

Salt deliquescence along boulder cracks in the Antarctic Dry Valleys: An overlooked source of moisture for rock weathering processes

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12 **Keywords**

13 Salt deliquescence; subcritical cracking; salt shattering; Antarctic Dry Valleys.

14 **Abstract**

15 Cracking is a primary rock-weathering mechanism in arid environments, where dry conditions
16 typically limit the efficacy of water-driven weathering processes. Here, we present results from a field-
17 based experiment in the hyper-arid and frigid Antarctic Dry Valleys (ADV) that documented recurring
18 periods of transient accumulation of liquid water along rock cracks during otherwise dry conditions.
19 This moisture was likely sourced from the deliquescence of hygroscopic salts during sub-saturated
20 humidity conditions. Analysis of meteorological data from 17 stations scattered throughout the ADV
21 revealed that near-surface atmospheric conditions across one of Earth's driest environments can
22 annually support tens of such deliquescence-efflorescence cycles of hygroscopic salts, e.g., CaCl_2 ,
23 NaNO_3 , NaCl , and MgCl_2 . This deliquesced moisture may have an important role in the cracking
24 processes of ADV rocks. In a broader context, the results from the ADV suggest that deliquesced
25 atmospheric humidity may be an overlooked source of moisture available for rock weathering processes
26 in otherwise extremely dry deserts on Earth and possibly Mars.

27 **1 Introduction**

28 **1.1 Rock weathering in hyper-arid environments**

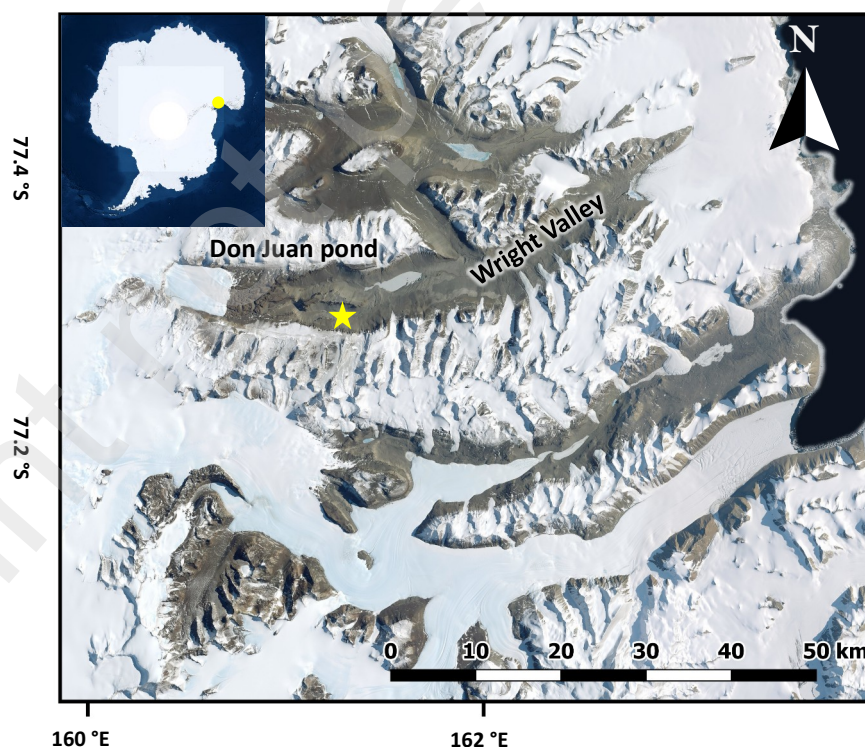
29 Rock weathering is broadly regarded as a key and often rate-limiting process in the subsequent
30 evolution of terrestrial landscapes. In hyperarid environments, physical disintegration, i.e., the breakup
31 of rocks through cracking, is typically a dominant mode of weathering because the characteristic dry
32 conditions in such settings limit the efficacy of water-dependent chemical, biological, and frost
33 weathering mechanisms (Cooke, 1981; Cooke & Smalley, 1968). When rocks or other brittle materials

