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Spectroscopic study of perchlorates and other oxygen chlorides in a Martian environmental chamber



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ABSTRACT

We report a study where the molecular spectral features of nine anhydrous and hydrous oxygen chlorides were analyzed both under Mars atmospheric pressure and temperature conditions in a Planetary Environment and Analysis Chamber (PEACh) and, for comparison, under ambient laboratory conditions. The goal is to understand the effect of Mars environmental conditions (mainly temperature T and CO_2 pressure P) on their spectral features as determined by both Raman and NIR spectroscopy. These results will be used for in situ simultaneous identification of the ClO_4^- and other intermediate oxygen chloride products generated during a dynamic electrostatic discharge (ESD) experiment. We have three major findings from the first phase of this study: (1) the v_1 Raman peak position is the most sensitive parameter for identifying the cation speciation in perchlorates (e.g., Na, Mg, Ca), the hydration state of magnesium perchlorate (e.g., $Mg(ClO_4)_2 \cdot xH_2O$, x = 0, 2, 4, 6), and the degree of oxidation of sodium oxygen chlorides (e.g., NaClO_v, y = 1, 2, 3, 4); (2) v_1 Raman peak positions of most tested hydrous and anhydrous oxygen chlorides show no detectable changes within the tested T and P ranges relevant to the environmental conditions at Mars surface and shallow subsurface, but water Raman peaks of the hydrated salts change following T decreases; (3) under the P & T conditions relevant to current surface and shallow subsurface at Mars mid-latitude regions, both Mg(ClO₄)₂ \cdot 6H₂O and Ca(ClO₄)₂ \cdot 2H₂O are stable against dehydration, while NaClO₄ \cdot H₂O dehydrates, with a dehydration rate that is a function of T which was quantified by in situ NIR spectroscopy. These results are useful for the interpretations of the data from current orbital remote sensing (Vis-NIR spectra) and from future landed missions (Raman spectra). Furthermore, we have designed a set of systematic ESD experiments to be conducted in PEACh for studying the pathways and the rates of oxygen chloride generation from chloride salts, as a potential mechanism to form oxygen chlorides during Martian dust storm. The results of the current study will be used for in situ simultaneous identification of the ClO_4^- and other intermediate oxygen chloride products generated during a dynamic ESD experiment.

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1. Introduction

The perchorate ion (ClO_4^-) was detected at the Phoenix landing site, with an average concentration 4.4 times of that of the chloride ion (Hecht et al., 2009). Further analysis suggested the observed data is a mixture of 60% Ca(ClO₄)₂ and 40% Mg(ClO₄)₂ (Kounaves et al., 2014a). At Gale crater, hydrated Ca-perchlorate was the best candidate to interpret the correlated releases of O₂ and chlorinated hydrocarbon observed during SAM (Sample Analysis at Mars) analyses (Glavin et al., 2013; Leshin et al., 2013). The existence of perchlorates at Viking sites was inferred (Navarro-González et al., 2010). The most recent relevant findings on Mars were spectral evidence that match with Mg-perchlorate, Mg-chlorate, and Naperchlorate at four sites during the season when Recurring Slope Lineae (RSL) were seen (Ojha et al., 2015). Furthermore, the analysis of Martian meteorite EETA79001 suggested a Martian origin of the detected ClO_4^- and ClO_3^- (Kounaves et al., 2014b). All these findings seem to support a hypothesis that perchlorates and other oxygen chloride species may exist ubiquitously on Mars (Archer et al., 2013). Nevertheless, the global distribution of oxygen chloride species are still largely unknown.

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On Earth, trace amounts of natural perchlorates and chlorates were found in the upper regolith of hyper-arid regions (such as Antarctica Dry Valleys, Kounaves et al., 2010). Supported by laboratory analysis tools, the current theory regarding the origin of naturally occurring perchlorates on Earth is centered on natural atmospheric processes (Catling et al., 2010), such as the photochemical reaction between sea-or-land based chloride and atmospheric ozone (Walvoord et al., 2003). Lightning was proposed to play a role and a set of laboratory simulation experiments was reported (Dasgupta et al., 2005).

On the basis of composition of Mars' atmosphere, a similar set of mechanisms for perchlorate generation on Mars has been suggested since 2009. A gas phase model between oxidants and volatile chlorine species on Mars was discussed (Catling et al., 2010). Using a 1D photochemical model, it was found that sufficient quantity of perchlorate can be modeled by gas phase photo chemistry to explain the abundance of CIO_4^- found in Atacama (Catling et al., 2010), while the modeled formation of perchlorate is insufficient by orders of magnitude ($\sim 10^7$) to explain the ClO_{4}^{-} concentration measured at Phoenix landing site (Smith et al., 2014). It suggests that non-gas-phase processes must play a major role in Martian perchlorate formation. The gas-solid reactions between oxidants and chloride-bearing solids were proposed, discussed, and tested. The conversion of chlorides to oxychlorides stimulated by UV radiation (Carrier and Kounaves 2015), and catalyzed by ice and TiO₂ (Kim et al., 2013; Schuttlefield et al., 2011), was reported. The molar yields of ClO_4^- through direct ozone oxidation of Cl-bearing solution and Cl-coated sand/glass were compared (Kang et al., 2008). Furthermore, the conversion of chlorides to oxychlorides stimulated by ESD on Mars was listed as a potential mechanism (Kounaves et al., 2010; Catling et al., 2010) without detailed experimental verification.

The electrification of surface dust and atmospheric species on Mars and the electrostatic discharge during Mars dust storms and dust devils has been a very active field of science investigation, including numerical modeling, laboratory experiments, and desert field tests (Atreya et al., 2006; Delory et al., 2006; Farrell et al., 1999). The required breakdown electric field strength on Mars (~25 kV/m) is much lower than that on Earth (~30,000 kV/m) (Zhai et al., 2006), and that breakdown electric field strength can be reached during Martian dust storms or dust devils (Delory et al., 2006). The predicted oxidant (e.g., H₂O₂) generation would be 200 times that produced by photochemistry (Atreya et al., 2006).

