Revision 1 Sulfate bearing deposits at Dalangtan playa and its implication for the formation and preservation of Martian salts W. G. Kong^{1*}, M. P. Zheng¹, F. J. Kong¹, and W. X. Chen¹ MLR Key Laboratory of Saline Lake Resources and Environments, Institute of Mineral Resources, CAGS, Beijing 100037, China

7 Abstract

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The sulfate bearing strata on Mars must have recorded rich information of its aqueous 8 history. However, the hydrated sulfates observed in the surface thin layer by remote 9 sensing, especially widespread kieserite, are likely weathering products other than 10 pristine deposits. Here we report the results from the mineralogical investigations and 11 environmental monitoring on the sulfate bearing Dalangtan Playa (an analogue site 12 with Mars-like environmental conditions in northern Tibetan Plateau) to examine the 13 depositional and secondary processes of hydrated sulfates. The regional deposition 14 characters of DLT Playa were described based on our mineralogical results. 15 Widespread kieserite was identified in situ by portable laser Raman spectrometer on 16 the weathered surface of the Mg-sulfates rich section, which formed from the 17 18 hexahydrite dehydration after exposed to the ambient conditions in six months covering the summer, and survived in the winter. During summer days, wind and 19 sunlight may have facilitated the dehydration process, leading the formation of 20 21 kieserite from dehydration. On the basis of the observed kieserite formation, the 22 recorded local environment conditions, as well as previously reported phase diagrams for Mg-sulfates, we suggest that the current diurnal relative humidity-temperature 23 24 circles at low latitudes of Mars favor the formation of kieserite through secondary 25 processes.

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Key words: Mars analogues; Tibetan Plateau; DLT Playa; sulfates deposits;
 Martian kieserite

31 Introduction:

Various minerals closely related to the aqueous history of Mars have been 32 33 identified or indicated, including clays (e.g. Bishop et al. 2008; Carter et al. 2010; 34 Ehlmann et al. 2009; Glotch et al. 2006; Mustard et al. 2008; Wang et al. 2006a), 35 carbonates (e.g. Boynton et al. 2009; Carter and Poulet, 2012; Ehlmann et al. 2008; Michalski and Niles 2010; Morris et al. 2010), sulfates (e.g. Arvidson et al. 2005; 36 Gendrin et al. 2005; Kounaves et al. 2010; Langevin et al. 2005; Lichtenberg et al. 37 2010; Murchie et al. 2009; Squyres et al. 2006; Wang et al. 2006b), and chlorides 38 39 (Glotch et al., 2010; Jensen and Glotch, 2011; Murchie et al. 2009a; Osterloo et al. 40 2008, 2010; Ruesch et al. 2012; Wray et al. 2009). It is reasonable to get information on the aqueous history of Mars from the detailed study of these minerals. 41

Abundant calcium sulfates, mostly gypsum occur near the north polar region of 42 Mars (Langevin et al. 2005). Mg-sulfates have the largest quantities and widest 43 distribution at low latitudes of Mars. For example, those discovered by Observatoire 44 pour la Minéralogie, l'Eau, les Glaces et l'Activité (OMEGA) fill most part of Valleys 45 Marineris and nearby lowlands (Gendrin et al. 2005). Stratigraphic relations of 46 sulfates with different hydration degrees (poly- and monohydrated sulfates) were 47 reported on the basis of comprehensive orbital data sets (Mangold et al. 2008), and 48 clarified for the Martian light-tone layered deposits (ILD) at various sites combining 49 50 the high resolution Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) with the Context Camera (CTX) data sets (e.g. Bishop et al. 2009; Flahaut et al. 2010; 51 Lichtenberg et al. 2010; Milliken et al. 2010; Murchie et al. 2009a, 2009b; Roach et al. 52 2009, 2010; Wiseman et al. 2010), and kieserite (monohydrated Mg-sulfate) was 53 specified to be widespread at low latitudes (e.g. Arvidson et al. 2005; Bishop et al. 54 2009; Gendrin et al. 2005; Mangold et al. 2008; Roach et al. 2009). 55

