (per)chlorate correlations along with $\text{NO}_3^-/\text{ClO}_4^-$ ratios to understand what nitrate and (per)chlorate detected in Hesperian rocks and unconsolidated surface sediments can tell us about the timing of nitrogen fixation on Mars and the extent to which nitrogen might have been mobilized by postdepositional processes, including biology.

2 Methods

2.1 Instrumentation

The data presented are from the analyses of solid Martian drilled and scooped samples by the Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) Curiosity rover. Sample Analysis at Mars is located in the body of the rover and receives samples that have been scooped or drilled (1.6 cm diameter \times 6 cm deep) and then processed on the end of Curiosity's robotic arm [Grotzinger *et al.*, 2012]. Sample Analysis at Mars performs evolved gas analysis (EGA), in which a sieved ($<150 \mu\text{m}$) and portioned sample is delivered into one of SAM's quartz-glass cups and is subsequently heated from Mars ambient to $\sim 870^\circ\text{C}$ at $35^\circ\text{C}/\text{min}$ in the SAM pyrolysis oven [Mahaffy *et al.*, 2012]. Gas evolved during pyrolysis is continuously monitored using the quadrupole mass spectrometer, and a portion of this gas can be sent to the hydrocarbon trap (Tenax®) for gas chromatograph-mass spectrometer (GC-MS) analysis. The SAM instrument and the quantification of nitrate, (per)chlorate, and sulfate have been described in detail elsewhere [Archer *et al.*, 2014; Stern *et al.*, 2015] and in the [supporting information \(SI\)](#) accompanying this manuscript.

2.2 Geological Setting

Curiosity has sampled both unconsolidated eolian drift material and sedimentary rocks at Gale Crater. Gale Crater is estimated to have formed between ~ 3.8 and 3.6 Ga, with sedimentary deposition occurring from ~ 3.6 to 3.2 [Grotzinger *et al.*, 2015]. Sediments were deposited in fluvial, lacustrine, and deltaic settings to an estimated height of 75 to several hundred meters above the crater floor [Grotzinger *et al.*, 2015], followed by exhumation by wind-driven erosion.

Curiosity's ~ 13.6 km traverse from Bradbury Landing to Marimba (Figure 1) covers ~ 110 vertical meters of stratigraphy representing 10,000 to 10,000,000 years (Figure 1), during which time intermittent bodies of standing water lasting from 100 to 10,000 years are thought to have been present [Grotzinger *et al.*, 2014; Grotzinger *et al.*, 2015]. These sedimentary materials are generally basaltic, with mineral assemblages including clays and amorphous materials. Sulfate veins as well as other minerals suggest varying degrees of chemical weathering and multiple episodes of diagenesis [Nachon *et al.*, 2017]. Briefly, the Yellowknife Bay (YKB) formation in the Bradbury Group (Figure 1)

represents a near-neutral lacustrine environment [*Grotzinger et al.*, [2014](#)] characterized by low water to rock ratios and minimal alteration [*McLennan et al.*, [2014](#)]. The Murray formation consists of finely laminated mudstones and contains a variety of diagenetic features [*Gellert et al.*, [2015](#); *Grotzinger et al.*, [2015](#); *Nachon et al.*, [2017](#)] and mineralogy indicating acidic (jarosite), alkaline (apatite), oxidizing (sulfate), and reducing (magnetite) conditions [*Rampe et al.*, [2016](#)]. The Stimson formation lies unconformably over the Murray formation and consists of eolian sandstone. Comprehensive descriptions of each of the 13 sampling locations can be found in the SI.

