Cryogenic origin of fractionation between perchlorate and chloride under modern martian climate

Dongdong Li1,2, Yu-Yan Sara Zhao3,4,5✉, Pierre-Yves Meslin6, Margaux Vals7, François Forget7 & Zhongchen Wu8

The high perchlorate (ClO₄⁻) to chloride (Cl⁻) ratios observed at the Phoenix landing site, northern polar region of Mars, have been puzzling since detection. However, a lack of understanding of perchlorate-chloride-water systems under cryogenic conditions makes it difficult to assess ClO₄⁻/Cl⁻ ratios during deliquescence-related processes. Here we quantitatively evaluate ClO₄⁻/Cl⁻ fractionation in deliquescence-induced brines of magnesium- and calcium-perchlorate-chloride salt mixtures under subzero conditions, by measuring solubility data and constructing temperature-dependent thermodynamic models. We find that under specific relative humidity (RH) and temperature (T) conditions, deliquescence of perchlorate-chloride mixtures may form brines with fractionated ClO₄⁻/Cl⁻ signatures. Appropriate RH-T, water-limited conditions, and aeolian processes are required to produce and preserve the elevated ClO₄⁻/Cl⁻ signatures in soils. Under the present climate, the north polar region can support ClO₄⁻/Cl⁻ fractionation and potentially enrich perchlorate for longer periods on global Mars. This highlights the uniqueness of Mars’ arctic environment and its implications for modern habitability.

1 Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining, China. 2 Key Laboratory of Salt Lake Resources Chemistry of Qinghai Province, Xining, China. 3 Center for Lunar and Planetary Sciences, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China. 4 CAS Center for Excellence in Comparative Planetology, Hefei, China. 5 International Center for Planetary Science, College of Geosciences, Chengdu University of Technology, Chengdu, China. 6 Institut de Recherche en Astrophysique et Planétologie (IRAP), Université de Toulouse, OMP-CNRS-UPS, Toulouse, France. 7 Laboratoire de Météorologie Dynamique (LMD/IPSL/CNRS), Sorbonne Université, Paris, France. 8 Institute of Space Sciences, Shandong University, Weihai, China. ✉email: zhaoyuyan@mail.gyig.ac.cn
Perchlorate (ClO$_4^-$) and chlorate (ClO$_3^-$) have important implications for the habitability of Mars, such as aqueous activities\textsuperscript{1-3}, redox capabilities\textsuperscript{4-6}, and bioavailability\textsuperscript{7}. Understanding the distribution and speciation of oxycarbonate species on Mars is also critical for understanding the chlorine cycle on the Martian soil-atmosphere interface\textsuperscript{8}, and critical for the detection of organic signals, and hazards and in situ resources for future human exploration\textsuperscript{9}. To date, perchlorate or oxycarbonate species (ClO$_x^-$; equivalent to ClO$_2^-$ + ClO$_3^-$) have been detected on Mars in surface soils, sedimentary rocks, and Martian meteorites\textsuperscript{10-16}. Natural perchlorate and chlorate are also observed in (hyper)arid environments on Earth (e.g., Atacama, Antarctic Dry Valleys) and in the surface samples of the moon and chondritic meteorites, indicating a ubiquitous presence of oxycarbonate species across the inner solar system\textsuperscript{7,18}.

