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# 1 Probing the Atmospheric Cl Isotopic Ratio on Mars: Implications for Planetary 2 Evolution and Atmospheric Chemistry

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## 28 29 Key Points:

- 30 • Cl isotopic ratio in atmospheric HCl on Mars is measured with NOMAD, finding a slight  
31 depletion of <sup>37</sup>Cl compared to Earth Standard.
- 32 • The atmospheric Cl isotopic ratio is compatible with surface values measured by MSL,  
33 not showing any fractionation beyond uncertainties.
- 34 • The majority of possible HCl depletion processes at Mars yield residual HCl with lighter  
35 Cl than its source.

36 **Abstract**

37 Following the recent detection of HCl in the atmosphere of Mars by ExoMars/Trace Gas  
 38 Orbiter, we present here the first measurement of the  $^{37}\text{Cl}/^{35}\text{Cl}$  isotopic ratio in the Martian  
 39 atmosphere using a set of NOMAD observations. We determine an isotopic anomaly of  $-6 \pm 78\%$   
 40 compared to Earth standard, consistent with the  $-51\%$  to  $-1\%$  measured on Mars' surface by  
 41 Curiosity. The measured isotopic ratio is also consistent with surface measurements, and  
 42 suggests that Cl reservoirs may have undergone limited processing since formation in the Solar  
 43 Nebula. The examination of possible sources and sinks of HCl shows only limited pathways to  
 44 short-term efficient Cl fractionation and many plausible reservoirs of “light” Cl.

45 **1 Introduction**

46 Halogens are among the fundamental components of protostellar clouds, and it is commonly  
 47 accepted that their main reservoirs in the early Solar System are hydrogen halides (i.e. HF, HCl,  
 48 HBr), as suggested in Dalgarno et al., (1974) and Jura (1974), given their chemical tendency to  
 49 form these compounds. For this reason, and for its ubiquitous presence, the detection and study  
 50 of the abundance and properties of HCl on various bodies of the Solar System is crucial to gain a  
 51 thorough understanding of their evolution in planetary systems.

52 Chlorine has two stable isotopes,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ , and as with other molecules, the isotopic  
 53 quantification of chlorine in HCl is recognized as an important metric for characterizing the  
 54 chemical processes and outgassing history of a planet. Moreover, this was one of the first  
 55 isotopic systems to be investigated by theoretical studies (Urey & Greiff, 1935). Across the Solar  
 56 System, the measurement of Cl isotopic composition in solid surface minerals is directly  
 57 connected to their current chemical composition and how this evolved from the initial reservoirs  
 58 (e.g. Catling et al. (2010); Eggenkamp et al. (1995)). In this context, volatilization and redox  
 59 reactions can efficiently induce long-term Cl fractionation, where molecules and complexes with  
 60 oxidized Cl ( $\text{Cl}^{n+}$ ,  $n=1,3,5,7$ ) will concentrate  $^{37}\text{Cl}$  relative to chlorides ( $\text{Cl}^-$ ). The variations  
 61 induced by these processes are measured as deviations from the average Cl isotopic ratio found  
 62 on Earth (Standard Mean Ocean Chlorine, or SMOC:  $(^{37}\text{Cl}/^{35}\text{Cl})_{\text{SMOC}}=0.31977$ , e.g. de Groot  
 63 (2009)), in units of parts per mil (‰):  $\delta^{37}\text{Cl} = ((^{37}\text{Cl}/^{35}\text{Cl})/(^{37}\text{Cl}/^{35}\text{Cl})_{\text{SMOC}} - 1) \times 1000$ , and can be  
 64 as significant as tens of ‰.

65 The value of the isotopic  $\delta^{37}\text{Cl}$  anomaly has been measured across the Solar System and in  
 66 other regions of stellar and planetary formation (e.g. de Groot, 2009); values are summarized in  
 67 Figure 1. Generally, variability of the  $^{37}\text{Cl}/^{35}\text{Cl}$  ratio is due to the conditions where  
 68 nucleosynthesis of the observed Cl takes place, which is produced almost entirely in core-  
 69 collapse supernovae. Higher metallicity core-collapse supernovae tend to produce higher  
 70  $^{37}\text{Cl}/^{35}\text{Cl}$  ratios (Kobayashi et al., 2006). In the Solar System, the average measured ratios  
 71 fluctuate between 0.29 and 0.33, while in neighboring star formation regions the measured value  
 72 can be significantly different. At formation, several mechanisms (primarily degassing and  
 73 oxidation) are able to increase the  $^{37}\text{Cl}/^{35}\text{Cl}$  ratio of planetary materials, while those that deplete  
 74 the heavier isotope are usually less efficient (Gargano & Sharp, 2019); therefore, the  
 75 composition of Cl may be a reliable metric to quantify how much a celestial body has evolved  
 76 from the original protosolar nebula composition (Dhooghe et al., 2017).

