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The geochemistry of Don Juan Pond: Evidence for a deep groundwater flow system in Wright Valley, Antarctica

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ABSTRACT

Don Juan Pond (DJP), Antarctica, is one of the most unusual surface waters on Earth because of its $CaCl_2$-rich composition. To investigate the evolution of pond waters during closed-basin evaporation and to understand the source of brines responsible for the chemistry of DJP, we apply a newly developed low-temperature aqueous model in the Na–K–Ca–Mg–Cl system to DJP. By modeling the closed-basin evaporation of DJP and comparing ionic ratios between DJP surface water, deep groundwater, shallow groundwater, and other surface chemistries in Wright Valley, we find that DJP is best explained by upwelling deep groundwater, as opposed to recent hypotheses proposing shallow groundwater sources. The early closed-basin evolution of brines in our model accurately predicts observed chemistries in DJP; however, late-stage closed-basin evaporation produces Mg–K-rich brines and salts that do not match the $CaCl_2$-rich brine in DJP. Based on groundwater inflow rates to DJP, we estimate that even the most concentrated brines in DJP have undergone closed-basin evaporation for less than a year. To explain the observed lack of Mg^{2+} and K^+ accumulation in DJP over time, and the surprisingly young age for the brines, we deduce that DJP is a localized upwelling from a regional groundwater flow-through system in which evaporated DJP brines are recycled back into the subsurface over yearly timescales. The existence of a regional groundwater flow system beneath DJP has implications for water and solute budgets in cold desert ecosystems, and may provide clues for the formation of groundwater and aqueous flows on Mars.

1. Introduction

Don Juan Pond (DJP), located in the south fork of Wright Valley within the McMurdo Dry Valleys (MDV), contains one of the most unique surface waters on Earth. DJP is composed of up to 40% salt by weight, 95% of which is $CaCl_2$ (Table 1), and occasionally precipitates antarcticite ($CaCl_2 \cdot 6H_2O$) (Torii and Ossaka, 1965). Owing to the high hygroscopicity and low eutectic temperature of the $CaCl_2$ brine in DJP ($-52\,^{\circ}C$), the pond waters never evaporate or freeze completely, even during the austral winter (Marion, 1997). The unique chemistry of DJP has been recognized since it was first discovered by Meyer et al. (1962), and has motivated extensive research in subsequent years (e.g. Dickson et al., 2013; Samarkin et al., 2010; Siegel et al., 1979; Webster, 1994).

The ability for perennial liquid water to persist in DJP despite the extremely cold and dry MDV environment, has generated interest in DJP as a niche for extremophiles and as a Mars analog site. Early biological investigations found evidence for microbial communities in DJP (Meyer et al., 1962; Siegel et al., 1979), although later studies questioned whether microbes actively grow in the hyper-saline core of the pond (Oren, 2013). Recent orbital images of the Martian surface have identified potential aqueous flow features such as Recurring Slope Lineae (RSL) (McEwen et al., 2011; Ojha et al., 2015), which are similar in appearance to features in the MDV above DJP (Head et al., 2007; Kreslavsky and Head, 2009; Levy, 2012). Given the cold and dry environment on Mars, the consensus is that aqueous flows on Mars are probably composed of brine. Several researchers have argued that aqueous flows on Mars may be $CaCl_2$ brines owing to their low eutectic and by analogy to DJP (Burt and Knauth, 2003; Chevrier and Rivera-Valentin, 2012; Stillman et al., 2016).

DJP was studied extensively during the Dry Valley Drilling Project (DVDP) in the 1970s with the drilling of the DVDP 13 borehole. Subsurface sediments and bedrock in DVDP 13 down to 75 m depth were discovered to be saturated with $CaCl_2$-rich groundwater having a composition similar to DJP, although lower in concentration (Table 1). At the time of drilling, this groundwater had positive hydraulic head above the ground surface (by up to 0.5 m), which caused the brine to upwell out of the borehole casing. In addition, Harris and Cartwright (1981) observed groundwater discharging from the eastern and western margins of DJP, which they attributed to upwelling deep groundwater. These ob-

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Table 1
Chemical analyses (mol kg^{-1}) and date of collection for DJP surface water, deep groundwaters from DVDP 13, shallow groundwaters east of DJP, and Lake Vanda groundwater.

