



Widespread occurrence of (per)chlorate in the Solar System



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ARTICLE INFO

Article history:

Received 29 January 2015

Received in revised form 25 August 2015

Accepted 1 September 2015

Available online xxxx

Editor: T.A. Mather

Keywords:

chlorate
perchlorate
meteorite
chondrite
Murchinson
Fayetteville

ABSTRACT

Perchlorate (ClO_4^-) and chlorate (ClO_3^-) are ubiquitous on Earth and ClO_4^- has also been found on Mars. These species can play important roles in geochemical processes such as oxidation of organic matter and as biological electron acceptors, and are also indicators of important photochemical reactions involving oxyanions; on Mars they could be relevant for human habitability both in terms of *in situ* resource utilization and potential human health effects. For the first time, we extracted, detected and quantified ClO_4^- and ClO_3^- in extraterrestrial, non-planetary samples: regolith and rock samples from the Moon, and two chondrite meteorites (Murchison and Fayetteville). Lunar samples were collected by astronauts during the Apollo program, and meteorite samples were recovered immediately after their fall. This fact, together with the heterogeneous distribution of ClO_4^- and ClO_3^- within some of the samples, and their relative abundance with respect to other soluble species (e.g., NO_3^-) are consistent with an extraterrestrial origin of the oxychlorine species. Our results, combined with the previously reported widespread occurrence on Earth and Mars, indicate that ClO_4^- and ClO_3^- could be present throughout the Solar System.

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1. Introduction

Until the late 20th century, perchlorate (ClO_4^-) was considered largely an anthropogenic compound, although its indigenous occurrence in the Atacama Desert had been already established (Ericksen, 1981). Now we know that natural ClO_4^- is ubiquitous across the surface of Earth, where it consistently co-occurs with chlorate (ClO_3^-) at roughly equimolar ratios in atmospheric deposition and soils, and both species reach their highest concentrations in semi-arid and arid areas (Jackson et al., 2015; Rao et al., 2010). ClO_4^- has also been found to be widespread and relatively abundant on Mars (Hecht et al., 2009; Ming et al., 2014; Kounaves et al., 2014). These species can play important roles in geochemical processes such as oxidation of organic matter and as biological electron acceptors, and are also indicators of important photochemical reactions involving oxyanions (Coates and Achenbach, 2004), and in the case of Mars they could be relevant for

human habitability both in terms of *in situ* resource utilization and potential human health effects (Davila et al., 2013).

It is now well established that terrestrial ClO_4^- and ClO_3^- are ubiquitously formed in the atmosphere, and are widely distributed by both wet and dry deposition (Rao et al., 2010; Rajagopalan et al., 2009; Jackson et al., 2010, 2012, 2015; Kounaves et al., 2010; Catling et al., 2010). ClO_4^- (and by inference ClO_3^-) is formed in the stratosphere by O_3 mediated oxidation of Cl^- and/or ClO_x^- , and possibly by photochemical oxidation of ClO_x , based on isotopic analyses ($\Delta^{17}\text{O}$ and $^{36}\text{Cl}/\text{Cl}$) of terrestrial ClO_4^- (Jackson et al., 2010; Sturchio et al., 2009). Heterogeneous oxidation of Cl^- may also contribute to terrestrial ClO_4^- based on laboratory studies (Carrier and Kounaves, 2015; Dasgupta et al., 2005; Kang et al., 2008) and the isotopic composition of some terrestrial ClO_4^- (Jackson et al., 2010). On the other hand, little is yet known regarding the origin of ClO_4^- on Mars, and the known terrestrial pathways of ClO_4^- synthesis cannot adequately explain its abundance or its distribution on that planet (Smith et al., 2014).

Here, we report the first detection of ClO_4^- and ClO_3^- in lunar samples and in two chondrite meteorites, and based on these results we suggest that these oxychlorine species are broadly dis-

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tributed in the Solar System. The presence of ClO_4^- and ClO_3^- in non-planetary materials could indicate new sources and pathways of formation not operational on Earth, with implications for our understanding of oxyanion photochemical production, and the chemical and photochemical oxidation of meteoritic organic compounds.