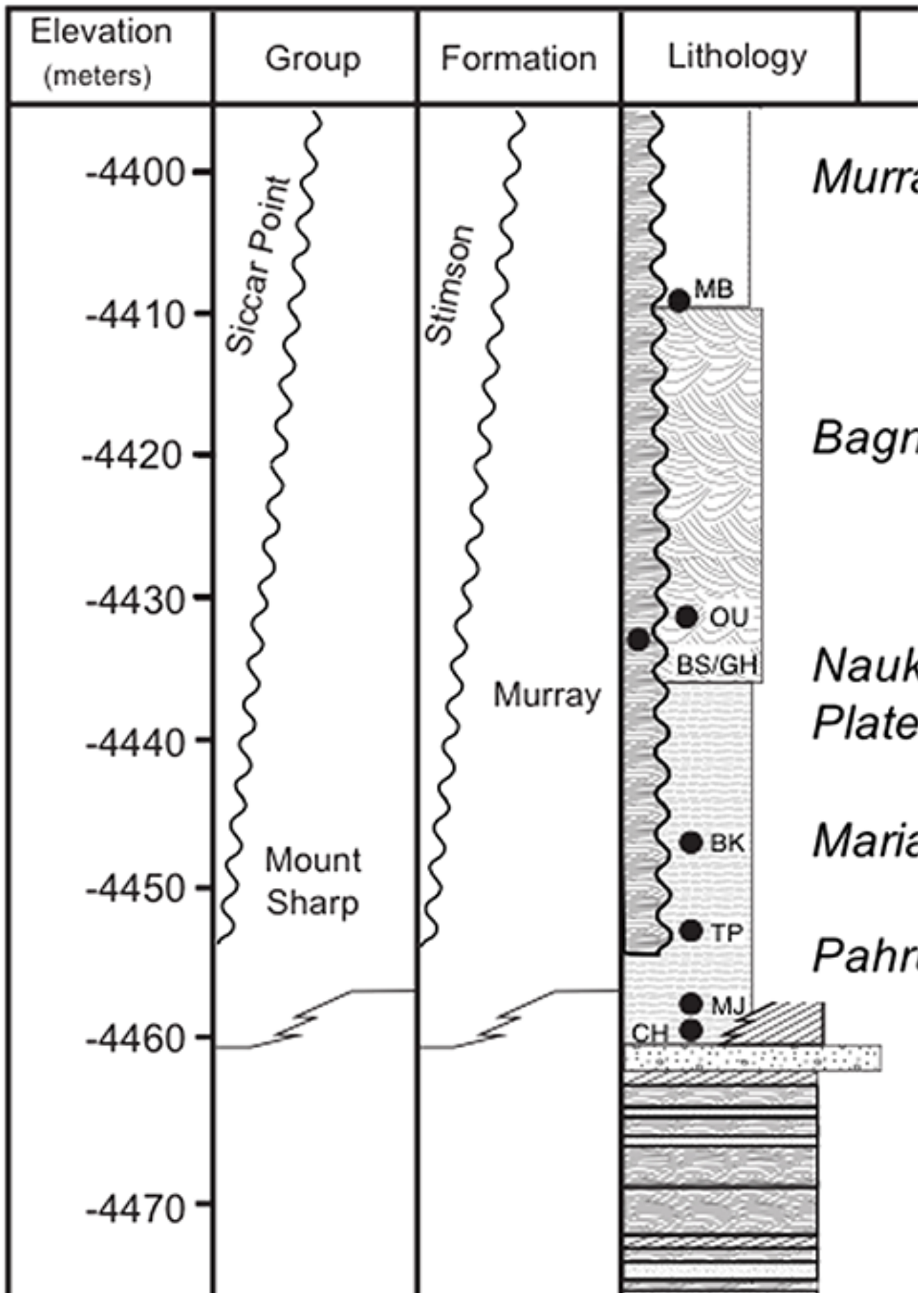


Figure 1.

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Gale crater stratigraphic column showing elevation of samples analyzed by SAM and map of Curiosity traverse. Figure constructed by John Grotzinger with input from the MSL sedimentary-stratigraphy working group. Map Credit: NASA/JPL-Caltech.

