

40 **Abstract**

41

42 We report laboratory experimental results that support a brine-related hypothesis for the
43 recurring slope lineae (RSL) on Mars in which the subsurface Cl-salts, i.e., hydrous chlorides
44 and oxychlorine salts (HyCOS) are the potential source materials. Our experiments revealed that
45 within the observed RSL temperature window T_{RSL} (250-300 K), the deliquescence of HyCOS
46 could occur in relative humidity ranges ($RH \geq 22\% - 46\%$) much lower than those for hydrous
47 (Mg, Fe)-sulfates ($RH \geq 75\% - 96\%$). In addition, we demonstrated that the RH values kept by
48 common HyCOS and hydrous sulfates in enclosures have a general trend as $RH_{sulfates} >$
49 $RH_{perchlorates} > RH_{chlorides}$ (with same type of cation) in wide T range. It means that the required
50 RH range for a Cl-salt to deliquesce can be satisfied by a co-existing salt of different type,
51 e.g., in the subsurface layers of mixed salts on Mars. Furthermore, we found a strong temperature
52 dependence of the deliquescence rates for all tested HyCOS, e.g., a duration of 1-5 sols for all
53 HyCOS at the high end (300K) of T_{RSL} , and of 20-70 sols for all tested HyCOS (except
54 $NaClO_4 \cdot H_2O$) at the low end (250K) of T_{RSL} , which is consistent with the observed seasonal
55 behavior of RSL on Mars. From a mass-balance point of view, the currently observed evidences
56 on Mars do not support *a fully-brine-wetted track model*, thus we suggest *a brine-triggered*
57 *granular-flow model* for the most RSL. Considering the recurrence of RSL in consecutive
58 martian years, our experimental results support the rehydration of remnant HyCOS layers during
59 a martian cold season through H_2O vapor-to-salt direct interaction. We found that the evidences
60 of HyCOS rehydration under Mars relevant P-T-RH conditions are detectable in a few minutes
61 by *in situ* Raman spectroscopy. This rehydration would facilitate the recharge of H_2O back into
62 subsurface HyCOS, which could serve as the source material to trigger RSL in a subsequent
63 warm season. The major limiting factor for this rehydration is the H_2O supply, i.e., the H_2O
64 vapor density carried by current Mars atmospheric circulation and the diffusion rate of H_2O
65 vapor into the salt-rich subsurface in a cold season. In a worst-case scenario, these H_2O supplies
66 can support a maximum increase of hydration degrees of two for totally dehydrated HyCOS,
67 whereas the full rehydration of subsurface HyCOS layers can be easily reached during a $>30^\circ$
68 obliquity period that has H_2O vapor density $10\times$ to $20\times$ times the value of current obliquity.
69 Overall, our results imply the existence of a large amount of Cl-salts in the subsurface at RSL
70 sites.

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74 **Key words:** Mars; hydrous Cl-bearing salts; deliquescence; rehydration; Raman spectroscopy;
75 recurring slope lineae;

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78 **Highlights**

79 • The deliquescence of Cl-salts requires mid-to-low RH that is easier to achieve than
80 sulfates on Mars.

81 • Mixed salts in subsurface can provide suitable RH at T_{RSL} to facilitate the deliquescence
82 of Cl-salts at $T > T_e$.

83 • The deliquescence rates of Cl-salts as function of T support the observed seasonal
84 behavior of RSL.

85 • The ultrahigh rehydration rate of Cl-salts does not limit the H₂O recharge, but the H₂O
86 supply on current Mars does.

87 • This study supports a Cl-brine-triggered granular-flow for most of RSL and the annually
88 partial recharge of H₂O.

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90

1. Introduction

Recurring slope lineae (RSL) on Mars are dark, narrow tracks on steep slopes that gradually lengthen in warm seasons, fade when inactive, and recur over multiple years (McEwen et al., 2011, 2014). RSL sites in southern mid-latitude regions on Mars (McEwen et al., 2011; Stillman et al., 2014) were first reported from MRO-HiRISE (Mars Reconnaissance Orbiter – High Resolution Imaging Science Experiment) observations (McEwen et al., 2007). Many more RSL sites are now confirmed in equatorial regions (especially Valles Marineris) and northern middle latitudes (McEwen et al., 2014; Stillman et al., 2014, 2016, 2017; Chojnacki et al., 2016).

RSL usually actively grow at the warmest times of the year for each latitude and slope aspect. This seasonality and tight correlation with local temperature (~ 250 to 300 K, McEwen et al., 2011, 2014) supports a general concept in which volatiles (especially H_2O) play a key role, while the source of H_2O remains an open question. Topographic observation shows that a groundwater origin is unlikely (Chojnacki et al., 2016). A rarefied gas-triggered granular flow model was suggested (Schmidt et al., 2017) but cannot explain the observation of spectral features of oxychlorines at RSL sites (Ojha et al., 2015). Dundas et al. (2018) studied the terminal slope of 151 RSL and concluded that the observed range of slope angles matches with the critical angles of granular flows, but further indicated that the seasonal behavior of RSL would be consistent with some role for water in RSL initiation.

In this paper we present experimental evidences from thermodynamics and kinetics of hydrous Cl-bearing salts to support a two-step hypothesis, in which the subsurface hydrous chlorides and oxychlorine salts (HyCOS) are potential contributors to RSL activity (Figure 1). This study addresses two critical characteristics of RSL that have not been fully explained by other models (Schmidt et al., 2017; Dundas et al., 2018): (1) the tight correlation of RSL occurrence with local temperature; and (2) the recurrence of RSL at the same sites in the same fashion during consecutive martian years (observed > 5 martian years hitherto).

Fundamentally, our hypothesis is based on the broad existence of Cl-bearing species on Mars, evidenced by the Cl-distribution map obtained by the Gamma-Ray Spectrometer (GRS) instrument on-board the Mars Odyssey orbiter (Keller et al., 2006), and by the detection of Cl in every surface sample during all Mars surface exploration missions (Clark et al., 1981, McSween et al., 1999, Gellert et al., 2006, Kounaves et al., 2010, McLennan et al., 2014). Furthermore, putative chloride deposits have been detected in wide regions of the southern hemisphere on Mars (Osterloo et al., 2008, 2010, 2015), although there is no obvious surface exposure at RSL sites (Mitchell and Christensen, 2016). Oxidized forms of Cl, especially perchlorate (ClO_4^-), were detected at the Phoenix landing site (Hecht et al., 2009; Kounaves et al., 2014). Their existence was demonstrated at Gale Crater (Glavin et al., 2013; Leshin et al., 2013, Sutter et al., 2017) and suggested at Viking sites (Navarro-Gonzalez et al., 2010). A widespread or global distribution of oxychlorine species on Mars has been proposed (Clark and Kounaves, 2016). Surface exposures of hydrated oxychlorine, however, appear to be quite rare in sufficient abundance to be detected from orbit by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) (Murchie et al., 2007; Ojha 2016), whereas the CRISM detection of oxychlorines at four RSL sites (Ojha et al., 2015) suggests a relation between RSL and Cl-salts.

137 For this study, we assume HyCOS salts in subsurface layers on Mars reached their highest (i.e.,
138 full) hydration states (Figure 1a) during a recent high-obliquity period ($>30^\circ$, about ~500 Kyr
139 ago, Laskar et al., 2004) when H₂O ice covered the surface in mid-low latitude regions on Mars
140 (Richardson and Wilson, 2002; Head et al., 2003), and lasted for tens of thousands of years.
141 Based on the experimental results (Wang et al., 2013, 2017), the full hydration of HyCOS and
142 hydrous sulfates at $T \leq 273\text{K}$ and 100% RH (controlled by H₂O ice) can be reached during time
143 periods much shorter than tens of thousands of years.

144
145 The first part of our hypothesis (step-one, Figure 1b) relates to the tight correlation of RSL
146 occurrence of with local temperature. I.e., during a warm season of the current obliquity cycle,
147 the deliquescence of subsurface HyCOS could generate Cl-bearing briny fluid that triggers RSL.
148 To test this hypothesis, three critical data sets are required: (1) the Relative Humidity (RH)
149 conditions for the deliquescence of HyCOS; (2) the RH ranges maintained by hydrous salts in an
150 enclosure in temperature window relevant to martian surface and subsurface; and (3) the
151 deliquescence rates of HyCOS as a function of temperature (T).

152
153 The second part of our hypothesis (step-two, Figure 1c) relates to the recurrence of RSL. I.e.,
154 during a cold season of the current obliquity cycle on Mars, when the H₂O vapor front moves
155 down from the Polar Region (Smith, 2002, 2009, Figure S4), H₂O would be recharged back to
156 the remnant subsurface HyCOS layers that have not been carried downhill by previous RSL
157 events. To test this hypothesis, two more critical data sets are required: (4) the feasibility of
158 HyCOS rehydration through direct H₂O vapor-salt reaction at extremely low temperature; (5) the
159 rehydration rates of HyCOS at relevant martian P-T-RH conditions.

160
161 We have obtained all five sets of critical data through experiments described in section 2 of this
162 paper. The experimental results that support our step-one hypothesis are reported in Section 3.
163 The experimental results that support our step-two hypothesis are reported in Section 4. The
164 implications of these experimental results are discussed in Section 5. We would emphasize that
165 the central goal of this manuscript is to presents the fundamental thermodynamic and kinetic
166 properties of HyCOS revealed by our laboratory experiments. On the basis of these newly found
167 properties, we developed two RSL-relevant implications, i.e., on its T-correlation and its annual
168 recurrence. Our experiment is not a RSL simulation, and we will not try to interpret every aspect
169 of RSL. Rather, we would use the newly found fundamental properties of HyCOS to provide a
170 one-step-forward understanding of potential source materials for RSL.