Among all the sites where perchlorate has been reported on Mars, the Phoenix landing site (68.2188°N, 125.7492°W) of the Vastitas Borealis is unique. The surface soil samples exhibit high ClO$_4^-$ abundance (0.62–0.67 wt%) and low Cl$^-$ abundance (0.03–0.05 wt%)\textsuperscript{15}, which results in an average ClO$_4^-$/Cl$^-$ molar ratio of 6.13. Assuming $C_{\text{total}} = Cl^-$ + ClO$_4^-$, the average ClO$_4^-$/Cl$^-$ molar ratio is equivalent to a ClO$_4^-$/Cl$_{\text{total}}$ molar ratio of 0.85. For comparison, such high ClO$_4^-$/Cl$_{\text{total}}$ molar ratios are rare and distinctive from any other Mars or terrestrial natural samples analyzed to date. Two aolian samples at Gale Crater (4.5895°S, 137.4417°E) contain comparable levels of ClO$_4^-$ (0.38 ± 0.16 wt% for Rocknest; 0.21 ± 0.06 wt% for Gobabeb)\textsuperscript{15}, but much lower ClO$_4^-$/Cl$_{\text{total}}$ ratios (0.20 ± 0.07 for Rocknest; 0.15 ± 0.04 for Gobabeb\textsuperscript{15}). Perchlorate (≤ 0.1 wt%) has also been suggested for soils at the two Viking landing sites (Viking 1: 22.27°N, 312.05°E; Viking 2: 47.64°N, 225.71°W)\textsuperscript{19}. Using the average Cl$_{\text{total}}$ of 0.8 wt%\textsuperscript{20} for calculation, the ClO$_4^-$/Cl$_{\text{total}}$ ratio is estimated to be 0.04. Sedimentary outcrops of Gale Crater show a large variation in ClO$_4^-$ abundances (from ~0 to 1.2 wt%), and the ClO$_4^-$/Cl$_{\text{total}}$ molar ratios are generally between 0.04 ± 0.02 and 0.18 ± 0.04, with only one exception of 0.27 ± 0.10 (mudstone sample “Cumberland”)\textsuperscript{15}. Martian meteorites “EET79001” (0.00006 wt% ClO$_4^-$; 0.00014 wt% ClO$_3^-$)\textsuperscript{14} and “Tissint” (0.00007 wt% ClO$_3^-$)\textsuperscript{16} report ClO$_4^-$/Cl$_{\text{total}}$ ratios of 0.20 and 0.01, respectively. Of the terrestrial soils/clalisches explored to date, Atacama samples contain the highest ClO$_4^-$/Cl$_{\text{total}}$ molar ratio of 0.0008\textsuperscript{37}. Other terrestrial and extraterrestrial soil/rock samples have ClO$_4^-$/Cl$_{\text{total}}$ molar ratios at least an order of magnitude lower than those of Atacama samples\textsuperscript{17,18}.

High ClO$_4^-$/Cl$^-$ and ClO$_4^-$/Cl$_{\text{total}}$ ratios found in Phoenix soils might be formed primarily via direct production of ClO$_4^-$ from Cl$^-$ (i.e., generation mechanisms) or some concentration pathways of already formed ClO$_4^-$ (i.e., enrichment mechanisms). However, the generation mechanisms are unlikely because Martian and terrestrial natural samples rarely contain ClO$_4^-$/Cl$_{\text{total}}$ molar ratios higher than 0.2, and simulation experiments producing ClO$_4^-$ species from chloride (via photochemistry, electrochemistry, and ozone oxidation) have not reported any ClO$_4^-$/Cl$_{\text{total}}$ molar ratios higher than 0.1\textsuperscript{21-24}. Enrichment mechanisms such as deliquescence of perchlorate salts (i.e., moisture-absorption and dissolution of the salts and eutectic melting of salt-ice mixtures) have been proposed to produce brines that may translocate and concentrate perchlorate\textsuperscript{25-27}. However, a lack of understanding of perchlorate-chloride-water ternary systems under cryogenic conditions makes it difficult to evaluate the ClO$_4^-$/Cl$^-$ signatures in such brines.

Here we quantitatively evaluate ClO$_4^-$/Cl$^-$ fractionation in deliquescence-induced brines of magnesium- and calcium-perchlorate-chloride salt mixtures under subzero conditions, by measuring solubility data (233.15 K to 273.15 K) and constructed phase diagrams (180 K to 300 K) with the aid of temperature-dependent thermodynamic models. We find that under specific relative humidity (RH) and temperature (T) conditions, deliquescence of perchlorate-chloride mixtures may form brines with fractionated ClO$_4^-$/Cl$^-$ signatures. Appropriate RH-T, water-limited conditions, and aeolian processes are required to produce and preserve the elevated ClO$_4^-$/Cl$^-$ signatures in soils. Under the present climate, the north polar region can support ClO$_4^-$/Cl$^-$ fractionation and potentially enrich perchlorate for longer periods on global Mars. Our work highlights that the high ClO$_4^-$/Cl$^-$ ratios detected in the Phoenix surface soil are produced by local environmental conditions and surface processes and may not be generalized to global Mars. It also indicates the uniqueness of Mars’ arctic environment and its implications for modern habitability. In addition, the high ClO$_4^-$/Cl$^-$ signatures might be further used as a chemical signature to infer deliquescence in a liquid water-limited environment for Mars.

Results and discussion

Thermodynamic constraints on deliquescence of perchlorate-chloride-water systems. We focus on the ternary systems Mg(ClO$_4$)$_2$ + MgCl$_2$ + H$_2$O and Ca(ClO$_4$)$_2$ + CaCl$_2$ + H$_2$O, which are the two most plausible systems suggested for soluted salts in Phoenix soils\textsuperscript{28-30}. Using isothermal solid-liquid equilibriums experiments, we experimentally measure solubility data at 273.15 K, 248.15 K, and 233.15 K for the Mg(ClO$_4$)$_2$ + MgCl$_2$ + H$_2$O system (Supplementary Table 1) and at 263.15 K, 248.15 K, and 233.15 K for the Ca(ClO$_4$)$_2$ + CaCl$_2$ + H$_2$O system (Supplementary Table 2), respectively. Supported by these ternary solubility data, we developed reliable temperature-dependent thermodynamic models for these ternary systems from 180 K to 300 K. The experimental and modeling results and validation of the thermodynamic models are available in the Supplementary Information (Supplementary Notes 1-5; Supplementary Tables 3-6; Supplementary Figs. 4-15).

