

## Hypersaline “wet patches” in Taylor Valley, Antarctica

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[1] Spatially isolated patches of soil located in Taylor Valley, McMurdo Dry Valleys, Antarctica, are sites of elevated salt content and soil moisture. During Antarctic spring, in the absence of snow melt, visibly wet (reduced albedo) patches of soil are present at the surface. The soil pore fluids are hypersaline and have average water activity of 0.74 (the water activity of a solution determines the equilibrium vapor pressure of that solution), and are an order of magnitude more saline than average soils in the Dry Valleys. These salty soils are 3–5 times more water rich than average soils. Geochemical and meteorological analyses show that these wet patches are sites of direct vapor emplacement into soil pore fluids that may ultimately be sourced by the deliquescence of soil salts. These wet patches represent a non-precipitation, non-groundwater source for water into Antarctic permafrost. **Citation:** Levy, J. S., A. G. Fountain, K. A. Welch, and W. B. Lyons (2012), Hypersaline “wet patches” in Taylor Valley, Antarctica, *Geophys. Res. Lett.*, 39, L05402, doi:10.1029/2012GL050898.

### 1. Background

[2] The McMurdo Dry Valleys (MDV, 77–78°S, 160–184°E) are an ice-sheet free portion of Antarctica surfaced by a mosaic of glaciers, permafrost, ephemeral streams, and ice-covered lakes [Lyons *et al.*, 2000]. The MDV is a cold, polar desert, with a mean annual temperature of  $\sim -18^\circ\text{C}$  and 3–50 mm of annual precipitation, all of which falls as snow and most of which sublimates [Doran *et al.*, 2002; Fountain *et al.*, 2010; Hunt *et al.*, 2010]. The high potential sublimation rate in the MDV region [Clow *et al.*, 1988; Gooseff *et al.*, 2006] results in desiccation of the soil to depths of 50–100 cm [Bockheim, 2002], resulting in the presence of “dry frozen” (ice-free) permafrost over  $\sim 43\%$  of the MDV [Bockheim *et al.*, 2007; Hunt *et al.*, 2010]. Ice cemented permafrost is present in  $\sim 55\%$  of the MDV, but even “ice cemented” permafrost is still commonly ice-free in the upper 10–20 cm [Bockheim *et al.*, 2007]. Ground ice, buried glacier ice, ice-cored moraines, and buried snow deposits constitute the remaining  $\sim 2\%$  of MDV permafrost deposits [Bockheim *et al.*, 2007; Marchant *et al.*, 2002; McKay, 2009; Stuiver *et al.*, 1981]. As a result of the extreme cold and aridity of the MDV, soil moisture is minimal and

spatially heterogeneous, averaging  $<1\%$  by mass for inland MDV soils [Campbell *et al.*, 1997].

### 2. Geomorphic Observations and Hypothesis

[3] Recent geomorphic observations in Taylor Valley, one of the MDV, have led to the identification of spatially isolated, dark-toned, damp soil patches (Figure 1). These “wet patches” are associated with neither perennial or seasonal snowbanks, nor with shallow groundwater or seasonal streams. Instead, they are surrounded by dry soil suggesting a lack of hydrological connectivity with surface/near-surface waters. Wet patches are typically found on topographic highpoints (small knolls) or on isolated hillslopes. They do not overlie buried excess ice (ground ice exceeding soil pore volume) in the upper 50 cm of the soil column. Wet patches are rare in the MDV, and likely cover  $<0.1\%$  of MDV soil surfaces. Wet patches have not been formally described before, however, they have been observed by several field parties working in Pearse and Wright Valleys, MDV (A. Davila and D. Andersen, personal communication, 2011).

[4] Direct (non-precipitation) condensation of water vapor to form saline brines has been proposed to occur at high elevations in the MDV [Wilson, 1979], a process termed “humidity separation.” This mechanism pulls moisture from the air during high humidity events, resulting in the hydration of hygroscopic salts (notably  $\text{CaCl}_2$  and  $\text{MgCl}_2$ ). A similar process occurs in warm deserts (e.g., Atacama) [Davila *et al.*, 2008; McKay *et al.*, 2003]. This process has not been previously observed at low elevations in the MDV. Here, we test the hypothesis that direct atmospheric deposition of water vapor into low-water activity saline intergranular fluids results in the growth and maintenance of seasonally wet patches of soil.

