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Widespread occurrence of (per)chlorate in the Solar System

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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.

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; Rajagopolan 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 ($\Delta^{17}O$ and $^{36}Cl/Cl$) 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 μg/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, 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.

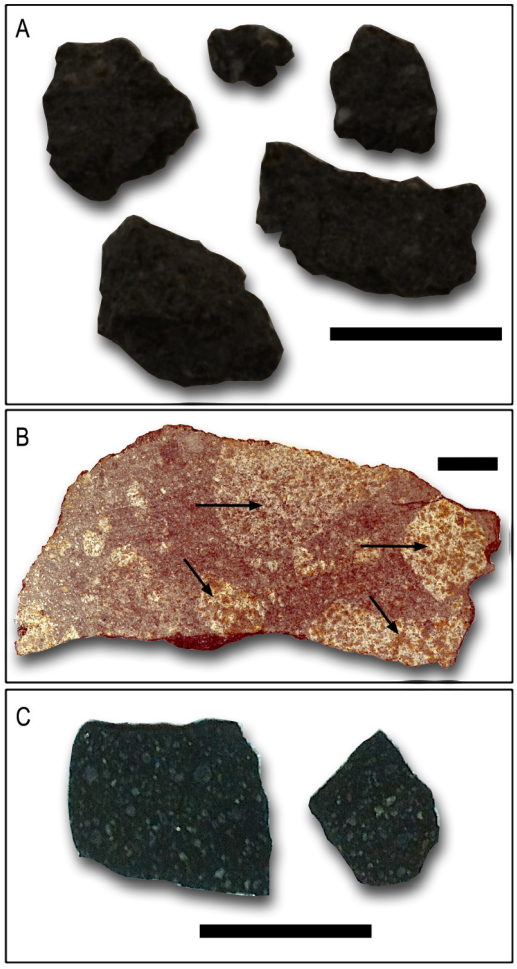

Fig. 1. Extraterrestrial samples analyzed in this study. (**A**) Subsamples of the Rusty Rock collected during the Apollo missions. Scale bar is 1 cm. (**B**) A fragment of the Fayetteville meteorite. Characteristic light clasts (arrows) are embedded in a dark matrix. Scale bar is 2 cm. (**C**) Two small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

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

Sample	Description	Mass of sample	Distance from fusion crust	ClO_3^-	ClO_4^-	Cl^-	NO_3^-–N	SO_4^{-2}
		(mg)	(cm)	(μg/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.