To follow up the above investigations, we designed a set of systematic ESD experiments to be conducted in Planetary Environment and Analysis Chamber (PEACh) to study oxygen chloride generation from chloride salts. This study would be separated into three phases. The first phase, i.e. this study, aimed at understanding the effect of Martian environmental condition (mainly temperature and CO_2 atmospheric pressure) on the spectral features of anhydrous and hydrous oxygen chlorides. This knowledge can then be used for *in situ* identification of the generated perchlorates and other intermediate oxygen chloride products during the ESD experiment. The second phase is to directly measure, identify, and quantify the oxidants generated by ESD in PEACh; The third phase is to study the pathways and the rates of oxygen chlorides generation during ESD. In this manuscript, we report the results from the first phase of our study.

2. Samples and spectroscopic measurements

Chlorine in oxygen chlorides can have four oxidation states, ClO^- (+1, hypochlorite), ClO_2^- (+3, chlorite), ClO_3^- (+5, chlorate), and ClO_4^- (+7, perchlorate). The former three can be the intermediate reaction products during the formation of the latter. Up to now, only ClO_3^- , in addition to ClO_4^- , has been suggested on Mars

(Ojha et al., 2015) and detected in a hyper-arid region on Earth (Kounaves et al., 2010).

On the basis of chemical features of perchlorates found on Mars, we selected Na-, Ca-, Mg-oxygen chlorides for this study, including NaClO_y (y = 1, 2, 3, 4), NaClO₄ · H₂O, Mg(ClO₄)₂ · xH₂O (x = 0, 2, 4, 6), and Ca(ClO₄)₂ · xH₂O (x = 0, 2, 4) (Table 1).

We use near-IR, mid-IR, and Raman in this study to gain comprehensive understanding of the vibrational spectral features and the P-T effect on them. Among them, Raman and near-IR spectra will be used for the *in situ* detection of oxygen chloride species during our third phase of the ESD experiments.

2.1. Sample and sample preparation

A total of twelve oxygen chlorides were studied. Among them, seven were purchased as pure chemicals; five were made by us.

The purchased pure chemicals are: sodium hypochlorite solution (NaClO, reagent grade, available chlorine 10–15%, Sigma-Aldrich, #MKBS7734V), sodium chlorite (NaClO₂, ~80%, Acros, #B0134726), sodium chlorate (NaClO₃, \geq 99%, Acros, #A0347735), sodium perchlorate (NaClO₄, \geq 98%, Sigma-Aldrich, #NO.M4992), sodium perchlorate hydrate (NaClO₄ \cdot *x*H₂O, \geq 99.99%, Sigma-Aldrich, #MKBT3054V), magnesium perchlorate hexahydrate (Mg(ClO₄)₂ \cdot 6H₂O, \geq 99%, Aalf Aesar, #127W005) and calcium perchlorate tetrahydrate (Ca(ClO₄)₂ \cdot 4H₂O, \geq 99%, Acros, #A0240689). The chemical purity of most purchased samples is good enough for molecular spectroscopic measurements, but the degree of hydration of some samples needed further confirmation.

The hydration state of NaClO₄ · xH_2O was first determined to be x = 1 by XRD measurement, and then verified by gravimetric measurements conducted before and after heating to 443 K, in dry N₂, for ~10 h. The hydration state of Mg(ClO₄)₂ · 6H₂O was confirmed by both XRD and similar weight loss experiments. We found the Ca(ClO₄)₂ · 4H₂O to be unstable under laboratory ambient conditions, The purchased Ca(ClO₄)₂ · 4H₂O became a mixture of Ca(ClO₄)₂ · 4H₂O and Ca(ClO₄)₂ · 2H₂O with the latter found to be the major component in the mixture.

Anhydrous $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ were obtained by heating $Mg(ClO_4)_2 \cdot 6H_2O$ (1.6682 g) and authenticated $Ca(ClO_4)_2 \cdot 4H_2O$ (2.3297 g) at 623 K (Devlin and Herley, 1986; Migdał-Mikuliet and Hetmańczyk 2008) in dry N_2 for 24 h. Then they were sealed in glass bottles. The gravimetric data before and after baking indicated the loss of about six and four waters per perchlorate molecule respectively. The subsequent Raman measurements through the glass wall of sealed sample bottles revealed Raman spectra without H_2O peaks in the 3000–4000 cm⁻¹ spectral range, confirming the formation of the anhydrous perchlorates.

In addition, based on the baking temperature (not Raman spectral features) stated by Devlin and Herley (1986), Migdał-Mikuliet and Hetmańczyk (2008), Bishop et al. (2014) and the stability diagram of Ca(ClO₄)₂ + H₂O (Nuding et al., 2014), we generated Mg(ClO₄)₂ · 2H₂O, Mg(ClO₄)₂ · 4H₂O, and Ca(ClO₄)₂ · 2H₂O by baking the purchased Mg(ClO₄)₂ · 6H₂O and Ca(ClO₄)₂ · 4H₂O in dry N₂. Raman spectra match the published values for these hydrated perchlorates (Table S1). Then these samples were stored in sealed glass bottles, and the homogeneity of the samples was determined by multi-spot Raman measurements through the glass wall of the sealed sample bottle.

2.2. Spectroscopic measurements

2.2.1. Measurements under laboratory ambient conditions

All twelve oxygen chlorides were studied first under laboratory ambient conditions using Raman spectroscopy through the glass wall of the sealed sample bottle. Then nine of them, stable in the laboratory, were analyzed by near-IR diffuse reflectance, mid-IR

Studied oxygen	Lab-é	mbient .	P & T		In PEACh														
chloride salts	IR			Raman	WIR + R	aman				Raman									
	н	DR	ATR		200 mbai	L .				200 mbai	L .			7 mbar					
					294 K	288 K	283 K	278 K	273 K	294 K	273 K	258 K	243 K	294 K	273 K	253 K	233 K	213 K	193 K
NaClO			>	>	>					>									
NaClO ₂	>	>	>	>	>				>	>		>	>				>	>	>
NaClO ₃	>	>	>	>	>				>	>		>	>				>	>	>
NaClO ₄	>	>	>	>	>				>	>		>	>				>	>	>
$NaClO_4 \cdot H_2O$	>	>	>	>	√ ^{7h}	✓ ^{7h}	ν ^{7h}	$\sqrt{7h}$	√ ^{7h}	>		>	>				>	>	>
$Mg(ClO_4)_2$				>															
$Mg(ClO_4)_2 \cdot 2H_2O$				>															
$Mg(ClO_4)_2 \cdot 4H_2O$				>															
$Mg(ClO_4)_2 \cdot 6H_2O$	>	>	>	>	✓ ^{7h}					>		>	>				>	>	>
Ca(CIO ₄) ₂				>															
$Ca(CIO_4)_2 \cdot 2H_2O$	>	>	>	>	√ ^{7h}					>		>	>				>	>	>
$Ca(ClO_4)_2 \cdot 4H_2O$				>															