### 3. Site and Sample Description

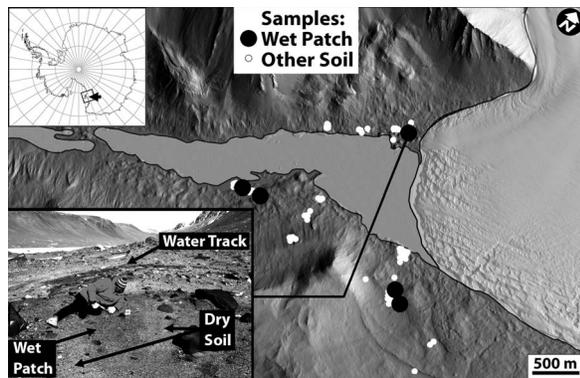
[5] Soil samples analyzed in this study were collected from the Lake Hoare basin, near 77.63°S, 162.92°E (Figure 1). Lake Hoare is a perennially ice-covered lake located in central Taylor Valley. Low elevation Taylor Valley soils are predominantly sandy haplorthels (typically 75–80% sand by mass), surfaced by a desert pavement of cobbles and pebbles [Campbell, 2003]. Depth to ice-cemented sediment ranges between 1–45 cm in the study site, and averages 28 cm for “dry” soils with less than 4% soil moisture by mass [Levy *et al.*, 2011]. Wet patch sample locations all lacked ice within 30 cm of the surface.

[6] Soil samples from the upper 10 cm of eight spatially isolated dark soil patches were collected during October 20–28, 2010 and November, 2010 (sample JLS10067). Ground surface temperatures measured in the Lake Hoare basin using a Campbell Scientific 107 temperature probe during

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**Figure 1.** Sampling sites in the Lake Hoare Basin, Taylor Valley, Antarctica (some sites yielded multiple soil samples from multiple wet patches). Glacier, lake, and soil contacts are highlighted. Inset map shows the general location of Southern Victoria Land, Antarctica (box) and the location of the MDV (arrow). Inset sampling example shows a wet patch with a water track  $\sim 10$  m behind it, and separated by a topographic divide.

October 20–28 average  $-17^{\circ}\text{C}$  with a maximum ground surface temperature of  $-6^{\circ}\text{C}$ . Analysis of Lake Hoare meteorological station records show clear conditions persisting through October 21–28, 2010, with clouds on October 14 and 20, 2010, however, low relative humidity values during these cloudy conditions argue against precipitation (www.mcmlter.org). The precipitation gauge at the nearby Lake Bonney station registered  $<0.9$  mm of water equivalent snowfall during this period, with an accuracy of  $\pm 1.5$  mm (ww.mcmlter.org). Any persistent winter snow or fresh (October) snow would sublimate, rather than melt, under these conditions [Hunt *et al.*, 2010].

[7] Soil sampling sites were identified by visual inspection of the landscape, and the upper 10 cm was sampled because damp, dark soil is concentrated in this depth horizon. Soil samples ( $\sim 200$  g) were collected using clean HDPE plastic scoops (rinsed in deionized, DI, water) and were placed into Whirl-Pak bags and homogenized by mixing in the bag. Reference samples of the upper 10 cm of 28 typical Lake Hoare basin soils also were collected during hillslope soil sampling traverses, including soils adjacent to wet patches, and represent soils spatially isolated from surface snow and ice or shallow groundwater [Levy *et al.*, 2011] (Figure 1).