During deliquescence of perchlorate-chloride salt mixtures, the substantial difference in solubility of perchlorate- and chloride-salts under specific RH-T conditions may result in fractionated ClO$_4^-$/Cl$^-$ signatures in the formed brines. Deliquescence surfaces of Mg- and Ca-perchlorate-chloride salt mixtures (i.e., Mg(ClO$_4$)$_2$+6H$_2$O + MgCl$_2$+4H$_2$O, x = 6, 8, 12; Ca(ClO$_4$)$_2$+6H$_2$O + CaCl$_2$+6H$_2$O) in the coordinates of ClO$_4^-$/Cl$_{\text{total}}$-RH-T are shown in Fig. 1 (Supplementary Data 1). For a specific salt mixture, the intersections of the deliquescence surface and the lower- and upper-T boundaries (i.e., dark cyan and dark red planes, respectively, in Fig. 1) constrain the RH-T conditions allowing for ClO$_4^-$/Cl$^-$ fractionation to occur. Deliquescence of perchlorate salt is preferred between the two boundaries while partial chloride salt remains solid, producing a brine with elevated ClO$_4^-$/Cl$^-$ ratios compared to its parent salt mixture. Above the upper T boundary, both perchlorate and chloride salts can fully deliquesc; under the lower T boundary, both perchlorate and chloride salts remain solids. Neither of the latter two cases would produce fractionated ClO$_4^-$/Cl$^-$ signatures.

Note that we did not include chloride (ClO$_3^-$) in our experiments and model, although it is an essential component of oxycarbonate species that may be present at both Phoenix site\textsuperscript{30} and Gale Crater\textsuperscript{29,31} on Mars, with equal or higher abundances than perchlorates\textsuperscript{24}. The rationales for not involving chloride in this work are mainly because (i) general lack of water activity, thermal and cryogenic solubility data for binary chlorate systems; (ii) the absence of ternary solubility data on chloride systems; and (iii) experimental complexities to include Cl$^-$, ClO$_4^-$ and ClO$_3^-$ in one system. Consequently, the subsequent discussion and conceptual model in the following sections are limited to the ClO$_4^-$/Cl$^-$-H$_2$O system without considering the potential interference of chloride. Future systematic experimental and
metastable state (under a thermodynamically stable state with the lowest eutectic of Ca(ClO₄)₂).

**Legend** are the interfaces for the phase transition of ternary ClO₄⁻-water system (i.e., ClO₄⁻-surfaces, below which deliquescence would occur. The upper- and upper-T boundaries for Mg(ClO₄)₂ are the deliquescence surfaces and the lower- and upper- T boundaries) for Mg(ClO₄)₂•6H₂O-MgCl₂•6H₂O (Fig. 2a-III) and Ca(ClO₄)₂•6H₂O-CaCl₂•6H₂O (Fig. 2a-IV), which may facilitate the formation of brines with elevated ClO₄⁻/Cl⁻ fractionation signs. The RH-T data are close but not in contact with the lowest eutectic points for the Mg(ClO₄)₂•6H₂O-MgCl₂•12H₂O or Mg(ClO₄)₂•6H₂O-MgCl₂•8H₂O cases (Fig. 2a-I and 2a-II). However, given the limited duration of the Phoenix mission (total lifetime 152 sols; Ls = 77° to Ls = 151°), we speculate that the RH-T conditions of Phoenix also likely support at least partial deliquescence and ClO₄⁻/Cl⁻ fractionation in the latter cases.

At Gale Crater, the Rover Environmental Monitoring Station (REMS) onboard the Curiosity rover recorded RH-T data. We examined the in situ RH-T data of the first four Martian years (Figure S17), which account for all the available data at the time of writing. Since the REMS data record the RH-T conditions at 1.6 m above the ground, surface brightness temperatures (Tsurf) modeling work on binary and ternary chlorate systems for cryogenic conditions is necessary to obtain fundamental insights.