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The Raman spectra were collected using a HoloLab5000-532 laser Raman spectrometer (KOSI, Kaiser Optical Systems Inc.). The Raman spectral range was 100-4000 cm⁻¹ with a spectral resolution of 4–5 cm⁻¹. The Raman spectrometer uses a continuous wave 532 nm laser as the excitation source, and a $20 \times$ microscope objective (0.4 NA, \sim 1 cm working distance) that focuses the laser beam onto a \sim 6 µm diameter spot with a power of \sim 3.5 mW at the sample surface. In order to prevent the change of hydration state of examined salts, all Raman measurements were made through the glass wall of a sealed sample bottle. The Raman spectrometer was wavelength-calibrated with a neon emission lamp, while the intensity calibration was made using a standard tungsten lamp calibrated at KOSI. The Raman spectrum of a silicon wafer (Raman peak at $520.7 \pm 0.2 \text{ cm}^{-1}$) was measured during each experimental day for calibrating the laser wavelength shift. The above calibrations ensure a better than 0.2 cm⁻¹ accuracy of the Raman peak position in the spectral region of interest.

A Nicolet Nexus 670 FTIR spectrometer (Thermo Fisher Scientific Inc.), with a MCT detector and a KBr beam splitter, was used to collect the mid and near IR spectra. near-IR diffuse reflectance spectra (NIR_DR, 2000–10,000 cm⁻¹) were collected directly from a powdered sample using a CricketTM reflectance accessory, and a gold-coated (200 µm thickness) rough surface plate was used as the 100% reflectance standard. mid-IR attenuated total reflectance spectrum (MIR-ATR, 4000–400 cm⁻¹) was recorded by pressing a few grains of sample on the diamond anvil of the golden-gate ATR unit. The mid-IR transmittance spectrum (MIR-T, 400–4000 cm⁻¹) was made by the standard KBr pressed pellet method. All IR spectra were recorded with a resolution of 4 cm⁻¹.

Near IR diffuse reflectance spectra $(1.4-2.5 \mu m)$ of samples were also collected directly from powdered samples using the brassboard-II of the WIR unit (to be described in section 2.2.2).

2.2.2. In situ spectral measurements in a Martian environment chamber Nine oxygen chlorides were studied by Raman and near-IR reflectance spectroscopy, with samples maintained under various Mars relevant pressure (P) and temperature (T) conditions in PEACh at Washington University in St. Louis as described below.

2.2.2.1. Planetary Environment and Analysis Chamber (PEACh) The building and testing of PEACh was reported by Sobron and Wang (2012). The pressure in the PEACh can range from ambient to 3×10^{-2} mbar. The simulated atmospheric composition and pressure are regulated via a combination of needle and ball valves connecting the PEACh with containers filled with premixed gases or pure CO₂. The temperature of the samples can be controlled from ambient to 173 K. The in situ analytical techniques for studying samples in the original design of the PEACh were laser Raman spectroscopy, laser-induced breakdown spectroscopy (LIBS), and microscopic imaging. For the current and next phases of this study, we re-designed and fabricated a new Teflon delivery plate and some larger copper sample cups (32 mm diameter and 1.0 mm depth). This was done to increase the reaction sample surface during ESD and to improve the measurement quality at low T. About 500 mg fine grinding powder sample could be filled into one cup and up to 17 sample cups can be sequentially presented for the in situ spectroscopic sensors in the PEACh (Fig. 1).

2.2.2.2. WIR, Near-IR reflectance spectrometer A new in situ sensor, the brassboard-II of the WIR unit (WIR-BB-II), was added to the PEACh. WIR is an near-IR reflectance spectrometer with a built-in light source designed for *in situ* measurements on planetary surfaces, and was developed by the *Planetary Spectroscopy Team* at Washington University in St. Louis, through a NASA ASTID program

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Fig. 1. Photograph of the interior of the PEACh (Planetary Environment and Analysis Chamber). Sample cups are carried by a rotating Teflon disk. The cup has a good thermal contact with the cold plate made of copper whose temperature is controlled by an active liquid–gas–nitrogen circulation path ($T_{min} = 173$ K *Sobron and Wang, 2012*). The rotation of Teflon disk would place the sample cup directly under the Raman probe or the WIR (Water-IR) unit, both are carried by a translational stage for focusing adjustment. *In situ* Raman and NIR measurements can be made throughout the study period in PEACh.

(Wang et al., 2010). Two brassboards of the WIR were successfully tested at various Martian analog sites (e.g., Atacama, Tibet, Wang et al., 2010). The WIR-BB-II unit installed in PEACh has a spectral range of 1.4–2.5 μ m over 128 spectral channels, which allows the direct detection of overtone and combinational modes of H₂O/OH in hydrous minerals or in other matrices. It uses six strong active IR sources (International Light Technologies, Inc. #MR3-4115) that can accomplish a measurement in a few seconds. It has a 2 cm working distance and ~1 cm diameter Field of View (FOV), and can be deployed directly on unprepared samples. A diffuse gold-coated reflectance standard was used for spectral reference, and InfraSpec WIR IIB operating software (Wilks Enterprise, Inc.) was used to collect spectral data. The wavelength was calibrated using calcite powder.

Before installing the WIR unit in PEACh, the extreme survival threshold of this unit was tested, using two IR sources of the same mode, by gradually lowering the PEACh pressure and temperature. The environmental survival threshold of the IR source was found to be 60 mbar and 243 K. The WIR-BB-II unit was mounted above the Teflon delivery plate, and used a vacuum electrical/signal feedthrough to connect with a laptop computer and the external power supply outside of the PEACh.