Description	Date	Ca^{2+}	Na^{+}	$1000 \times Mg^{2+}$	$1000 \times K^{+}$	Cl^{-}
Don Juan Pond[b]	12/18/1975	4.127	0.442	105.00	5.00	9.173
DVDP 13, 5.48 m[b]	1/9/1975	1.285	0.254	27.68	2.11	2.860
DVDP 13, 8.8 m[b]	1/9/1975	1.362	0.259	28.89	2.15	3.056
DVDP 13, 15 m[a]	1/20/1976	1.903	0.318	43.59	2.47	4.184
DVDP 13, 58 m[a]	1/20/1976	2.062	0.348	48.27	2.86	4.753
Shallow groundwater, upper[a]	12/27/1975	0.043	0.052	17.28	0.85	0.159
Shallow groundwater, lower[a]	12/27/1975	0.103	0.101	41.43	1.47	0.352
Shallow groundwater. upper[a]	1/7/1976	0.035	0.042	14.01	0.75	0.130
Shallow groundwater, lower[a]	1/7/1976	0.073	0.074	29.43	1.18	0.255
Shallow groundwater[c]	1/20/1974	0.460	0.439	293.45	16.55	1.765
Lake Vanda, 80 m[a]	11/1/1973	0.979	0.571	487.64	37.29	3.837

[a] Flows east of DJP (Harris and Cartwright, 1981), where 'upper' and 'lower' designate relative position in a flow system. The Lake Vanda sample is groundwater collected 80 m below the lake surface and 10 m below the lake bottom.
[b] Torii et al. (1977).
[c] Flow east of DJP (Wilson, 1979).

servations, as well as other hydrogeological arguments (Harris and Cartwright, 1979, 1981), led to a view that DJP is the result of closed-basin evaporation of groundwater upwelling from a deep, confined aquifer.

Dickson et al. (2013) proposed an alternative hypothesis that shallow groundwater fluxes control the chemistry of DJP. This idea is based on (1) observations of shallow groundwater flows east of DJP (Cartwright and Harris, 1981; Wilson, 1979) and (2) time-lapse photography showing regular brine discharges at the eastern and western margins of DJP during the austral summer and winter (Dickson et al., 2013, 2016). Shallow groundwater flows east of DJP are enriched in $CaCl_2$ (i.e., Ca^{2+} in excess of $SO_4^{2-} + CO_3^{2-}$) (Table 1) and are thought to be hydrologically connected to moist streaks of soil (termed "water tracks" or "slope streaks") that occur on north facing slopes in Wright Valley (Cartwright and Harris, 1981; Dickson et al., 2013; Head et al., 2007). These moist streaks of soil are thought to derive from subsurface water traveling downslope along the top of impermeable ice-cemented soil, and subsequent wetting of the soil surface by upwards wicking water. Dickson et al. (2013) found that outflow occurrences to DJP in the austral summer were correlated with surface temperature increases and greater water contents in nearby moist streaks, which suggested that shallow groundwater flows found east of DJP, not deep groundwaters, are responsible for the $CaCl_2$ component in DJP.

To test hypotheses of shallow vs. deep groundwater inputs against observed chemistries in DJP, we model closed-basin evaporation of DJP using a recently developed geochemical model in the Na–K–Ca–Mg–Cl system (Toner and Catling, 2017), and compare ionic ratios in DJP to surface and groundwater chemistries throughout Wright Valley. We find that salts in DJP are dominated by deep groundwater inputs, in contrast with shallow groundwater hypotheses. Furthermore, by modeling the closed-basin evaporation of upwelling groundwater, we deduce that DJP is fed by a regional flow-through groundwater system, potentially analogous to other deep groundwaters that have been detected in the MDV (Mikucki et al., 2015).

2. Methods

2.1. Study site

The MDVs are extremely cold and dry, with mean annual temperatures near $-20\,°C$ (Doran et al., 2002) and <100 mm of water per year in the form of snow (Fountain et al., 2010), most of which sublimates in the dry air (Liu et al., 2015). Temperatures in the winter have lows near $-40\,°C$, while summer temperatures occasionally rise above freezing. DJP is located at 117 m elevation above sea level within a small closed-basin in the South Fork of Wright Valley (77.565 S, 161.174 E) (Fig. 1A). The pond occupies a closed-basin in the middle of a salt pan about 800 m long (E–W) and 350 m wide (N–S), and typically has a maximum depth of 10–30 cm, although the depth fluctuates from year to year (Harris and Cartwright, 1981; Torii et al., 1977). On the west, DJP is bounded by a rock glacier that hosts a small meltwater stream in the summer. To the east of DJP, the valley floor rises in a series of small basins, terminating in a major valley floor threshold at ∼190 m elevation and 5 km distance from DJP. During the austral summer, ephemeral shallow groundwaters draining from the east flow into DJP basin. To the north and south, DJP is bounded by steep colluvial slopes.