77 As seen in Figure 1, the Solar System is characterized by a few notable exceptions to SMOC.  
78 Mass spectrometric measurements of lunar rock samples (Boyce et al., 2015; Shearer et al.,  
79 2014) have shown that the Moon contains chlorine that is isotopically unlike any other body in  
80 the Solar System (J. J. Barnes et al., 2019; Sharp et al., 2010). This anomaly has been recently  
81 suggested to be the result of degassing of the lunar magma ocean early in the Moon's history,  
82 rather than of lava degassing, as initially thought. In a number of cases, instead, the surface  $\delta^{37}\text{Cl}$   
83 is found to be significantly lower than SMOC. Besides Mars' perchlorates, observations of  $\delta^{37}\text{Cl}$   
84 at comet 67P by Rosetta/ROSINA (Dhooghe et al., 2017) indicate  $\delta^{37}\text{Cl}=-93\%$ , consistent with  
85 the value in the protosolar nebula (Anders & Grevesse, 1989; Kama et al., 2015; Lodders, 2010).  
86 On Earth, the only large exception to the SMOC are the Atacama Desert perchlorates (Böhlke et  
87 al., 2005), whose composition is likely due to atmospheric photochemical reactions and  
88 subsequent dry deposition onto an arid environment.

89 The role of atmosphere-surface interactions in determining the variation and present values  
90 of  $\delta^{37}\text{Cl}$  on Mars is an outstanding scientific question, which can only be solved by atmospheric  
91 measurements supporting existing modeling efforts. While on Earth these dynamics are well  
92 studied (e.g. Keppler et al. (2020); Laube et al. (2010)) there is no definite explanation of the  
93 peculiarly "light" Cl isotopic composition found at Mars' surface. The widespread observation of  
94 perchlorates by the Phoenix lander (Hecht et al., 2009) and by the Sample Analysis at Mars  
95 (Mahaffy et al., 2012) onboard Curiosity rover (Glavin et al., 2013) suggested mechanisms  
96 similar to those in place for the Atacama perchlorates. Those arid-environment perchlorates are  
97 produced by oxidation of Cl species by ozone, or oxygen-containing species (e.g., O or OH)  
98 derived from chemical processes involving ozone (Catling et al., 2010), with little or no  
99 subsequent evolution. Yet, it was later found that these mechanisms cannot explain - under  
100 Martian conditions - the perchlorate abundance measured on Mars (Smith et al., 2014).

101 The systematically negative values of  $\delta^{37}\text{Cl}$  measured on surface by Curiosity in various  
102 locations of Gale Crater (Farley et al., 2016) have at least two plausible explanations related to  
103 the thermal evolution of Cl: First, if the measured Cl derived directly from oxychlorine  
104 compounds, then the "light" Cl comes from long-term atmospheric chemical transformations  
105 involving oxygen compounds. Second, if Cl comes from chloride, partial reduction of  
106 isotopically "heavy" perchlorate can fractionate HCl yielding lower  $\delta^{37}\text{Cl}$  (Farley et al., 2016).  
107 Because of the depletion in  $^{37}\text{Cl}$ , it seems logical to exclude that the origin of the low surface  
108  $\delta^{37}\text{Cl}$  observed is outgassing and subsequent atmospheric escape, which would yield an  
109 enrichment in the heavier isotope (Jakosky et al., 2017).

110 Recently, the Trace Gas Orbiter Atmospheric Chemistry Suite (ACS) and the Nadir  
111 Occultation for MArS Discovery (NOMAD) spectrometers reported the first detection of HCl in  
112 the Martian atmosphere (Korablev et al., 2021; Aoki et al., 2021). In Martian Year (MY) 34, HCl  
113 has been detected by NOMAD in about 50 vertical profiles at  $L_S = 210-330$  right after the most  
114 intense phase of the Global Dust Storm (GDS), when the dust content in the atmosphere was still  
115 heavily enhanced (Smith, 2004; Smith et al., 2013). Observations show that the enhancement of  
116 the HCl abundance in the atmosphere is only transient, in fact previous studies were able to set  
117 only upper limits for HCl (e.g. Villanueva et al., 2013) using ground based observations that  
118 were acquired around the Northern Spring Equinox ( $L_S 0$ ), after the period where HCl is reported

119 by ACS and NOMAD. The detection of HCl therefore constitutes the proof of active exchange of  
120 Cl between the surface and the atmosphere in specific conditions.

121 Here we show the measurement of the  $^{37}\text{Cl}/^{35}\text{Cl}$  isotopic ratio in the atmosphere of Mars  
122 obtained with NOMAD, and discuss the implications of this result. To date, this is only the third  
123 case in which a value is obtained for a planetary atmosphere (besides Earth and Venus (Iwagami  
124 et al., 2008)). The purpose of the present work is two-fold: first, the measured isotopic ratio will  
125 be discussed in light of the processes that explain the transient presence of HCl in the Martian  
126 atmosphere, discussed in Aoki et al. (2021), Korablev et al. (2021) and Olsen et al. (2021).  
127 Second, the significance of the retrieved isotopic ratio is contextualized in connection with the  
128 surface value, offering some clues about the atmosphere-surface interaction, and compared to the  
129 other values measured in the Solar System.