2. Methods

We investigated the occurrence of ClO_4^- , ClO_3^- , chloride (Cl^-), sulfate (SO_4^{2-}) and nitrate (NO_3^-) in two lunar samples and in two chondrite meteorites (Fig. 1). Lunar samples included sample 66041, a regolith sample from the Cayley Plain near Stone Mountain at the Apollo 16 landing site, and sample 66095, a portion of “bulk sample” from the “Rusty Rock”, also at the Apollo 16 landing site. The meteorite materials included subsamples of the Murchison meteorite, a carbonaceous chondrite (class CM2) recovered in Victoria, Australia, and the Fayetteville meteorite, an ordinary chondrite (class H4) regolith breccia recovered in Arkansas, USA.

The protocol for sample preparation and analysis has been described previously (Rao et al., 2010; Jackson et al., 2010). Soluble salts were extracted from lunar and meteorite samples by leaching in pre-cleaned and pre-tested containers using pre-tested filtered (0.2 μm) deionized distilled water (DDI) to avoid contamination. Lunar regolith (Lunar 1) was leached as received without processing. The “Rusty Rock” lunar sample (Lunar 2) was first leached without processing, by soaking the unaltered sample in DDI. Subsequently, the sample was removed from the water and crushed in a stainless steel vessel using a stainless steel rod to produce a fine powder. The powder was then leached with new DDI water. Meteorite samples were crushed as described above (without pre-leaching). Both the rod and vessel were pre-cleaned and tested for residual ClO_3^- and ClO_4^- by extraction with DDI water. Unless specifically mentioned, all extractant solutions were filtered with either 0.2 μm syringe filters or disc filters. In all cases, syringes, filters, and filtration units were pre-rinsed with DDI water and the rinse water tested for ClO_3^- and ClO_4^- prior to each use. Ratio of solid to liquid in the extraction suspension varied from 5:1 to 40:1 (by wt.) based on the mass of the sub-sample and required volume for analysis. Masses of leached subsamples varied from 0.2 to 1.2 g (Table 1). To test for contamination due to extraction, transfer, filtering or other influence of the method, a pre-washed and dried (500 °C) sample of silica sand was subjected to the complete extraction procedure including crushing and filtering. Concentrations of ClO_4^- and ClO_3^- in the sand extract solution were less than 0.001 $\mu\text{g/L}$, the lowest level of quantification (LLQ).

ClO_4^- and ClO_3^- were quantified using IC-MS/MS. The IC system (LC20, Dionex Corp., Sunnyvale, CA) consisted of a GP50 pump,

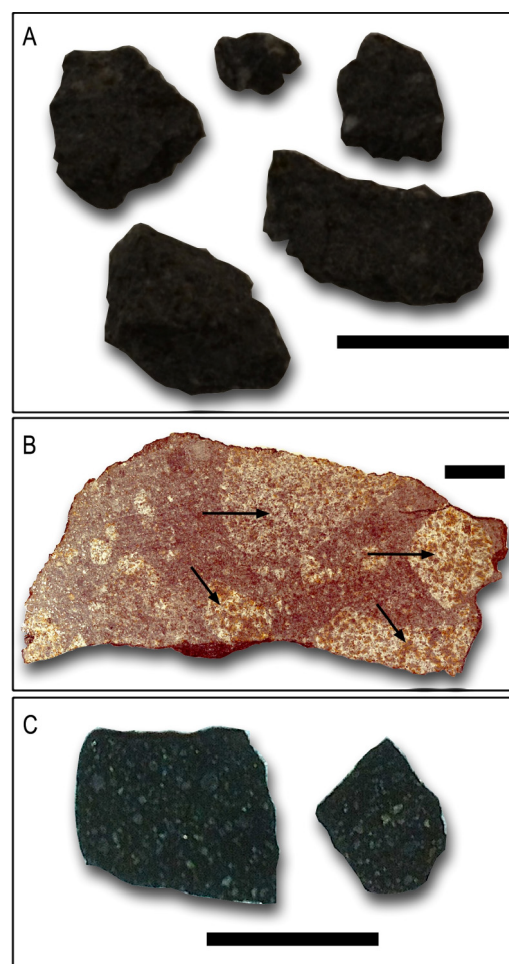


Fig. 1. Extraterrestrial samples analyzed in this study. (A) Subsamples of the Rusty Rock collected during the Apollo missions. Scale bar is 1 cm. (B) A fragment of the Fayetteville meteorite. Characteristic light clasts (arrows) are embedded in a dark matrix. Scale bar is 2 cm. (C) Two small fragments of the Murchison meteorite. Scale bar is 1 cm.