171 172 **2. Samples and experiments**

173
174 We used nine HyCOS salts, six hydrous chlorides, and three hydrous perchlorates as the starting
175 phases. We designed four sets of experiments to study their thermodynamic and kinetic
176 properties and used these results to test the two-step hypothesis described in introduction.

177 178 2.1. HyCOS samples selected for experiments

179
180 The selection of six hydrous chlorides, MgCl₂·6H₂O, FeCl₂·4H₂O, FeCl₃·6H₂O, CaCl₂·4H₂O,
181 AlCl₃·6H₂O, and KMgCl₃·6H₂O, was based on three lines of reasoning. First is the observed
182 existence of hydrous chlorides in terrestrial salt deposits in hyperarid regions (Antarctica,

183 Atacama Desert, and the Qaidam Basin on the Tibet Plateau (e.g., [Torii et al., 1965](#), [Wang et al.,](#)
184 [2018](#)). Second is the potential existence of HyCOS on Mars, with an order of cation abundances
185 (high in Mg and Fe, moderate in Ca, and poor in Al, Na, K) as observed in martian secondary
186 minerals, indicating a lower degree of alteration ([McLennan, 2012](#); [Hurowitz et al., 2006](#)). The
187 third is the stability of these hydrous chlorides in the observed T range of RSL sites (~250-300 K,
188 [McEwen et al., 2011, 2014](#)). For this study, NaCl·2H₂O and KCl were not selected because the
189 former is not stable at T > 273K, and the latter does not have a hydrate. The selection of hydrous
190 perchlorates, Mg(ClO₄)₂·6H₂O, Ca(ClO₄)₂·4H₂O, and NaClO₄·H₂O was based on the same
191 reasoning.

192
193 Eight hydrous chlorides and oxychlorine salts were purchased as pure chemicals, i.e.,
194 Mg(ClO₄)₂·6H₂O and MgCl₂·6H₂O from Sigma-Aldrich (CAS:13446-19-0 and CAS:7791-18-6);
195 Ca(ClO₄)₂·4H₂O and CaCl₂·4H₂O from ACROS (CAS:15627-86-8 and CAS:10035-04-8);
196 NaClO₄·H₂O from Fisher (CAS:7791-07-3); FeCl₂·4H₂O and FeCl₃·6H₂O from MP Biomedicals
197 LLC (LOT:8655KA and LOT:6237K); AlCl₃·6H₂O from Sigma (LOT:118H0299). The sample
198 of KMgCl₃·6H₂O was synthesized in our laboratory. The chemical and structural identification
199 of these HyCOS were verified by XRD and by laser Raman spectroscopy ([Wang et al., 2013b](#);
200 [Wu et al., 2016](#)).

201 202 2.2. Selected temperature ranges for experiments

203
204 We used the observed Mars surface temperature (T) data at Gale Crater ([Gómez-Elvira et al.,](#)
205 [2012](#)) to constrain our selection of temperature ranges in the experiments. In addition, we used at
206 least three temperatures in each set of Experiment 1 and Experiment 4, which enabled us to
207 reliably extrapolate to lower temperatures at which it becomes impractical to conduct laboratory
208 experiments.

209
210 Experiment 1 and Experiment 2 are relevant to the deliquescence of HyCOS in the warm season,
211 i.e., for the generation of RSL. We used two sets of mission-observed temperature data to
212 constrain the temperature range selection. They are: (1) the temperature window T_{RSL} ~250-300
213 K based on THEMIS data ([McEwen et al., 2011, 2014](#)) obtained at RSL sites in southern mid-
214 latitudes and Valles Marineris, (2) a T_{ground}=200-290 K and T_{air}=207-280 K during the summer at
215 Gale Crater, measured by the temperature sensor in REMS (Rover Environmental Monitoring
216 Station) on the Curiosity rover ([Gómez-Elvira et al., 2012](#)).

217
218 Experiment 3 and Experiment 4 are relevant to the recharge of H₂O back into subsurface HyCOS
219 in the cold season, i.e., to support the recurrence of RSL. We used the mission-observed lowest
220 temperature to constrain the temperature range selection. They are T_{ground}=175-260 K and
221 T_{air}=188-250 K measured by the same temperature sensor during winter at Gale Crater ([Gómez-
222 Elvira et al., 2012](#)).

223 224 2.3. Experiment 1 – to seek for RH-T conditions for the deliquescence of HyCOS

225
226 Experiment 1 is a set of T-RH driven deliquescence/dehydration reactions for nine HyCOS. Ten
227 RH levels (ranging 6-100%) and three temperatures (323 K, 294 K, 278 K, the last two are
228 within the observed T_{RSL} window, [McEwen et al., 2011, 2014](#)) were used for each salt, with a

229 total of 270 experiments for nine HyCOS. For each experiment, dry powder of the sample
230 (~0.12 g for chlorides and ~0.25 g for perchlorates, corresponding to approximately similar
231 numbers of moles) was placed in a reaction vial (~1 cm diameter and 4 cm height). The unsealed
232 reaction vial was placed into a glass bottle (~2.5 cm diameter and 5 cm height) half-filled with an
233 RH buffer solution and tightly sealed. Ten RH buffer solutions were used (Table S1, Greenspan,
234 1977). For each HyCOS, 30 pairs of reaction vials and RH-buffer bottles were placed in three
235 environments with controlled temperatures, i.e., 323 ± 1 K in an oven, 294 ± 1 K on a laboratory
236 bench top, and 278 ± 1 K in a dedicated experiment refrigerator.

237
238 An early study by Vaniman and Chipera (2006) has demonstrated that the grain-size effects on
239 the deliquescence/dehydration processes only show up in the first few minutes to hours, but have
240 no effect in long-term results that take days to months to reach equilibrium. Based on this
241 observation, we used the purchased or synthesized HyCOS directly as the starting materials
242 without grain-size selection.

243
244 Our Experiment 1 was conducted at Earth atmosphere pressure. Theoretically, the enthalpy of a
245 reaction is a function of pressure. The small pressure difference between Mars and Earth,
246 however, has only a negligible effect (Chou and Seal II, 2007). Therefore the results of
247 Experiment 1 are applicable to Mars, similar to the deliquescence/dehydration experiments
248 conducted by our group and others on hydrous sulfates (Chou and Seal II, 2003a, 2003b, 2004,
249 2005a, 2005b, 2007; Chou et al., 2002, 2013; Chipera and Vaniman 2007; Vaniman and Chipera,
250 2006; Wang et al., 2006, 2009, 2011, 2012; Wang and Connor 2014; Wang and Zhou 2014).

251
252 The majority of 180 experiments for six chlorides lasted over 18 months and the majority of 90
253 experiments for three perchlorates lasted over 6 months. Most experiments reached equilibrium
254 either by showing the total disappearance of solid salt into brine (i.e., full deliquescence), or
255 “plateaued” mass (within measurement uncertainty) in gravimetric measurements of solids. In all
256 nine plots of Figure 4, an experiment leading to deliquescence is marked with an orange-colored
257 spot; an experiment leading to no-change or dehydration or rehydration is marked by a spot of
258 another color and an annotation whose phase identification was made using non-invasive laser
259 Raman spectroscopy. Note all annotations above the non-orange colored spots at 278 K in Figure
260 4a-i are suggestive only, because the lack of standard Raman spectra of some HyCOS with
261 different hydration degrees.

262
263 Some trials in Experiment 1 on hydrous chlorides at 278 K and $\text{RH} \leq 33\%$ show continuous
264 mass increases after nearly 60 months (Fig. 4a-i), suggesting the slow development to either
265 higher hydration degrees or to deliquescence. Long-term experiments on the stability fields and
266 phase boundaries among these solid phases of HyCOS are ongoing and are not covered here.

267
268 The middle and final products of each experiment were measured at 12 to 16 intermediate stages
269 with regulated time intervals. At each intermediate stage, the reaction-vial was removed from the
270 RH-buffer bottle, sealed immediately, and then non-invasive gravimetric measurements of
271 reaction vials and laser Raman spectroscopic measurements on solid phases through the glass
272 wall of the reaction vials were made.

273

274 We used gravimetric measurements to follow the loss or gain of H₂O per chloride/perchlorate
275 molecule from its starting degree of hydration. In order to obtain information on the rate of
276 deliquescence and thus to link to the observed RSL development, it is important to record the
277 length of time (from the start of experiment) for the full deliquescence of a HyCOS under
278 selected T-RH conditions. Accordingly, we used visual inspections to monitor the progress of
279 deliquescence until full deliquescence was attained. We emphasize that the length of time for full
280 deliquescence ($t_{100\%}$) of a HyCOS was quantitatively validated using gravimetric measurement.
281 This validation is based on the concept that, at a given temperature, the solubility of a salt in H₂O
282 is a fixed value. Thus the total gain in mass (as % per molar mass), at $t_{100\%}$, is about the same
283 across the ten RH levels for a HyCOS at a given T.

284
285 During Experiment 1, we recorded the time when a brine became visible in the reaction vial that
286 typically involved >30% of the tested amount of a HyCOS salt ($t_{>30\%}$), and then recorded the
287 time when full deliquescence (i.e., without remaining salt) of that HyCOS was reached ($t_{100\%}$). In
288 [section 3.3](#), we use the time duration between these two timing points, $\Delta t = t_{100\%} - t_{>30\%}$, to
289 represent the development of a macroscopic manifestation of deliquescence of a HyCOS at a pair
290 of T-RH conditions.