## 130 **2 Measurement of $\delta^{37}\text{Cl}$ in HCl with NOMAD onboard Trace Gas Orbiter**

131 The ExoMars Trace Gas Orbiter (Vandaele et al., 2018) NOMAD spectrometer operates in  
132 the spectral ranges between 0.2 and 4.3  $\mu\text{m}$ . The two infrared channels of NOMAD, one  
133 dedicated to Solar Occultations (SO) and one primarily to Limb and Nadir Observations (LNO)  
134 combine the optical setup of an echelle grating with an Acousto Optical Tunable Filter (AOTF),  
135 which is a feasible way to select diffraction orders during repeated acquisitions (Neefs et al.,  
136 2015). During a Solar Occultation measurement, the instrument observes solar radiation as it is  
137 attenuated by the atmosphere at different altitudes, switching between five or six diffraction  
138 orders every second, providing information about the vertical structure of the atmosphere at a  
139 high vertical sampling ( $\sim 1$  km) and spatial resolution ( $\sim 2$  km) from the surface to 200 km. The  
140 resolving power of the SO channel is close to 20,000 and obtains vertical profiles of the  
141 atmospheric constituents (Vandaele et al., 2015), such as  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$  and their isotopologues  
142 (Aoki et al., 2019; Vandaele et al., 2019; Villanueva et al., 2021). Pertinent to this work, it also  
143 performs a sensitive search of organic species (Korablev et al., 2019), such as hydrocarbons  
144 ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ , Knutsen et al. 2021), and other trace species (e.g.  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{OCS}$ ,  
145  $\text{SO}_2$ ).

146 Following the first detection of HCl in the Martian atmosphere reported by ACS (Korablev et  
147 al., 2021) and NOMAD (Aoki et al., 2021), we derive the  $^{37}\text{Cl}/^{35}\text{Cl}$  isotopic ratio on a set of  
148 occultations where high HCl abundance has been detected, increasing the likelihood of obtaining  
149 a statistically significant Cl isotopic ratio estimate. Specifically, we have selected all the  
150 detections of HCl during MY34 using the NOMAD spectra that cover the interval 2898 – 2921  
151  $\text{cm}^{-1}$  (order 129), which display the R0 lines for the two Cl isotopes (2904.11 and 2906.25  $\text{cm}^{-1}$ ).  
152 Among the  $\sim 50$  detections of MY34, a number of occultations at mid to high southern latitude  
153 ( $30\text{-}75^\circ\text{S}$ ) show the largest HCl abundance, up to 4 ppbv below 40 km. To maximize the signal  
154 to noise ratio (SNR) of both the  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$  lines, we focus on those observations, and  
155 select a total of 7 independent occultations where HCl is detected between 2 and 40 km of  
156 altitude, at  $L_S = 250$  to 320 in MY34. It is important to point out that in most cases the  $\text{H}^{37}\text{Cl}$  line  
157 has intensity below or comparable to the single-spectrum noise level; therefore, a vertical profile  
158 of  $^{37}\text{Cl}/^{35}\text{Cl}$  cannot be consistently retrieved. Instead, the data are used to derive an average,  
159 global value of  $\delta^{37}\text{Cl}$  in two steps: first, single spectra are analyzed to derive the  $\text{H}^{35}\text{Cl}$   
160 abundance by only probing the lines of the main isotopologue. Second, we build an average of  
161 all those spectra where HCl is detected, weighing them with the SNR of the  $\text{H}^{35}\text{Cl}$  detection, and

162 retrieve a single value for the  $^{37}\text{Cl}/^{35}\text{Cl}$  isotopic ratio from this “grand average” spectrum. All the  
163 analysis is done taking into account the known instrument systematics, such as temperature-  
164 induced frequency shifts and resolving power variability, which are modeled and accounted for,  
165 according to the instrument calibration (Liuzzi et al., 2019).

166 Retrievals are performed with the Planetary Spectrum Generator (PSG, Villanueva et al.,  
167 (2018)) which incorporates an Optimal Estimation retrieval scheme (Liuzzi et al., 2016; Rodgers,  
168 2000) and models the above mentioned instrument systematics (details in Supplementary  
169 Materials). Besides HCl, we retrieve the vertical profiles of H<sub>2</sub>O and HDO, which have distinct  
170 absorption lines in the spectral interval considered herein. The other variables, including  
171 atmospheric pressure and temperature, are assumed a-priori from the GEM-Mars model (Neary  
172 & Daerden, 2018), using a modeled scenario for the MY34 GDS (Liuzzi et al., 2020; Neary et  
173 al., 2020).