56 The hydration states of sulfates are strongly influenced by the relative humidity

57 (RH) and temperature (T) of ambient environments. Thus the hydrated sulfates on Martian surface might be the products from the weathering of primary deposits under 58 Mars atmosphere. Many studies through laboratory experiments or thermodynamic 59 modeling have been carried out to investigate the stability properties under different 60 RH and T conditions for sulfates (e.g., Chipera and Vaniman 2007; Chou and Seal 61 62 2003, 2007; Grevel et al. 2012; Kong et al. 2011; Steiger et al. 2011; Vaniman et al. 2004, 2006b; Wang et al. 2009, 2011; Xu and Parise 2012), as well as for sulfates 63 associated with smectites under Mars-like RH and T conditions (Wilson and Bish, 64 2012). These studies have provided critical information for discussing how these 65 observed hydrated sulfates originate. 66

In nature, complex factors might be involved to constrain the occurrence of specific sulfate species, thus studies on terrestrial analogue sites with similar mineralogy and environmental conditions are needed to help linking these fundamental studies with Mars observations.

71 Terrestrial analogue studies have focused on various aspects and have served critical information for Mars explorations (e.g. Bishop et al. 2001, Marchant and Head 72 2007) Since 2008, we have started the expedition at saline playas in a hyperarid 73 74 region on Tibet Plateau, a terrestrial Mars analogue site, to investigate the mineralogy, geology, bio-signatures, and climatic conditions (Kong et al. 2009, 2013a, 2013b; 75 76 Mayer et al. 2009; Sobron et al. 2009; Wang and Zheng 2009; Zheng et al. 2009). In this report, we focus on the depositional and weathering processes of hydrated 77 78 sulfates in one of these saline playas (i.e., Dalangtan Playa).

79 Dalangtan Playa on Tibetan Plateau

Dalangtan (DLT) Playa formed from the drying up of sulfate brine in the centered depression of the DLT secondary basin (38°0′-38°40′N, 91°10′- 92°10′E, Figure 1) 82 that locates on the north-west of Qaidam Basin, northern margin of the Tibetan Plateau. The Tibetan Plateau (average elevation of about 4500 m) blocks the humid 83 air carried by the Indian monsoon, leading to the hyperarid (Aridity Index (AI) ≤ 0.04) 84 Qaidam Basin (32-35° N, 90-100° E) (Zheng et al. 2009). DLT basin is the 85 86 depositional center of the western Qaidam Basin and the high elevation (~ 3000 m) of the DLT Playa induces a low mean annual temperature (276-278 K) as well as the 87 large diurnal, seasonal temperature variation (from 303 K to 253 K) (Kong et al. 88 2013a). The combination of these factors (sulfate rich sediments, cold and dry weather, 89 90 low pressure, and high UV radiation) makes the DLT Playa one of the best sites to carry out Mars analogue studies. 91

92 Samples and methods

93 Sample collection

In the recent two expeditions to DLT Playa (September 2012, and January 2013), four vertical sections (i.e. DP1, 2, 3, and 4; 2-4 meters depth) have been sampled at locations with different distances to its depositional center (Figure 1). The sections were made during mining activities and have a depth of 2-4 m. All these four sections exhibit obvious interbedded layers (e.g. Figure 2 for DP2), and fresh samples were systematically collected and numbered on the each layer after removing the weathered crust.

101 In situ Raman analysis at DLT:

During the expeditions, we used a portable Raman spectrometer (iRaman 532, BW Tec, spectral resolution 4cm⁻¹) for *in situ* characterization of the original deposition sequence as well as the weathered surface for the sulfate-bearing sections (Figure 2). For sections DP1, 3, 4, the Raman spectrometer was used to measure the fresh digged surfaces before sampling. For DP2 section, the Raman spectrometer was used to 107 carefully examine the mineral phases in the weathered materials on the outer surface.

108 Laboratory mineralogical analysis of collected samples:

Samples were well sealed and stored in a 233 K freezer to prevent unexpected phase change due to dehydration or rehydration after delivered back (about one week for delivery). For mineralogy characterization, each sample was analyzed by X-ray diffraction (XRD), laser Raman spectroscopy and polarizing petrographic microscopy. The samples used for these measurements were carefully chosen, for example, we only use coarse blocky samples that did not show any feature from dehydration or rehydration.