291
292 We used laser Raman spectroscopic measurements to do molecular phase identification of
293 dehydrated or unchanged HyCOS (in solid form) based on previous Raman studies ([Bakker,](#)
294 [2004](#); [Uriarte et al., 2015](#); [Wu et al., 2016](#)). Our Raman measurements were made through the
295 glass wall of sealed reaction vials. At least three spots on each sample were measured at each
296 intermediate stage to determine the homogeneity of reaction products.

297 2.4. Experiment 2 – to measure the RH level maintained by a hydrous salt in an enclosure

298
299
300 The goal of the Experiment 2 is to measure the approximate RH level that can be maintained by
301 a hydrous salt (in the form of dry grains) in an enclosure at a given temperature. Fifteen hydrous
302 salts (six sulfates, six chlorides, and three perchlorates) were used ([Table 1](#)).

303
304 In this experiment, we placed a salt, in the form of dry grains, into a bottle of 4 cm diameter and
305 10 cm height, half filled with the salt and sealed. We inserted the sensor head of a TRH10 data
306 logger into the head space of each sealed bottle. All fifteen bottles were placed first at $238.7 \pm$
307 0.1 K in a first freezer, then at 258.2 ± 0.5 K in a second freezer, then at 272.2 ± 0.3 K in a
308 research experiment refrigerator, and then at 294 ± 1 K on the laboratory bench.

309
310 T and RH values were recorded every five minutes during 2-3 days at each temperature. We
311 collected 500-1000 data points for each salt at a given temperature. We used 80-90% of the
312 collected data (after a system reached its equilibrium) to calculate the average RH ([Table 1](#)).

313 2.5. Experiment 3 – to validate HyCOS rehydration at dry-ice temperature (195 K)

314
315
316 The goal of Experiment 3 was to validate the feasibility of HyCOS rehydration through direct
317 H₂O vapor-salt reaction at a temperature near the lowest T_{ground} during the coldest season in Mars
318 equatorial regions (e.g., at Gale Crater, [Gómez-Elvira et al., 2012](#)).

319

320 Five fully dehydrated HyCOS (MgCl_2 , CaCl_2 , NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$, and $\text{Ca}(\text{ClO}_4)_2$) (generated
321 by heating the corresponding HyCOS in oven) were used as the starting samples, whose
322 identifications were done using multipoint Raman measurements through the glass wall of sealed
323 bottles prior to Experiments 3 and 4.

324
325 During Experiment 3 (Figure 2), a dehydrated HyCOS powder sample was put into a cup (5 cm
326 diameter and 4 cm height) covering only the bottom of the cup (sample thickness < 5 mm). The
327 sample cup (Fig. 2a) was inserted in a Styrofoam box filled with dry ice (195 K) up to the edge
328 of sample cup, and then was placed in a vacuum chamber (Fig. 2a). The vacuum in the chamber
329 (~33 mbar) was dynamically maintained between a continuous vacuum pumping and an input
330 flow of mixed dry CO_2 and H_2O vapor. The H_2O vapor pressure was monitored using a RH
331 meter in the chamber and was adjusted (to be 30-40% RH) by a water bath system at 30°C (Fig.
332 2a). The sample cup within the dry-ice-filled Styrofoam box was removed after a reaction time
333 of 5-6 hours. Laser Raman measurements on each sample were taken immediately, while the
334 sample cup was kept within a pile of dry ice (Fig. 2b) and isolated from laboratory air using a
335 plastic film. Raman measurements were made on > 50 spots for each sample.

336
337 2.6. Experiment 4 – to find the rehydration rate of HyCOS in a Mars chamber

338
339 The goal of the Experiment 4 was to evaluate the rehydration rates of HyCOS in a Mars chamber,
340 at various P, T and RH conditions. These experiments were conducted in the PEACH (Planetary
341 Environment and Analysis Chamber, Sobron and Wang, 2011), with an *in-situ* Raman probe for
342 simultaneous phase identification (Fig. 3). A fully dehydrated HyCOS sample was put into a
343 copper cup that was in tight thermal contact with a copper plate that is cooled by a cycle of cold
344 N_2 -gas flow from a LN_2 dewar. The temperatures of the sample cup can be set and monitored
345 from ambient temperature down to 173 K using a controlled-heating resistor in the LN_2 dewar
346 (Fig. 3). The RH level in the PEACH was monitored using a RH meter and controlled by a water
347 bath system outside of the PEACH, shown in Figure 3 (circled by a blue dotted line). Continuous
348 vacuum pumping was maintained. A total of 35 experiments were conducted at T = 236 to 296 K,
349 RH ~5 to 44% (with larger uncertainties than those listed in Table 1), and P=14 to 41 mbar on
350 five dehydrated HyCOS samples.

351
352 In these experiments, the starting time of the rehydration of a HyCOS was determined by
353 simultaneous *in situ* Raman measurements, using a Raman probe in the PEACH with a sampling
354 spot of ~20 μm diameter. The Raman measurements were made every 9 seconds on the reaction
355 product in the PEACH from the beginning of each experiment. Using a motorized rotation stage,
356 at least five spots on each HyCOS sample were checked repeatedly every 9 seconds.

357 358 **3. Results of Experiments 1 & 2 to Support the Step-one Hypothesis**

359 360 3.1. RH range for the deliquescence of HyCOS

361 From 270 RH-T driven deliquescence/dehydration experiments on nine HyCOS, Experiment 1,
362 we observed the deliquescence, hydration, non-change, and dehydration processes of nine
363 HyCOS at ten RH levels and three temperatures. The final phases (at the time of this writing) are
364 shown in Figure 4 (a to i), with deliquescence marked by orange spots (brine) and the hydrated,

365 unchanged, or dehydrated phases marked by other colors whose hydration degrees were
366 annotated in each plot as determined by Raman measurements.

367
368 Except for $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ that show complicated phase changes (Fig. 4e, 4f),
369 we can plot the deliquescence boundaries of seven HyCOS species in Figure 5a & 5b, and
370 compare them with the deliquescence boundaries of sulfates generated by previous studies (Chou
371 and Seal II, 2007; Wang et al., 2012; Wang and Connor 2014). The deliquescence boundary of
372 each HyCOS was plotted as a colored band, through the middle space between two sets of RH
373 values in the T-RH field, where deliquescence was seen at the higher RH values (right side of
374 band) but not seen at the lower RH values. The width of each colored bar reflects the uncertainty
375 of phase boundary in RH. Filled orange data points indicate occurrence of deliquescence.
376 Unfilled points indicate dehydration, or no-change, or rehydration, against the deliquescence
377 boundary at the lowest RH (e.g., those of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ in Figure 5a and those of $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$
378 in Figure 5b). Similar deliquescence boundaries for hydrous sulfates were drawn based on data
379 in Figure S1, S2, S3 and relevant publications in supporting documents.

380
381 When compared with hydrous sulfates (Fig. 5, S1, S2, S3), the most prominent characteristic of
382 HyCOS deliquescence is that it occurs at mid-to-low RH levels. For example, at $T \leq 294$ K, the
383 deliquescence of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ requires $\text{RH} \geq 22$ -33% only,
384 and the deliquescence of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ requires
385 $\text{RH} \geq 43$ -46% only. In comparison, the deliquescence of three typical hydrous sulfates,
386 melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), and ferricopiapite
387 ($\text{Fe}_{4.67}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$), requires much higher RH levels, i.e., ≥ 94 -96%, ≥ 90 -92%, and \geq
388 75-79% (Fig. 5, S1, S2, S3), respectively. These data suggest that the RH conditions for
389 deliquescence of HyCOS would be more easily met than for the deliquescence of hydrous
390 sulfates, in a dry environment such as on present-day Mars.

391
392 The deliquescence boundaries derived from our Experiment 1 (Fig. 5) are consistent with the
393 DRH (deliquescence relative humidity) of NaClO_4 (51% at 273K, 64% at 228K), $\text{Mg}(\text{ClO}_4)_2$ (42%
394 at 273K, 55% at 223K), and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ($15.3 \pm 3.5\%$ in 223-273K) observed by Gough et al.,
395 (2011, 2016). The DRH ($63.3 \pm 12.5\%$) of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ reported by Gough et al (2016) is higher
396 than the DRH (≥ 30 -33% at 278-323K, Fig. 4a) of our study, but our conclusion is supported by
397 the observed continuous mass increase beyond the highest hydration degree of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (Fig.
398 4a, a point at 278 K and $\sim 33\%$ RH, marked as $>7w \rightarrow$ brine), thus indicating a slow
399 development of deliquescence at low T. The observation of wide DRH (5% to 55%) of
400 $\text{Ca}(\text{ClO}_4)_2$ and no efflorescence observed at 1% RH by Nuding et al (2014) are consistent with
401 our observation of deliquescence of $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ at 7.4-11.3% RH and 278 K (Fig. 4h).

402
403 Compared with those early studies, our 270 RH-T driven deliquescence/dehydration experiments
404 on nine HyCOS revealed an overall picture of approximate deliquescence boundaries of four
405 (Mg, Ca, Fe^{3+} , Al^{3+}) hydrous chlorides and three (Na, Mg, Ca) hydrous perchlorates, with a
406 direct comparison among them (Fig. 5a, 5b) and a direct comparison with the deliquescence
407 boundaries of hydrous (Mg, Fe^{2+} , and Fe^{3+}) sulfates (Fig. 5, S1, S2, S3). Based on these
408 comparisons, we conclude that on present-day Mars, the RH conditions for the deliquescence of
409 HyCOS would be more easily met than for the deliquescence of hydrous sulfates.