**Table 1.** Major Ion Data for Wet Patch Soil Samples Determined by Ion Chromatography of Soluble Phase Extracts<sup>a</sup>

Sample	$\text{Cl}^-$ (mM) <sup>1</sup>	$\text{NO}_3^-$ (mM) <sup>1</sup>	$\text{SO}_4^{2-}$ (mM) <sup>2</sup>	$\text{Na}^+$ (mM) <sup>1</sup>	$\text{K}^+$ (mM) <sup>1</sup>	$\text{Mg}^{2+}$ (mM) <sup>1</sup>	$\text{Ca}^{2+}$ (mM) <sup>1</sup>	$\text{HCO}_3^-$ (mM) <sup>3</sup>	TDS (mg/L) <sup>1</sup>	Total M <sup>1</sup>
JLS10013	70.07	1.98	1.67	12.47	2.16	20.09	10.49	0.40	3952	0.12
JLS10021	52.02	0.74	1.25	10.44	2.14	13.23	8.26	0.32	2951	0.09
JLS10021C	157.57	2.44	0.92	34.22	4.28	35.18	27.30	1.60	8612	0.26
JLS10022	155.43	1.66	6.23	64.62	5.07	23.22	27.67	1.92	9490	0.28
JLS10039	22.39	0.52	0.28	7.76	0.65	5.33	2.00	-0.42	1241	0.04
JLS10047	95.78	3.91	2.94	33.16	4.14	15.17	18.97	0.02	5787	0.17
JLS10047A	66.12	2.73	0.72	21.46	3.21	8.91	13.42	-0.96	3825	0.12
JLS10067	165.90	7.59	4.09	89.66	8.51	23.82	20.48	5.05	10176	0.32
Average	98.16	2.69	2.26	34.22	3.77	18.12	16.07	0.99	5754	0.18
Typical Soil	3.89	0.17	0.63	3.30	0.25	0.44	0.47	1.06	340	0.01

<sup>a</sup>TDS is total dissolved solids and Total M is the sum of molarities. P values for wet patches vs. typical soil single-ended ANOVA: <sup>1</sup>P  $< 0.0001$ , <sup>2</sup>P  $< 0.06$ , <sup>3</sup>No Difference.

**Table 2.** Table of Derived Products<sup>a</sup>

Sample	W:R	GWC <sup>b</sup> (%)	CF	$\text{Cl}^*$ (mM)	TDS* (g/L)	Total M*	$a_w$
JLS10013	1.98	2.95	67.20	4710	266	7.99	0.82 <sup>c</sup>
JLS10021	3.01	2.55	118.33	6160	349	10.42	0.73 <sup>c</sup>
JLS10021C	2.99	4.17	71.63	11290	617	18.76	0.52 <sup>d</sup>
JLS10022	2.00	3.40	58.69	9120	557	16.66	0.67 <sup>d</sup>
JLS10039	2.00	1.32	151.21	3390	188	5.89	0.88 <sup>c</sup>
JLS10047	2.02	4.14	48.93	4690	283	8.52	0.80 <sup>c</sup>
JLS10047A	2.01	4.90	41.05	2710	157	4.78	0.91 <sup>c</sup>
JLS10067	2.03	0.91	221.39	36730	2250	70.9	0.61 <sup>d</sup>
Average	NA	3.04	97.31	9850	584	18.0	0.74 <sup>c</sup>
Typical Soil	2.00	1.17	377.39	900	92	0.03	0.94 <sup>c</sup>

<sup>a</sup>W:R is water to rock mass ratio in the extracts. GWC% is the field gravimetric water content of the soil samples. CF is the concentration factor described in the text.  $\text{Cl}^*$ , TDS\*, and Total M\* are CF-corrected IC results. FPD is freezing point depression. Note,  $\text{H}_2\text{O}\%$  for JLS10067 is extrapolated from a 2/5-strength solution.

<sup>b</sup>For wet patches vs. typical soil single-ended ANOVA: P  $< 0.005$ .

<sup>c</sup>CF-corrected pore solution water activity determined by PHREEQC and FREZCHEM.

<sup>d</sup>CF-corrected pore solution water activity determined by FREZCHEM only due to high solution strengths.

Samples were kept frozen and were transported to McMurdo Station for analysis.