2.2.2.3. Raman probe The other in situ spectroscopic sensor in PEACh that we used is a laser Raman probe. It is connected with a Raman spectrometer outside of PEACh through an optical fiber cable, which was installed using a vacuum optical fiber feedthrough (Sobron and Wang, 2012). This optical fiber cable uses a 6×1 configuration with a single-mode fiber to deliver the 532 nm laser beam onto the sample in PEACh, and 6 multi-mode fibers to collect Raman photons from the sample and send them to the Raman spectrometer, a Kaiser Nexun-E spectrometer (Kaiser Optical System, Inc.). The Raman signal is detected using an Andor CCD camera (DU401A-BV-132 iDus). A diode-pumped solid-state laser (532 nm, 25 mW, CrystaLaser) was used as excitation source. A total of 2.56 mW laser power was focused on the target surface with a beam diameter of about \sim 22 µm (Sobron et al., 2010). This Raman system was calibrated in the same way as the Holo-Lab5000-532 used for the Raman measurements under laboratory ambient conditions. The Raman probe in PEACh can work under much more harsh conditions (to 173 K and 0.1 mbar, Sobron and Wang, 2012) than the WIR-BB-II unit.

3. Experimental results

Table 1 lists all spectral measurements that we conducted in this study on all twelve oxygen chlorides, including Raman, NIR-DR, MIR-T and MIR-ATR measurements under laboratory ambient conditions, and the *in situ* NIR-R and Raman measurements in PEACh at 10 different *T* levels and at three CO_2 atmosphere *P* levels.

The Raman, NIR, and MIR spectra are intrinsically connected. Raman and MIR bands are a direct measure of the fundamental vibrational modes of a molecule, while NIR bands are generated by the overtones and combinations of the fundamental modes. Therefore, we use the Mid-IR spectral data (*T* or ATR) to elucidate Raman and NIR spectral features.

The Raman, NIR, and MIR spectral features observed under laboratory ambient conditions formed the basis for our understanding of the Martian environmental effects on the samples. Table S1 lists the positions of major Raman bands of the oxygen chlorides both at ambient laboratory P and T, and at low CO₂, P and T in PEACh. Table S2 lists the position of their major NIR-DR bands, at ambient laboratory P and T (using Nexus670) and those at low CO₂, P, and T in PEACh (using the WIR-BB-II). Fig. S1 and Fig. S2 show the typical Mid-IR (T and ATR) spectra of some oxygen chlorides that are stable at ambient laboratory P and T.

Unlike the Raman measurements under ambient conditions made through the glass wall of sealed sample bottles, the NIR-DR and MIR-T/ATR measurements were made in the open air of our laboratory. Some hydrous perchlorates can change their hydration state. In Table S2, Fig. S1 and Fig. S2, we only list the data for the salts that are stable under ambient laboratory conditions.

The purchased NaClO is in the form of an aqueous solution (10-15% concentration). Raman and MIR-ATR measurements were made at ambient *P* and *T*, and a Raman measurement in PEACh was taken from a 2.0 ml sample in a 3 mm-deep sample cup made of copper (Table 1). These measurements were made to distinguish Cl–O bonding from other oxygen chlorides.

Because the limited survival thresholds of the WIR-BB-II unit (60 mbar and 243 K), the *in situ* NIR-R measurements were conducted at 200 mbar in PEACh while the *in situ* Raman measurements were conducted down to 7 mbar and 193 K (Table 1). As will be discussed in section 4, the pressure effects (in tested, Mars relevant, *P* range) on both NIR-R and Raman spectral features of anhydrous oxygen chlorides (exclusive of NaClO solution) were found to be negligible.

Unlike MIR and NIR, the Raman measurements use a 6 μ m diameter laser spot in the laboratory and a 22 μ m diameter laser spot in PEACh. For all measurements, unless otherwise specified, at least three Raman spectral measurements were taken per sample, to verify the sampling homogeneity and spectral reproducibility.

4. Discussion

From the detailed analyses of the obtained data we have three major findings, which will be discussed separately in following sections.

4.1. Distinguishing oxygen chlorides

4.1.1. Oxygen chlorides with different oxidation degrees

The most distinct Raman spectral feature of NaClO, NaClO₂, NaClO₃, and NaClO₄ is the systematic up-shift of their strongest peaks from 712.8 cm⁻¹ to 952.5 cm⁻¹ (Fig. 2) which gives a total of 239.7 cm⁻¹ upshift over the change of the oxidation state





Fig. 2. Raman ν_1 peaks of anhydrous sodium oxygen chloride salts measured under laboratory ambient conditions. The change from Cl⁺ to Cl⁷⁺ causes 239.7 cm⁻¹ upshift of Raman ν_1 peak.

from +1 to +7. On the basis of structures of ClO⁻, ClO⁻₂, ClO⁻₃, and ClO_4^- ionic groups in these salts, we would assign these Raman peaks to the symmetric stretching vibration mode (v_1) of ClO^- , ClO_2^- , ClO_3^- and ClO_4^- (Robinson, 1963). Generally speaking, a larger force constant of a chemical bond (Cl-O in these salts) generates higher vibrational energy, which shifts the peak position to a higher wavenumber. In this case, the force constants of NaClO_y (y = 1, 2, 3, 4) are 3.3×10^{-8} Nm⁻¹, 5.33×10^{-8} Nm⁻¹, 6.96×10^{-8} Nm⁻¹ and 7.3×10^{-8} Nm⁻¹ (Robison, 1963) respectively. Structurally, the increasing force constants are directly related to the reducing Cl–O bond length from 1.56 Å in ClO_2^- , to 1.49 Å in ClO_3^- , and to 1.44 Å in ClO_4^- (no reported data of bond length of ClO) (Robinson, 1963). These two parameters-force constants and bond length-correlate directly with the observed v_1 peak up-shift of oxygen chlorides with increasing degree of oxidation.