The subsurface of DJP was investigated during drilling of the DVDP 13 borehole on the southwest margin of the pond (Fig. 1). Drilling commenced January 8th 1975 and was finished on January 13th (Mudrey et al., 1975). DVDP 13 penetrated 12.67 m of silty–sandy sediments, followed by a fractured dolerite sill (Ferrar dolerite) from 12.67 to 52.2 m depth. The base of the core was comprised of a crystalline basement complex from 52.2 to 75 m depth (Mudrey et al., 1975). All core units were found to be saturated with brine, which was corroborated by electrical depth soundings and seismic profiles (McGinnis et al., 1973). Brine samples were taken from sediments in the upper portion of DVDP 13 during drilling on January 9th 1975 (Torii et al., 1977), and two brine samples were collected one year after DVDP 13 drilling from the top and bottom of the dolerite sill (Harris and Cartwright, 1981). 21 additional samples in the dolerite sill were collected between December 3rd 1975 and January 20th 1976 and were analyzed for their full chemistry, but only Cl^- concentrations are given (Harris and Cartwright, 1981). The composition of DVDP 13 groundwaters was found to be the same with respect to both depth and time.

2.2. Modeling

To model the chemistry of brines in DJP, we use the Pitzer model of Toner and Catling (2017) in the Na–K–Ca–Mg–Cl system. This model is valid from 25 to $< -70\,°C$ and includes as solid phases ice, halite (NaCl), hydrohalite ($NaCl{\cdot}2H_2O$), sylvite (KCl), antarcticite ($CaCl_2{\cdot}6H_2O$), bischofite ($MgCl_2{\cdot}6H_2O$), $MgCl_2{\cdot}8H_2O$, $MgCl_2{\cdot}12H_2O$, carnallite ($KCl{\cdot}MgCl_2{\cdot}6H_2O$), and tachyhydrite ($CaCl_2{\cdot}2MgCl_2{\cdot}12H_2O$). This model is a significant improvement over previous models in the Na–K–Ca–Mg–Cl system at subzero temperatures (e.g. Marion and Farren, 1999; Spencer et al., 1990) because it includes enthalpy and heat capacity data, which con-

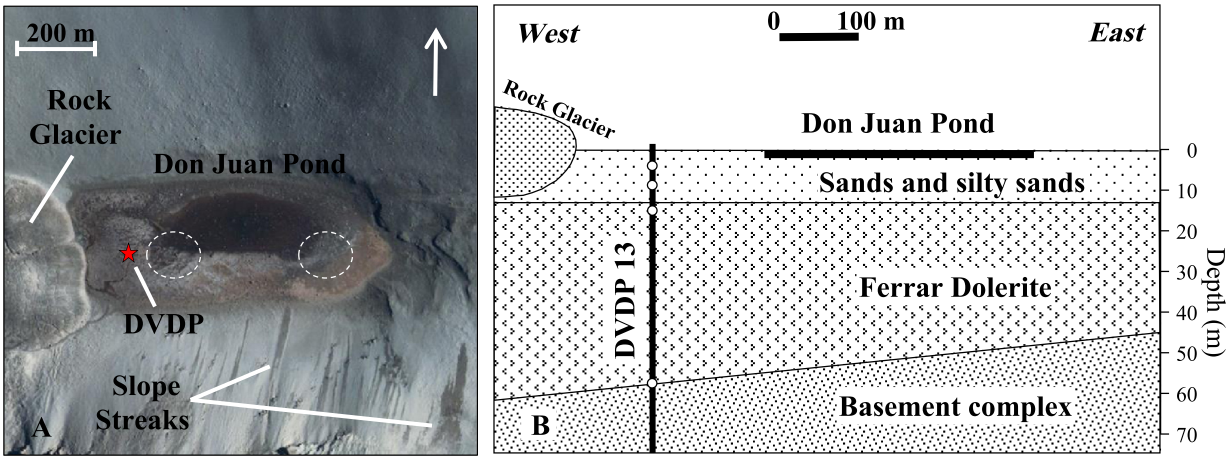

Fig. 1. (A) A satellite image of DJP, showing the location of DVDP 13 (red star) and discharge zones observed on the southwest and eastern margins of the pond (dashed circles) (Dickson et al., 2013, 2016; Harris and Cartwright, 1981). The arrow points north. (B) A west–east geologic cross section of DJP, showing the location of DVDP 13 and major geologic units. The depths at which groundwater was sampled from DVDP 13 (5.48, 8.8, 15, and 58 m) are shown as white circles. Adapted from Harris and Cartwright (1981). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

strain the temperature dependence of modeled water and ion activity coefficients. Furthermore, this model includes a more accurate representation of the thermodynamic properties of $CaCl_2$ up to saturated concentrations, which is important given the $CaCl_2$-rich composition of DJP. We implement our model using the geochemical program PHREEQC (our model is now distributed with PHREEQC as the 'ColdChem.dat' database), which calculates phase equilibria at different temperatures using Gibbs free energy minimization (Appelo and Postma, 2005). Our model does not include SO_4^{2-} chemistries; however, DJP contains trace SO_4^{2-} due to the high Ca^{2+} concentrations, so SO_4^{2-} can be neglected.