#### 4. Methods

[8] Samples were analyzed for water content and soil major ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{F}^-$ ). Water content was measured by weighing out a  $\sim 100$  g split of each sample and drying the sample at  $105^{\circ}\text{C}$  for 24 hours in an oven. Dried samples were re-weighed to determine the gravimetric water content (GWC, in  $\text{g}_{\text{water}}/\text{g}_{\text{sample}}$ ). Volumetric water content (VWC) was determined for each sample by multiplying GWC by the average bulk density of Lake Hoare basin soils ( $1.8 \text{ g/cm}^3$ ) [Levy *et al.*, 2011]. For major ion analysis,  $\sim 100$  g dried sample splits were mixed with DI water in a 1:3 ratio of sediment to water by mass and agitated for  $\sim 1$  minute. These soluble phase extracts were then filtered using  $0.45 \mu\text{m}$  HT Tuffryn membrane filters into pre-cleaned polyethylene bottles. Major ion concentrations were determined by ion chromatography as described in [Welch *et al.*, 2010], resulting in a total analytical error of  $<4\%$ . Bicarbonate,  $\text{HCO}_3^-$ , was determined through charge balance for each sample. Major ion analysis gives a measure of total solution extract molarity and total dissolved solids (TDS). Geochemical analyses for wet patch soils and non-wet-patch soils are presented in Tables 1 and 2.

[9] Because the major ion data reflect the composition of a dilute extract and not the composition of the actual wet patch pore fluids, it is necessary to calculate how much more concentrated wet patch pore fluids were in the field than in the extracts. Initially, we assume that all of the salt present in the soil samples is concentrated in the pore fluids (this assumption is addressed later in the discussion section). This is a reasonable simplifying assumption, given that the amount of soluble matter dispersed through typical MDV soil is small compared to the high concentrations of salts in wet patch samples (Table 1). This assumption allows us to calculate a concentration factor (CF), which is the water-to-rock ratio used in the extracts times the ratio of the dry bulk density of the soil (1.8 g rock per 1 cm<sup>3</sup> soil) to the field volumetric water content of the soil. The inferred concentration of an ion in the pore fluid,  $X^*$ , is calculated by multiplying  $X$  (the measured concentration) by the CF. This calculation is illustrated in Table 2.

[10] From the estimated composition of the wet patch pore fluids, the water activity ( $a_w$ ) of the solution may be calculated. Water activity is the key thermodynamic parameter for testing the hypothesis that wet patch moisture derives from atmospherically-emplaced water vapor. Water activities for CF-corrected solutions were determined using the PHREEQC and FREZCHEM geochemical models, assuming solution temperatures of 1°C (typical summer soil surface temperature—lower temperatures will typically act to reduce water activity, although the critical deliquescence relative humidity for many salts will also increase at lower temperatures) [Charlton *et al.*, 1997; Marion and Grant, 1994; Tang and Munkelwitz, 1993] (Table 2). Where PHREEQC produced anomalously low  $a_w$  values due to high solution strengths, only FREZCHEM results are reported (FREZCHEM is optimized for low-temperature brines).

## 5. Results

[11] Geochemical measurements and calculations are summarized in Tables 1 and 2. Average wet patch soils are three times more water rich than typical Taylor Valley soils, and have solute loads over ten times greater. Unfrozen water content due to matric effects in these soils is expected to be less than 0.02% over the temperature range considered in this study [Ugolini and Anderson, 1973]. Calculated water activities for average wet patch pore water solutions are 0.74 (identical to a relative humidity of 74%), and range from 0.52 to 0.91 ( $a_w = 1.0$  for pure water—see discussion for details). Typical Taylor Valley soil intergranular fluids have a water activity of 0.94 based on PHREEQC and FREZCHEM modeling.

## 6. Discussion

[12] Are the calculated CFs realistic? To evaluate whether the CF-corrected solution strengths were meaningful, CF-corrected wet patch solutions were modeled using the FREZCHEM and PHREEQC geochemical models as described above [Charlton *et al.*, 1997; Marion and Grant, 1994]. Average wet patch solutions were found to be initially saturated with respect to dolomite, gypsum and halite. The later two minerals are found extensively in saline soils in the MDV [Keys, 1979] and these minerals also can be

associated with MDV hypersaline brines [Lyons *et al.*, 2005]. For determining pore fluid water activity, the geochemical models determine the fluid composition in equilibrium with these crystallized solid phases, which can be understood to represent salts distributed throughout the soil sample that are not contained in the pore fluids. Because the 3% GWC of wet patches is sufficient to wet the sand grains, the pore fluid  $a_w$  is calculated for a solution in equilibrium with both dissolved and crystalline phases. In evaporation models, the solution becomes successively saturated with anhydrite, carnallite (a K-Mg chloride), magnesium chloride, magnesite, and calcium chloride. These are all commonly occurring MDV surface soil salts [Keys, 1979].