In mid-IR spectra (*T* and ATR) of these oxygen chlorides, the strongest peak in 800–1500 cm⁻¹ split to 2–3 sub-peaks (Fig. S1) due to the variation of local symmetry of the crystal structure (Chabanel et al., 1996). Our results are consistent with the reported IR spectral characteristics of ClO_4^- (Gadsden, 1975) and ClO_3^- (Gadsden, 1975). More importantly, there is a similar systematic up-shift observed on the central positions of MIR-T/ATR peaks of NaClO₂, NaClO₃, and NaClO₄, from 820 cm⁻¹ to 1120 cm⁻¹. The much larger shift ($\Delta \sim 300$ cm⁻¹) in MIR relative to the Raman shifts ($\Delta \sim 150$ cm⁻¹) indicates that MIR peaks are derived from different vibrational modes that are IR-active only.

There are no real features in near-IR reflectance spectra of these anhydrous NaClO_y (y = 1, 2, 3, 4) except forming adsorbed water on those salt grains.

4.1.2. Perchlorates with different cations

The most distinct Raman spectral feature of anhydrous NaClO₄, Mg(ClO₄)₂, and Ca(ClO₄)₂ is the systematic position up-shift of their v_1 peaks from 952.5 cm⁻¹ to 984.6 cm⁻¹ (Fig. 3) leading to a total upshift of ~32.2 cm⁻¹ for these salts. The effect of cation changes on the Raman v_1 peak position is obvious, whereas the cause can be complicated. Because v_1 peak is derived from the stretching vibration of ClO₄⁻ tetrahedra, the effect of the cation (M) occurs through a very weak linkage between the cation (M) and the oxygen ion in ClO₄⁻. The total effect of different cations (M) is due to combination of the effects of their ionic radii, masses, charges, and the polarity of the weak M–O–Cl linkage. A similar Raman peak shift induced by a cation substitution was observed in silicates, carbonates, and sulfates (Wang et al., 2001; Kuebler et al., 2006).

Due to the rapid rehydration of anhydrous $Mg(ClO_4)_2$, and $Ca(ClO_4)_2$ in open air, we did not obtain their MIR-T/ATR and NIR-



Fig. 3. Raman v_1 peak of perchlorates with different cations.

DR spectra. Bishop et al. (2014), however, have found their mid-IR spectral bands are also sensitive to the type of cation, and have discussed the detailed causes(charge and radius of the cation) of this phenomenon.

The NIR-DR spectra of hydrous perchlorates NaClO₄ · H₂O, Mg(ClO₄)₂ · 6H₂O, and Ca(ClO₄)₂ · 2H₂O all have strong and distinct absorption features near 1.17 µm, 1.40 µm, and 1.90 µm (Table S2) contributed by the overtones and combinational water vibrational bands. These data are consistent with the published NIR reflectance spectra by Hanley et al. (2014) and Bishop et al. (2014). These features permit us to monitor the *P*–*T* effects on these salts in our experiments in PEACh (section 4.2).

4.1.3. Perchlorates with different hydration degrees

Very similar to hydrous sulfates, perchlorates with different hydration states have distinct Raman v_1 peaks and H₂O peaks. Fig. 4a shows a set of Raman spectra from Mg(ClO₄)₂ · *x*H₂O (x = 0, 2, 4, 6). We observed a systematic v_1 peak down-shift from 982.8 cm⁻¹ to 933.4 cm⁻¹ ($\Delta \sim 49.4$ cm⁻¹) following the increasing hydration states of Mg-perchlorates. A similar v_1 peak down-shift was observed following the increasing hydration states in Ca(ClO₄)₂ · *x*H₂O (x = 0, 2, 4) series ($\Delta \sim 49.3$ cm⁻¹, Table S1). Fig. 4b shows the changes of H₂O Raman peak shapes and positions of four Mg-perchlorates. Data of Na- and Ca-perchlorates are listed in Table S1.

The same trend of ν_1 Raman peak down-shifts with increasing hydration states in perchlorates was found previously in hydrous Mg-sulfates (Wang et al., 2006), Ca-sulfates (Wang et al., 2009), and Fe²⁺-sulfates (Chio et al., 2007). Based on a detailed analysis of the structural characteristic of Mg-sulfates, Wang et al. (2006) concluded that the increased hydrogen bonding effect of the structural H₂O molecules on the oxygen ions in SO₄ tetrahedra is the major cause of Raman ν_1 peak down-shift in hydrous Mg-sulfates. We believe that hydrogen bonding is also the cause of the observed Raman ν_1 peak down-shift in perchlorates with increasing hydration states.

Hydrous NaClO₄ · H₂O has a very small Raman ν_1 peak shift (<1 cm⁻¹) from anhydrous NaClO₄, but a single strong H₂O Raman peak at 3533 cm⁻¹. The similar phenomenon was found in their MIR-ATR spectra, where the hydration of NaClO₄ leads to 10 cm⁻¹ shift of major peak and the appearance of strong H₂O doubt peaks in 3000–3600 cm⁻¹ spectral range (Fig. S1).

4.1.4. Applications of the different spectroscopic tools

Based on the above discussion, the Raman spectra of oxygen chlorides provide the most distinct characterization for their degree of oxidation, cation species, and hydration states. In addition, the single, sharp, and strong v_1 Raman peak serves as the best tool to identify individual oxygen chloride salts in sample mixtures in the laboratory or during a landed mission on Mars. For our study,



Fig. 4. Raman spectra of Mg-perchlorates with different hydration degrees under laboratory ambient conditions: (a) Raman ν_1 peaks. (W₀ = Mg(ClO₄)₂; W₂ = Mg(ClO₄)₂ · 2H₂O; W₄ = Mg(ClO₄)₂ · 4H₂O; W₆ = Mg(ClO₄)₂ · 6H₂O); (b) Raman H₂O peaks.

it would be especially powerful for *in situ* monitoring the generation of ClO_4^- and other intermediate oxygen chloride products during EDS experiments in the PEACh. The NIR-DR spectroscopy generates characteristic spectra from bulk sample of the hydrated oxygen chlorides. It is suitable for quantitative studies and useful for interpreting spectra from the orbital remote sensing data from Mars. The mid-IR spectra supplement the link between Raman and NIR, due to the intrinsic connection of the three vibrational spectroscopies.