CD25 conductivity detector, AS40 automated sampler, and IonPac AS20 (250 × 2 mm) analytical column. The IC system was coupled to a triple quadrupole mass spectrometer (MDS SCIEX API 2000, Applied Biosystems, Foster City, CA) equipped with a Turbo Ion Spray source. A 45 or 20 mM ClO_4^- or ClO_3^- , respectively) NaOH eluent at 0.2 mL min^{-1} was followed by a 90% acetonitrile (0.3 mL min^{-1}) post-column solvent. To account for matrix effects all samples were spiked with ClO_4^{18-} or ClO_3^{18-} internal standard.

Table 1
Abundances of soluble ClO_4^- , ClO_3^- , Cl^- , NO_3^- and SO_4^{2-} in extraterrestrial samples.

Sample	Description	Mass of sample (mg)	Distance from fusion crust (cm)	ClO_3^-	ClO_4^-	Cl^-	NO_3^- -N	SO_4^{2-}
				($\mu\text{g/kg}$)	($\mu\text{g/kg}$)	(mg/kg)		
Lunar 1	Regolith			0.06	<0.01	4.6	<5	58
Lunar 2	Rusty Rock ^a			0.5	0.03	6.6	<1.2	13.5
FV1a	LC	1205	0.5–1	2.1	2.2	8.3	<0.2	41
FV1b	LC	831	0–0.5	310	4.1	45	<0.3	38
FV1c	LC	247	0–0.2	12	6.0	48	<0.1	50
FV1d	LC	425	0.2–0.5	15	1.7	11	<.05	39
FV2a	DM	1759	0.5–1	20	0.91	20	17	63
FV2b	DM	269	<0.2	0.45	2.6	67	24	96
M1		207	Unknown	1.0	0.06	215	<5	1.9×10^4
M2		386	>0.2	15	1.2	230	<0.3	2.2×10^4

Lunar 1 = Moon regolith-66041; Lunar 2 = Moon rock-66095; FV = Fayetteville; M1 = Murchison (1) USNM 5451-2; M2 = Murchison 2. LC = Light Clast (F-10); DM = Dark Matrix (F-141).

^a Analysis after initial surface extraction and crushing.

Table 2
Stable isotopic composition of NO_3^- extracted from the Fayetteville meteorite.

Sample	Description	Method	$\delta^{15}\text{N}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\delta^{17}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)
FV2a	DM below fusion layer (aliquot 1)	N_2O	28.2	32.3	NA	NA
FV2a	DM below fusion layer (aliquot 1)	$\text{N}_2 + \text{O}_2$	27.5	32.1	16.7	0.0
FV2a	DM below fusion layer (aliquot 2)	N_2O	29.8	31.8	NA	NA
FV2b	DM + fusion layer + small clast layer	N_2O	24.6	32.0	NA	NA

NA = Not analyzed.

FV2a (aliquot 1) had $\text{NO}_2^-/\text{NO}_3^-$ molar ratio of 0.014.

A 200 μL loop was used for sample loading with a ClO_4^- and ClO_3^- method detection limit (MDL) of 0.0002 $\mu\text{g/L}$. The MDL was determined by multiplying the standard deviation of 7 sequential 0.001 $\mu\text{g/L}$ standards by the “*t*” value for 99% confidence level and 6 degrees of freedom. Our LLQ is 0.001 $\mu\text{g/L}$, equal to our lowest calibration standard. Analytical spike recoveries were 90–110%. Cl^- , SO_4^{2-} , and NO_3^- were analyzed following EPA Method 300.0 using a Dionex LC20, an IonPac AS14A column (4 × 250 mm), 8 mM $\text{Na}_2\text{CO}_3/1$ mM NaHCO_3 eluent, and an Anion Atlas electrolytic suppressor. Initially, samples were run using a 25 μL loop resulting in a LLQ of 500 $\mu\text{g/L}$ $\text{NO}_3\text{-N}$. As most samples did not contain NO_3^- above the LLQ, when sufficient filtered extracts were available we re-analyzed the solutions using a 500 μL injection loop, which produced a LLQ of 10 $\mu\text{g/L}$ of $\text{NO}_3\text{-N}$. The concentration of nitrite (NO_2^-) was measured in Fayetteville dark matrix extract sample FV2a by a NO_2^- selective version of the bacterial reduction method (Böhlke et al., 2007).