[13] What do these results imply about vapor flux into wet patches? The water activity of a solution determines the equilibrium vapor pressure that the solution supports. Because water vapor moves from areas of high water vapor partial pressure to areas of low water vapor partial pressure, it will move from the atmosphere into the wet patch solutions if the vapor pressure in the atmosphere is greater than the vapor pressure of the wet patches and vice versa.

[14] For an isothermal environment, water will move from zones of high relative humidity (RH) to zones of low RH. The relative humidity for air in the Lake Hoare basin during the representative year 2009, measured ~100 m from sample site JLS10067, is plotted in the auxiliary material.<sup>1</sup> For most of the year, atmospheric RH is higher than the average wet patch  $a_w$ . Notably, this is true even in summer, when atmospheric water vapor pressures are highest, permitting the largest potential fluxes of water vapor into wet patches. This is consistent with our observations that wet patches become darker and more pronounced during the transition from austral spring (October/November) into austral summer (December). For the year preceding the October/November 2010 sampling window, RH at the Lake Hoare station averaged  $74 \pm 3\%$ , which is consistent with vapor flux into average wet patches, and wet patches more concentrated than average (RH uncertainty reflects instrument measurement accuracy).

[15] It should be noted that the RH comparison in the auxiliary material discounts the fact that ground temperature and air temperature are not always identical in the MDV. In order to determine whether wet patch soils would be expected to hydrate under the exact air/ground temperature and RH conditions that preceded sampling, water vapor flux directions were calculated using temperature and relative humidity data collected at 15 minute intervals by the LTER meteorological station adjacent to Lake Hoare ([www.mcmlter.org](http://www.mcmlter.org)) during the interval spanning September 1, 2010 to October 31, 2010. For temperatures above 0°C, a parameterization of the Clausius-Clapyron equation was used to compute vapor pressure [World Meteorological Organization, 2008], while for temperatures below 0°C, the empirical Goff Gratch equation was used [List, 1984]. The vapor pressure above pure water in thermal equilibrium with the soil surface beneath the weather station was also calculated, along with the vapor pressure above an  $a_w = 0.74$  solution (the composition of an average wet patch pore fluid), a high-salt wet patch pore fluid composition ( $a_w = 0.61$ , similar to JLS10067), and an  $a_w = 0.35$  solution (e.g.,

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2012GL050898.

one saturated with  $\text{CaCl}_2$ ). During that interval, atmospheric water vapor pressure exceeded soil pore fluid water vapor pressure 69% of the time for average wet patch pore solutions, 76% of the time for concentrated wet patch pore solutions, and 97% of the time for saturated  $\text{CaCl}_2$  solutions. These calculations suggest that direct emplacement of water vapor into intergranular fluids, in the absence of snow melt, is a strong candidate mechanism for the hydration of the sampled wet patches.

[16] What do the meteorological measurements suggest about long-term stability of wet patches? Using the methods described above, the daily average atmospheric water vapor partial pressure measured at 3 m, soil water vapor pressure, and solution water activities for average and concentrated wet patch pore waters were calculated for the Lake Hoare basin from 2003–2010. Water vapor pressures were then converted to water vapor masses to determine the mass flux into or out of the wet patches. From 2003–2010, vapor flux is net-out of the soil for salt-free fluids in the Lake Hoare basin, consistent with previous modeling of ground ice sublimation [Hagedorn *et al.*, 2007; Kowalewski *et al.*, 2006; McKay *et al.*, 1998]. However, vapor flux out of soils is significantly reduced in an average wet-patch-composition soil (vapor flux out of soils is reduced from  $\sim 19 \text{ kg/m}^2$ , or  $-10\%$  GWC assuming a 10 cm mixing depth, to  $\sim 10 \text{ kg/m}^2$ , or  $-6\%$  VWC assuming a 10 cm mixing depth). Vapor flux out of the 61% water solution (e.g., JLS10067) reduced to  $6 \text{ kg/m}^2$ , or  $-3\%$  GWC, assuming a 10 cm mixing depth.