are subjected to low stresses, cracks can propagate subcritically (Anderson, 2005; Atkinson, 1984). Natural stresses in arid climates are likely dominantly subcritical in magnitude and commonly attributed to repeated cycles of thermal expansion/contraction in response to diurnal insolation dynamics (e.g., McFadden et al., 2005) or salt weathering (Desarnaud et al., 2016; Sperling & Cooke, 1985; Steiger et al., 2008; Winkler & Wilhelm, 1970). Nonetheless, laboratory, as well as field-based studies, have shown that even a slight increase in moisture can significantly increase the rates at which these otherwise ‘dry’ rock-cracking mechanisms can operate (Eppes et al., 2020; Eppes & Keanini, 2017; Meredith & Atkinson, 1985; Yoshitaka Nara et al., 2010, 2012; Waza et al., 1980). Here, we present field-based evidence from one of Earth’s driest and coldest deserts that the deliquescence of atmospheric humidity by hygroscopic salts is an effective pathway for water delivery to rock cracks. This moisture delivery pathway to rock cracks may have an important and previously overlooked pace-setting role in the cracking process of rocks in hyper-arid environments.

1.2 The Antarctic Dry Valleys

The Antarctic Dry Valleys (ADV) (Fig. 1) are amongst the coldest and driest ‘ice-free’ regions on Earth (Doran et al., 2002; Fountain et al., 2010; Obryk et al., 2020). The mean annual air temperatures on the valleys floors range between -15°C and -30°C , depending on the location (Obryk et al., 2020), and precipitation is limited to less than 50 mm/yr that occurs primarily as snowfall (Fountain et al., 2010). These hyperarid and frigid conditions have prevailed in the ADV since the Pliocene (Fielding et al., 2011; Scopelliti et al., 2013), resulting in one of the slowest eroding landscapes on Earth with estimated bedrock erosion rates below 1 m/m.y. (Balco & Shuster, 2009; Brook et al., 1995; Margerison et al., 2005; Marrero et al., 2018; Staiger et al., 2006; Sugden et al.,

1999; Summerfield et al., 1999). As such, the ADV environment is also regarded as a prime analog site for the present-day hyperarid and cold surface conditions on Mars (Head & Marchant, 2014; Sletten et al., 2003; Tamppari et al., 2012). Rock weathering processes in the ADV have been previously attributed to thermal stress mechanisms (Campbell & Claridge, 1987; Hall, 1999; Lamp et al., 2017) or to hygroscopic salts (Campbell & Claridge, 1987; Johnston, 1973; Selby & Wilson, 1971; Wellman & Wilson, 1965), that accumulate at or near the ADV surface due to the extremely dry conditions (Bisson et al., 2015; Keys, 1979; Keys & Williams, 1981). The presence of up to ~30 salt phases was previously reported in the ADV soils, including hygroscopic salts, such as NaCl, MgCl₂, NaNO₃, and CaCl₂ (Bisson et al., 2015; Claridge & Campbell, 1977; Goudie & Cooke, 1984; Keys, 1979; Keys & Williams, 1981; Miotke & von Hodenberg, 1983; Tamppari et al., 2012; Wilson, 1979).



65 **Figure 1: Annotated satellite image of the Antarctic Dry Valleys. Yellow star marks the field site near Don**
66 **Juan pond in Wright valley. The satellite image was obtained through the QuickMapServices QGIS**
67 **plugin, from ESRI server (ArcGIS/World_Imagery).**