Laboratory laser Raman analysis was conducted using a Renishaw System-2000 spectrometer (514 nm laser and spectral resolution, 1-2 cm⁻¹) for point measurement on all samples. The laser wavelength calibration was made using a Si wafer and resulted in Raman peak position accuracy of 1 cm⁻¹ and precision of 0.5 cm⁻¹.

120 XRD measurements were carried out on an X-ray diffractometer (Y500 by 121 CDRIG Ltd.) with Cu X-ray source, and all the XRD patterns were collected in the 20 122 range of 3-80 °, with step size of 0.05 °. The peak positions were calibrated using the 123 Si (111) spacing of a standard Si reference powder. All samples were measured 124 immediately after they were grounded into powder by either an electric grinder or by 125 an agate mortar. The total duration for the preparation and measurement of single 126 sample is less than one hour.

127 A Zeiss Axio Scope A1 polarized petrographic microscope was used to determine 128 the mineralogy for all samples, and sulfates with different hydration states can be 129 distinguished based on their different optical properties.

130 **Relative humidity and temperature (RH-T) monitoring**

A RHT10 data logger with a capacitance sensor by Extech was placed at the

surface of studied areas for more than two years (since 2010) to record the RH-T
conditions near the surface. RH-T conditions were measured and recorded
simultaneously every per hour, and the recorded data were collected manually for
every 3-6 months.

The RH values at subzero temperatures measured by the RHT10 logger were defined by actual H₂O partial pressure in the air over saturated H₂O partial pressure of ice, and these RH values were transformed to actual H₂O partial pressure in the air over saturated H₂O partial pressure of hypothetical supercooled pure water (i.e. RH% defined by the World Meteorological Organization) based on the Goff–Gratch equation (McDonald, 1965). And the RH values at subzero temperatures in this study all follow the definition by the World Meteorological Organization.

Depositional characters

Table 1 shows the chemical formula for the minerals involved in this study. The 144 145 minerals identified in different layers of four sampled sections are listed in Table 2, and the order of appearance of each mineral indicates the estimated relative 146 147 abundance (from large to small) in the layers. Epsomite can be easily dehydrated to hexahydrite even by grinding in XRD sample preparing (Wang et al., 2009), and the 148 149 pristine Mg-sulfate phase in DP2 was determined to be hexahydrite based on the facts 150 that: 1) hexahydrite was found to be the only Mg-sulfate in the analysis of well stored 151 DP2 samples using petrographic microscope; and 2) none of XRD patterns of DP2 152 samples showed any signal of epsomite.

The uppermost layer (i.e. the weathered crust), rich in aeolian sands, is thicker in DP 3, 4 sections than in DP1 and 2, indicating an earlier dry up time at the edge of the depression, which is consistent with previous studies (e.g. Wang et al. 1993). Mirabilite dominates in the lower layers for DP 3 and DP 4, followed by the halite dominating layers, while hexahydrite dominates in DP 2, showing an evolution of sulfate brine from the stage for mirabilite precipitation to that for hexahydrite precipitation, which is common on earth for both lacustrine and marine sediments. Halite occurs in almost all the deposited layers, which indicates that the sulfate brines that formed the studied sections are saturated with NaCl.

The Mg-sulfate bearing DP2 is of the greatest interest among four sections for this study, which serves good opportunity to compare with Mg-sulfates on Mars. Five hexahydrite layers have been noticed in this section (Table 2), and carnallite was found to co-occur with hexahydrite in two of these five layers. Although K-Mg-Cl-SO₄ brines had reached a late stage for the co-precipitation of hexahydrite and carnallite, the brines need to be further concentrated to reach the stage for kieserite precipitation (e.g. Braitsch 1971; Harvie and Weare, 1980).

Apparent mineralogical differences have been found among the interbedded layers for section DP2 (Figure 2). Dark colored layers are rich in clays, which indicate increased supply of fresh waters under relatively wet climates. Whitish layers, dominated by hexahydrite and halite, have less or even no clays, thus would have formed under relatively dry climates with little or no fresh water supply (Zheng et al. 1997).