3 Martian Nitrate and (Per)Chlorate

Nitrate abundance reported by SAM in situ measurements ranges from nondetection to 681 ± 304 mg/kg [Stern *et al.*, 2015], while (per)chlorate was present from nondetection up to 11 ± 5 g/kg (~1.1 wt %) [Archer *et al.*, 2014; Ming *et al.*, 2014] in the samples examined to date (Table 1). Samples from the rest of the Murray and Stimson formations were relatively low in both nitrate and (per)chlorate when compared to eolian materials, with the exception of Buckskin (BK) in the Murray formation.

Table 1. Nitrate and (Per)Chlorate Abundances and $\text{NO}_3^-/\text{ClO}_4^-$ Measured in Gale Crater Sedimentary Rocks and Eolian Materials^a

Sample	Formation	NO_3 (mg/kg)	ClO_4 (g/kg)	NO_3/ClO_4 (mol)
Rocknest average (RN)	Eolian with dust	274 ± 96	3.71 ± 0.68	0.12 ± 0.04
John Klein 4 (JK)	Yellowknife Bay	209 ± 94	0.87 ± 0.39	0.39 ± 0.11
Cumberland 3 (CB)		681 ± 304	10.5 ± 4.5	0.10 ± 0.03
Windjana (WJ)	Kimberley	85 ± 35	2.27 ± 0.94	0.06 ± 0.01
Confidence Hills (CH)	Murray	143 ± 59	0.47 ± 0.23	0.49 ± 0.15
Mojave (MJ)		170 ± 71	1.00 ± 0.42	0.27 ± 0.05
Telegraph Peak (TP)		143 ± 59	0.80 ± 0.35	0.29 ± 0.06
Buckskin (BK)		290 ± 120	1.48 ± 0.65	0.31 ± 0.07

^aError term reflects analytical uncertainties associated with instrument background and mass estimates.
 bn.d. indicates that nitrate or (per)chlorate was not detected in the sample.

Sample	Formation	NO ₃ (mg/kg)	ClO ₂ (g/kg)	NO ₃ /ClO ₂ (mol)
Oudam (OU)		85 ± 35	n.d.	-
Marimba (MB)		n.d. ^b	n.d.	-
Big Sky (BS)	Stimson	186 ± 77	1.21 ± 0.55	0.25 ± 0.06
Greenhorn (GH)		151 ± 62	1.13 ± 0.47	0.22 ± 0.03
Gobabeb 1 (GB1)	Bagnold Dunes/Eolian	305 ± 126	2.14 ± 0.94	0.23 ± 0.05
Gobabeb 2 (GB2)		Sample mass unknown		0.17 ± 0.03

Evolved gas measurements from Oudam (OU) and Marimba (MB) in the Murray formation represent the first samples in which (per)chlorate was below the SAM limit of detection, which was ~100 ppm. The absence of (per)chlorate could have fundamental implications on the geochemical history of Mars, and these measurements may be the first definitive evidence that (per)chlorate formation has not been pervasive at all times and places, challenging previous implications of Curiosity's analysis [Archer *et al.*, 2015]. The fact that (per)chlorate was below detection limits at both MB and OU also has major implications for the detection of organics in these sediments. The lack of (per)chlorate salts in the samples would prevent combustion or chlorination of any native organic molecules released from the samples during heating in the SAM oven [Freissinet *et al.*, 2015], leading to a greater recovery of organics should they be present. Nitrate and (per)chlorate abundances vary by at least 2 orders of magnitude (Table 1) and are generally correlated ($R^2 = 0.83$, Figure 2). The highest (per)chlorate and nitrate contents are found in YKB mudstone in the Cumberland (CB) sample. Yellowknife Bay mudstone likely represents a lacustrine depositional environment favoring the concentration and preservation of nitrate and (per)chlorate. Although the John Klein (JK) sample near CB in YKB does have a significantly lower nitrate concentration than CB, JK contains evidence of aqueous alteration via diagenetic flow through fractures [Vaniman *et al.*, 2014], so low abundances of both species at JK could represent postdepositional leaching. All other drilled samples lay stratigraphically above CB and JK and have significantly lower abundances of both nitrate and (per)chlorate, suggesting either lower rates of deposition of these salts or higher degrees of aqueous alteration. Although it is difficult to constrain relative ages of the YKB and Murray formations, they are separated by ~60 m of stratigraphy (Figure 1), which could represent tens of thousands to millions of years [Grotzinger *et al.*, 2015]. Therefore, the YKB and Murray formations may represent different parent materials, different hydrological conditions, and even different global atmospheric conditions. Complex diagenetic histories have been implicated for Murray formation sediments [Nachon *et al.*, 2017], suggesting that