4.2. Pressure and temperature effect on spectral features

As listed in Table 1, seven oxygen chlorides were measured using *in situ* Raman probe and the WIR-BB-II unit in PEACh, to investigate the pressure and temperature effects on Raman and NIR-DR spectral features. The peak positions in Raman and NIR-DR spectra measured at different temperature and pressures in PEACh are listed in Table S1 and S2.

4.2.1. Pressure effect on spectral features

Using fixed calibration procedures and measurement conditions, the repeatability of Raman peak position measurement of our Raman system is ~0.2 cm⁻¹. However, in view of several less precise parameters of the PEACh, e.g., the pressure (±1 mbar), the temperature (±0.5 K) and the potential sample inhomogeneity (especially their hydration states), the reproducibility of multi-point Raman measurements in our study is about ±0.5 cm⁻¹ which serves as the limit of uncertainty for detecting the effect of pressure and temperature on the Raman spectra.

At room temperature (294 \pm 0.5 K), five stable oxygen chlorides (except NaClO₄ · H₂O that goes through a phase transition in tested P-T range, section 4.3) were tested in CO₂ atmosphere at 1 atm, 200 mbar and 7 mbar. These Raman measurements were usually taken about 30 min after the desired pressure in PEACh ensuring that the atmospheric equilibrium had been reached. In addition, at least three Raman measurements were taken at different spots for each sample. Fig. 5 plots the Raman peak positions $(v_1 \text{ and } H_2O \text{ peaks})$ of the oxygen chlorides measured at different pressures (Table S3). A blue colored box in the plot of Fig. 5 represents the distribution of Raman peak position measurements at different spots of tested samples, with a red colored solid line represents the averaged value. With the help of two black dotted lines marking the $\pm 0.5~{\rm cm^{-1}}$ distance from a selected value in each plot, we found that there is no meaningful position shift beyond measurement uncertainty ($\pm 0.5 \text{ cm}^{-1}$), as function of CO₂ atmospheric pressure, for both v_1 peak and H₂O peak of the studied oxygen chlorides.

This set of measurements shows that in CO_2 atmosphere, down to current average pressure on Mars (7 mbar), no obvious pressure



Fig. 5. Position variations of ν_1 peak and H₂O Raman peaks of anhydrous and hydrous oxychlorine salts as function of atmospheric pressure in PEACh (at 294 K). At least three Raman measurements were taken at different sampling spots for each sample and at each pressure. The distributions of Raman peak position are shown as a "box". Two dotted lines for each plot mark ± 0.5 cm⁻¹, i.e. the reproducibility of Raman measurement in this study. This data set demonstrates that there is no obvious pressure effect on the Raman peak positions in the tested pressure range.

effect was found in Raman spectral features of the tested oxygen chlorides. In another words, the pressure difference between Earth and Mars atmosphere would not induce the uncertainty when identifying these oxygen chlorides salts through their Raman peak positions.

The recorded NIR reflectance spectra using the WIR-BB-II were limited to 200 mbar. No pressure effect on these spectra is observable.

4.2.2. Temperature effect on spectral features

The six plots in Fig. 6 show the Raman ν_1 peak positions of six oxygen chlorides at seven temperatures from 294 K to 193 K (P = 200 mbar or 7 mbar, considering the pressure effect is neglectable) (Table S4). To ensure the thermal equilibrium, these Raman measurements were taken on a sample about 30 min after the cold plate in PEACh reached the desired *T*. The peak position data was plotted in the same way as in Fig. 5. By the help of two black dotted lines (± 0.5 cm⁻¹) in each plot, we determine that there is no measurable shift of ν_1 Raman band as function of tem-



Fig. 6. Position variations of Raman ν_1 peak of anhydrous and hydrous oxychlorine salts as function of temperature in PEACh, at 200 mbar above 243 K, and at 7 mbar below 243 K. At least three Raman measurements were taken at different sampling spots for each sample and at each temperature. The distributions of Raman peak position are shown as a "box". Two dotted lines for each plot mark ± 0.5 cm⁻¹ range, i.e. the reproducibility of Raman measurements in this study. This data set demonstrates that there is no obvious temperature effect on the ν_1 peak position of these samples, except for NaClO₄ · H₂O whose ν_1 peak shows a sudden down-shift at 233 K.

perature, for all oxygen chlorides, except NaClO₄ · H₂O. The three boxes of NaClO₄ · H₂O at 233 K, 213 K, 193 K all shifted below the lower dotted line. This shift is suggestive of a phase change, which would be consistent with the model prediction of the stability of NaClO₄ · H₂O (down to 258 K) by Chevrier et al. (2009) and by Gough et al. (2011), while acknowledging that the instrumental resolution is insufficient to confirm the finding. In Fig. 6, three boxes of Mg(ClO₄)₂ · 6H₂O at 233 K, 213 K, 193 K also shifted slightly below the lower dotted line, i.e., shift >0.5 cm⁻¹. However, we have learned that the hydration state changes in Mg(ClO₄)₂ · xH₂O system would cause much large ν_1 shift, shown in Fig. 4. Thus we do not claim a phase change in Mg(ClO₄)₂ · 6H₂O based on these data.

Fig. 7a plots the down-shift of H₂O Raman peak positions of NaClO₄ \cdot H₂O and Mg(ClO₄) \cdot 6H₂O following the decrease of sample temperature in PEACh. Originally, NaClO₄ \cdot H₂O and Mg(ClO₄)₂ \cdot 6H₂O each has a single H₂O peak, at ~3531.9 cm⁻¹ and ~3529.5 cm⁻¹, with the H₂O peak of NaClO₄ \cdot H₂O nar-

rower than that of Mg(ClO₄)₂ · 6H₂O. From 294 K to 193 K, about 5.5 cm⁻¹ and 7.0 cm⁻¹ down-shift occur for the H₂O peaks of NaClO₄ · H₂O and Mg(ClO₄) · 6H₂O, respectively.