410

411 The question remains as to where on Mars these mid-to-low RH % ranges might exist.

412

413 3.2. RH ranges maintained by hydrous salt in an enclosure

414

415 At the martian surface, RH is controlled by the partial pressure of H₂O in the atmosphere (P_{H₂O})
416 and the local temperature. The daytime RH at the martian surface is extremely low. The potential
417 high RH in early morning on Mars is accompanied by extremely low T (mostly < T_e of common
418 salts). Surface salts thus are not expected to form briny fluid. On the other hand, salt layers in the
419 martian subsurface could have a very different RH. We used Experiment 2 to provide a
420 quantitative evaluation of this concept. The measured RH values maintained by fifteen hydrous
421 salts in enclosures are listed in Table 1 (with the manufacturer-specified uncertainties). Only the
422 measured RH values at 272.2 ± 0.3 K were listed, because we found that the differences of
423 measurement RH value of a salt at different temperatures are smaller than the uncertainties in
424 RH measurement specified by the manufacturer of data logger.

425

426 First, we found that the measured RH value maintained by a hydrous salt (in the form of dry
427 grains) in the head space of a sealed bottle closely approaches its RH_{buffer}(T) value (Table S1), a
428 fixed RH value at a given temperature maintained by a saturated aqueous solution of that salt in a
429 closed system (Greenspan, 1977). This RH_{buffer}(T) value is consistent with the deliquescence-
430 phase boundaries defined by stability-field experiments (Fig. 5, S1, S2, S3). Theoretically, the
431 stability field of a hydrous salt would suggest a range of RH maintained by dry grains of that salt,
432 e.g., 95-40 % RH at 278 K for MgSO₄·7H₂O based on Fig. S1. While the actual measurements
433 made in the head space of sealed bottles (half-filled with one of 15 hydrous Mg-, Fe-, Ca-, Al-,
434 NaK-salts in form of dry grains, Table 1) in Experiment 2 revealed RH levels very near the high
435 end of RH (~ RH_{buffer}(T)) of their stability fields, e.g., 95±5 % for MgSO₄·7H₂O (Table 1).

436

437 Secondly, we found a general trend in the RH-maintaining capability among the tested common
438 sulfates, chlorides, and perchlorates with the same type of cation (e.g., column Mg-salts, Fe-salts,
439 Ca-salts, Al-salts, and NaK-salts in Table 1). We found that the RH range maintained by a
440 sulfate in an enclosure is higher than that maintained by a perchlorate with the same cation, and
441 the RH range maintained by a perchlorate is higher than that maintained by a chloride with the
442 same cation. For example, the RH range of 95±5 % is maintained by MgSO₄·7H₂O, 49±3 % by
443 Mg(ClO₄)₂·6H₂O, 38±3 % by MgCl₂·6H₂O. The similar trend exists for Fe-, Ca-, Al-, NaK-salts.

444

445 This trend suggests that subsurface layers with mixed salts would be beneficial for HyCOS
446 deliquescence to occur. For example, the required RH range for the deliquescence of chlorides
447 (Fig. 5a) can be readily provided by co-existing perchlorates or sulfates (Table 1).

448

449 This *matching of RH ranges* (e.g., DRH_{chlorides} < RH_{buffer-sulfates}, Fig. 5 vs. Table 1) reflects the
450 *fundamental properties of these salts* and provides a critical basis to support the feasibility of
451 HyCOS deliquescence in a subsurface salty layer with mixed salts, at temperatures higher than
452 the eutectic temperature (T_e) of a salt (Table 4).

453

454 In other word, the two conditions for the deliquescence of a salt to occur, i.e., an environmental
455 relative humidity > DRH and a temperature > T_e (Toner et al., 2014; Möhlmann 2011a, 2011b;
456 Möhlmann and Thomsech, 2011; Janchen et al., 2010) that seem very hard to be met

457 simultaneously at the surface of Mars (Möhlmann 2011a), can actually be met within a
458 subsurface layer filled with mixed salts on Mars. Combining the results shown in Figure 5 and
459 Table 1, we conclude that the salt mixtures in a realistic field site have the potential to generate
460 Cl-bearing brine, at temperature $> T_e$ (e.g., 278-323 K, Figure 4).

461
462 A logical follow-up question is: are the subsurface salty layers, buried by ordinary Mars surface
463 regolith, in a quasi-closed environment?

464
465 The answer is yes, as given by a thermal-model study (Mellon et al, 2004) and validated by the
466 shallow ground-ice observed at the Phoenix site (Mellon et al., 2009). This model calculates the
467 vertical temperature profile of an ice-cemented regolith layer (40% porosity) covered by a layer
468 of martian ordinary surface dust. Owing to the large difference in their thermal inertia (TI) values
469 ($TI_{\text{surface-dust}} = 250 \text{ J m}^{-2}\text{K}^{-1}\text{s}^{-1/2}$, $TI_{\text{H}_2\text{O-ice}} = 2290 \text{ J m}^{-2}\text{K}^{-1}\text{s}^{-1/2}$, nearly tenfold), the subsurface ice-
470 rich layer would be less affected by the large diurnal T fluctuation at the surface. This layer
471 would have a very narrow temperature range ΔT (e.g., $\Delta T = 175\text{-}185 \text{ K}$ when $\Delta T = 150\text{-}240\text{K}$ at
472 the surface) and a much lower maximum temperature T_{max} (e.g., $T_{\text{max}} = 185 \text{ K}$ when $T_{\text{max}} = 240 \text{ K}$
473 at the surface, Mellon et al., 2004, Fig.1).

474
475 Because many salts have high TI values, similar to the ice-cemented soil (e.g., $TI_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}} =$
476 $2218 \text{ J m}^{-2}\text{K}^{-1}\text{s}^{-1/2}$, $TI_{\text{NaCl}} = 3326 \text{ J m}^{-2}\text{K}^{-1}\text{s}^{-1/2}$) (Mellon, 2008), this thermal model can be
477 extrapolated to a subsurface salt-rich-layer (Wang et al., 2013a). Thus the subsurface salty layer
478 would be isolated from atmospheric temperature fluctuations at the surface, i.e., it would be in a
479 quasi-closed environment.

480
481 This extrapolation was validated by two field observations. On Mars, the highly hydrated ferric
482 sulfates (including $\text{Fe}_{4.67}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$) were found in the shallow subsurface (dug up by
483 the action of a rover wheel) at Gusev crater (Johnson et al., 2007; Campbell et al., 2008; Wang et
484 al., 2008). In addition, the dehydration of these ferric sulfates, after being exposed to surface
485 atmosphere, was revealed by their color change in Pancam images (Wang & Ling, 2011), which
486 implied an original high RH environment in the salty layer of subsurface. On Earth, highly
487 hydrated Mg-sulfates ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) were found in the subsurface of a saline playa in a
488 hyperarid region (Aridity Index < 0.04) on the Tibet Plateau (Wang et al., 2013a, Wang et al.,
489 2018). These two sulfates, $\text{Fe}_{4.67}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, would dehydrate within
490 hours in the laboratory when RH is 11 % (Wang et al., 2009, 2012). However, they remain intact
491 for thousands-to-millions of years in the subsurface of hyperarid regions (Earth and Mars).

492
493 In conclusion, Table 1 indicates that the required RH range for the deliquescence of chlorides or
494 perchlorates (Fig. 5) can be readily provided by co-existing salts of other types, such as sulfates,
495 in a subsurface layer containing mixed salts.

496
497 Whether the deliquescence of subsurface hydrous salts could occur and could be macroscopically
498 observed in a warm season on Mars, the kinetics of the deliquescence process is the determining
499 factor, which is revealed by the second set of results from our 270 RH-T driven
500 deliquescence/dehydration experiments on nine HyCOS.

501
502

503 3.3. The rate of HyCOS deliquescence

504

505 The development of the deliquescence process of each tested HyCOS is presented as Δt ($= t_{100\%}$ -
506 $t_{>30\%}$) vs. T in [Figure 6](#), where $t_{100\%}$ is the time of full deliquescence of a tested HyCOS counting
507 from the start, under a pair of T-RH conditions, marked by a symbol (a square for $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
508 in [Fig. 6a](#); a triangle for $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ in [Fig. 6b](#); etc.) on the top of a colored vertical bar.
509 Whereas the low end of this vertical bar ($t_{>30\%}$) represents the appearance time of observable
510 brine of that HyCOS (often $>30\%$ brine/salt ratio).

511

512 Because the Δt s at the different RH and the same T of the same HyCOS overlap considerably, we
513 calculated a mean value of Δt for an RH (e.g., 6.6 sols for 59% RH for $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at 278 K,
514 [Fig. 6a](#)), then averaged over the means of all seven Δt s of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at seven RH levels and
515 the same T, and get a $\Delta t_{\text{ave}}(278 \text{ K}) = 3.9$ sols (red dot in overlapped vertical bars at 278 K in [Fig.](#)
516 [6a](#)), for the purpose of following discussion. In [Fig. 6a](#), this Δt_{ave} represents an average time for
517 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ deliquescence to manifest at 278 K over a wide RH range (45-100%). An
518 exponential regression line (black dotted line in [Fig. 6](#)), in the form of $\Delta t_{\text{ave}}(T) = a \cdot e^{b \cdot T}$, was
519 calculated using $\Delta t_{\text{ave}}(323 \text{ K})$, $\Delta t_{\text{ave}}(294 \text{ K})$ and $\Delta t_{\text{ave}}(278 \text{ K})$ for each HyCOS, with R^2 reflecting
520 the quality of regression. The parameters of derived regression lines for seven HyCOS are listed
521 in [Table 2](#), as well as the calculated $\Delta t_{\text{ave}}(240 \text{ K})$, $\Delta t_{\text{ave}}(250 \text{ K})$ and $\Delta t_{\text{ave}}(300 \text{ K})$ in sol for each of
522 the tested HyCOS, using the regression parameters.