174 The derived isotopic ratio, average spectrum, and retrieved HCl profiles are shown in Figure  
175 2. The average of  $\delta^{37}\text{Cl}$  (relative to SMOC) from all of the measurements taken at altitudes  
176 between 2 and 40 km (a total of 351 spectra), where both isotopes are detectable, is  $-6 \pm 78 \text{ ‰}$   
177 ( $^{37}\text{Cl}/^{35}\text{Cl} = 0.3179 \pm 0.0192$ ). The uncertainty on this value is directly produced by Optimal  
178 Estimation and reflects the equivalent radiometric noise on the grand average of the spectra  
179 considered. However, the reported confidence interval is also as large as most variations induced  
180 by eventual instrumental and temperature profile systematics (details in the Supplementary  
181 Materials). The limited precision of the measurement is essentially set by the level of accuracy of  
182 the retrieval of H<sup>37</sup>Cl isotope, which is close to 13-sigma, in contrast to the H<sup>35</sup>Cl, whose  
183 precision is around 20-sigma. It is important to stress again that this value refers to specific  
184 environmental conditions: all the spectra used in this study are acquired at latitudes between 30-  
185 72 °S, sparse longitudes and L<sub>S</sub> 250-320 in MY34.

186 The confidence interval of the retrieved value encompasses all the values measured at the  
187 surface by Curiosity (Farley et al., 2016), and shows in average only a slight depletion in  $^{37}\text{Cl}$   
188 compared to SMOC. There are no measurements at the surface at the same latitudes where this  
189 dataset is acquired, therefore a direct comparison is not technically possible. This isotopic ratio is  
190 an average over a relatively large range of pressures, preventing from ruling out stronger  
191 fractionation at higher altitudes or to resolve its vertical behavior.

### 192 **3 Discussion: atmospheric chemistry and reservoirs**

193 Despite the relative uncertainty in the derived atmospheric  $\delta^{37}\text{Cl}$ , we can contextualize it with  
194 respect to hypotheses formulated to explain the transient atmospheric HCl enhancement, the  
195 chemical and physical relation with isotopic ratios at surface, and what conclusions can be drawn  
196 about the historical evolution of Mars. First, the observed atmospheric fractionation does not  
197 suggest significant Cl escape. Already evident from Curiosity measurements, this agrees with the  
198 confidence interval for the atmospheric  $\delta^{37}\text{Cl}$ , which is well below the fractionation observed for  
199 gases of similar molar mass, such as Ar, a strong indicator of atmospheric loss through solar  
200 wind sputtering (Jakosky et al., 2017). Even if HCl enhancement in the atmosphere is only  
201 transient, the retrieved value of  $\delta^{37}\text{Cl}$  is compatible with the hypotheses that crustal Cl reservoirs  
202 that contribute to form HCl in the atmosphere have gone through limited or no degassing,  
203 otherwise the average atmospheric (and surface)  $\delta^{37}\text{Cl}$  would have been much higher (as for the

204 Moon). The fact that HCl is quickly removed from the atmosphere after L<sub>S</sub> 330 indicates that the  
205 physical or chemical processes that create and sequester HCl from the atmosphere must be  
206 dominant over its escape, not surprising given the chemical reactivity of Cl compounds. On long  
207 temporal scales (~Myr), redox reactions involving Cl can yield measurable <sup>37</sup>Cl/<sup>35</sup>Cl  
208 fractionation, particularly if Cl is reduced from perchlorate salts (e.g. Ader et al., 2008).

209 As observed by Aoki et al. (2021), the vertical distribution of HCl is very similar to water  
210 vapor, and in MY34 is observed between the GDS and the regional storm mostly at mid-latitudes  
211 in the Southern hemisphere, where both water vapor and dust are abundant during the declining  
212 phase of the GDS (Aoki et al., 2019; Liuzzi et al., 2020). The HCl abundances observed during  
213 the same season in MY35 are comparable to MY34, suggesting that the simultaneous presence of  
214 dust and water vapor – rather than the abundance of dust itself – is key to HCl production. There  
215 are two main channels to produce atmospheric HCl: either directly from Cl<sup>-</sup> stored in the form of  
216 chloride salts (e.g. NaCl, KCl) in lifted dust particles by reaction with HO<sub>2</sub>, or by release from  
217 the reaction between oxyanions such as perchlorate salts (ClO<sub>4</sub><sup>-</sup>) and OH, whose presence is  
218 expected from the odd hydrogen cycle of water vapor.

219 In the first case, atmospheric HCl is produced when Cl is released by dust. Cl release may  
220 happen either by direct UV irradiation of dust particles lifted in the atmosphere during the GDS,  
221 or as recently suggested (Wang et al., 2020) by electrostatic discharge of dust particles  
222 containing chlorides during very intense dust activity. This last mechanism may account to some  
223 of the HCl observed in MY34, and be less relevant in MY35 (Aoki et al., 2021). Regardless, the  
224 released Cl would subsequently react with HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>: H<sub>2</sub>O<sub>2</sub> + Cl → HCl + HO<sub>2</sub>; HO<sub>2</sub> +  
225 Cl → HCl + O<sub>2</sub> (Lefèvre & Krasnopolsky, 2017) and H<sub>2</sub> + Cl → HCl + H. In Martian conditions  
226 (Smith et al., 2014), the reaction rate with HO<sub>2</sub> is 10<sup>-3</sup>-3·10<sup>-3</sup> s<sup>-1</sup> between 0 and 40 km and the one  
227 with H<sub>2</sub> is 4·10<sup>-5</sup>-2·10<sup>-3</sup> s<sup>-1</sup>, 2 orders of magnitude larger than the H<sub>2</sub>O<sub>2</sub> channel (4·10<sup>-6</sup>-10<sup>-4</sup> s<sup>-1</sup>).  
228 Regardless, these mechanisms would not alter the isotopic composition of Cl in HCl with respect  
229 to the one in the dust because Cl does not change its oxidation state.