**Deliquescence and potential perchlorate/chloride fractionation at the Phoenix site versus Gale Crater.** Combining the thermodynamic constraints and in situ RH-T measurements, we can further constrain the deliquescence behavior of Mg- and Ca-perchlorate-chloride salt mixtures at the Phoenix site and Gale Crater on Mars. At the Phoenix site, the surface RH-T conditions recorded by the Thermal and Electrical Conductivity Probe (TECP; recalibrated data) can support the deliquescence of Mg- and Ca-perchlorate-chloride salt mixtures (Fig. 2a; Supplementary Data 2). Of the four salt mixtures, the RH-T data of the Phoenix site overlap well with the RH-T condition ranges supporting the ClO₄⁻/Cl⁻ fractionation (i.e., intersections of the deliquescence surfaces and the lower- and upper- T boundaries) for Mg(ClO₄)₂•6H₂O-MgCl₂•6H₂O (Fig. 2a-III) and Ca(ClO₄)₂•6H₂O-CaCl₂•6H₂O (Fig. 2a-IV), which may facilitate the formation of brines with elevated ClO₄⁻/Cl⁻ fractionation signs.

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measured by the Ground Temperature Sensor (GTS) were also processed for comparison. We find that the REMS and GTS datasets show no difference in terms of supporting deliquescence at Gale Crater, but the GTS data contain higher uncertainties that would propagate to the derived RH data (Supplementary Figs. 18 and 19). Therefore, we use the REMS data to discuss the Gale Crater environments (Fig. 2b). The variation in RH–T conditions along the traverse of the Curiosity rover is primarily due to the change in ground properties (e.g., thermal inertia and porosity) from loessened regolith to solid bedrock, as the rover started to climb the Mount Sharp (sol 1800 onwards)34. Consequently, the RH–T conditions of the first three Martian years at Gale Crater would support the deliquescence of Ca(ClO$_4$)$_2$·6H$_2$O–CaCl$_2$·6H$_2$O but not for any of the Mg salt mixtures (Fig. 2b; Supplementary Fig. 17). In the fourth Martian year, deliquescence and ClO$_4$−/Cl$^-$ fractionation can occur for both the Mg(ClO$_4$)$_2$·6H$_2$O–MgCl$_2$·6H$_2$O and Ca(ClO$_4$)$_2$·6H$_2$O–CaCl$_2$·6H$_2$O systems (Supplementary Fig. 17). The O$_2$ and HCl evolution patterns during pyrolysis of the aeolian samples “Rocknest” and “Gobabe” suggest that the cations of the oxychlorine species are likely Na, K and Ca39. We find that the absence of ClO$_4$−/Cl$^-$ fractionation in these samples during the first three Martian years might further rule out Ca-perchlorate. The lack of pyrolysis analyses for oxychlorine in soil/aeolian samples after “Gobabe” (elevation −4.424 km)9 makes it difficult to evaluate the possible ClO$_4$−/Cl$^-$ molar ratios at higher elevations along the rover traverse. Note that ClO$_4$−/Cl$^-$ ratios detected in the drilled samples from the bedrock mainly represent rock characteristics influenced by aqueous processes rather than atmosphere–solid interactions and thus are irrelevant to the model we discuss in this study.

Deliquescent brine at the Phoenix site would contain substantially elevated ClO$_4$−/Cl$^-$ signatures compared to their parent salt mixtures. For example, the deliquescence of the Mg(ClO$_4$)$_2$·6H$_2$O–MgCl$_2$·6H$_2$O salt mixture would produce a brine with a nearly fixed ClO$_4$−/Cl$^-$ molar ratio of 2.5 (Fig. 3a; Supplementary Data 3). The Ca(ClO$_4$)$_2$·6H$_2$O–CaCl$_2$·6H$_2$O salt mixture would form a brine with a ClO$_4$−/Cl$^-$ molar ratio ranging from 9.0 to 13.3 (Fig. 3b). For MgCl$_2$·6H$_2$O and MgCl$_2$·12H$_2$O instead of MgCl$_2$·6H$_2$O, using the inferred lowest eutectic points for calculation, the formed brines would have ClO$_4$−/Cl$^-$ molar ratios of 14.4 and 62.6, respectively. Our calculations assume complete separation of formed brines and residual chloride salts and thus provide the upper limit for the deliquescence-induced ClO$_4$−/Cl$^-$ molar ratios. The measured ClO$_4$−/Cl$^-$ of 6.1315 in Phoenix soil can form via either Mg or Ca salt mixtures, but the Mg(ClO$_4$)$_2$·6H$_2$O–MgCl$_2$·6H$_2$O system is unlikely to be the parent salt mixture since it cannot produce a ClO$_4$−/Cl$^-$ ratio higher than 2.5.