68 **1.3 Salt deliquescence in the ADV**

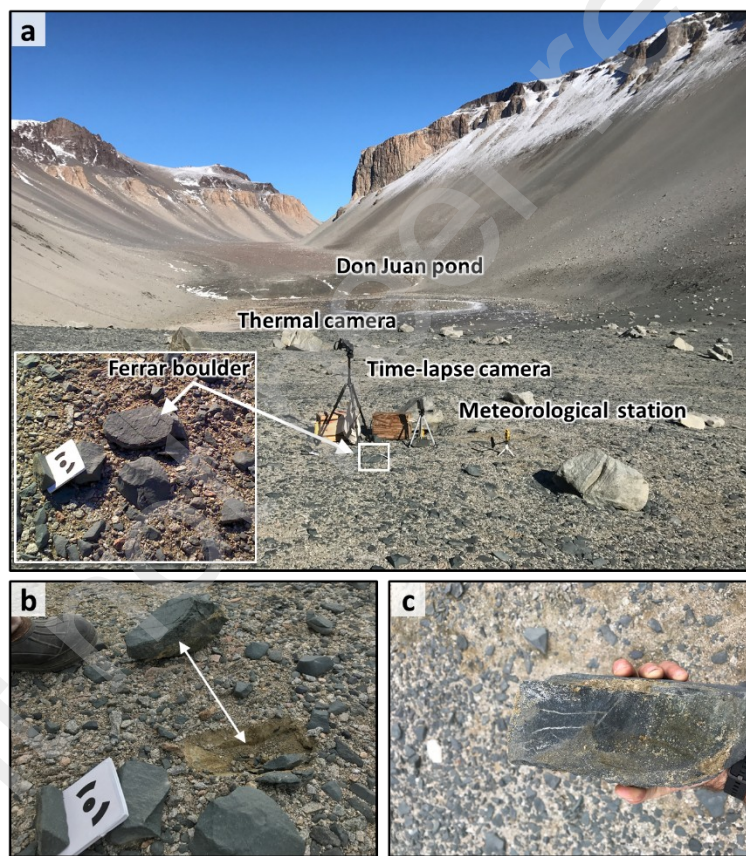
69 Deliquescence occurs when the relative humidity (RH) of the air mass exceeds the
70 deliquescence relative humidity (DRH) of a specific salt or a salt mixture, and atmospheric water is
71 absorbed and forms a brine that can further adsorb water. Efflorescence is the reverse process that
72 occurs when relative humidity is reduced below the efflorescence relative humidity (ERH) and
73 recrystallization occurs. Salt deliquescence/efflorescence dynamics have been previously documented
74 in the ADV soils as the appearance of transient ‘wet patches’ (Gough et al., 2016; Harris & Cartwright,
75 1981; Head et al., 2007; Levy, 2021; Toner et al., 2022) or ‘wet slope streaks’ (Toner et al., 2022)
76 during events of increased atmospheric humidity. The present study tests whether and how such
77 deliquescence/efflorescence dynamics can facilitate rock-cracking processes in the ADV.

78 **2 Methods**

79 **2.1 Field experiment and laboratory analyses**

80 A field-based 10-day experiment was performed using local meteorological measurements
81 (Kestrel 5500), time-lapse photography (Brinno TLC 200), and thermal imaging (FLIR SC430) of a
82 Ferrar Dolerite boulder with incipient cracks near the Don Juan pond in Wright Valley (Fig. 1, 2). After
83 the experiment, extraction of the boulders revealed light-toned salts along the rock cracks that were
84 embedded in the soil during the experiment (Fig. 2b, c). Mineralogical and chemical analyses of the

85 salts were performed at the Geological Survey of Israel. Salts samples taken from a crack in the boulder
86 were dissolved in distilled water, and chemical analysis for major cations was conducted using
87 inductively coupled plasma-optical emission spectrometry (Perkin Elmer, Optima 5300) and major
88 anions using ion chromatography (Dionex ICS-2000). Mineralogic analysis was performed using bulk
89 X-ray diffraction. Mineral phase identification and semi-quantification were performed using
90 HighScore Plus® software based on the ICSD database.



91 **Figure 2: a) Field experiment setup near Don Juan pond (in the background, west of the experiment site)**
92 **in Wright Valley. White arrows mark the imaged boulder. The length of the boulder is 25 cm. Monitoring**
93 **equipment includes: a time-lapse optical camera used to detect wetting events, a mobile meteorological**

94 station, and a thermal camera. b) Image of the Ferrar dolerite boulder removed from the soil after the
95 experiment (white arrow). c) The underside of the Ferrar dolerite boulder showing accumulation of salts
96 in cracks.