175 Kieserite formation at DLT Playa

The DP2 section was created in April 2012 by local mining activities and has been exposed to the ambient atmosphere for about 6 months before our first expedition (Sept. 2012). Kieserite was identified by *in situ* Raman measurements (e.g. the kieserite spectra in Figure 3C) from the whitish materials covering the surface of all five hexahydrite bearing layers in DP2 (Figure 2) for the two expeditions. The kieserite must have formed from the weathering of the hexahydrite layers during the six months before the first expedition in Sept. 2012, and survived in the winter untilthe second expedition in Jan. 2013.

Some in situ Raman spectra acquired on the pseudomorphic whitish materials 184 (Figure 3B) that came from the hexahydrite dehydration do not show any spectral 185 186 feature, and further observations under petrographic microscope for these whitish 187 materials suggested the existence of amorphous Mg-sulfates. The Raman spectra of amorphous Mg-sulfates obtained in the laboratory laser Raman measurements do 188 show a broadened peak at 1030 cm⁻¹, however, this peak did not show up in our 189 spectra due to the low sensitivity of the portable Raman spectrometer. Kieserite was 190 191 also identified several millimeters deeper in these pseudomorphic materials.

192 We excavated a horizontal section (at 1.5 meter depth) at DP2, from surface to 193 interior for about 15 centimeters. In situ Raman measurements were made at 194 individual spots on this section. The hydrous Mg-sulfates identified on the horizontal 195 section show a trend of increasing hydration degree from the outermost weathered 196 surface to the fresh interior, and they are kieserite and sanderite, starkeyite, 197 pentahydrite, and finally hexahydrite (Figure 3). This clear trend from monohydrated 198 kieserite to the primary hexahydrite indicates a gradient of RH-T conditions within 199 the subsurface that controlled the dehydration/rehydration processes of Mg-sulfates at 200 DP2 site.

The RH-T stability fields of hydrated Mg-sulfates were substantially studied by different experimental methods at temperatures above 263 K (Chou et al. 2003, 2007; Chipera and Vaniman 2007; Peterson and Wang 2006; Steiger et al. 2011; Wang et al. 2009, 2011), and was extrapolated to as low as 175K through thermodynamic calculation (Figure 4, Steiger et al. 2011). Although their results are consistent with each other in general, difference exists referring to the formation of kieserite through

207 dehydration processes.

208 In the experiments by Wang et al. (2009) and Chipera and Vaniman (2007), 209 kieserite can only form from dehydration of epsomite or hexahydrite at temperatures above 323 K, and the dehydration stop at starkeyite under DLT relevant temperatures. 210 211 Starkeyite is metastable under all RH-T conditions (e.g. Chou et al 2007, Steiger et al. 212 2011), and the dehydration process for starkeyite to kieserite is extremely slow (Steiger et al. 2011). This should be the reason why the dehydration seems to stop at 213 214 starkeyite in these two sets of experiments (Wang et al. 2009; Chipera and Vaniman 2007). At DP2, the hexahydrite dehydration product, starkeyite, continued to 215 216 dehydrate at relatively low temperatures (mean annual T 276-278 K, Kong et al. 217 2013a), and formed widespread kieserite on the outermost surface. In their 218 experiments, constant RH-T conditions were controlled for the dehydration reaction. At DP2, more factors such as wind and sunlight may have been involved in the 219 220 dehydration process. Wind and sunlight are effective factors to speed up evaporation, 221 and the strong wind and sunlight at DLT Playa (e.g. > 3 m/s for monthly average wind 222 speed at summer, Kong et al. 2013a) may have facilitated the dehydration of starkeyite by quickly removing the water vapor produced from dehydration and by 223 224 serving more energy for the dehydration reaction respectively, thus kieserite formed at 225 DLT. In the laboratory experiment by Wang et al. 2009, amorphous Mg-sulfates form 226 in the quick dehydration processes, and it cannot form under DLT relevant RH-T 227 conditions. Thus the occurrence of amorphous Mg-sulfates at DLT playa indicates 228 very quick dehydration processes, which was probably induced by wind and sunlight. Wang et al. (2011) suggested that kieserite can form from the amorphous 229 230 Mg-sulfates that firstly formed from dehydration under Mars relevant temperatures.