For reference, we also analyzed relevant data from McMurdo Dry Valleys (MDV), Antarctica. The MDV is considered an excellent analog site for the northern plains of Mars because of the arid conditions, intense UV solar radiation, diurnal freeze/thaw cycles, sparse snowfall, cryogenic processes, low mean temperatures, and Mars-like surface topography35. Our results show that the RH–T conditions of Antarctica would produce substantial liquid water and dissolve both ClO$_4$− and Cl$^-$ and may not result in ClO$_4$−/Cl$^-$ fractionation (Supplementary Note 6 and Supplementary Fig. 20). This result is consistent with the absence of ClO$_4$−/Cl$^-$ fractionation found in samples of MDV35,36.

**RH–T conditions of global Mars that can support perchlorate/chloride fractionation.** Using the RH–T constraints obtained from the phase diagrams (Supplementary Fig. S1; Supplementary Table 7), we map the Martian surface for regions of which the RH-

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**Fig. 2 Deliquescence-induced brine formation at the Phoenix landing site and Gale Crater.** a) In situ RH–T data of the Phoenix landing site are overlaid onto the deliquescence surfaces of the salt mixtures. I: Mg(ClO$_4$)$_2$·6H$_2$O–MgCl$_2$·12H$_2$O; II: Mg(ClO$_4$)$_2$·6H$_2$O–MgCl$_2$·6H$_2$O; III: Mg(ClO$_4$)$_2$·6H$_2$O–MgCl$_2$·6H$_2$O–CaCl$_2$·6H$_2$O. The dark gray regions are the projection of the ternary deliquescence surfaces, and the dark cyan and dark red horizontal lines are the projections of the lower- and upper- T boundary planes, respectively, as shown in Fig. 1. The green dots are in situ RH–T measurements. The thick solid dark-cyan curve is the best fit line, and the thin dashed dark-cyan curves are the 10 K uncertainty boundaries. Salt mixtures of Mg(ClO$_4$)$_2$·6H$_2$O–MgCl$_2$·6H$_2$O and Ca(ClO$_4$)$_2$·6H$_2$O–CaCl$_2$·6H$_2$O may facilitate the formation of brines with elevated ClO$_4$−/Cl$^-$ signatures. b) In situ RH–T data of Gale Crater overlaid on the deliquescence surfaces of the salt mixtures. The dark gray ternary deliquescence surfaces and the lower- and upper- T boundary lines of subfigures I to IV are the same as shown in (a). The colored dots are the in situ RH–T data (REMS; sols 526, 531, 548, 549, 551, and 554 to 561 with maximum yearly humidity). The RH–T conditions of the first Martian year at Gale Crater would support the deliquescence of Ca(ClO$_4$)$_2$·6H$_2$O–CaCl$_2$·6H$_2$O but not for any of the Mg salt mixtures.
A conceptual model for the formation and preservation of high perchlorate/chloride ratios on the Martian surface. Three essential factors are crucial for the formation and preservation of fractionated ClO$_4^-$/Cl$^-$ signatures. First, the RH-T conditions should be suitable for deliquescence to occur. Second, the water source should be limited in quantity since any substantial liquid-water interactions would dissolve both ClO$_4^-$ and Cl$^-$ and obliterate the fractionation signatures. Third, subsequent separation of the perchlorate-enriched brines and chloride-enriched salts is necessary for the ClO$_4^-$/Cl$^-$ signatures to be detected. In this scenario, the transient brines formed under water-limited conditions would be primarily confined onto the particle surface or intergranular pores, and thus, their spatial translocation would be substantially constrained. We suggest that translocation of the salts with soil/dust particles via aeolian processes may be a more practical way to form a locally homogeneous ClO$_4^-$/Cl$^-$ signature, as detected in Phoenix soils.

We propose a conceptual model for forming and preserving high ClO$_4^-$/Cl$^-$ ratios on the present Martian surface (Fig. 5). (1) Aeolian processes (e.g., dust storms/dust devils) continuously transfer dust/soil particles coated with perchlorate-chloride salt mixtures (ClO$_4^-$/Cl$^-$ ratios presumably at the global-average level) to some region (e.g., the Mars arctic region). Dust is likely to be the primary carrier of perchlorates and chlorides, given the high efficiency in converting chlorides to perchlorates on the dust particles. (2) Under appropriate RH-T conditions (e.g., the Phoenix landing site), deliquescence of the perchlorate-chloride salt mixture by interaction with water-vapor or water-ice produces transient brines containing fractionated ClO$_4^-$/Cl$^-$ signatures. The specific ratios depend on the parental salts and the RH-T conditions. (3) Dust/soil particles cemented with brines would be more resistant to aeolian translocation (e.g., during the impact of saltating particles) than dry ClO$_4^-$-depleted dust/soil particles. In this way, perchlorates preferentially accumulate while chlorides are more likely to be transported locally or regionally. The texture of the Phoenix soils supports this conceptual model well—a geologically young soil (for the current RH-T conditions to remain applicable), with active reworking (by dust deposition/lifting) and without interaction with extensive liquid water. The
cohesive and cloddy nature of the soils indicates an interaction between ice/absorbed water and salty soil in place. The soil profile demonstrates homogeneity in terms of soil microstructure, and no substantial difference in soil particles is observed above and below the ice table. Microscopic analysis of the Phoenix soil particles suggests that the soil is aeolian in origin and the particles may have undergone long-distance translocation (>500 km) via air-fall dust processes or saltation. The three soil samples “Rosy Red”, “Sorceress 1”, and “Sorceress 2”, composing the topmost ~5 cm of the soil profile, each contain evenly distributed ClO$_4^-$ concentrations and high ClO$_4^-$/Cl$^-$ ratios.