Considering that there is no meaningful shift observed for v_1 peak of Mg(ClO₄) · 6H₂O in tested temperature ranges, the downshift of its H₂O peaks could be caused by the thermal contraction of octahedra [Mg(H₂O)₆] in its crystal structure. The reduction in the length of Mg–OH₂ bond in [Mg(H₂O)₆] could increase the mass effect applied by Mg on the H₂O vibration, thus down-shifting the peak gradually with *T* decrease. A similar H₂O Raman peak downshift at low temperature was also observed by Chio et al. (2007) on FeSO₄ · H₂O. From 190 K to 8 K, a 12 cm⁻¹ down-shift was found in H₂O Raman peak, with the v_1 Raman peak position showing almost no change from 1017 cm⁻¹ to 1015 cm⁻¹ (the peak position accuracy of that study was stated as ± 2 cm⁻¹).

The H₂O Raman peak of Ca(ClO₄)₂ \cdot 2H₂O at 294 K consists of at least three sub-peaks, at 3478.1 cm⁻¹, 3524.9 cm⁻¹, and 3608.4 cm⁻¹ (Fig. 7b). Following the decrease of temperature, these sub-peaks shift to opposite directions and generate more splits (dotted black thin lines in Fig. 7b help to see these two types of changes). The visual inspection suggests the appearance of seven sub-peaks at 193 K, which is very similar to the phenomenon observed at 223 K by Fischer et al. (2014). Spectral deconvolution generated eight Gaussian sub-peaks, with the peak positions slightly different from those of Fischer et al. (2014).

On the basis of two previous studies, the split of H₂O Raman peak of a low-symmetry crystal can be caused by a structural modification at low temperature. At room T, the H_2O peak of MgSO₄ · 7H₂O has two sub-peaks. At 194.5 K, they further split into four sub-peaks (Fig. 2 of Wang et al., 2011), while its v_1 Raman peak has <1 cm⁻¹ peak shift. It is interesting that the XRD measurements taken at 194.5 K also show that each of the four XRD lines in $2\theta = 10-25^{\circ}$ range further splits into 4, 3, 2, and 3 sub-lines respectively (Fig. 5 of Wang et al., 2011). This phenomenon was interpreted to have been caused by differential contractions at low T along the different crystallographic axes of the unit cell, which actually results in a decrease of structural symmetry. A similar example is the symmetry reduction from $P2_12_12_1$ to $P2_1$ in sodium ammonium sulfate dehydrating with T change from 300 K to 20 K, reported by Lipinski et al. (2001). In the case of MgSO₄ \cdot 7H₂O, the decrease of structural symmetry introduces more crystallographic non-equivalent sites for structural water. The H₂O at each nonequivalent site would generate a sub-peak at different positions in 3200–4000 cm⁻¹ spectral range that resulting in the overall peak splitting. This phenomenon was also seen in FeSO₄ · 4H₂O (Fig. 8 of Chio et al., 2007), where its H₂O peak with original six sub-



Fig. 7. Position variations of H_2O Raman peak of hydrous Ca^{2+} , Mg^{2+} , Na-perchlorates as function of temperature in PEACh, at 200 mbar above 243 K and at 7 mbar below 243 K. (a) H_2O peaks of hydrous Na^+ and Mg^{2+} perchlorates show an obvious down-shift following the decrease of temperature; (b) The temperature effect on H_2O peaks of $Ca(ClO_4)_2 \cdot 2H_2O$ is mainly the gradual increase in sub-peak separation.



Fig. 8. In situ NIR ($1.4-2.6 \mu m$) spectra obtained by the WIR unit in PEACh. (a) Comparison of the spectra of Mg(ClO₄)₂ · 6H₂O and Ca(ClO₄)₂ · 2H₂O taken at 294 K and 243 K in PEACh (200 mbar, RH about 1%) shows no obvious temperature effect on NIR spectra. (b) Spectra of hydrous oxychlorine salts during 8 h continuous monitoring in PEACh at Room *T* and 200 mbar (RH about 1%). Dehydration of NaClO₄ · H₂O was evidenced, while no dehydration occurred in Mg(ClO₄)₂ · 6H₂O and Ca(ClO₄)₂ · 2H₂O.

peaks at room *T* further splits into ten sub-peaks at 8 K, with no shift of its v_1 Raman peak at 990 cm⁻¹. Our observation of the Raman spectral changes of Ca(ClO₄) · 2H₂O at 193 K is very similar to the above two observations, i.e., the splitting of H₂O Raman peaks and no measureable shift of v_1 Raman peak beyond the experimental uncertainty. We assign the decrease of structural symmetry at low *T* as the cause of these spectral changes.

On the basis of above discussion, we conclude that the temperature effect on the Raman spectra of Mg(ClO₄) \cdot 6H₂O and Ca(ClO₄) \cdot 2H₂O does exist, but only affecting H₂O Raman peaks. Because ν_1 Raman peak position demonstrated the best correlation with the change in degree of oxidation, cation, and hydration state of tested oxygen chlorides, the temperature difference would not interfere to identify them either in the laboratory experiment or during the exploration on Mars.

The details of NIR reflectance spectra taken using the WIR-BB-II will be discussed in section 4.3.

4.3. The stability of perchlorates in tested P-T range

4.3.1. $Mg(ClO_4)_2 \cdot 6H_2O$ and $Ca(ClO_4)_2 \cdot 2H_2O$

Thermodynamic modeling suggests that the Mg(ClO₄)₂ · 6H₂O phase would be stable down to 206 K at a relative humidity >44% (Chevrier et al., 2009). This prediction was validated by a rapid rehydration experiment (within 12 h) from anhydrous Mg(ClO₄)₂ to Mg(ClO₄)₂ · 6H₂O at 263 K and 0.5% RH by Robertson and Bish (2011) using XRD for the phase ID.

Our experiments on these two perchlorates at 193 K and 7 mbar CO₂ atmospheric pressure (RH < 1%) in PEACh support above predictions, which demonstrates no ν_1 Raman peak shifts beyond experimental uncertainty (Figs. 5 and 6). This conclusion is further confirmed by our NIR reflectance measurement using the WIR-BB-II taken at low *P*–*T* in PEACh. The perfect overlap of two NIR spectra taken at 294 K and 243 K (*P* = 200 mbar) is reached for both Mg(ClO₄) \cdot 6H₂O and Ca(ClO₄)₂ \cdot 2H₂O (Fig. 8a). Our NIR reflectance observations are consistent with those made by Hanley et al. (2014) on Mg(ClO₄) \cdot 6H₂O (down to 80 K).