At DP2, the amorphous Mg-sulfates overlay or mix with kieserite (Figure 3), and this

occurrence does not support that amorphous Mg-sulfates had formed prior to kieserite.
Thus we believe that the kieserite at DLT playa mostly formed directly from the
dehydration of hexahydrite, and the starkeyite identified (Figure 3) might be the
intermediate product of the hexahydrite-kieserite dehydration process.

In the work by Steiger et al. (2011), the epsomite-kieserite transition boundary was obtained by a different experimental technique, which suggests kieserite can form from dehydration under DLT relevant temperatures. Our field observation that kieserite formed from the dehydration of hexahydrite at DLT Playta (mean annual T 276-278 K and relative humidity < 30%, Kong et al. 2013) give terrestrial evidence to support their results.

Implications for the observed Mg-sulfates on Mars

Although starkeyite is a metastable phase under all RH-T conditions, the 243 dehydration of starkeyite is extremely slow as observed by many experimental studies, 244 245 thus starkeyite has been suggested to have the most common occurrence under current diurnal RH-T circles on Martian surface (e.g. Steiger et al. 2011 Wang et al., 2011). 246 247 However, this does not help much on explaining whether the widespread Martian kieserite came from deposition or from the weathering of higher hydrated Mg-sulfates. 248 249 Our observations of kieserite formation at DLT playa might be able to give some clues 250 referring to this question.

The diurnal surface RH-T conditions of a typical summer and a winter day at the DLT playa are shown in Figure 5, and the diurnal RH-T circles have been plotted in Figure 4 for comparison. A typical summer diurnal RH-T circle locates wholly in the RH-T stability field of kieserite (Figure 4), with a diurnal average T of 294 K, and kieserite have formed from hexahydrite dehydration under such conditions in less than 6 months, neglecting the less kieserite favored spring and autumn conditions. 257 The typical winter diurnal RH-T circle locates wholly outside the kieserite RH-T stability field (diurnal average T of 257 K, Figure 4), however, the previously formed 258 259 kieserite survived the winter and was detected all over the weathered surfaces of DP2 in our second expedition in Jan. 2013. These facts support previous observation 260 261 through laboratory experiments that the kieserite formation from dehydration at 262 higher temperatures in the kieserite RH-T stability field is much easier than 263 rehydrating to other phases at lower temperatures outside kieserite field (e.g. Vaniman 264 and Chipera 2006a). And factors such as wind and sunlight make it feasible to observe the kieserite formation from dehydration at DLT Playa. 265

266 As indicated by Figure 4, the diurnal RH-T conditions in the Martian summer at 267 low latitudes covers the RH-T stability fields of three stable Mg-sulfates, i.e. kieserite, 268 epsomite, meridianite. At summer daytime on Martian surface, the RH-T conditions locates in the RH-T stability field of kieserite, and wind (with maximum of 7 m/s, 269 270 Hess et al., 1977) and sunlight can also facilitate the dehydration process of hydrated 271 Mg-sulfates, leading to the formation of kieserite. Although the maximum 272 temperature (255 K) used in this study for Mars is about 48 K lower than that at DLT 273 Playa (303K), the formation of minor amount of kieserite can be expected. Once 274 kieserite had formed during the summer daytime, it has great chance to survive in the 275 low temperature nighttime due to low rehydration rates at the minimum temperature 276 of 195 K, which is about 58 K lower than the minimum temperature in the winter 277 night at DLT Playa (Figure 4). Although the diurnal RH-T circle discussed here is 278 adapted from a summer day, it would be easier for the summer formed kieserite to survive a much colder winter on Mars than that at DLT Playa (Smith et al. 2006; 279 280 Spanovich et al. 2006). Thus the current diurnal RH-T circles might favor the formation of kieserite. 281

282 Beside, RH deviation from equilibrium can also have influence on the dehydration or rehydration rates. However, to our knowledge, no reliable data are available on 283 how much the influence is. For dehydration, there seems no big difference between 284 the RH derivations from equilibrium in daytime on Mars and that in summer at DLT 285 286 Playa (Figure 4). For rehydration, the RH derivation from equilibrium seems to be 287 larger in nighttime on Mars than that in winter at DLT Playa. However, the temperature decreases as the RH derivation from equilibrium goes larger, which may 288 289 lead to stronger influence on decreasing the rehydration rates. Thus we believe temperature variations dominate the dehydration or rehydration rates for Mg-sulfates 290 291 referring to the kieserite formation under current diurnal RH-T conditions on Mars.