97 2.2 Meteorological data

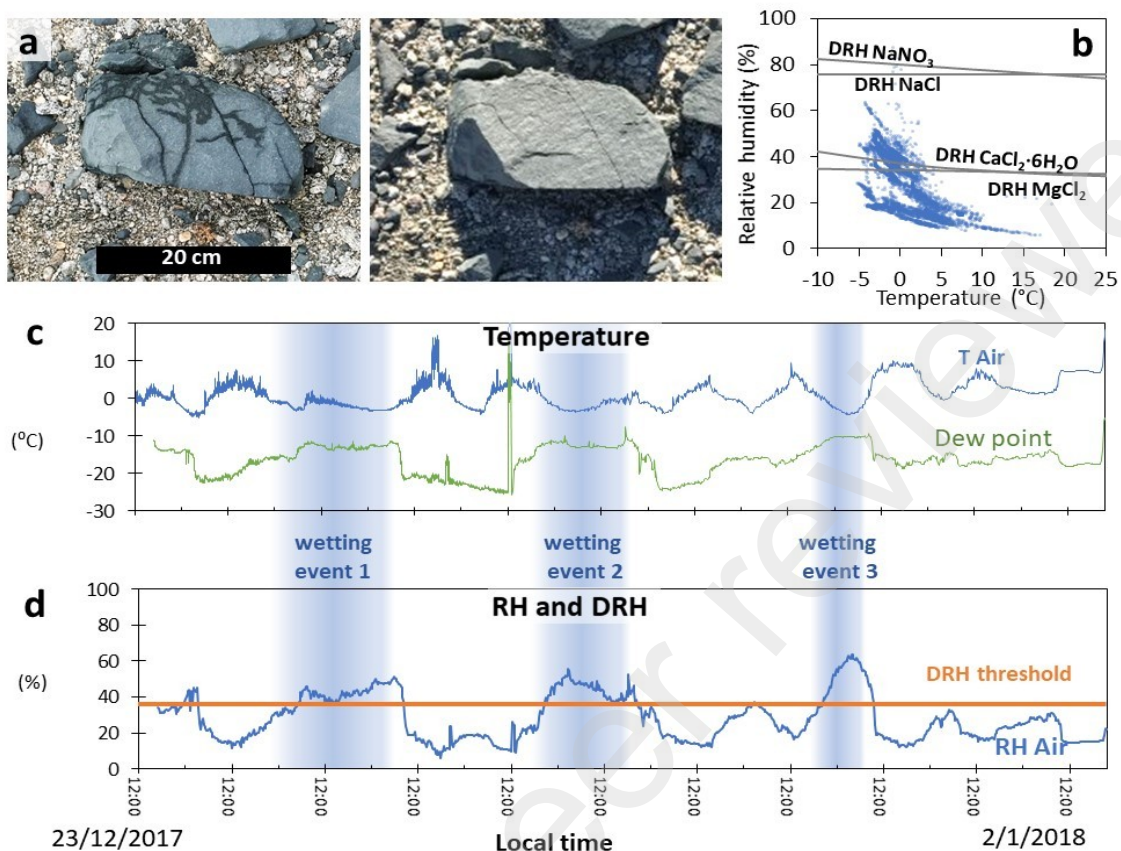
98 Meteorological data from 17 weather stations scattered throughout the ADV were used to
99 examine the occurrence of deliquescence-efflorescence conditions for NaNO_3 , CaCl_2 , NaCl , and MgCl_2 .
100 The weather stations are part of the McMurdo Long Term Ecological Research Project (MCM LTER)
101 in the ADV. Most stations (11 out of 17) have been operating for over 20 years at 1-hour temporal
102 recording resolution. Analysis of these data was conducted to quantify the occurrence of supra-DRH
103 conditions for these salt phases in the ADV environment through time. Deliquescence conditions were
104 defined as the durations in a year when RH values exceed the DRH of the specific salt phase. A
105 Deliquescence/efflorescence cycle was defined as a period between the increase of RH above DRH to
106 when RH decreases below DRH. A minimum duration threshold of 3 hours and a minimum of 5%
107 excess humidity above DRH were used to filter out short events and those with marginal excess RH.
108 The DRH value of CaCl_2 used in the analysis refers to the hexahydrate phase - $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
109 ('Antarcticite'), which was first described in the ADV (Torii & Ossaka, 1965).