230 In the second case, HCl production would occur by a reduction mechanism, which can  
231 change the oxidation state of Cl in Cl oxyanions (ClO<sub>x</sub><sup>-</sup>) to HCl, and induce formation of HCl  
232 with an isotopic composition lighter than the surface perchlorates. However, the lifetime of HCl  
233 (90 Sols below 15 km, see Aoki et al. (2021)) would be inconsistent with the timescale of  
234 fractionation processes due to redox reactions. Importantly, the modeling of Cl Rayleigh  
235 distillation (Farley et al., 2016; Schauble et al., 2003) suggests that a reduction >30% of the  
236 perchlorates in dust, with a fractionation factor of 0.95, is able to lower the δ<sup>37</sup>Cl by 50‰ in the  
237 produced HCl over the geologic history of the crust. Yet, a depletion of tens per ‰ of <sup>37</sup>Cl in  
238 atmospheric HCl is within the confidence interval of our retrievals and therefore does not  
239 conclusively exclude this interpretation for long-term fractionation.

240 On Earth, O<sub>3</sub> plays an important role in the atmospheric Cl chemistry, as seen in Atacama.  
241 However, O<sub>3</sub> at Mars is reportedly absent at L<sub>S</sub> 250-320 at latitudes where HCl is most abundant  
242 (Perrier et al., 2006; Clancy et al., 2016; Willame et al., 2017), thus the presence of other sources  
243 of perchlorates beyond those in the lifted dust is unlikely. Because of oxidation, such sources  
244 would be enriched in <sup>37</sup>Cl, varying the isotopic composition of Cl in HCl significantly.

245 NOMAD and ACS data suggest that HCl is abundant below the hygropause. As shown in  
246 Figure 3, there are at least four mechanisms that, in principle, could efficiently deplete HCl in the  
247 middle atmosphere, and each yields a different isotopic signature in the observed HCl compatible  
248 with the confidence interval we retrieved for  $\delta^{37}\text{Cl}$ :

249 **1)** Given the high abundance of water vapor where HCl is detected (Aoki et al., 2021), a first  
250 chemical pathway to destroy HCl could be the reaction with OH:  $\text{OH} + \text{HCl} \rightarrow \text{Cl} + \text{H}_2\text{O}$ . This is  
251 the major sink for HCl in the stratosphere at Earth (Michelsen et al., 1996), and preserving the  
252 oxidation state of Cl, it would not modify its isotopic composition in the residual HCl. Yet, this  
253 process is much slower than the production process involving OH (Aoki et al., 2021);

254 **2)** HCl could be adsorbed by deposition on ice particles and condensed. Based on what is  
255 expected from fractionation of other elements (e.g. H, O), this would deplete  $^{37}\text{Cl}$  of HCl, but  
256 only above the altitudes at which HCl is detected in this study and to a limited extent (1-2‰, as  
257 in Luo et al., 2012). As mentioned, the vertical distributions of HCl and  $\text{H}_2\text{O}$  are very similar,  
258 therefore HCl is expected to be trapped in growing water ice particles (Kippenberger et al.,  
259 2019). While no water ice has been detected simultaneously with HCl observations, it has a  
260 diurnal cycle, and the frequency of water ice clouds following the regional dust storm at  $L_S$  320  
261 increases at mid-southern latitudes (Liuzzi et al., 2020), and could play a role in HCl depletion;

262 **3)** Similarly to what happens on Earth with Polar Stratospheric Clouds, there may be  
263 heterogeneous chemistry on water ice by reaction with  $\text{ClONO}_2$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HOCl}$  (Solomon, 1999).  
264 In this case, HCl could be oxidized in  $\text{Cl}_2$  or  $\text{ClNO}_2$ . At isotopic equilibrium, the oxidation of Cl  
265 would further deplete  $^{37}\text{Cl}$  from HCl, to an extent that depends on temperature and abundance of  
266 the reagents. However, even if such processes favor the production of  $\text{OCIO}$  and ultimately  
267 perchlorates and their deposition on the surface (Wilson et al., 2016), it is expected that  
268 heterogeneous chemistry involving water ice is too slow to be considered an efficient sink of  
269 HCl and  $^{37}\text{Cl}$ , and to dominate over the other processes. Alternatively,  $\text{Cl}_2$  and  $\text{ClNO}_2$  would be  
270 destroyed on timescale of a few tens of minutes; Cl would then be produced, which would in turn  
271 react quickly with  $\text{HO}_2$  to produce HCl (which means that Cl would be reduced to HCl, as  
272 before).