292 If the surface diurnal RH-T circles at low latitude regions on current Mars truly 293 favor the formation of kieserite through dehydration, why are there polyhydrated 294 Mg-sulfates in the vicinity of kieserite bearing regions on Mars as indicated by 295 OMEGA and CRISM observations (e.g. Bishop et al. 2009; Flahaut et al. 2010; 296 Gendrin et al. 2005; Lichtenberg et al. 2010; Milliken et al. 2010; Roach et al. 2009). 297 As reviewed by Murchie et al. (2009a), the polyhydrated sulfates (including Mg 298 bearing phases) tend to occur at stratigraphically higher parts, while kieserite tends to 299 occur at lower parts. We propose that the temperature difference between the 300 atmosphere hundreds of meters above the surface and the surface (about 10 K 301 difference for the first two hundred meters for the Martian atmosphere, Sorbjan et al. 302 2009) might be one important factor that causes this observed stratigraphic relation 303 for monohydrated and polyhydrated Mg-sulfates. As shown in Figure 4, the hydrated Mg-sulfates on the stratigraphically higher parts have less chance to experience 304 305 relative high temperatures, thus has a less possibility for dehydrating to kieserite. However, this observed stratigraphic relation is not strict, even interbedded layers of 306

monohydrated and polyhydrated Mg-sulfates were noticed (Roach et al. 2009), and 307 308 this can be explained by other factors that influences the Mg-sulfate stability 309 properties, such as various abundance of coexisting smectites, which can buffer local RH and prevent the dehydration of coexisting Mg-sulfates (Wilson and Bish 2012). 310 311 Our scenario for the kieserite formations suggests that the widespread kieserite 312 may have formed through the weathering of hydrated Mg-sulfates under current Mars conditions, which does not require the observed kieserite to be the direct precipitation 313 product from Mg-S-bearing brines. 314 315 Summary Two expeditions have been carried out on DLT Playa (mean annual T 276-278 K, 316 RH < 30%) in Sept. 2012 and Jan. 2013. The mineralogy of four sulfate bearing 317

sections (DP 1-4) (2-4 meters depth) in this playa were investigated both in situ and on the collected samples in the laboratory. On the basis of obtained mineralogical results, the evolution of the sulfate brines in this region is discussed. All these four sections contain obvious interbedded layers, and hexahydrite was determined to be the major minerals for five layers in section DP2.

Hydrated magnesium sulfates including kieserite, sanderite, starkeyite, and pentahydrite have been observed following a trend of increasing hydration state from the weathered surface to the fresh interior.

Widespread kieserite was identified on the weathered surface of five hexahydrite bearing layers in DP2 through *in situ* measurements by a portable laser Raman spectrometer for both expeditions. Based on mineralogical results, it is concluded that kieserite observed at DLT came from the dehydration of hexahydrite, and possibly with intermediate product of starkeyite. On the basis of the occurrence of kieserite and stability properties of Mg-sulfates determined by previous studies, we suggest that

factors such as wind and sunlight may have facilitated the dehydration of Mg-sulfates,

leading to the quick formation of kieserite at DLT Playa.

334 Combining our field observations, the surface RH-T data recorded for the DLT Playa, and the RH-T phase diagram of Mg-sulfates determined by previous studies, a 335 336 scenario is proposed for the formation of widespread Martian kieserite. Our scenario 337 states that the current Mars surface diurnal RH-T circles at low latitudes favor the formation of kieserite through dehydration. The temperature difference between the 338 339 atmosphere at hundreds of meters above the surface and the surface might be one important factor that controls the stratigraphic trend for monohydrated and 340 341 polyhydrated Mg-sulfates observed on Mars. In this scenario, the Martian kieserite 342 does not need to be the deposition product from brines, which might be favored by the atmospheric modeling studies for past Mars. 343