the measured abundances may reflect the redistribution of these similarly soluble salts by water and not necessarily changes in atmospheric processes producing nitrate and (per)chlorate. Therefore, an alternative explanation for the nondetection of both (per)chlorate and nitrate at MB would be the aqueous removal of these species. Under this scenario, it is likely that any soluble organics would also have been leached from the sediments.

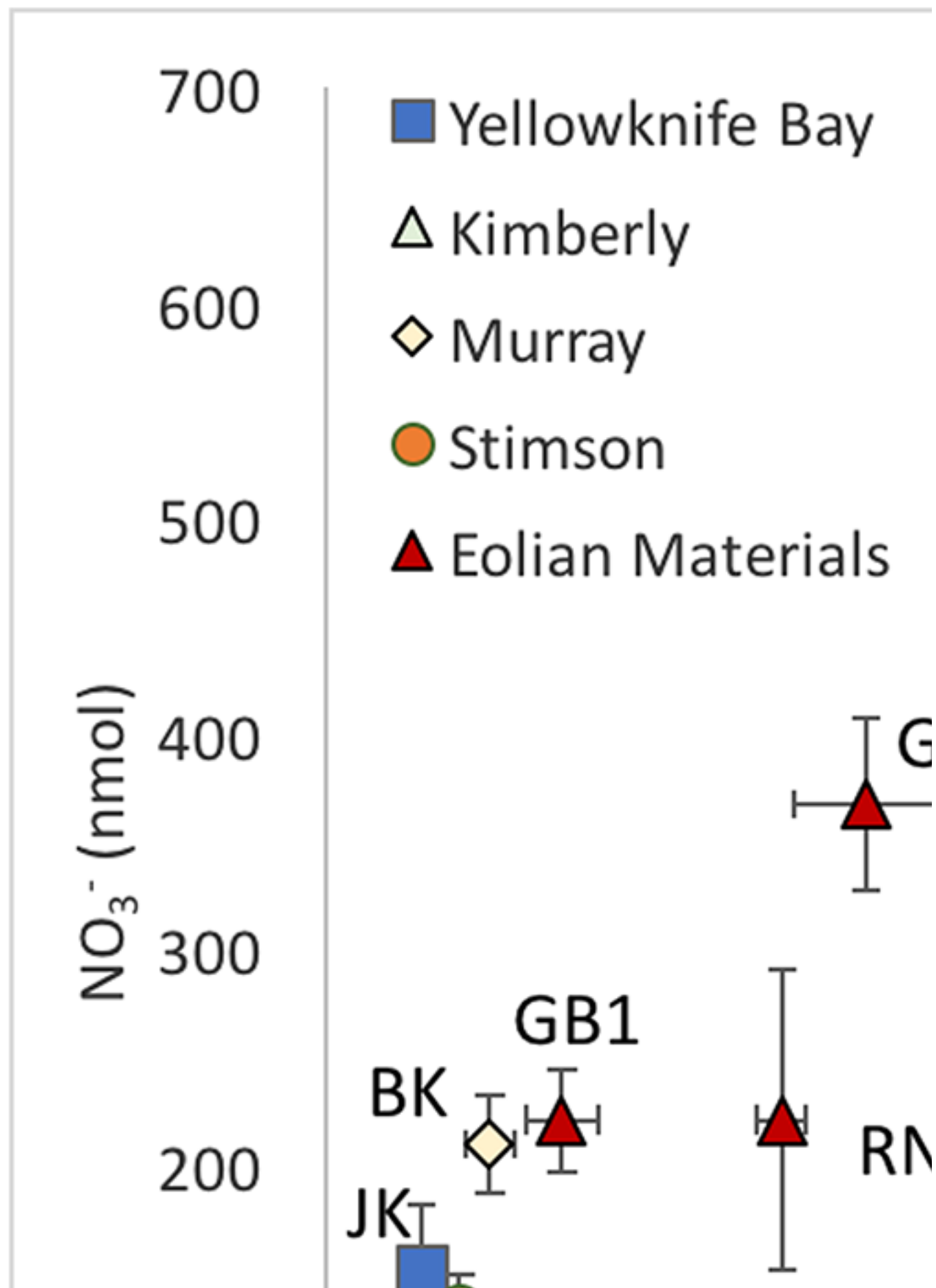


Figure 2.

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Total nitrate versus (per)chlorate amounts in Gale crater materials as determined from detections of evolved NO and O₂ by SAM-EGA analysis.

The similarity in NO₃⁻/ClO₄⁻ ratio among all sedimentary rock samples (average NO₃⁻/ClO₄⁻ = 0.25 ± 0.13) measured at Gale crater suggests either that deposition rates were constant or that postdepositional processes, such as redistribution by aqueous alteration as described above, erased any evidence of variable depositional rates. The similar NO₃⁻/ClO₄⁻ ratio is consistent with steady state processes of atmospheric production and possibly loss of both species over the time of sediment deposition represented by the formations sampled by SAM at Gale crater. Such steady state processes have been observed in the most hyperarid places on Earth such as the University Valley in the MDV [Jackson *et al.*, 2016]. An alternative scenario for the consistent ratios could be the result of an averaging of initially variable (per)chlorate and nitrate deposition rates due to temporal variations in atmospheric or surface production rates of (per)chlorate and nitrate. In this scenario, postdepositional impact, fluvial, eolian, aqueous, and/or other erosive processes could have acted to mix and redistribute similarly soluble (per)chlorate and nitrate resulting in the observed constant ratio.