4.3.2. NaClO₄ · H₂O

For NaClO₄ · H₂O, changes in its NIR reflectance spectra were observed at 200 mbar, appearing as the gradual reduction with time in band depths of its NIR bands at 1.43 µm, 1.93 µm, 2.14 µm. The decrease of NIR band depth is an indication of dehydration process that worth further study. These NIR bands only appear in the spectra of tested hydrous oxygen chlorides. The band at 1.43 µm is assigned to the H₂O stretching overtone and the band at 1.93 µm is assigned to the combination of the H₂O stretching mode and the H₂O bending mode.



Fig. 9. (a) The decrease of absorption band area near 1.5 µm of NaClO₄ · H₂O as function of time in PEACh (200 mbar) at different temperatures (W₀ = NaClO₄; W₁ = NaClO₄ · H₂O; W_x = NaClO₄ · xH₂O (0 < x < 1)); (b) Dehydration rate of NaClO₄ · H₂O at different temperatures, showing the decrease of dehydration at low *T*.

To further study the dehydration process, we conducted a set of six experiments in PEACh, at room temperature (294 K) and low pressure (200 mbar) in CO₂ atmosphere (the RH < 1%), with NaClO₄ · H₂O, Mg(ClO₄)₂ · 6H₂O and Ca(ClO₄)₂ · 2H₂O as starting phases. NIR reflectance spectra and Raman spectra were taken at selected time intervals as 0 h, 1.1 h, 2.3 h, 4.0 h, 6.3 h, 8.3 h. Fig. 8b shows the sequentially recorded NIR spectra from three hydrous perchlorates. The perfect spectral overlap was observed for Mg(ClO₄)₂ · 6H₂O and Ca(ClO₄)₂ · 2H₂O, while a very obvious dehydration of NaClO₄ · H₂O was noticed. Also the Raman spectra of NaClO₄ · H₂O showed a gradual reduction of the intensity of H₂O Raman peak at ~3531 cm⁻¹.

In order to quantify this dehydration process of NaClO₄ · H₂O with function of temperature, we added another four sets of dehydration experiments at 288 K, 283 K, 278 K and 273 K in the PEACh, accompanied with five to seven NIR measurements at ~1 h interval. The H₂O absorption band at 1.43 µm was selected and its band area was calculated by the InfraSpec WIR-BB-II software after translating the reflectance into absorbance. The band area values changed as function of time duration (hour) at different temperatures were shown in the Fig. 9a, which revealed the kinetics of this dehydration process.

As seen in Fig. 9a, the area value of H_2O NIR band declined more quickly at higher temperatures (294 K or 283 K). When the

temperature dropped to 273 K, almost no dehydration was observable in the 7.5 h experiment. To enhance the presentation of this kinetic character, the slope of each curve in Fig. 9a was calculated using the first-order least square linear fitting of Matlab (version 7.0, Eigenvector Research, Inc., Manson, WA). A strong negative correlation was shown between the curve slopes and the temperature (Fig. 9b). Unfortunately, the 7–8 h time duration in PEACh was not enough for NaClO₄ · H₂O to reach total dehydration, even at 294 K evidenced by remaining H₂O Raman peak at 3531 cm⁻¹. Thus we could not use these data to derive the activation energy E_a . Nevertheless, the general trend of this dehydration matches with Arrhenium equation, i.e., an inversed temperature dependence of dehydration rate.

The fact that $NaClO_4 \cdot H_2O$ was nearly total dehydrated in 7-8 h at 200 mbar and 294 K with RH < 1% suggests that Naperchlorates, if present at the Mars surface, would be in the anhydrous form with no NIR spectral features. This conclusion based on the stability of NaClO₄ \cdot H₂O poses a doubt on the assignment made by Ojha et al. (2015) on the NIR spectra features of NaClO₄ \cdot H₂O observed from one RSL site (on the wall of Horowitz crater). The <1% RH level in our experiment matches the daytime RH levels measured at Viking lander-1 site, two MER-sites, and MSL-site. It suggests the dehydration of NaClO₄ · H₂O would go to completion at surface of Mars during the daytime hours. The higher RH levels (100% for Viking and MERs, 50% for MSL, Savijärvi, 1995; Harri et al., 2014) were only found in a few early morning hours at those sites. Whether the rehydration of NaClO₄ can happen and can reach the completion in a few hours at such low temperature depends on its rehydration rate (would slow down quickly with T decreases). Experimental studies have demonstrated the impossibility of rehydrating Mg-sulfates during a few early morning hours in a diurnal cycle (Wang et al., 2011, 2013). Based on current knowledge, we think NaClO₄ should be in anhydrous form at Mars surface.

5. Conclusions

S and Cl were detected in every samples analyzed by all Mars surface exploration missions, with H implied in many. H, S, Cl are three highly mobile elements in the near surface atmosphere, the surface, and the shallow subsurface on Mars, which make the studies of the sulfur, chlorine and hydrogen cycles extremely important for fundamental science of Mars.

Up to now, oxygen chlorides were detected at four landing sites and at four active RSL regions. However, the global distribution of perchlorates and their concentration relative to other chlorine species are largely unknown (except at Phoenix site). Laboratory simulation experiments will provide scientific knowledge that can help to fill the knowledge gaps.

The three findings in the experiments, i.e (1) the v_1 Raman peak position to identify the cation speciation, hydration state and oxidation state; (2) the *T* and *P* effect on v_1 and H₂O Raman peak position; (3) the phase transition properties of Mg(ClO₄)₂ · 6H₂O and Ca(ClO₄)₂ · 2H₂O and NaClO₄ · H₂O under simulated Martian conditions, reported here provide a fundamental characterization of these materials, which will be needed for further *in situ* study of the pathways and rates of oxygen chlorides generation as stimulated by ESD during dust storms and dust devils on Mars. The NIR and Raman spectral features of perchlorates and other oxygen chlorides can provide critical information to interpret some orbital remote sensing data and to identify their oxidation states, hydrous states and cation species during future landed missions on Mars. The characterized low temperature effect on Raman spectral features is also useful for the explorations of other planetary bodies.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2016.07.044.

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