273 **4)** Differential photolysis could increase the  $\delta^{37}\text{Cl}$  in atmospheric HCl. On Earth, this effect  
274 is as large as 8‰ in  $\text{CF}_2\text{Cl}_2$  (e.g. Laube et al., 2010). UV radiation of wavelength  $\sim 185$  nm can  
275 even reach Mars' surface, and this process has its maximum efficiency between 5 and 25 km of  
276 altitude in Martian conditions, with  $\text{H}^{35}\text{Cl}$  photolysis rate being around  $10 \text{ cm}^{-3} \text{ s}^{-1}$ , rivaling with  
277 the efficiency of the  $\text{OH}+\text{HCl}$  reaction. This process would yield "heavier" HCl on timescales  
278 typical of photolysis (weeks), yet photolysis alone is not able to explain HCl depletion, because  
279 it happens on timescales much longer than production by  $\text{HO}_2$  (Catling et al., 2010; Heays et al.,  
280 2017).

281 Overall, this set of NOMAD observations of  $\delta^{37}\text{Cl}$  is in agreement with the surface values,  
282 and the majority of plausible depletion processes yield lighter residual HCl. The isotopic  
283 composition of HCl, even with the large uncertainty involved in the data, is mostly consistent  
284 with the hypothesis that HCl is produced through Cl directly released from lifted dust particles  
285 during the GDS (by UV irradiation or electrostatic discharge). Efficient fractionation with  
286 respect to the source can occur only via reduction of oxyanions/perchlorates by hydroxyl

287 radicals, but is unlikely to be significant on the short timescales in which HCl is observed. If the  
288 atmospheric isotopic composition is mostly consistent with surface minerals, the atmospheric  
289 value can be considered significant to characterize Cl reservoirs where no surface measurement  
290 is available. We find no univoque indication of  $^{37}\text{Cl}$  enrichment, consistent with the possibility  
291 that Cl reservoirs have undergone little processing after planetary formation.

292 Despite the global circulation of dust during the GDS, potential reservoirs co-located with  
293 detections would include southern highland location, a soil bearing negative  $\delta^{37}\text{Cl}$ , and  
294 seasonality. Of the 7 detections shown here 6 occur at high latitude (60–72.5°S), where  
295 thermodynamics suggests that Ca-perchlorate brine are metastable at surface (Rivera-Valentin et  
296 al., 2020). There, a simple cycle may exist, in which Cl precipitates to perchlorate  $\text{ClO}_4^-$  (Catling  
297 et al., 2010). Once at surface, it can either deliquesce and evaporate, releasing Cl (Rivera-  
298 Valentin et al., 2020), or be lifted by dust devils, frequent in this season (Balme et al., 2003),  
299 where Cl recombines to HCl following one of the reactions mentioned earlier. However,  
300 perchlorate may instead percolate downward to the top of the cryosphere, where it can melt and  
301 transforms to a shallow brine nappe (e.g., Clifford et al., 2010). Furthermore a site located at  
302 30°S is too close to the Equator for perchlorate brine metastability. If generated there, Cl may  
303 rise up from a deep reservoir to the surface using tectonic paths, as suggested by magmatic dykes  
304 propagation and extensional fracturing from the Tharsis region during the Hesperian (Mège and  
305 Masson, 1996). Moreover, 3 of the 6 high-latitude detections are also associated with deep-  
306 rooted crustal fracturing, following another Tharsis-related fracture swarm, and in one case  
307 polygonal ground fractures also show resurfacing. Several Cl detections reported by Aoki et al.  
308 (2021) also coincide with Tharsis grabens in the northern hemisphere. Overall, the Cl cycle on  
309 Mars may involve other reservoirs across the planet in the crust, at the surface, and in the  
310 atmosphere. Crustal reservoirs may supply chlorine with  $\delta^{37}\text{Cl}$  down to  $\sim -5\%$ , which processed  
311 may decrease to even lower values.

312 The strong link between the atmospheric  $\delta^{37}\text{Cl}$  and Cl reservoirs may indicate that Mars has  
313 moved from a primordial reducing environment to its current oxidizing one, as suggested by  
314 previous studies (Farley et al., 2016; Smith et al., 2014). The atmospheric measurement  
315 presented here is lower than most of the inner Solar System, though compatible with both Venus  
316 and Earth's values. Further studies to discern the vertical structure and to map the  $\delta^{37}\text{Cl}$  in HCl  
317 will be key to assessing the relation between the atmospheric Cl isotopic composition and that at  
318 surface and subsurface, and to address whether or not significant fractionation occurs with  
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 349 <https://nomad.aeronomie.be/index.php/data>.