523

524 [Figure 6](#) and [Table 2](#) first revealed that the deliquescence rates of all seven HyCOS have strong
525 temperature dependences, i.e., rapidly declining Δt_{avg} when temperature increases. For example,
526 a 10 K increase from 240 K ([Table 2](#)) to 250 K (low end of T_{RSL} window, [McEwen et al., 2011,](#)
527 [2014](#)) can cause a Δt_{avg} shortening of 12 sols for $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 399 sols for $\text{NaClO}_4 \cdot \text{H}_2\text{O}$
528 (column 7, 8, 9 of [Table 2](#)). At 300K (high end of T_{RSL} window, [McEwen et al., 2011, 2014](#)), the
529 deliquescence of all seven HyCOS would occur within 1-5 sols (column 10 of [Table 2](#)). This
530 property is consistent with the tight temperature correlation of observed RSL ([McEwen et al.,](#)
531 [2011, 2014](#)).

532

533 Secondly, as shown in [Figure 6](#) and [Table 2](#), different HyCOS species have very different slopes
534 of the regression lines in $\Delta t(\text{sol})$ vs. $T(\text{K})$. For example, the $\Delta t_{\text{avg}}(323\text{K})$ for $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ([Fig.](#)
535 [6a](#)) and $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ ([Fig. 6b](#)) are almost the same, ~ 0.2 - 0.3 sol, but the $\Delta t_{\text{avg}}(278 \text{ K})$ is 7.7 sols
536 for $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ ([Fig. 6b](#)) and 3.3 sols for $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ([Fig. 6a](#)), i.e., $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ is ~ 2 times
537 slower in deliquescence rate. This means that the reduction of the deliquescence rate of
538 $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ at low temperature is much faster than that of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. In other words, at low
539 temperature, the deliquescence of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ occurs more readily than that of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$.

540

541 These findings can be used to derive a quantitative comparison among different HyCOS,
542 especially in the temperature range lower than the observed T_{RSL} window (250-300K) at the
543 surface, i.e. the subsurface T.

544

545 For this purpose, we use 172(=688/4) sols (a green dotted line in each plot of [Figure 6](#)) to set a
546 virtual limit for a warm season on Mars, while understanding that the actual time-durations of the
547 RSL are very different at different locations on Mars (can be a full year at some places, [Stillman](#)
548 [et al., 2016, 2017](#)). Using the green dotted 172 sols line, the T=300 K line (high end of T_{RSL}

549 window, red rectangle in Figure 6), and the black dotted regression line, we can draw a gray-
550 shaded area in Δt (sol) vs. T(K) plot of each HyCOS in Figure 6. The size of the gray-shaded area
551 represents approximately the susceptibility of a HyCOS to deliquescence. Quantitatively, the
552 $T_{\text{low-end}}$ of the gray-shaded area (defined by the intersection point of the regression line and 172-
553 sols line in Fig. 6, and listed in column 5 of Table 2) gives a straightforward prediction. This
554 means that during a warm season, if the environmental T of a subsurface HyCOS layer rises
555 above the $T_{\text{low-end}}$ of, e.g., > 238 K for $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (Fig. 6b, Table 2), with the suitable RH range
556 provided by co-existing salt mixture, the macroscopic manifestation of deliquescence of
557 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ would occur in less than 172 sols.

558
559 Nevertheless, environmental $T > T_e$ (Eutectic T_e values of many salts based on literature were
560 listed in Table 4) is required for deliquescence of a salt to occur. Among the seven HyCOS
561 shown in Figure 6, six of them have the $T_{\text{low-end}} > T_e$ (T_e was shown by a vertical blue dotted line
562 in each plot of Fig. 6), thus the above statement applies to all of them. For $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, whose
563 T_e (240K, Table 4) dictates that its deliquescence can only start when the environmental T in
564 subsurface rising to 240K, although its less steep regression line in Δt vs. T plot ends with a $T_{\text{low-}}$
565 $\text{end} \sim 208\text{K}$ (column 5 of Table 2).

566
567 When the T of a subsurface layer begins to rise in a warm season from its original T (assuming
568 $T_{\text{max}}=185\text{K}$ when $T_{\text{max}}=240\text{K}$ at surface, Mellon et al., 2004), with the suitable RH range
569 provided by co-existing salt mixture, the deliquescence of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and
570 $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ would start earlier than other HyCOS because they require less temperature
571 increases (column 6 of Table 2) by seasonal changes.

572
573 A further comparison of regression lines in Fig.6, however, shows that the deliquescence rate of
574 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is the fastest among the seven HyCOS. For example at 240K (column 7 of Table
575 2), the macroscopic manifestation of deliquescence of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ would take about 29 sols
576 (averaging over a RH range, Fig. 6a), while the similar manifestation of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ would take
577 an average 71 sols. Using the calculated sol numbers at 240K (column 7 of Table 2) to compare
578 the deliquescence rates of seven HyCOS, an order in the deliquescence susceptibility is:
579 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} > \text{AlCl}_3 \cdot 6\text{H}_2\text{O} > \text{FeCl}_3 \cdot 6\text{H}_2\text{O} > \text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O} > \text{CaCl}_2 \cdot 4\text{H}_2\text{O} >$
580 $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} > \text{NaClO}_4 \cdot \text{H}_2\text{O}$. The same order would be derived if using the values of $T_{\text{low-end}}$.

581
582 Overall, the results of Experiments 1 (270 RH-T driven deliquescence/dehydration experiments)
583 and 2 (quantification of RH values maintained by 15 common salts in enclosure) demonstrated
584 that the deliquescence of subsurface HyCOS layers could occur on Mars (our step-one
585 hypothesis) with temperature increases. The time ranges for brine manifestation in a salt-rich
586 subsurface in the observed T_{RSL} (250-300 K) (or modeled T window of salt-rich subsurface, gray
587 rectangles in Fig. 6) are in the same order of magnitude with the observed development of RSL
588 in warm seasons on Mars.

589 4. Results of Experiment 3 & 4 to Support the Step-two Hypothesis

590
591 A key question is how the deliquescence of HyCOS recurs at the same sites in the same fashion
592 (i.e., from the top of a crater rim or the top of a cliff) during consecutive years (> 5 martian
593 years). Now we use the results of Experiment 3 and 4 to test our hypothesized mechanism, i.e.,
594

595 the direct H₂O vapor-to-salts reaction that enables the recharge of H₂O back to the subsurface
596 HyCOS layer, so the deliquescence of HyCOS layer can occur in a subsequent martian warm
597 season.

598 4.1. Feasibility of HyCOS rehydration at 195 K

600
601 Results of Experiment 3 (Figure 7) demonstrated the feasibility of the rehydration of MgCl₂,
602 CaCl₂, NaClO₄, Mg(ClO₄)₂, Ca(ClO₄)₂ through direct H₂O vapor-to-salt reaction, at 195 K, a low
603 T that is practical to maintain in the laboratory using dry ice and also close enough to the lowest
604 T_{ground} measured (~175 K (Gómez-Elvira et al., 2012)) on Mars.

605
606 Figure 7 (a to e) shows the Raman spectra measured on the dehydrated HyCOS samples before
607 and after Experiment 3. The starting anhydrous CaCl₂ and MgCl₂ both have no Raman peak in
608 the 2800-3800 cm⁻¹ range (top black spectrum in Fig. 7a and 7b). After 5-6 hours of CO₂ + H₂O
609 flow while maintaining the anhydrous chlorides at 195 K, the ending Raman spectra shows the
610 H₂O peaks of hydrous chlorides (marked by black dotted lines). Among the checked (>50) spots
611 for each ending product, multiple hydration degrees were found (Bakker, 2004; Uriarte et al.,
612 2015). The highest hydration degrees for both chlorides, CaCl₂·6H₂O and MgCl₂·12H₂O, were
613 reached at some checked spots, which suggest not only a direct H₂O vapor-to-salt reaction but
614 also a very fast attainment of equilibrium at 195 K.

615
616 The starting anhydrous Ca(ClO₄)₂, Mg(ClO₄)₂, and NaClO₄ all have a finger-print Raman peak
617 belonging to the ClO₄ fundamental mode at 985, 983, and 952 cm⁻¹ (top black spectrum in Fig.
618 7c, 7d, 7e, based on Wu et al., 2016). After Experiment 3, the formation of hydrous perchlorates
619 was revealed by additional peaks in the fundamental spectral range 900-1050 cm⁻¹ (marked by
620 dotted lines), such as a new Raman peak at 942 cm⁻¹, in addition to 952 cm⁻¹ peak of anhydrous
621 NaClO₄, and by additional Raman peaks of H₂O vibrational modes (marked by black dotted lines)
622 in the 3800-2800 cm⁻¹ spectral range (Fig. 7c, 7d, 7e). These observations support the
623 rehydration of Ca(ClO₄)₂, Mg(ClO₄)₂, and NaClO₄ to Ca(ClO₄)₂·xH₂O (x=2, 4), Mg(ClO₄)₂·xH₂O
624 (x=2, 6), and NaClO₄·xH₂O (x=1, 2, and more) at 195K.

625 4.2. The rate of HyCOS rehydration under Mars conditions

626
627
628 The goal of Experiment 4 is to evaluate the rehydration rates of five dehydrated HyCOS (MgCl₂,
629 CaCl₂, NaClO₄, Mg(ClO₄)₂, Ca(ClO₄)₂) under Mars relevant conditions. We conducted 35
630 experiments in the PEACH with a simultaneous phase identification made using an *in situ* Raman
631 probe inside of the PEACH (Section 2.6). Based on the *in situ* Raman sensing (every 9 s), the
632 timing of the onset of rehydration of a HyCOS (i.e., when a H₂O peak appears in the Raman
633 spectrum, detection limit ~1 mol %) was determined.