Eolian materials RN, GB1, and GB2 (Figure 1) have NO₃⁻/ClO₄⁻ ratios similar to drilled sedimentary samples in Gale crater. The RN material is a mixture of local, regional, and global sources that yields a bulk basaltic chemistry that is similar to eolian material at other landing sites [Blake *et al.*, 2013; Minitti *et al.*, 2013]. Its NO₃⁻/ClO₄⁻ ratio is consistent with the CB and JK samples from nearby YKB. The GB1 and GB2 materials are surface sands from the informally named Bagnold Dunes (Figure 1), an active dune field that unconformably overlies Murray formation mudstone. The overall mineralogy of GB is similar to RN, although GB materials lack the dust component seen in RN [Minitti *et al.*, 2013]. In terms of abundance, eolian samples fall between the nitrate and (per)chlorate rich CB and the rest of the sedimentary rock samples bearing lower abundances of these salts. These intermediate abundances may represent physical mixing between two end-member parent materials representing relatively higher and lower abundances of these salts. They may also be more representative of a global baseline for abundances of these salts.

While little is known regarding the timescales over which nitrate and (per)chlorate deposition has occurred, comparisons of NO₃⁻/ClO₄⁻ ratios measured in rocks of various ages and in global Martian dust could provide a better understanding of when these processes were active and if they are still active today. Although production of NO in the ionosphere has been reported [Fox, 2015; Mahaffy *et al.*, 2015], it is unclear whether NO persists in the lower atmosphere where it could undergo photochemical reactions leading to dry deposition of nitrate. Therefore, it is possible that all nitrate on Mars is relic, forming during or even prior to the Gale forming impact and mobilized during deposition, with no modern contribution. Likewise, although (per)chlorate formation has been modeled as a steady state process on Mars [Carrier and Kounaves, 2015; Catling *et al.*, 2010; Wilson *et al.*, 2016] and has been detected on the Martian surface at multiple surface exposed sites [Archer *et al.*, 2014; Hecht *et al.*, 2009] and in Hesperian aged sediments [Ming *et al.*, 2014], it is possible that these (per)chlorate detections represent