As a result of strong winds induced by baroclinic transient waves occurring at high northern latitudes in the autumn and winter seasons, most regional-scale dust storms originate from the northern plains. Frequent local and regional-scale dust storms take place between latitudes ~30–80°N. These dust storms enable regional or global circulation of dust across latitudes and facilitate material exchange in and out of the north polar region. Dust storm simulations (e.g., for MY25 and MY34) indicate the general north polar region and the Phoenix site to be an active region in terms of dust activity, which may facilitate dust/soil translocation in that region. Interestingly, the Acidalia-Chryse and Utopia Planitiae regions, which also stand out in Fig. 4, are known to be “storm tracks” where regional-scale dust storms develop, which acts in favor of the proposed scenario in these regions.

The essential factors required for the formation and preservation of fractionated ClO$_4^-$/Cl$^-$ signatures in turn impose environmental constraints on the site where high ClO$_4^-$/Cl$^-$ signatures are detected. At the Phoenix site, for instance, we estimated that the deposition of an ~5-cm thick dust layer requires ~1.5 kyr to 13.7 kyr (Earth years) by using the rate of dust settling measured during the Phoenix mission lifetime (“fiducials” data of 0.05 ± 0.04 μm per sol, representing any random patch on the lander deck). Additionally, by using the north polar dust sedimentation rates (0.6~1 mg cm$^{-2}$ yr$^{-1}$) and assuming a bulk density of 1.2 g cm$^{-3}$ of the dust, we obtained a consistent estimated 6–10 kyr (Earth years) for a 5-cm dust accumulation. This estimated time-scale is consistent with the time proposed for ground ice formation by diffusive equilibrium (hundreds to thousands of years) and the formation of a shallow ice table within ~100 kyr under the current Martian climate regime. Therefore, the active dust processes and the specific RH- T conditions may have lasted for approximately a few to tens of kyr at the Phoenix site.

Our study indicates that environmental conditions and surface processes operate cooperatively to produce and preserve fractionated ClO$_4^-$/Cl$^-$ signatures under the present climate of Mars. The north polar region of Mars, in particular, is a region that can best support ClO$_4^-$/Cl$^-$ fractionation and ClO$_4^-$/Cl$^-$ enrichment. Such fractionation and enrichment of perchlorates, if lasting for a few tens to hundreds of kyr or longer, would support the

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**Fig. 4 Time fraction of a Mars year under the present climate where surface RH-T conditions can support ClO$_4^-$/Cl$^-$ fractionation for Mg- or Ca-perchlorate-chloride salt mixtures.** a-c are for the Mg-salt mixture, with the hydrated state of Mg-chloride varying from 12H$_2$O, 8H$_2$O, and 6H$_2$O, respectively. d is for Ca(ClO$_4$)$_2$·6H$_2$O-CaCl$_2$·6H$_2$O. A ClO$_4^-$/Cl$_{total}$ molar ratio >0.2 is used as the indicator of perchlorate/chloride fractionation and the corresponding boundary conditions for each salt mixture are shown in Supplementary Fig. 19 and Supplementary Table 7. PHX represents the Phoenix landing site; VL1 and VL2 represent Viking Landers 1 and 2, respectively; GC represents the Gale Crater. Regions without colors indicate that the surface RH- T conditions would never support ClO$_4^-$/Cl$^-$ fractionation. Globally, the north polar region can maintain ClO$_4^-$/Cl$^-$ fractionation for the longest time with both Mg- and Ca- salt mixtures. Compared to the Phoenix site, Viking Landers 1 and 2 and Gale Crater are located in regions with a shorter time fraction. Dynamics of the water cycle and parental salts are critical controlling factors. See the text for discussion.
Dust/soil particles. In this way, perchlorates preferentially accumulate in brines would resist aeolian translocation better than dry ClO$_4^-$ (e.g., the Mars arctic region). Deliquescence of the perchlorate-chloride salt mixture by interaction with water-vapor or water-ice can produce transient brines containing fractionated ClO$_4^−$ (Cl$^−$) signatures. The specific ratios depend on the parent salts and the RH-T conditions. Dust/solid particles cemented with brines would resist aeolian translocation better than dry ClO$_4^−$ -depleted dust/solid particles. In this way, perchlorates preferentially accumulate in place while chlorides are more likely to be transported away.