634
635 We have found that the Raman peaks of rehydrated HyCOS appeared *within minutes* after the
636 beginning of an experiment. For example, the peak of CaCl₂·2H₂O (3445 cm⁻¹) occurred at 4 min
637 and 50 s (Figure 8a) and the peaks of Ca(ClO₄)₂·2H₂O (3491 cm⁻¹) and Ca(ClO₄)₂·4H₂O (3550
638 cm⁻¹) appeared at 10 min and 14 min (Figure 8b), respectively.

639

640 A relevant aspect is the very high rehydration rate of sulfates, considering their effect in
641 facilitating the deliquescence of Cl-salts when they co-exist (section 3.2). In previous studies
642 (Wang et al., 2009, 2011, 2012, 2013), we observed the rehydration of sulfates within a few
643 hours at the lowest temperature tested. For example, the rehydration of $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ occurred (to
644 form $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ at various RHs and 278K) after 1 hour
645 into the experiment (Wang et al., 2009, Table 4).

646
647 The results of Experiment 4 demonstrated that the rehydration rates of HyCOS under Mars-
648 relevant P-T-RH conditions are extremely fast, *minutes to hours*. When compared with the time-
649 scale of a martian cold season (> 100 sols), we conclude that the rehydration rate of HyCOS is
650 *not a limiting factor* for the recharge of H_2O back to HyCOS during the length of a cold season
651 on Mars. We discuss limiting factors in the next section.

652 653 **5. Implication to RSL -- an understanding built upon the experimental results and the mass** 654 **balance calculations**

655
656 Our experiments generated five sets of data that provided critical basis for the interpretation of
657 two essential characteristics of RSL, which have not been fully explained by other models
658 (Schmidt et al., 2017; Dundas et al., 2018), i.e., the tight temperature correlation of RSL
659 occurrence and the recurrence of RSL in the subsequent warm season.

660
661 Through the experiments, we discovered: (1) the subsurface layers of mixed salts can provide the
662 mid-to-low RH range to facilitate the deliquescence of HyCOS in RSL relevant T window; (2)
663 the T dependence of the deliquescence rates of HyCOS supports the observed seasonal behavior
664 of RSL; (3) the rehydration of dehydrated HyCOS at extremely low T is feasible through direct
665 H_2O vapor-to-salt interaction; (4) the rehydration rates of tested HyCOS under Mars conditions
666 are extremely fast, thus would not be a limiting factor for the recurrence of RSL. Based upon
667 these results, we discuss additional details, especially from a mass-balance perspective, to
668 develop a one-step-forward understanding on the potential source materials of RSL on Mars.

669 670 5.1. The generation of RSL

671
672 A direct comparison of RH-T conditions for deliquescence (Fig. 5) indicates that Cl-bearing salts,
673 HyCOS, are more likely (than sulfates) to be the source materials to trigger RSL. This
674 conclusion is consistent with the detection of oxychlorine salts at RSL sites (Ojha et al., 2015),
675 as well as the rare-to-absent sulfate features in Vis-NIR spectra from RSL sites (Ojha et al.,
676 2013). Anhydrous chlorides (as desiccation products of Cl-brine) have no Vis-NIR spectral
677 features and thus are not observable by CRISM.

678
679 The seasonal behavior of RSL on Mars is fundamentally supported by the strong temperature
680 dependence of the deliquescence rates of HyCOS (Fig. 6).

681
682 During most of the time in a martian year, even at a locality where the environmental RH is in a
683 suitable range for deliquescence of a HyCOS (Fig. 4, 5, Table 1), low environmental
684 temperatures (even when $T > T_e$) would dictate a very low deliquescence rate (Fig. 6). The
685 limited amount of brine, if ever generated, might coat grain surfaces but not form a briny flow.

686 Only when a locality enters the warmest period, e.g., a few mid-afternoon hours in a warm
687 season on Mars, would the peak temperature experienced by the subsurface HyCOS layer induce
688 a large increase of the deliquescence rate (Fig. 6, Table 2), which would abruptly generate a
689 larger amount of brine through a high %-to-full deliquescence of HyCOS in a short time, with
690 brine volume > 60-118% of original HyCOS volume (at least, when counting only the structural
691 H₂O in HyCOS, shown in the last column of Table 3).

692
693 When some quantity of briny fluid forms abruptly, flows, and reaches a steep slope, its down-hill
694 motion may trigger an RSL flow. Now we need to consider the volume of a subsurface HyCOS
695 layer that would be required to generate the observed RSL (the sizes and the occurrence of >10
696 RSL at most RSL sites, McEwen et al., 2011, 2014), through two flow models: *a fully-brine-*
697 *wetted track model* and *a brine-triggered granular-flow model*

698 699 5.1.1. A fully-brine-wetted track model

700
701 This model assumes that the observed albedo reduction in RSL tracks was mainly caused by
702 gradual wetting of surface regolith by HyCOS brine. We need to estimate the required volume of
703 Cl-bearing brine and the required volume of subsurface HyCOS layer for a typical RSL track, to
704 test this model.

705
706 Two parameters have to be constrained for this estimation: (1) the percentage of brine per
707 volume of regolith that enabled the observed albedo change at an RSL site; (2) the percolation
708 depth of a Cl-bearing brine at an RSL site.

709
710 The best way to constrain the first parameter is to refer the investigation on “water tracks” in the
711 Antarctic Dry Valley (ADV) (Dickson et al., 2013; Head et al., 2007; Kreslavsky and Head,
712 2009; Levy, 2012; Levy et al., 2014; Marchant and Head, 2007). ADV has the most Mars-like
713 temperature-precipitation environment on Earth, with widespread permafrost and extremely low
714 erosion rates. Similar to RSL on Mars, tracks with low albedo were seen in satellite imaging on
715 north-facing slopes of valley walls. These tracks occur on steep slopes (10-30°), elongated down
716 slope, usually > 60 m in width, extend ~100-400 meter in length, and show no detectable relief.
717 Field exploration found that the most fundamental difference between the subsurface soils in the
718 tracks and inter-tracks was a difference in their water content (Head et al., 2007).

719
720 Laboratory analysis (Levy et al., 2014) of collected samples from ADV revealed that the
721 gravimetric water contents (GWC) of two water-track samples were 2.5% and 4.2%. The GWC
722 of typical ADV hill slope soils are 1.2% and 0.5%. Levy and co-authors also found that the soil
723 darkening occurs rapidly as soil moisture increases from 0% to about 5%. The presence of salts
724 or soil moisture above 5% did not result in additional darkening. Based on these ADV
725 observations, we set a conservative 10 vol. % as the lower limit for brine content in the regolith
726 required for a *fully-brine-wetted track model*.

727
728 The second parameter to be constrained is the percolation depth of Cl-bearing brine into regolith.
729 In general, the percolation of brine would be terminated at the top of an impervious layer, similar
730 to the ground ice layer terminating the percolation of liquid H₂O in ADV water tracks. When
731 considering the percolation of brine, an impervious layer would be formed by the precipitation of

732 a salt with the highest eutectic temperature (T_e) among all species in the brine. [Table 4](#) lists the
733 T_e values, with sulfates having the highest T_e ($\Delta T=273-T_e \sim 1.2 - 3.8$ K), and perchlorates having
734 the lowest ($\Delta T=273-T_e \sim 34 - 67$ K).

735
736 When a brine containing sulfates and HyCOS forms and starts to flow downhill, the percolation
737 of the brine would occur at the same time. The temperature of the regolith on the slope would
738 decrease with the increase of depth ([Mellon et al., 2004](#)). At a depth when $T_{\text{regolith}} \sim T_e$ of sulfates,
739 an impervious layer of sulfates would form, thus preventing further percolation of the remaining
740 brine. Based on the T_e of Ca-, Mg-, Na-, and K-sulfates (272 K to 269 K, [Table 4](#)), the measured
741 T_{RSL} window, and the measured ordinary T_{ground} at equatorial regions (e.g., Gale Crater) on Mars
742 ([Gómez-Elvira et al., 2012](#)), the impervious sulfate layer would form at very shallow depths,
743 which would limit the percolation depth of Cl-bearing brine in an RSL track. For this reason, it is
744 reasonable to use 5 cm diurnal skin depth of dry regolith ([Grimm et al., 2014](#); [Stillman et al.,](#)
745 [2014](#)) to constrain the percolation depth of a Cl-bearing brine at an RSL site.

746
747 Using the above two constrained parameters, we made a rough estimate of the amount of brine
748 required by a *fully-brine-wetted track model*. An RSL of 0.5 m width, 100 m length, and 5 cm
749 depth, with 10 vol. % brine content, would require a brine of 0.250 m³ in volume. Based on the
750 known mineral density values of hydrous and anhydrous chlorides and perchlorates ([Table 3](#)),
751 and counting conservatively only the structural H₂O in HyCOS for contributing the brine volume,
752 we obtained a required subsurface pure HyCOS layer of 0.5 m × 0.5 m × 1.0 m in volume (as the
753 high limit), in order to generate an RSL of the size described above. Since ≥10 RSL tracks were
754 observed at most RSL sites, a *fully-brine-wetted track model* would require quite a large amount
755 of subsurface HyCOS layer at each RSL site. On the basis of the current observations (remote
756 sensing and surface exploration) from Mars, the evidences that satisfy this requirement are hard
757 to establish. Therefore, we would suggest a different model that requires a lesser amount of
758 subsurface HyCOS materials at an RSL site, i.e., a *brine-triggered granular-flow model*.