Stable isotope ratios ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$) of NO_3^- in Fayetteville meteorite dark matrix extracts were determined by the bacterial reduction method (Casciotti et al., 2002; Sigman et al., 2001), with and without conversion of N_2O to N_2 and O_2 (Kaiser et al., 2007). Data were calibrated by analyzing NO_3^- isotopic reference materials USGS32, USGS34, and USGS35 as samples and normalizing results to be consistent with reported values (Böhlke et al., 2003).

3. Results

ClO_4^- and (or) ClO_3^- concentrations were measurable in all extracts from both lunar and meteorite samples. ClO_3^- was detected in lunar samples 66041 (regolith) and 66095 (“Rusty Rock”) at concentrations of 0.06 $\mu\text{g/kg}$ and 0.5 $\mu\text{g/kg}$, respectively (Table 1). ClO_4^- was also measured in the “Rusty Rock” (0.03 $\mu\text{g/kg}$) but was below the limit of detection (<0.01 $\mu\text{g/kg}$) in the regolith sample. ClO_4^- and ClO_3^- were also detected in all subsamples analyzed of the Murchison meteorite and the Fayetteville meteorite at concentrations of up to two orders of magnitude higher than in lunar samples (Table 1). In both meteorites, subsamples varied with respect to the inclusion of, and/or distance from, the fusion crust. ClO_4^- and ClO_3^- were detected in two independent samples of Murchison, one of them taken ~2 cm below the fusion crust, and in multiple samples of the Fayetteville meteorite including the dark matrix (F-141) and light clast (F10) (Fig. 1C). Generally, ClO_3^- was more abundant than ClO_4^- by a factor 1 to 100. The sole exception was one subsample of the Fayetteville meteorite (FV2b) consisting of material adjacent to the fusion crust, which contained more ClO_4^- than ClO_3^- . The highest ClO_3^- concentration was found within a light clast of Fayetteville (310 $\mu\text{g/kg}$); but significantly, both ClO_4^- and ClO_3^- were detected also in the dark matrix of the same meteorite. The dark matrix is composed of comminuted clast material that has been darkened by space exposure, is characterized by large amounts of implanted solar wind atoms (such as inert gases), and has experienced radiation damage (e.g. by charged particle tracks) (Pellas, 1972; Rieder and Wänke, 1969; Suess et al., 1964). ClO_3^- was observed to be unstable in the Fayetteville meteorite extractant suspension,

likely because of reduction by solid phase reduced Fe, including Fe^0 , but was stable in the filtered extracts (Jarosewich, 1990; Engelbrektson et al., 2014).

Because of the observed instability of ClO_3^- in non-filtered extractant suspensions, we further investigated the possible reduction of ClO_3^- during extraction. Two small subsamples of Fayetteville light clast (F-10) were leached but not filtered, one composed mainly of fusion crust (scraped from surface) and the other of light clast material directly below the fusion crust to a depth of <5 mm, and the concentration of ClO_3^- was monitored over time. ClO_3^- in the sample composed of light clast material below the fusion crust was reduced by 90% after 24 h compared to the initial concentration measured after ~10 min of exposure in the extractant solution (DDI water). However, the concentration of ClO_3^- in the surface sample composed of oxidized fusion crust increased by ~10 times compared to the initial concentration (~10 min), likely because of increased efficiency of extraction due to diffusion of ClO_3^- out of the solid particle matrix and no reduction due to the oxidized state of the material. We also observed >90% loss of ClO_3^- in 24 h after addition of ClO_3^- solution (1 $\mu\text{g/L}$) to the residual FV1a solids that were leached previously. Residual solids in all non-crust samples clearly reflected iron oxidation in the laboratory by progressive alteration in color from grey to orange.