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592 **Captions for Figures and tables**

- 593 Figure 1. Location of Dalangtan (DLT) Playa in the Qaidam Basin on Tibetan Plateau.
- 594 Samples were systematically collected on four sections (DP 1, 2, 3, 4) with different distances
- 595 to the depositional center of DLT Playa.
- 596
- 597 Figure 2. Photo of DP2 section and *in situ* Raman measurements
- 598

599	Figure 3. Occurrence of hydrated Mg-sulfates at section DP2. A) Photo of a plane
600	perpendicular to the weathered surface of DP2 section excavated for in situ Raman
601	investigation. B) Photo of weathered material from section DP2, whitish pseudomorphic
602	crystals come from hexahydrite dehydration, and darker colored halite crystals persist from
603	weathering. C) In situ Raman spectra of Mg-sulfates (assigned based on Wang et al. (2006c))
604	and the markers on photo A (Ks, kieserite; Sa, sanderite; St, starkeyite; Pt, pentahydrite, and
605	Hx, hexahydrite) show where the spectra were obtained. Epsomite cannot be distinguished in
606	situ from hexahydrite due to limited spectral accuracy of the portable Raman spectrometer
607	(Wang et al. 2006c), and epsomite was ruled out after the XRD and petrographic microscope
608	analysis on collected samples. D) Major sulfate peaks of Raman spectra in C with peaks
609	indicated.

9/11

- 611 Figure 4. Phase diagram of MgSO₄-H₂O system at low temperatures (adapted from Steiger
- et al. (2011)). Dashed curves are the phase boundaries for $11H_2O-7H_2O$, $7H_2O-6H_2O$,
- 613 7H₂O-4H₂O and 6H₂O-4H₂O, and the dotted line represents the boundary for 6H₂O-1H₂O
- 614 (above 293 K) and the 7H₂O-1H₂O boundary (below 293 K). Solid loop represents a daily cycle
- 615 of present-day Mars conditions in summer at the Viking Lander 1 site (Savijärvi 1995). The
- dashed loop shows the diurnal change of the atmospheric conditions hundreds of meters
- 617 above the surface inferred by Mini-TES on Spirit rover (Sorbjan et al. 2009). Dotted loops
- 618 indicate the diurnal change of the surface conditions of DLT Playa for a typical summer and
- 619 winter day, and the specific date is noted in the figure.
- 620
- 621 Figure 5. Diurnal surface RH-T conditions of the DLT Playa for a typical summer and winter
- 622 day (specific dates are marked in the figure).
- 623
- Table 1. Chemical formulas for salt minerals involved in this study.
- 625

Table 2. Minerals identified in each layer from the top surface to the bottom of four sections.
 The order of appearance for each mineral indicates the estimated relative abundance (from large to small) in the layers.













Minerals	Chemical formula
meridianiite	MgSO ₄ •11H ₂ O
epsomite	MgSO ₄ •7H ₂ O
hexahydrite	MgSO ₄ •6H ₂ O, 6W
pentahydrite	MgSO ₄ •5H ₂ O, 5W
starkeyite	MgSO ₄ •4H ₂ O, 4W
sanderite	MgSO ₄ •2H ₂ O, 2W
kieserite	MgSO ₄ •1H ₂ O, 1W
halite	NaCl
carnallite	KCI•MgCl ₂ •6H ₂ O
gypsum	CaSO ₄ •2H ₂ O
anhydrite	CaSO ₄
mirabilite	Na ₂ SO ₄ •10H ₂ O
glauberite	Na ₂ Ca(SO ₄) ₂

Vertical section s	Layers from the top surface to the bottom					
DP1	hexahydrit e halite clays	halite	clays halite	halite clays	halite	clays halite
DP2	clays carnallite halite	hexahydrit e halite carnallite clays	clays halite hexahydrit e	hexahydrite halite clays	halite hexahydrit e clays	hexahydrit e halite clays carnallite halite clays
DP3	clays anhydrite	halite clays anhydrite glauberite	halite gypsum clays mirabilite	mirabilite halite gypsum		
DP4	clays anhydrite	halite clays anhydrite glauberite	halite gypsum clays mirabilite	mirabilite halite gypsum		