759 760 5.1.2. A brine-triggered granular-flow model

761
762 This *brine-triggered granular-flow model* assumes the main portion of an RSL track would be
763 dry granular flow on a steep slope, triggered by the downhill motion of a briny subsurface fluid
764 (that reduced internal friction) that was generated from the deliquescence of subsurface HyCOS.
765 By this model, once such briny fluid forms and reaches a steep slope, it can stimulate slope
766 instability that initiates flow of overlaying dry grains that in turn spreads the HyCOS spectral
767 signature (and low albedo as darkening) along the flow path at the surface of a steep slope. The
768 details of such flow would need more experimental simulations (e.g., [Imamura et al., 2019](#)),
769 which is beyond the scope of this study.

770
771 The detected hydrous oxychlorine salts at four RSL sites ([Ohja et al., 2015](#)) could be the salts
772 from nearly dried-up brines from accumulated RSL activities through many martian years. The
773 observed rapid fading of many RSL, when the season changes, can be explained by efflorescence
774 of the brine ([Gough et al., 2011, 2014](#)). Dust deposition requires decades to brighten dark
775 features on Mars ([Aharonson et al., 2003](#)).

776

777 Dundas et al. (2018) studied the terminal slope of 151 RSL, and concluded that the observed
778 range of slope angles matches with the critical angles of granular flows. Their model, however,
779 cannot explain the seasonal behavior of RSL, for which they suggested the potential role of water
780 for RSL initiation. Our *brine-triggered granular-flow model* would be a natural match with
781 Dundas model, i.e., a Cl-bearing-brine-triggered granular flow for most RSL.

782

783 5.2. The recurring of RSL in consecutive years

784

785 The recurring of RSL from the same RSL sites in the same fashion in consecutive years is a more
786 challenging phenomenon to interpret. Based on our experiments, we suggested the recharge of
787 H₂O through the rehydration of subsurface HyCOS layer, which interacted with atmospheric
788 H₂O vapor front that moves down from the Polar Region during a cold season (Smith, 2002;
789 Smith et al., 2009; Figure S4). Our experimental results (Figure 8) demonstrated that the
790 rehydration rate of HyCOS under Mars-relevant P-T-RH conditions would not be a limiting
791 factor. Now we need to consider, from a mass-balance perspective, the H₂O supply through Mars
792 atmospheric circulation in the current obliquity period.

793

794 We first note that the HyCOS salts brought downhill by an RSL in the previous warm season
795 would be mostly spread on the slope. These HyCOS salts cannot contribute to RSL in the
796 following year because RSL always begin from the top of crater rims or the top of cliff.

797

798 Secondly, the potential source materials for the next year's RSL would be *the remnant*
799 *subsurface HyCOS in RSL source regions*. There can be two types of remnant HyCOS, either the
800 subsurface HyCOS dehydrated during the previous warm season, i.e., the unfilled points in
801 Figure 5 (corresponding to the non-orange colored data points in nine plots of Figure 4), or a
802 subsurface HyCOS layer that underwent deliquescence in the previous warm season but the
803 generated brine did not move far enough to reach a downhill slope, thus the brine simply
804 solidifies in place when the cold season starts.

805

806 Thirdly, during a cold season when atmospheric H₂O front moves down from Polar Region and
807 passes through the equatorial and low-latitude region (Smith 2002; Smith et al., 2009; Figure S4),
808 some H₂O molecules would diffuse down into subsurface where HyCOS layer would be a cold-
809 trap for H₂O, because HyCOS have high thermal inertia (TI) and thus at low temperature (based
810 on Mellon et al., 2004).

811

812 In order to determine quantitatively the increase of hydration degree of a subsurface HyCOS
813 layer from an atmospheric H₂O supply, we need to estimate two values: (1) the quantity of H₂O
814 being carried by the seasonal H₂O vapor front; (2) the quantity of H₂O diffusing into the
815 subsurface during the length of a cold season.

816

817 Related to the amount of H₂O supplied by current atmospheric circulation, a moderately high
818 column value of 15 precipitable-microns (pr- μ m) was found for low latitude and equatorial
819 regions during the cold season on Mars, with a value of 90 pr- μ m near the North Polar Region,
820 extracted from MGS-TES (Thermal Emission Spectrometer) and Viking-MAWD (Mars
821 Atmospheric Water Detection) data (Smith, 2004; Jakosky and Haberle, 1992; Jakosky 1985).

822

823 We thus use a range of 15 - 90 pr- μm as the input H₂O vapor density, with 90 pr- μm as the
824 original column value when the H₂O vapor front leaving the North Polar Regions (Jakosky and
825 Haberle, 1992), and the 15 pr- μm to be the result of absorption by cold subsurface materials in
826 equatorial and low latitude regions. This range of input H₂O vapor density, assuming it is well
827 mixed with CO₂, translates to about 1.5×10^{-6} - 9.0×10^{-5} kg m⁻³ (as N_{atm}) at the soil surface.

828
829 The flux of H₂O vapor from the atmosphere to the subsurface is limited by H₂O vapor diffusion
830 through any overlying soil. For our purpose, we ignore diurnal oscillations in ground
831 temperatures and the buffering effects of adsorption, and consider only the average conditions of
832 temperature and vapor density (e.g., Mellon and Jakosky, 1993; Mellon et al., 2004; Aharonson
833 and Schorghofer, 2006). The mean flux is then given by

$$834 \bar{F} = -D \overline{dn/dz}, \quad (1)$$

835
836 where D is the effective diffusion coefficient (m²/s), that can vary depending on local soil
837 structure, n is the vapor density (kg/m³), and z is the depth downward into the subsurface (m)
838 (Mellon and Jakosky, 1993 and references therein). Assuming a set of reasonable values of 10
839 μm pores, 50% porosity, and a tortuosity of 1.75 (Sizemore and Mellon, 2008), we estimate a
840 typical diffusion coefficient to be $\sim 3 \times 10^{-4}$ m² s⁻¹. The mean gradient in H₂O vapor density,
841 $\overline{dn/dz}$, may be approximated as $\overline{\Delta n}/z$ between the atmosphere and a subsurface depth z .

842
843 To estimate $\overline{\Delta n} = N_{\text{atm}} - N_z$, we need to select a suitable subsurface vapor density value (N_z), which
844 is controlled by local temperatures at depth Z and the specific HyCOS species present. As
845 mentioned in the beginning of this section, there are two types of remnant HyCOS as the
846 potential source materials to trigger RSL of the following year. In the following calculations, we
847 consider the worst-case scenario, a bone-dry subsurface HyCOS layer. We assume that at the
848 beginning of a cold season, this layer would have a H₂O vapor density similar to that of
849 atmospheric vapor density during the previous warm season. A range of average atmospheric
850 vapor density 4-10 pr- μm was found for season of Ls 270-0-135, and 15-12 pr- μm for the season
851 of Ls180-225 (Smith et al., 2009). Based on equation (1), a larger N_z yields a smaller $\overline{\Delta n}$ thus a
852 lower mean flux \bar{F} . To start with a conservative assumption, we selected a larger N_z value, 10 pr-
853 μm , that corresponds 1.0×10^{-6} kg m⁻³, for our calculation.

854
855 From this calculation, taking 172 sols as a virtual season limit for comparison purpose, for
856 diffusion of H₂O vapor downward to a subsurface HyCOS layer, we obtained a flux of H₂O in
857 the range of 0.22 to 3.47 kg m⁻² at 1 cm depth, and 0.04 to 0.69 kg m⁻² at 5 cm depth in 172 sols.
858 Using the flux to 1 cm depth subsurface, we calculated the increase of hydration degree for seven
859 HyCOS (density data are in Table 3) during one cold season (172 sols). We use Figure 9 to
860 illustrate the result of our calculation, in which we assumed the immediate rehydration based on
861 the ultrafast rehydration rate found in Experiment 4, i.e., the rehydration rates of dehydrated
862 HyCOS under Mars relevant conditions.

863
864 The solid symbols on the left side of Figure 9 show the increased hydration degrees of seven
865 totally dehydrated HyCOS (the worst case scenario) by the end of 172 sols in current obliquity
866 period, with an input H₂O vapor density range of 15-90 pr- μm . We found that the largest
867 increase of hydration degree is 1.95 by the end of 172 sols. We also found that this conclusion
868

869 does not change much even using a less conservative assumption. For example, the largest
870 increase of hydration degree would be 2.09 when using the smallest possible starting water vapor
871 density, $N_z = 4 \text{ pr-}\mu\text{m}$ based on [Smith et al., 2009](#).

872
873 This calculation indicates that at the current obliquity, the supply of H_2O molecule in 172 sols
874 from the polar cap through atmospheric circulation and downward diffusion is limited, which
875 will support the partial rehydration of subsurface HyCOS, with the largest increase of hydration
876 degree to be two. In other words, if the starting HyCOS being totally dehydrated, they will not
877 reach their highest hydration degrees (which are 2 to 12, marked on the right-side of [Fig. 9](#)) by
878 the end of 172 sols.

879
880 At specific locations on Mars, however, the cold season (or high H_2O vapor density) could last
881 longer than 172 sols, which would enable a large increase in the hydration degree of HyCOS. In
882 order to have a quantitative comparison with the results of 172 sols ([Figure 9](#)), [Table 5](#) shows
883 that the full hydration of seven HyCOS (from totally dehydrated states) can be reached in about
884 0.8 to 3.8 martian years, with the input H_2O vapor density at $90 \text{ pr-}\mu\text{m}$.