Cl^- , SO_4^{2-} and NO_3^- were also analyzed in the extraction solutions from all meteorite fragments and lunar samples. Cl^- and SO_4^{2-} concentrations were similar to those previously reported for these types of meteorites and lunar materials (Table 1). NO_3^- concentrations were 24 and 17 mg/kg $\text{NO}_3\text{-N}$ in two subsamples of the dark matrix in the Fayetteville meteorite obtained at different distances from the surface (<0.2 cm and 0.5–1 cm, respectively). NO_3^- was below our detection limit (<0.05 to <5 mg/kg) in all other meteorite and lunar samples (Table 1). Stable isotope ratios of N and O in NO_3^- from two Fayetteville dark matrix extracts analyzed in two different laboratories were similar (Table 2). Mean values for all samples, aliquots, and methods were $+27.4 \pm 2.0\text{‰}$ for $\delta^{15}\text{N}$ ($n = 4$), $+32.4 \pm 0.3\text{‰}$ for $\delta^{18}\text{O}$ ($n = 4$), and 0.0‰ for $\Delta^{17}\text{O}$ ($n = 1$).

4. Discussion

We report for the first time the occurrence of ClO_4^- and ClO_3^- in non-planetary materials. Several lines of evidence suggest that the detected species are extraterrestrial in origin. The two lunar samples were collected by astronauts during the Apollo mission, and were kept under stringent clean conditions (Heiken, 1991). As such, the extraterrestrial origin of ClO_4^- and ClO_3^- in these samples appears certain. As for the meteorite samples, both Murchison and Fayetteville were recovered immediately after falling to Earth: within days for Murchison and <1 day for Fayetteville (Lovering et al., 1971; Schwarz and Sears, 1988), which largely precluded the risk of contamination by terrestrial processes after the falls. The instability of ClO_3^- in Fayetteville unfiltered extracts also indicates the meteorite was not substantially exposed to liquid water after falling to Earth and thus minimizes the likelihood of post-fall terrestrial contamination.

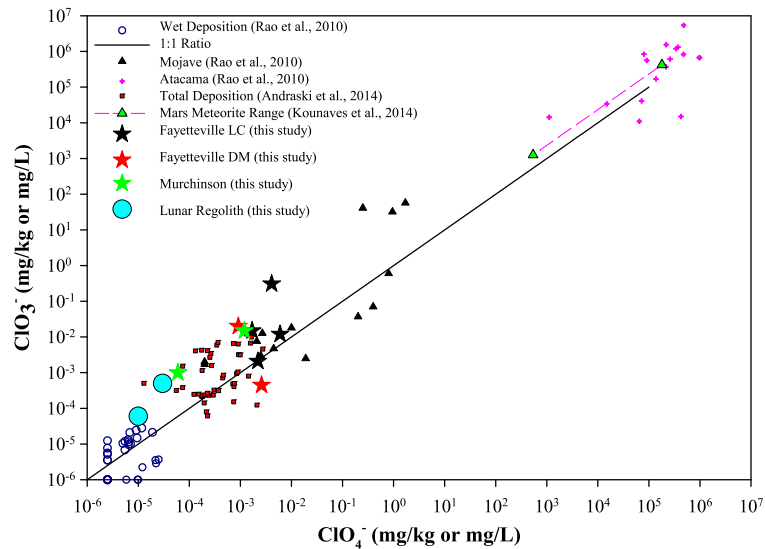


Fig. 2. ClO_3^- and ClO_4^- concentrations of lunar and asteroidal meteorites presented with published data from terrestrial and extra-terrestrial samples. Ranges of values for Mars meteorite based on total mass and mass of salt-enriched material (Kounaves et al., 2014). For Fayetteville, LC refers to light clast and DM refers to dark matrix.