formation of a lubricating brine in the basal ice layer and facilitate the flow of the northern ice cap36. The enrichment of perchlorates in the north polar region also offers implications for modern habitability. On the one hand, the (meta)stable brines that were formed are likely high in salinity and low in water activity, which are not habitable to any known terrestrial life55,56. On the other hand, concentrated perchlorates can facilitate water adsorption due to their hygroscopic characteristics and result in the regolith holding a substantial fraction of the water inventory57. Such water-rich regolith may shelter against radiation doses and provide safe habitats underground for potential extant life58.

Methods

Experimental measurements of ternary solubility at subzero temperatures. An isothermal method was used to determine the solid-liquid phase equilibria in the ternary systems Mg(ClO$_4^-$)$_2$ - MgCl$_2$ - H$_2$O and Ca(ClO$_4^-$)$_2$ - CaCl$_2$ - H$_2$O. The experiments were conducted at 273.15 K, 263.15 K, 248.15 K, and 233.15 K, respectively. Magnesium chloride hexahydrate and calcium chloride dihydrate (MgCl$_2$·6H$_2$O, purity ≥99.0 wt%, CAS No. 7758-18-6; CaCl$_2$·2H$_2$O, purity ≥99.0 wt%, CAS No. 10035-04-9; Shanghai Sinopharm Chemical Reagent Co., Ltd) were purified by one-time recrystallization with an approximately 60% salt recovery. The final purity, as analyzed by Inductively Coupled Plasma Emission Spectrometry was >99.95 wt%. Magnesium perchlorate hexahydrate (Mg(ClO$_4^-$)$_2$·6H$_2$O, purity ≥99.99 wt% metals basis, CAS No. 13446-19-0, Aladdín Industrial Co.) and calcium perchlorate tetrahydrate (Ca(ClO$_4^-$)$_2$·4H$_2$O, purity ≥99.8 wt%, CAS No. 13627-98-8, Acros) were directly used without further purification. Ultrapure water (18 MQ) was used in all experiments. A thermostatic water bath with a refrigerating machine (Lauda Command and DLK45, Germany) was used to perform the cryogenic phase equilibria experiments (Supplementary Fig. 1). The temperature uncertainty of the whole thermostat system was controlled within 0.05 K. A 250 ml flat-bottom glass tube with a PTFE stopper and overhead mechanical stirrer was used as the container (i.e., solubility cells in Supplementary Fig. 1). The reaction mixtures were prepared by weighing ultrapure water and the appropriate amount of perchlorate and chloride reagents to fill 1/4 of the reaction container. The container with the reaction mixture was lowered into a water bath until the water covered most of the container. The experiments were conducted at 273.15 K, 263.15 K, 248.15 K, and 233.15 K, respectively. The mixtures were equilibrated for five days at 273.15 K and for at least ten days at 263.15 K, 248.15 K, and 233.15 K, due to the slow rates in reaching equilibrium at subzero temperatures. Throughout the experiments, the reaction mixtures were stirred thoroughly.

As a conventional analysis method used by physical chemists in thermodynamic experiments, the chemical compositions of the supernatants filtered using 0.45 μm syringe filters were determined by mass titration of Mg$^{2+}$, Ca$^{2+}$, and Cl$^−$, and subsequent subjection of ClO$_4^−$ according to charge balance. Mg$^{2+}$ and Ca$^{2+}$ were titrated by EDTA solution calibrated using ZnO and CaCO$_3$ primary standards, respectively. Anion Cl$^−$ was titrated by AgNO$_3$ solution calibrated using a NaCl primary standard. The relative uncertainties of the chemical analysis were within 0.5% for Mg$^{2+}$, Ca$^{2+}$, and Cl$^−$, and 0.6% for ClO$_4^−$.

The chemical compositions of wet solids (i.e., directly scooped out of the reaction container without further processing) were also determined using the same analytical methods as for the supernatants. Solid phases in equilibrium with the solution at 273.15 K were identified using an X-ray diffractometer (XRD; XPert PRO, 200 PANalytical with Cu Ka radiation and λ = 0.15406 nm) at room temperature (Supplementary Fig. 2). For solid phases in equilibrium with the solution at temperatures lower than 273.15 K, Schreinemakers’ wet residues method39 was used instead of XRD analysis to avoid possible melting or decomposition of hydrated salts at room temperature. The Schreinemakers’ wet residues method was a classical method in the phase diagram experimental determination for the salt-water system and its principle is illustrated in Supplementary Fig. 3. The overall relative uncertainties of the liquid and wet residual compositions in the experiments were within 2%. The details of the experimental methods and results are available in Supplementary Notes 1 and 2, respectively.