110 3 Results

111 3.1 Salt deliquescence during the field experiment

112 Time-lapse photography revealed an accumulation of moisture along cracks in the imaged
113 boulder (identified visually by the darkening of the rock, Fig. 3a) during three discrete periods spanning

114 between approximately 6-12 hours each (Fig. 3a, supp. Time-lapse video). Since no precipitation was
115 observed during the experiment, we can overrule snow melt as a potential source, although it is a
116 recognized source of water for rocks and soils during the austral summers (Hagedorn et al., 2010; Liu et
117 al., 2015). These periods of moisture stability along the boulder cracks coincided exclusively with RH
118 values that exceeded 35~40% but did not reach the dew point and included sub-zero air temperatures
119 (Fig. 3c, d). During these moisture accumulation events, RH values coincided with supra DRH
120 conditions for chloride salts, such as CaCl_2 and MgCl_2 (Fig. 3b, d). Chemical analysis of the salts
121 samples taken from a crack in the boulder shows that the major anions are Cl^- , SO_4^{2-} and (55%, 45%,
122 respectively) and that the major cations are Ca^{+2} , Na^+ , K^+ , Mg^{+2} , SiO_2 , and Sr^{+2} (71%, 23%, 3%, 2%, 1%,
123 1% respectively). Excess of Cl^- and Ca^+ after accounting for the complete precipitation of halite and
124 gypsum, which were the dominant salt phases found in X-ray diffraction, points to the presence of
125 CaCl_2 and possibly other chlorides, which is not unexpected considering the proximity of the
126 experiment site to the Don Juan pond – a saline lake rich in CaCl_2 (Dickson et al., 2013; Toner et al.,
127 2017). Therefore, the most likely explanation for the observed wetting events in the experiment appears
128 to be the deliquescence of such salts. Altogether moisture sourced from deliquesced atmospheric
129 humidity was found to be stable along the boulder cracks for ~25% of the otherwise ‘dry’ 10-day span
130 of the experiment.



131 **Figure 3: Moisture delivery to rock cracks via salt deliquescence. a) Images of a Ferrar dolerite boulder**
 132 **during (left) and between (right) wetting events. b) Data from field measurements of air temperature vs.**
 133 **relative humidity during the 10 days experiment. Black lines indicate the DRH of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, NaNO_3 ,**
 134 **NaCl , MgCl_2 salts as a function of temperature. c) Ambient air T (blue), and dew point (green) through**
 135 **time. Note that air T does not reach the dew point during observed wetting events and that wetting events**
 136 **(blue shading) persist through sub-zero temperatures. d) Relative humidity (blue) and the DRH threshold**
 137 **of 35%~40% (orange). All three wetting events were initiated after supra-DRH conditions were achieved**
 138 **and ended when RH declined below the DRH threshold.**

139 3.2 Analysis of meteorological data

140 Results from analysis of 17 meteorological stations in the ADV show that the conditions for
141 deliquescence of the salt phases that were examined, i.e., CaCl_2 , NaNO_3 , NaCl , and MgCl_2 , prevail on
142 average for 69% (range 43%-85%), 16% (range 4%-25%), 32% (range 10%-51%) and 83% (range
143 43%-85%) of the year, respectively (Fig. 4, Fig. supp. S1-3). In addition, the conditions for discrete
144 deliquescence events happen on average 55 (range 25-83), 30 (range 12-48), 50 (range 20-76), and 39
145 (range 15-36) times per year, respectively (Fig. 4, Fig. supp. S1-3). For simplicity, deliquescence
146 conditions for single-phase salt-brine systems were assumed. However, laboratory experiments show
147 that the DRH of salt mixtures is expected to be even lower than that of the same single salts (e.g. Yang
148 et al., 2002). Thus, the duration of deliquescence conditions is potentially longer than calculated herein.