ancient atmospheric processes. The RN sample had a small component of global Martian dust based on observation of dust-sized grains ($<20\ \mu\text{m}$) and theoretically should have some modern material which has been in continuous contact with the atmosphere. Based on the fact that $\text{NO}_3^-/\text{ClO}_4^-$ ratio and abundances in RN are quite similar to all other eolian and sedimentary samples, there is no evidence in this sample for significant accumulation of either nitrate or (per)chlorate since the consolidation and burial of Gale crater sedimentary rocks in the early Hesperian. However, it is also possible that the dominance of locally sourced materials in RN obscures the contributions of the dust component.

3.1 Comparison of Nitrate/(Per)Chlorate Ratio and Abundances on Mars to Earth

Gale crater nitrate abundances measured thus far fall within the range of abundances reported for hyperarid areas on Earth such as the Atacama Desert and University Valley in the MDV [Jackson *et al.*, 2015b; Lybrand *et al.*, 2016] (Figure 3). The range of abundances in Gale crater (85–681 mg/kg) is very similar to the 10^2 – 10^3 mg/kg range reported for the University Valley permafrost [Jackson *et al.*, 2016], which may be the best analog for nitrate on Mars due to the near absence of biological activity [Goordial *et al.*, 2016] and lack of lateral fluid transport [Jackson *et al.*, 2016]. A survey of the lower elevation valleys in the MDV showed greater nitrate abundances at 10^4 – 10^5 mg/kg [Lybrand *et al.*, 2016], which may reflect the small amount of biological activity that has been demonstrated in Taylor, Beacon, and Wright Valleys [Bakermans *et al.*, 2014]. Although the Atacama Desert generally receives less precipitation than the MDV, flood events such as the one that occurred in March of 2016 [Wilcox *et al.*, 2016] and those associated with the El Niño–Southern Oscillation [Magilligan *et al.*, 2008] allow for maintenance of low levels of biological activity as well as episodic transport of soluble surface materials. In addition, there are differences in relative exposure ages of surfaces as well as changes in paleoclimate, resulting in varying degrees of accumulation. This may account for the large variability of nitrate and (per)chlorate concentrations (Figure 3) reported for the Atacama [Jackson *et al.*, 2015b]. Similar variability has been reported for the Mojave Desert, which receives more water than the Atacama or MDV [Jackson *et al.*, 2010, 2015b; Lybrand *et al.*, 2013].