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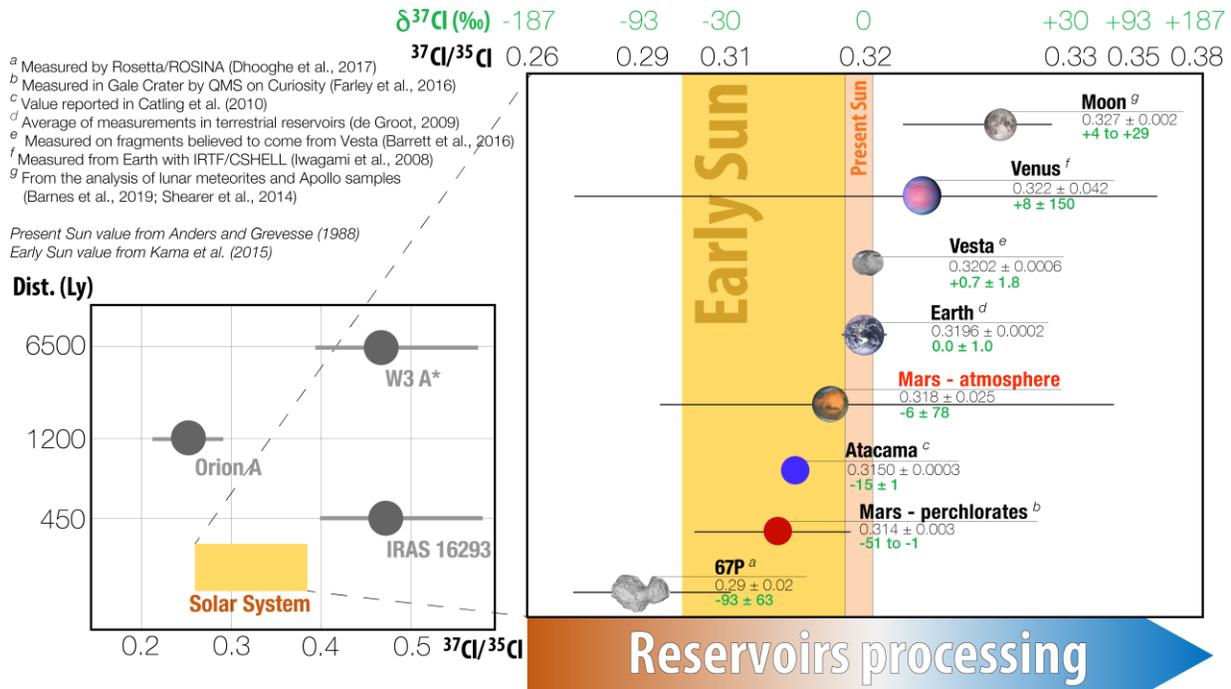
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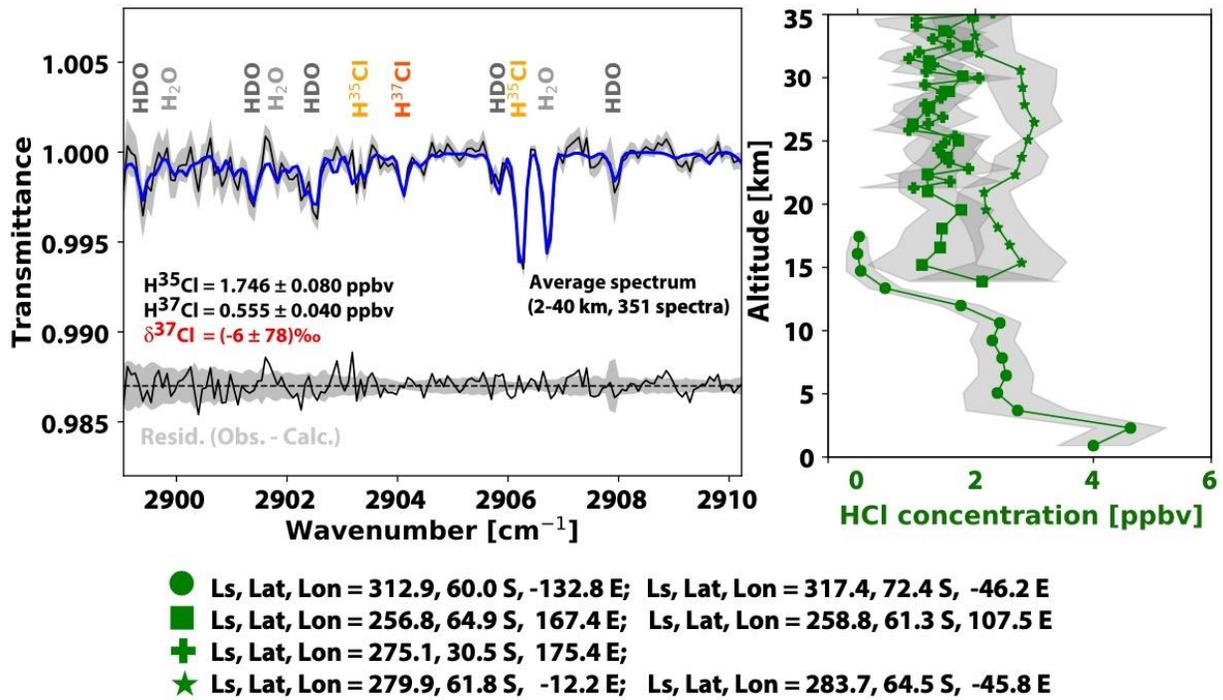
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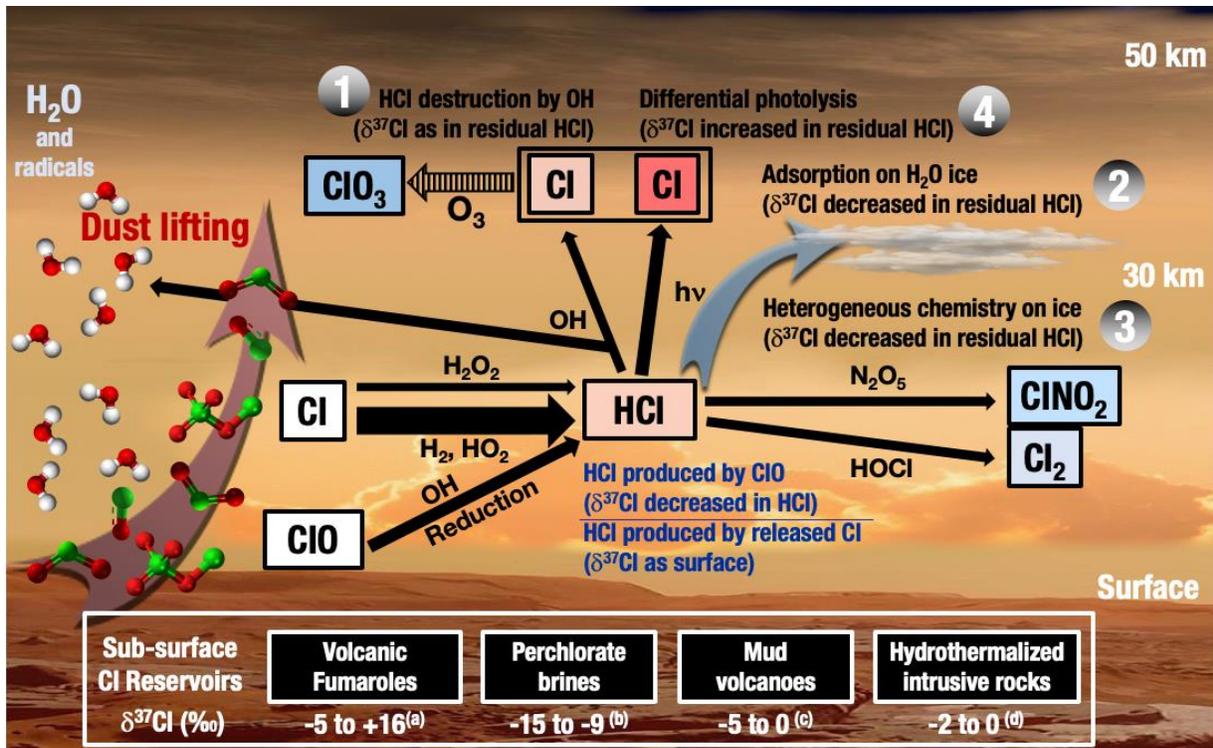
**Figure 1.** The isotopic abundances of Cl exhibit a relatively large variability across different regions of our galaxy. Values measured within the Solar System are on the right plot, compared to modeled primordial Sun value. The value from this work is in red text. Values range from the isotopically “heavy” Moon, and the “light” comet 67P. The value measured for Venus and this work are the only cases of infrared spectroscopy measurements, while the others are obtained from mass spectrometry. For the Solar System, values are reported both in terms of absolute ratio, and deviation from SMOC. X-axis is not in linear scale.

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**Figure 2.** Average NOMAD spectrum and retrieval of  $\delta^{37}\text{Cl}$  value. Left panel: observed spectrum (black), best-fit model (blue) and noise (grey). Residuals are on the bottom, and spectral lines are labeled on top. Right panel: vertical profile of HCl retrieved from the seven occultations considered in this study. Season and location of the occultations are labeled on the bottom. Each profile is an average of two occultations, with the exception of the one at Ls 275-276.

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**Figure 3.** Proposed HCl physics and chemistry and relation with the Cl isotopic composition and reservoirs. Once produced, HCl is then either deposited after photo- or chemical dissociation or processing through heterogeneous chemistry (involving HOCl, N<sub>2</sub>O<sub>5</sub>) or adsorption on water ice. The more efficient processes (under Martian conditions) have thicker arrows; the chemistry of O<sub>3</sub> (dashed arrow) is likely not active at the observations' time. Products with the same isotopic composition as the possible surface reservoirs are in white boxes, those that could be depleted in <sup>37</sup>Cl compared to sources are in red boxes, and those enriched in <sup>37</sup>Cl are in blue. References: (a) Sharp et al. (2010); (b) Böhlke et al. (2005); (c) Godon et al. (2004); (d) Barnes & Cisneros (2012).