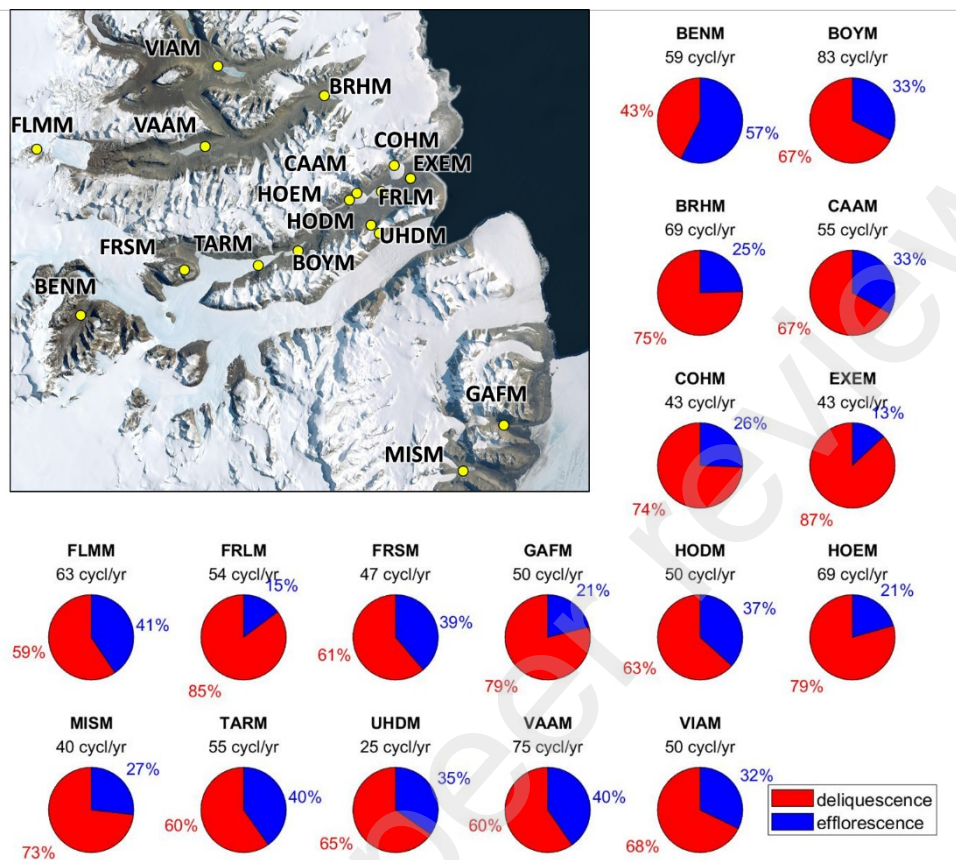


Figure 4: Results of deliquescence conditions of CaCl_2 in 17 meteorological stations in the ADV. The pie plots show the time fraction of deliquescence conditions (red). The number of estimated deliquescence-efflorescence cycles per year is marked below the station name. A full description of the stations is found at <https://mcm.lternet.edu/meteorology-data-sets#met-15>.

4 Discussion

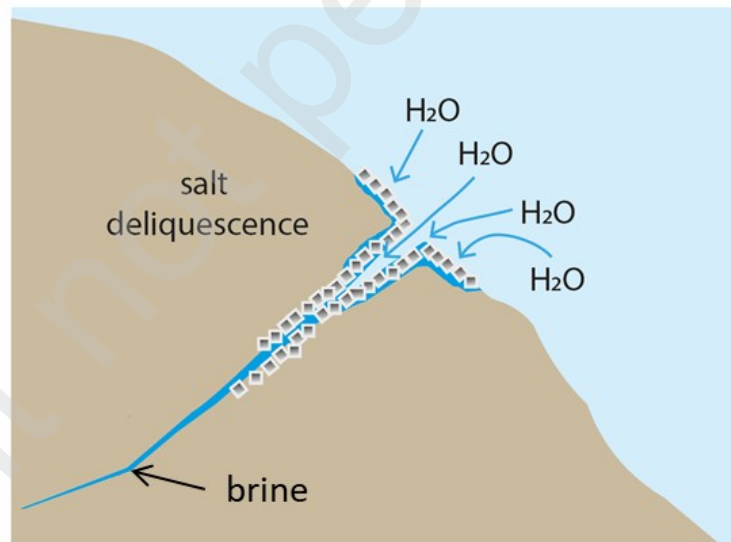
The results of the field-based experiment show evidence that salt deliquescence is an effective mechanism of moisture delivery to the rock surface and cracks in the hyper-arid and frigid conditions of the ADV. Deliquescence/efflorescence cycles such as those observed during the experiment (Fig. 3) are