Thermodynamic modeling methods and results validation. The ISLEC software, i.e., Institute of Salt Lakes Equilibrium Calculator, was used in this study to model the solubility isotherms and generate the phase diagrams for the ternary Mg(ClO$_4^-$)$_2$ - MgCl$_2$ - H$_2$O and Ca(ClO$_4^-$)$_2$ - CaCl$_2$ - H$_2$O systems. The thermodynamic model used in the study was based on the classical Pitzer model updated by the Pitzer’s group60. The ISLEC software used the Gibbs energy minimization (GEM) approach for solving the phase equilibria. The ISLEC software has successfully modeled extensive binary systems, ternary systems, and multicomponent systems down to ~200 K (see Code Statement for accessible link). A detailed description, parameters, and equations implemented by the ISLEC software for the studied ternary systems Mg(ClO$_4^-$)$_2$ - MgCl$_2$ - H$_2$O and Ca(ClO$_4^-$)$_2$ - CaCl$_2$ - H$_2$O are summarized in Supplementary Note 3. The experimental data collected from the literature for regressing the temperature-dependent binary perchlorate parameters are shown in Supplementary Table 3. All the thermodynamic parameters used are listed in Supplementary Tables 4 and 5. Details of validations of the modeling results are presented in Supplementary Notes 4 and 5.

Phase diagram calculation. Deliquescence occurs when the relative humidity (RH) in the gas-phase environment is at or above the mutual deliquescence relative humidity (MDRH) of a salt mixture. The MDRH data points therefore belong to the deliquescence surfaces of a salt mixture62. In a salt-solution model, RH can be derived using the water activity (a$_w$). At a given temperature, R = 100 * a$_w$ = 100 * p$_w$/p$_0$ where p$_w$ and p$_0$ are the vapor pressure of the saturation solution and pure water, respectively. When a$_w$ is a solution of a salt with a vapor pressure of the saturated solution equal to RH, the MDRH is MDRH. The a$_w$ can be calculated using equation 816 in the Supplementary Information. The deliquescence surface data in an x-Y-RH coordinate system were generated using the C codes (i.e., islec_mars_mdrh_mc, i.e., islec_mars_mdrh_cac; see Code Statement for accessible link). The x was calculated from the equilibrium mobility of perchlorate and chloride in aqueous solution. This code can be compiled using the GCC compiler on the Linux platform or the Dev-Cpp compiler on the Windows platform. The awk script can be used to format the output data produced by islec_mars_mdrh_mc for further visualization. These output data were then visualized with Gnuplot software for 2D and 3D plots. Detailed instructions can be found in the README file included in the source code package (link provided in Code Statement).

Mapping global Mars for the regional environments that may support ClO$_4^−$/Cl$^−$ fractionation. The regions that meet the RH-T$_{mrdh}$ requirements for ClO$_4^−$/Cl$^−$ fractionation, i.e., where environmental conditions overlap with the phase diagram of a specific salt mixture and can produce brine with ClO$_4^−$/Cl$^−$ = 0.2 (Supplementary Fig. 17 and Supplementary Table 7), were mapped using the outputs of the
LMD General Circulation Model is available on request from the LMD team. The LMD GCM simulates water and dust transport, including the microphysics and radiative effects of water ice clouds, dust/ice sedimentation and condensation/sublimation of water/ice at the surface. The model has also been used to predict and analyze the night-time near-surface relative humidity on Mars. The model is continuously confronted with available observations to validate its results.

Software/gawk; the GCC compiler: gcc.gnu.org; the Dev-Cpp compiler: sourceforge.net.

Data availability
Rover Environmental Monitoring Station (REMS) data are available in the Planetary Data System (PDS) https://atmos.nmsu.edu/PDS/data/mlrem_1001/DATA. Underlying data for the main figures are included as Excel files in the source data. All data used for plotting the main figures and supplementary figures and those presented in Supplementary Tables are available at Science Data Bank, https://doi.org/10.1122/sciencedb.09911. The softwares used in this study are accessible at following links provided. The awk: www.gnu.org/software/gawk; the GCC compiler: gcc.gnu.org; the Dev-Cpp compiler:.sourceforge.net/projects/orwelldevcpp. The Gnuplot: www.gnuplot.info. The ISLECl software and models can be accessed from a PHP based Web interface with a single point calculation module (www.islecnet.islecl-web/isle-web-mg-cl-dcot, www.islecnet.islecl-web-ca-cl-dcot). The LMD General Circulation Model is available on request from the LMD team.

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