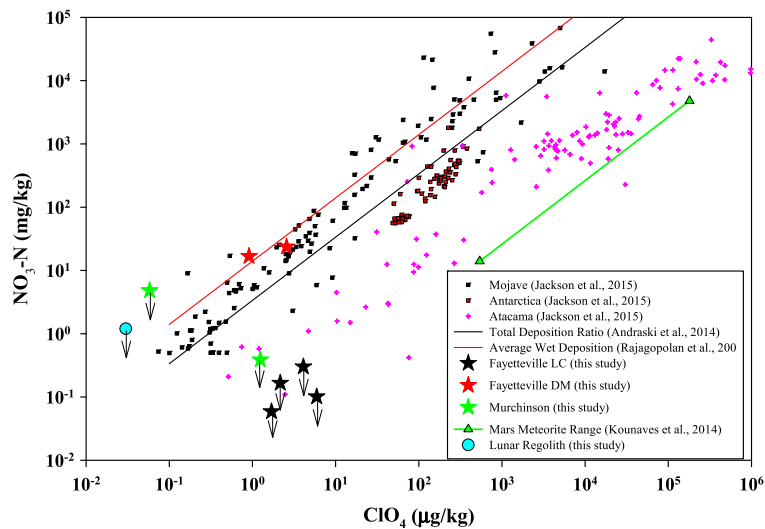


Fig. 3. NO_3^- and ClO_4^- concentrations of Lunar and asteroidal meteorite samples presented with published terrestrial and extra-terrestrial samples. Ranges of values for Mars meteorite based on total mass and mass of salt-enriched material (Kounaves et al., 2014). For Fayetteville, LC refers to light clast and DM refers to dark matrix. NO_3^- concentrations less than the detection limit are indicated by symbols with downward pointing arrows.

The relative abundances and heterogeneous distributions of the different anions within the Fayetteville meteorite also support an extraterrestrial origin, particularly when considering the relative distribution and abundance of these species on Earth (Figs. 2, 3). Terrestrial ClO_4^- , ClO_3^- , and NO_3^- are globally distributed, and NO_3^- and ClO_4^- abundances are strongly correlated worldwide in arid and semi-arid environments, with $\text{NO}_3^-/\text{ClO}_4^-$ molar ratios typically of the order of 10^4 to 10^5 , except in the Atacama Desert (10^3) (Jackson et al., 2015). ClO_4^- and ClO_3^- concentrations in meteorite and lunar samples are similar to or lower than the lower range of terrestrial soil and caliche concentrations (Fig. 2). However, samples of the Fayetteville meteorite light clast contained measurable ClO_4^- but no detectable NO_3^- (Table 1), a scenario never encountered so far in terrestrial samples. Assuming a maximum NO_3^- concentration based on our LLQ ($10 \mu\text{g/L}$), the maximum possible molar $\text{NO}_3^-/\text{ClO}_4^-$ ratios in the light clast samples would have been <100 , lower than those of any reported terrestrial samples, but closest to those of Atacama Desert soils (Fig. 3). In contrast, the dark matrix contained both NO_3^- and

ClO_4^- , with $\text{NO}_3^-/\text{ClO}_4^-$ ratios at least two orders of magnitude higher than in the light clast. Finally, the molar $\text{ClO}_3^-/\text{ClO}_4^-$ ratios in the lunar and meteorite samples fall within the range of all other previously published and unpublished terrestrial samples and similar to those observed in Martian meteorite samples with ratios generally 1:1 to 10:1 (Fig. 2; Rao et al., 2010; Carrier and Kounaves, 2015). However, the observed reactivity of ClO_3^- in unfiltered aqueous extracts from the Fayetteville meteorite is important because it suggests that its actual concentrations could be higher than the measured values by a factor of 10 or more. Future analysis should carefully evaluate the potential for oxy-anion reactivity during extraction. As such, the reported ClO_3^- concentrations should be viewed as minimum values and this may explain the relatively large variations in ClO_3^- concentrations compared to ClO_4^- , which is relatively unreactive (Engelbrekton et al., 2014).

The isotopic composition of NO_3^- leached from the dark matrix of the Fayetteville meteorite does not preclude, but is difficult to reconcile with terrestrial sources. The $\delta^{15}\text{N}$ value of Fayetteville