[17] Because the water vapor pressure above a saline fluid varies linearly with the  $a_w$  of the fluid, it is possible to calculate a “break-even”  $a_w$  of 0.44, at which no net flux exists and the wet patches are stable. This is well above the  $a_w$  of a saturated  $\text{CaCl}_2$ - $\text{NaCl}$ - $\text{MgCl}_2$ - $\text{KMgCl}_3$  solution, which suggests that salt-saturation of wet patch soils buffers them against complete desiccation, particularly given that atmospheric relative humidity is typically higher than 44% in the Lake Hoare basin. Indeed, during the 2003–2010 period, mean daily RH at Lake Hoare was  $66 \pm 3\%$ . Interestingly, mean daily RH has been increasing  $\sim 0.7$  percentage points per year since the instrumental record began in 1988 at Lake Hoare [Doran *et al.*, 2002]. These results suggest that the recognition of wet patches may be a relatively modern phenomenon, driven by enhanced water vapor content in the MDV. Finally, combining the meteorological and geochemical data, these results suggest that only modest amounts of evaporative concentration of salts are enough to stabilize wet patches against evaporation, and that boundary layer temperature and water vapor conditions may dominate the hydration state of MDV wet patches, resulting in hydration of wet patches by direct atmospheric water vapor deposition during high humidity conditions.

## 7. Origins of Wet Patches: A Role for Deliquescence?

[18] Here, we have provided geochemical and meteorological evidence for the direct deposition of atmospheric water vapor into saline ground water during high humidity periods in Antarctic wet patches. However, the ultimate geological source of wet patches—the mechanism that initially concentrates the soil salts—remains unknown. Possible explanations for the formation of these unusual salt

maxima include ponding and evaporation of paleo-lakes [e.g., Hendy, 2000], ponding and evaporation of saline water tracks [e.g., Levy *et al.*, 2011], or glacially rafted concentrates of marine salts [e.g., Clayton-Greene *et al.*, 1988].

[19] Likewise, the initial source of water to form wet patch intergranular fluids remains undetermined. Hygroscopic salts such as calcium-, sodium-, potassium-, and magnesium-chloride are common in the Dry Valleys [Keys, 1979], and are particularly abundant in wet patches (A. Davila, personal communication, 2011). These salts will deliquesce (form a saturated brine with moisture derived from the atmosphere) when atmospheric water vapor pressure reaches a critical relative humidity [Edgar and Swan, 1922; Yang *et al.*, 2006]. The critical RH is salt-dependent (for example, 87% for KCl, 75% for NaCl, 38% for  $\text{MgCl}_2$  and 30–35% for  $\text{CaCl}_2$ ), and the critical RH is lower for mixtures of salts than for pure phases [Smith *et al.*, 1999; Tang and Munkelwitz, 1993; Yang *et al.*, 2006]. Such salt mixtures would be found in evaporated wet patches, based on the modeling described above. Deliquescence of hygroscopic salts is rapid, occurring over several hours [Cohen *et al.*, 1987]. The presence of hygroscopic soil salts in a polar desert environment in which nearly all seasonal snow sublimates, rather than melting, implies that the deliquescence of these salts may be the initial source of water for wet patches. This inference is consistent with the observation that the critical deliquescence RH for a  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{KMgCl}_3$  mixture is well below the mean annual RH for Lake Hoare, implying that, where present, any initially dry salts such as these will be rapidly hydrated via deliquescence.

## 8. Conclusions

[20] Wet soil patches in Taylor Valley, Antarctica, were found to be approximately an order of magnitude more enriched in salts than typical Taylor Valley soils. This high salt content, composed of hygroscopic species including  $\text{CaCl}_2$ ,  $\text{NaCl}$ , and  $\text{MgCl}_2$ , results in the formation of hypersaline intergranular pore fluids that have low (average 0.74) water activities. In the absence of snowmelt, deliquescence of soil salts and fluid growth by vapor deposition is the most likely source for this moisture. Low water activities result in a flux of water vapor from the atmosphere into the salty soil, creating spatially isolated “wet patches.”

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