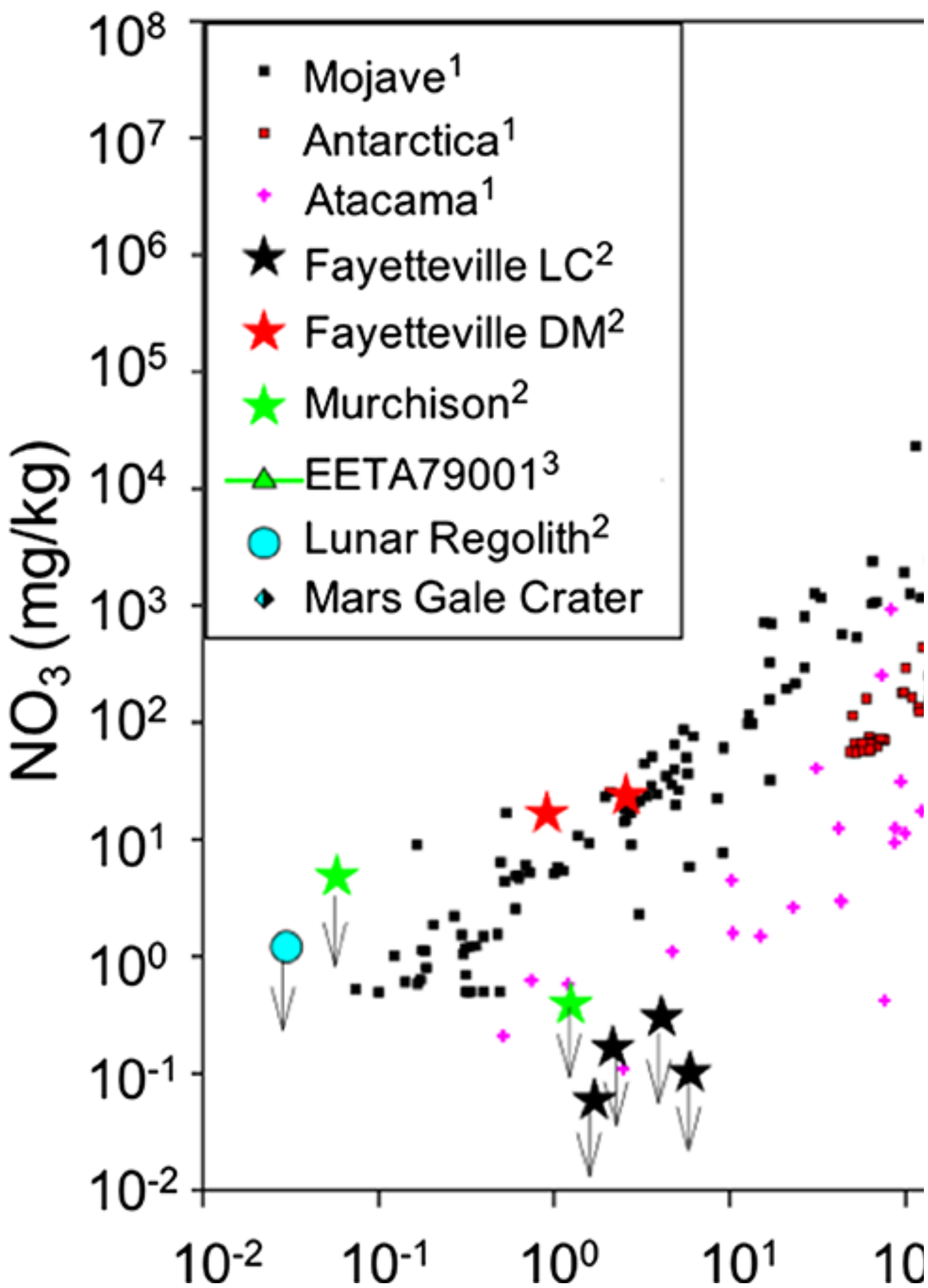


Figure 3.

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Nitrate and (per)chlorate data from 1) *Jackson et al.* [2015b], 2) *Jackson et al.* [2015a], 3) *Kounaves et al.* [2014], and this study. In situ Mars measurements at Gale crater indicate that (per)chlorate abundance on Mars is higher than other extraterrestrial samples and most of Earth, with the exception of the Atacama Desert. Gale crater nitrate abundances are similar to those found in arid Mars analog environments. Nitrate and (per)chlorate concentrations less than the detection limit of the analytical technique are indicated by symbols with downward and left pointing arrows. For more discussion of extraterrestrial materials, see the [SI](#).

While Gale crater nitrate abundances are comparable to those on Earth, (per)chlorate abundance in Gale crater materials (10^6 – 10^7 $\mu\text{g}/\text{kg}$) is generally greater than terrestrial soils (10^{-1} – 10^5 $\mu\text{g}/\text{kg}$), and only in the Atacama does (per)chlorate abundance approach that reported for Mars [*Catling et al.*, 2010]. The much greater (per)chlorate abundances in Gale crater sediments than on Earth may indicate faster (per)chlorate accumulation rates on Mars and/or longer accumulation times. Furthermore, these high abundances may point to (per)chlorate formation mechanisms unique to Mars, particularly those that depend on radiolysis [*Wilson et al.*, 2016].