157 expected to promote rock cracking by ‘salt shattering’, which is regarded as an important weathering
158 mechanism in arid soils (Amit et al., 1993; A. Goudie & Viles, 1997; Andrew S. Goudie, 2013;
159 Rodriguez-Navarro & Doehne, 1999), including the ADV (Johnston, 1973) and Mars (Jagoutz, 2006;
160 Malin, 1974). Salt shattering requires that the amount of water is low enough to limit the leaching of
161 the salts from the surface/soils, and yet sufficient for salt-water interactions that support cycles of
162 dissolution and crystallization of salts that can exert local stress when confined within rock pores or
163 fractures (Amit et al., 1993; Desarnaud et al., 2016; Sperling & Cooke, 1985). In addition, recent studies
164 have demonstrated that even the rates of ‘dry’ mechanical weathering processes, such as those induced
165 by salt hydration or cyclic thermal stress-loading (Lamp et al., 2017; McFadden et al., 2005; Richter &
166 Simmons, 1974; Viles et al., 2010), may accelerate by orders of magnitude in the presence of small
167 amounts of moisture (Eppes et al., 2020; Eppes & Keanini, 2017). This acceleration is associated with
168 the weakening of bonds by water molecules at the tip of cracks that propagate slowly in response to
169 subcritical stresses (Atkinson, 1984; Eppes et al., 2020; Meredith & Atkinson, 1985; Nara & Kaneko,
170 2006; Voigtländer et al., 2018). The delivery of moisture to the tips of cracks, via salt deliquescence,
171 can thus also accelerate crack propagation under external subcritical stress. The analysis of data
172 obtained from permanent ADV meteorological stations (Fig. 4) shows that the atmospheric conditions
173 that enabled the deliquescence events in our field site near the Don Juan pond are prevalent throughout
174 the ADV and therefore suggest that deliquesced moisture during otherwise ‘dry’ conditions can be an
175 important moisture delivery pathway for rock weathering throughout the ADV soil.

176 Laboratory experiments show that ERH can be lower than DRH for a given salt and temperature
177 due to a kinetic barrier for the nucleation of a crystalline phase (Gough et al., 2016; Martin, 2000). In

178 our experiment, there is no evidence for the reported hysteresis between DRH and ERH. This could be
179 because of the heterogeneity and impurity of natural brines that can readily facilitate the nucleation of
180 salt crystals. Furthermore, the onset and termination of the deliquescence events that were documented
181 during the field experiment were not driven by diurnal oscillations in air temperature and resulting
182 changes in RH and instead appeared to be more closely associated with pulses of increased vapor
183 pressure (Fig. Supp. S4).

184 We thus propose that deliquescence/efflorescence cycles may be an important driver of rock
185 weathering in the ADV and potentially other hyper-arid regions where an accumulation of hygroscopic
186 salts is observed. This includes Mars, where the presence of deliquescent salts was previously suggested
187 (Gough et al., 2019; Toner et al., 2015).



188 **Figure 5: illustration of moisture delivery into rock cracks by salt deliquescence. Deliquesced moisture**
189 **(brine) within rock cracks can accelerate the propagation of cracks by weakening rock chemical bonds by**

190 water molecules at the tip of cracks that propagate slowly in response to subcritical stresses. Such stresses
191 can originate from cycles of salt crystallization (deliquescence/efflorescence cycles) and/or thermal
192 expansion/contraction in response to diurnal insolation dynamics.

193 **5 Conclusion**

194 Based on our results from a field experiment that show discrete wetting events of a rock surface
195 in sub-saturated air and sub-freezing conditions, following an increase in air RH, we conclude that salt
196 deliquescence may be an effective and overlooked mechanism of water delivery into rock cracks in
197 hyper-arid and cold conditions on Earth and possibly Mars as well. An analysis of data from 17
198 permanent meteorological stations shows that conditions for the deliquescence of several salt phases
199 that are found in the ADV prevail throughout the region and that such moisture delivery may be
200 widespread in the ADV. We suggest a dual role that salt deliquescence plays in the acceleration of rock
201 cracking in arid regions. The first is a source of stress load, as cycles of dissolution and crystallization
202 of salts exert local stress when confined within rock pores or fractures (Sperling and Cooke, 1985;
203 Desarnaud et al., 2016; Amit et al., 1993). The second is the acceleration of subcritical rock cracking in
204 the presence of even small amounts of water at the tip of cracks (Eppes et al., 2020; Eppes & Keanini,
205 2017; Meredith & Atkinson, 1985; Yoshitaka Nara et al., 2010, 2012; Waza et al., 1980).

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