NO_3^- is within the range of values reported for both terrestrial and extraterrestrial solid N (Coplen et al., 2002; Füri and Marty, 2015). The low $\Delta^{17}\text{O}$ value (0‰) is unlike that of terrestrial atmospheric NO_3^- (typically of the order of +60 to +90‰) but similar to that of other terrestrial NO_3^- formed in soils and aquatic systems. However, the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values are higher than those of most terrestrial NO_3^- that has not been isotopically fractionated by partial reduction. Therefore, the isotopic data are not consistent with either terrestrial atmospheric NO_3^- , or with common NO_3^- in normal terrestrial soils such as those near the area of recovery, or with mixtures of those two sources. It is possible the Fayetteville NO_3^- once had $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ values near 0 if it was reduced subsequently with a $\Delta\delta^{15}\text{N}/\Delta\delta^{18}\text{O}$ ratio of 1 (Granger et al., 2008). For example, for an assumed fractionation effect of -25% ($\epsilon^{15}\text{N}$), a change in $\delta^{15}\text{N}$ from 0‰ to 27‰ could be consistent with loss of 62% or more of the initial NO_3^- . One possible, but rather complicated, scenario is that the observed isotope ratios were a result of chemical processes during the fall itself; for example, if atmospheric N_2 or soil organic N were oxidized before or during Earth impact. NO_3^- formed before, during, or after the fall could have had $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ near 0 and, if subsequently partially volatilized or reduced, could then have approximately equally elevated $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, as observed. Alternatively, it is possible that some NO_3^- isotopic fractionation occurred during solute extraction, if NO_3^- was subject to similar reactions that apparently reduced ClO_3^- concentrations, but the isotopic similarity between two different extractions would then be fortuitous. In summary, the rapid recovery of the meteorite, the large differences in NO_3^- concentrations and $\text{NO}_3^-/\text{ClO}_4^-$ ratios between the light clast and dark matrix, the occurrence of NO_3^- at depth below the meteorite surface, and the stable isotopic composition of the NO_3^- , are not readily explained by terrestrial NO_3^- contamination or production during or after the fall.

The presence of extraterrestrial ClO_4^- and ClO_3^- in lunar and meteoritic samples would imply a mechanism of formation in the environment of space, different from the main processes for synthesis on Earth, and which operates on non-planetary bodies with different chemical and mineralogical composition, and dissimilar histories of alteration. It is considered unlikely that gas phase reactions could be responsible for the presence of ClO_4^- and ClO_3^- in lunar samples or in chondrites; instead, heterogeneous photocatalytic or radiation-induced mineral-surface reactions involving chlorine-bearing phases may be responsible (Dasgupta et al., 2005; Kang et al., 2008; Kim et al., 2013; Carrier and Kounaves, 2015). For example, chlorine oxides carrying the $-\text{ClO}_3$ and $-\text{ClO}_2$ groups can form via the interaction of energetic electrons and carbon dioxide-rich chlorine-bearing ices in the solid phase (Kim et al., 2013). Schuttlefield et al. (2011) showed that highly oxidizing valence band holes produced by UV illumination of naturally occurring semiconducting minerals are capable of oxidizing Cl^- to ClO_4^- in aqueous solutions, a non-atmospheric pathway that could operate on the surface of minerals. This heterogeneous production has been demonstrated for Cl^- coated silica under atmospheric conditions similar to those on Earth (Dasgupta et al., 2005) and Mars (Carrier and Kounaves, 2015).

In the case of the Moon, Cl^- has been detected in some samples. For example, sample 66095 has leachable Cl^- (in H_2O) ranging from 29 to 117 mg/kg (Sharp et al., 2010). El Goresy et al. (1973) recognized that the volatile metals were probably “salts” such as a Cl-bearing sulfate, because Cl was mostly leachable in hot water. More recently, Shearer et al. (2014) reported substantial metal chlorides in the same sample, and attributed them to deposition from degassing of an impact ejecta blanket, which may have experienced multiple episodes of oxy-hydration. In such a scenario, UV illumination of Cl-bearing minerals around water ice

or adsorbed water could be a possible endogenous source of the Cl^- , ClO_4^- and ClO_3^- . Reported temperatures for the mineral phase formation in sample 66095 are above ClO_4^- and ClO_3^- decomposition temperatures (Shearer et al., 2014), and strongly suggest that both species would postdate the rock formation event. A radiation-induced origin could be reflected in the vertical distribution of ClO_4^- and ClO_3^- , such that both species should be absent or at much lower concentrations below the average depth of the lunar regolith (c.a. 2–16 m), a mixed layer of fine-grained lunar soil and ejecta deposits (Zhang et al., 2015). There are also possible exogenous sources, such as the impact of terrestrial and Martian meteorites, albeit the contribution of these sources would likely be small. Water-extractable SO_4^{2-} from the Murchison and other CM chondrites possesses positive $\Delta^{17}\text{O}$ values supporting the role of photochemical processes that could be conducive to the formation of ClO_4^- and ClO_3^- (Airieau et al., 2005); however, NO_3^- from the Fayetteville meteorite does not have a positive $\Delta^{17}\text{O}$ value. Further study of the abundances and isotopic compositions of various anions in these meteorites may help resolve uncertainties about the alteration of their parent bodies, potentially involving salt rich fluids.