The Gale crater $\text{NO}_3^-/\text{ClO}_4^-$ average ratio (0.23 ± 0.12) is vastly lower than all terrestrial ratios including the Atacama and MDV (Table 2). On Earth, the $\text{NO}_3^-/\text{ClO}_4^-$ ratio has been studied as a tool to assess biological cycling in an environment. Recently, a comprehensive study by *Jackson et al.* [2015b] presented a global survey of $\text{NO}_3^-/\text{ClO}_4^-$ ratios in arid and semiarid environments. The hyperarid sites, which included the MDV (University Valley) and Atacama Desert, had the lowest ratios at 10^3 – 10^4 and the largest component of unaltered atmospheric nitrate. Broader surveys of the MDV have reported much higher ratios of 10^4 – 10^5 [*Lybrand et al.*, 2016]. These higher ratios are likely due to the fact that these locations represent lower elevations in the MDV where low levels of biological activity have been demonstrated [*Bakermans et al.*, 2014].

Table 2. Nitrate/(Per)Chlorate Ratios in Terrestrial Mars Analogs and Solar System Materials

Location	$\text{NO}_3^-/\text{ClO}_4^-$	Reference
U.S. wet deposition	100,000	<i>Rajagopalan et al.</i> [2009]
MDV, Antarctica	60,000–123,000	<i>Lybrand et al.</i> [2016]
U.S. Mojave	85,000	<i>Jackson et al.</i> [2015a]
University Valley, Antarctica	14,000	

Location	$\text{NO}_3^-/\text{ClO}_4^-$	Reference
Atacama	1400	
Fayetteville meteorite, light clast	<100	<i>Jackson et al.</i> [2015b]
Fayetteville meteorite, dark clast	>1000	
EETA 79001	~40	<i>Kounaves et al.</i> [2014]
Mars in situ materials	<1	<i>Stern et al.</i> [2015], <i>Ming et al.</i> and <i>Archer et al.</i> [2014]

4 Conclusions

The vast differences between $\text{NO}_3^-/\text{ClO}_4^-$ ratios on Earth and Mars are likely the result of mechanisms that produce these species and the length of time over which they were active. On Earth, biological and atmospheric nitrate production is ongoing, and low levels of nitrate in Earth environments usually indicate active biology and/or hydrology. In the hyperarid Mars analog environments, the absence of biology and hydrology allows accumulation of photochemical nitrate on the order of millions of years, similar to what Gale crater sediments may have experienced prior to burial. The surface landscape of Mars has been stable for billions, not millions, of years, suggesting that if ongoing steady state processes contributed significant amounts of nitrate, eolian materials would contain more nitrate than sedimentary rocks. The similar amounts of nitrate in eolian materials and rocks on Mars suggest that nitrate on Mars is the preserved product of relict processes such as impact [*Manning et al.*, [2009](#)], which would have limited nitrate formation to the first ~1 Ga of Martian history [*Carr and Head*, [2010](#)].

Conversely, the modern Martian environment may enhance the production of (per)chlorate through surface heterogeneous processes coupled with UV and/or ionizing radiation. This is supported by laboratory studies [*Carrier and Kounaves*, [2015](#); *Quinn et al.*, [2013](#); *Wu and Wang*, [2016](#)]. The mystery, then, is why exposed Martian eolian materials and drilled rocks both contain comparable amounts of (per)chlorate, despite the fact that rocks should not have accumulated (per)chlorate postburial in the Hesperian, while surface sediments would continue to accumulate (per)chlorate on modern Mars. This suggests that a destruction mechanism may balance the production of (per)chlorate on Mars, maintaining relatively consistent levels of (per)chlorate in Martian surface materials. Ionizing radiation [*Quinn et al.*, [2013](#); *Wilson et al.*, [2016](#)], which both produces and destroys (per)chlorate, may be the mechanism responsible for an active (per)chlorate cycle on Mars.

Acknowledgments

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Ancillary