885
886 Studies have suggested that H_2O ice would be stable at Mars equatorial region when obliquity
887 exceeds 45° , and would be stable at mid-latitude regions when obliquity $>30^\circ$ ([Richardson and](#)
888 [Wilson, 2002](#); [Head et al., 2003](#)). The most recent obliquity $>30^\circ$ period occurred 500 kyrs ago
889 and lasted for 10's of Kyrs ([Laskar et al., 2002, 2004](#)). During these periods, the increased polar
890 cap sublimation is expected to increase the global humidity ([Jakosky et al., 1993](#)) by $10\times$ to $20\times$
891 at obliquity 30° , possibly as high as $100\times$ at obliquity 35° (e.g., [Mellon and Phillips 2001](#);
892 [Chamberlain and Boynton 2007](#)).

893
894 With the input H_2O vapor density calculated to $900 \text{ pr-}\mu\text{m}$ ($10\times$ times of current value, [Mellon](#)
895 [and Phillips 2001](#); [Chamberlain and Boynton 2007](#)), the hollow symbols on the right side of
896 [Figure 9](#) show the results of our calculation for a high obliquity period ($>30^\circ$) in the recent past.
897 It revealed that all HyCOS in our consideration can reach their highest hydration degrees in a
898 very short time (< 172 sols in [Fig. 9](#)). Provided that some of the hydrated salts could survive to
899 the present day (dehydration rates of Mg-sulfates reported by [Wang et al., 2013a](#); comparison of
900 dehydrations of Mg, Fe, Ca, Al sulfates reported by [Wang and Zhou, 2015](#)), this H_2O could then
901 be available for episodic deliquescence of subsurface HyCOS that triggers RSL in the current
902 epoch.

903 904 **5. Conclusions**

905
906 The results from our five sets of experimental results support a brine-related hypothesis for RSL,
907 with subsurface HyCOS as the most likely source materials. Specifically, the strong temperature
908 dependence of the deliquescence rates of HyCOS ([Figure 6](#)) matches with the seasonal behavior
909 of RSL. Our calculation on the required volume of HyCOS layer for a typical RSL track and the
910 current observational evidences on Mars does not support *a fully-brine-wetted track model*, thus
911 we suggested *a brine triggered granular flow model* for most observed RSL that is consistent
912 with Dundas' model ([2018](#)) based on the analysis of terminal slope of 151 RSL. Consider the
913 recurrence of RSL, the ultrahigh rehydration rates of HyCOS under Mars relevant P-T-RH
914 conditions ([Figure 8](#)) supports the recharge of H_2O back into HyCOS in cold seasons on Mars

915 such that deliquescence of salts in the following warm season could be a trigger for RSL in
916 consecutive martian years. Nevertheless, at current Mars obliquity during an annual cycle, the
917 diffusion rate of atmospheric H₂O vapor into the salt-rich subsurface indicates a limited H₂O flux
918 supply, which supports the partial rehydration of the subsurface remnant HyCOS in a worst-case
919 scenario.

920
921 On the other hand, establishment of a full-scale H₂O reservoir for RSL could be achieved quickly
922 during the recent >30° obliquity period based on previous studies about the H₂O vapor density of
923 that period (Figure 9). It is worth to notice, however, that implication of our rehydration and
924 rehydration rate experiments is limited to the H₂O recharge through atmospheric H₂O cycle. In
925 order for the subsurface HyCOS reservoir to last until the recent episode, the mechanisms for
926 replenishing subsurface salts (Cl and S) will have to exist to support a brine-related hypothesis
927 for RSL, which belongs to a next step investigation. Overall, our results imply that large amounts
928 of Cl-salts exist in the martian subsurface at RSL sites.

929

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931

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943

944 **7. Author contributions.**

945 AW designed the experimental study, with the help from ASM. AW, ZCL, and YCY conducted
946 the experiments and the data analysis. ASM contributed in the development of flow models.
947 MTM made the mass-balance calculations. MDS provided the data and Figure S4 for
948 atmospheric H₂O vapor circulation. JH guided the referencing of ADV water track study. BLJ
949 helped in the proof reading of manuscript. All co-authors contributed in the discussions,
950 interpretations, and the development of implications.

951

952 **8. Competing financial interests.**

953 Declarations of interest: none.

954 **9. Additional information**

955 The data to support the figures in this manuscript will be available at a public FTP site at
956 <http://epsc.wustl.edu/public-data/>, with a folder named as /2019_ICARUS_Wang_paper/. No
957 user ID and password are required for the access of these data.

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1375 **11. Tables**
1376

1377 **12. Table and Figure captions**

1378

1379 Table 1. RH values (average over > 400 collected data points \pm manufacture specified
1380 uncertainty*) of 15 sealed hydrous salts at 272.2 ± 0.3 K

1381

1382 Table 2. Comparison of deliquescence rates of seven tested HyCOS, $\Delta t_{\text{avg}}(\text{sol})$ at 250K and
1383 260K were calculated using the regression line $\Delta t_{\text{ave}}(T) = a * e^{b * T}$

1384

1385

1386 Table 3. The least additional brine volume of some HyCOS deliquescence, counting only their
1387 structural H₂O.

1388

1389 Table 4. Eutectic temperatures of some sulfates, chlorides, and perchlorates collected from the
1390 literature.

1391

1392 Table 5. Martian years needed for full rehydration of totally dehydrated HyCOS with 90 μm
1393 input H₂O vapor density.

1394

1395 **Figure 1. Illustration of the hypothesis** (HyCOS=Hydrous Chlorides and Oxychlorine Salts).

1396 (a) During high obliquity period (> 30° about ~500 Kyr ago; > 45 ° about ~5 Myr ago, lasted >
1397 10's Kyr), H₂O ice covered mid-low latitude regions on Mars. H₂O vapor from H₂O ice diffused
1398 into subsurface HyCOS layer. As the result of > Kyr diffusion, subsurface HyCOS reached their
1399 full hydrations. (b) Warm season during current obliquity, when local T rises ($T_{\text{RSL}} = 250\text{-}300\text{K}$).
1400 Deliquescence rates of subsurface HyCOS increased quickly with T, generated Cl-bearing brine
1401 that reduced internal friction and triggered the instability at steep slope. The combined wet-dry
1402 flow spread HyCOS spectral features onto some slopes. (c) Cold season during current obliquity,
1403 H₂O vapor front moves down from polar region to mid-low latitude region on Mars (Smith et al.,
1404 2009). Atmospheric H₂O vapor diffused into remnant subsurface HyCOS layer. Depending on
1405 $P_{\text{H}_2\text{O}}$, duration of cold season, type of HyCOS and their hydration degrees, they reached partial or
1406 full hydrations, which will serve as the source materials for RSL in next warm season.

1407

1408 **Figure 2. Laboratory set-up for Experiment 3.** (a) Left side is a vacuum chamber, in which a
1409 dynamic vacuum was kept by a vacuum pump and the input of CO₂ gas flow with well-
1410 controlled H₂O vapor supplied by a system on the right (circled by a blue dotted line). The
1411 sample cup, with dehydrated HyCOS powder covering only the bottom, was inserted in to a dry-
1412 ice (-78°C) filled Styrofoam box. (b) Raman measurements were taken immediately after the
1413 removal of Styrofoam box from vacuum, with sample cup being kept within a pile of dry ice and
1414 isolated from laboratory air using a plastic film.

1415

1416 **Figure 3. Laboratory set-up for Experiment 4.** Left side is the PEACH (Planetary
1417 Environment and Analysis Chamber), in which a dynamic vacuum was kept by a vacuum pump
1418 and the input of CO₂ gas flow with well-controlled H₂O vapor supplied by a system on the right
1419 (circled by a blue dotted line). A fully dehydrated HyCOS sample was put into a copper cup that
1420 was in tight thermal contact with a copper plate that is cooled by a cycle of cold N₂-gas flow
1421 from a LN₂ dewar. Raman measurements were made using an *in situ* probe inside of PEACH
1422 directly on the sample (insert photo). A motorized rotation stage ensured five spots on each

1423 HyCOS sample to be checked by Raman probe repeatedly every 9 seconds during the whole
1424 duration of an experiment.

1425

1426 **Figure 4. Results of Experiment 1: deliquescence-dehydration-rehydration of nine HyCOS**
1427 **in T-RH space base on 270 experiments.**

1428

1429 **Figure 5. Deliquescence phase boundaries of HyCOS compared with those of hydrous**
1430 **sulfates.**

1431

1432 **Figure 6. Time range Δt (from $t_{>30\%}$ to $t_{100\%}$) of the observed macroscopic manifestation of**
1433 **deliquescence of a HyCOS, as a function of T and RH.**

1434

1435 **Figure 7. Evidence of HyCOS rehydration at 195 K.** Black colored spectra on top are from the
1436 started anhydrous phase. All other colored spectra are from the products of Experiment 3, i.e.,
1437 rehydration phases.

1438

1439 **Figure 8. Evidence of extremely fast rehydration of chlorides and perchlorates measured at**
1440 **different T and RH in a Mars environment chamber in Experiment 4.** (a) Rehydration of
1441 CaCl_2 at 251 K, 23.6 % RH, and 16.4 mbar. (b). Rehydration of $\text{Ca}(\text{ClO}_4)_2$ at 296 K, 4.8 %RH,
1442 and 19.7 mbar.

1443

1444 **Figure 9. The rehydration of HyCOS is not limited by their rehydration rate, but by**
1445 **atmospheric H_2O supply.** With the measured H_2O vapor density of current obliquity (15-90 μm),
1446 the largest increase of hydration degree is two for the HyCOS. With the estimated H_2O
1447 vapor density for $>30^\circ$ obliquity period (10x to 20x of current), all HyCOS can reach their
1448 highest hydration degrees in a very short time (< 172 sols). Five colored lines at the right indicate
1449 the highest hydration degree of a HyCOS, with color code matches with the HyCOS in legend.
1450 For example, the highest hydration degree of NaCl and NaClO_4 (green color) is two H_2O per
1451 molecule.