Our findings could also help explain the presence, abundance and distribution of ClO_4^- near the surface of Mars (Hecht et al., 2009; Ming et al., 2014). There, a purely atmospheric origin via gas-phase oxidation of volcanically-derived chlorine appears unlikely given the small amount of ozone in the atmosphere, and the colder, drier conditions, which cause low rates of gas phase oxidation reactions (Smith et al., 2014). Instead, heterogeneous photocatalytic or radiation induced surface reactions involving chlorine-bearing phases, and the direct input via meteoritic delivery may be additional, or alternative sources of ClO_4^- that could have been active for billions of years. In addition, our results suggest that ClO_3^- , which has not yet been detected on Mars, is likely also present, locally perhaps even at higher abundances than ClO_4^- .

Ionizing radiation in the environment of space can also cause the partial decomposition of ClO_4^- and ClO_3^- into O_2 and reactive chlorine species (RCS) such as ClO^- and ClO_2 (Prince and Johnson, 1965; Quinn et al., 2013). The formation of RCS could explain in part the diagenetic history of some meteorites, and in particular the unexplained origin of chlorinated organic compounds in some carbonaceous chondrites, including Murchison (Schöler et al., 2005).

5. Conclusion and implications

Our findings indicate that ClO_4^- and ClO_3^- , and perhaps other more transient oxychlorine species, may be ubiquitous in the Solar System, as they have been reported on Earth and Mars, and now in lunar samples and in two chondrite meteorites. The contribution of meteorites to the ClO_4^- content of Mars and Earth surface material is likely negligible even over a time period of 1 billion years based on estimated meteorite mass inputs ($\sim 10^7$ kg/yr) (Flynn and McKay, 1990) and our measured concentrations of ClO_4^- in meteorites (~ 0.01 – 0.06 mg/kg) but it could represent a significant fraction, perhaps even the dominant source, of ClO_4^- in lunar surface material based on an estimated 1–2% meteorite material in indigenous lunar mare soils (Anders et al., 1973). We recognize that these are preliminary estimates based on a small number of data. With the available information we cannot estimate the timing for the origin of ClO_4^- and ClO_3^- in the meteorites, but potentially they could be as old as the meteorites themselves, or even pre-date them as part of the original parent body from which the meteorites formed. In either case considering that carbonaceous chondrites may represent the most primitive solar system materials known, the ClO_4^- and ClO_3^- described here might be the most

ancient natural occurrences reported so far. The presence of ClO_4^- and ClO_3^- in meteorites as well as on Earth, the Moon and Mars implies they may be present to varying degrees throughout the Solar System.

Acknowledgements

We would like to acknowledge the CAPTEM (Curation and Analysis Planning Team for Extraterrestrial Materials) and the lunar sample curators at NASA Johnson Space Center for providing the Moon samples. We acknowledge the Smithsonian Institution for providing samples of the Murchison meteorite, and the University of Arkansas for providing samples of the Fayetteville meteorite. Janet Hannon and Andrew Schauer assisted with NO_3^- isotope analyses. David Stonestrom, Balaji Rao, Mark Claire, and an anonymous reviewer provided helpful reviews of the manuscript. AFD acknowledges funding from the NASA Astrobiology program (Grant NNX12AD61G), and the NASA Astrobiology Institute (NAI Grant NNX15BB01A to the SETI Institute). Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Author contributions

W.A. Jackson, N. Estrada, and M. Brundrett processed the samples and performed the analyses. D. Sears provided meteorite samples and interpretation of meteorite results. C. McKay, A. Davila, D. Sears, J. Coates, J.K. Böhlke, and W.A. Jackson designed the study and wrote the paper. All authors discussed the results and commented on the manuscript.

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