In closed-basin lake systems, salts carried in surface or groundwater flows accumulate over time in evaporating basin waters until they are precipitated from solution as crystalline salts or other secondary minerals. To model closed-basin evaporation in DJP, we assume a constant flux of brine to the pond balanced by continual evaporation of water and equilibrium precipitation of salts. The initial condition in our model is a pond that is identical in composition to the inflowing groundwater (either shallow or deep groundwater). We then continually add more groundwater brine, and at the same time remove water to simulate evaporation, keeping the total mass of water in the pond constant (i.e. the influx of water from groundwater is equal to water loss due to evaporation and precipitation in hydrated salts). To present our model results, we plot modeled ion concentrations against the 'filling/evaporation cycle', where one filling/evaporation cycle represents the addition of groundwater equal to the starting brine content of the pond balanced by continuous evaporation so that the water mass remains constant.

We consider two possibilities for the brine influx to DJP: (1) shallow and (2) deep groundwater. For the shallow groundwater flux, we use the brine composition from Wilson (1979) (Table 1), adjusting Cl^- concentrations to achieve charge balance and neglecting trace SO_4^{2-} concentrations: $Ca^{2+} = 0.46$, $Na^+ = 0.439$, $Mg^{2+} = 0.293$, $K^+ = 0.0165$, and $Cl^- = 1.963$ mol kg^{-1}. For the deep groundwater flux, we use the average chemistry measured in DVDP 13 at 15 and 58 m depth, similarly adjusting Cl^- concentrations: $Ca^{2+} = 1.983$, $Na^+ = 0.333$, $Mg^{2+} = 0.046$, $K^+ = 0.0027$, and $Cl^- = 4.393$ mol kg^{-1}. Based on average temperatures measured in DJP during the austral summer (Marion, 1997), we model closed-basin evaporation at 5 °C. We expect that most closed-basin evaporation will occur during the austral summer because the evaporation rate from a solution strongly depends on the water vapor pressure, which increases exponentially with increasing temperature.

3. Model results: closed-basin evaporation in Don Juan Pond

Our deep groundwater model of closed-basin evaporation indicates that halite precipitates early after only one filling/evaporation cycle (Fig. 2A, see methods for the definition of a filling/evaporation cycle). The early precipitation of halite is consistent with its abundance in DJP and nearby soils (Torii et al., 1977). After only ~1.5 filling/evaporation cycles, antarcticite precipitates from solution, a mineral also found in DJP basin (Torii and Ossaka, 1965). After 50 filling/evaporation cycles, Mg^{2+} and K^+ concentrations increase to the extent that carnallite and later bischofite precipitate from solution, neither of which have been found in DJP basin. The final residual brine at ~100 filling/evaporation cycles is a Mg–Ca-rich brine. To determine if our model is consistent with DJP, Fig. 2A shows Na^+, K^+, Ca^{2+}, and Mg^{2+} concentrations measured in DJP against filling/evaporation cycle, where the filling/evaporation cycle of a measured brine is set equal to the filling/evaporation cycle of the modeled brine having the same Cl^- concentration (hollow symbols). Modeled trends in ion concentration closely follow ionic concentrations in DJP, including the decrease in Na^+ due to halite precipitation.

If we use shallow groundwaters as input to our closed-basin evaporation model (Fig. 2B), we find that carnallite and bischofite precipitate much earlier at 6 and 12 filling/evaporation cycles respectively (compared to 39 and 85 filling/evaporation cycles respectively in the deep groundwater model). Carnallite precipitates before antarcticite in the shallow groundwater model, which conflicts with observations of antarcticite, and not carnallite, in DJP basin. Overall, ionic compositions in our shallow groundwater model do not match measured compositions in DJP. Compared to DJP, modeled Na^+, Mg^{2+}, and K^+ concentrations are much higher and Ca^{2+} concentrations are lower; however, our model is roughly consistent with the decrease in Na^+ concentrations due to halite precipitation.

In our modeling, we assume equilibrium crystallization, in which phases precipitated during an earlier model iteration may redissolve into solution. Another possible evolution pathway is via fractional crystallization, which removes precipitated phases from the system. Differences between equilibrium and fractional closed-basin pathways in our model will only arise if a precipitated phase redissolves; however, neither the deep nor shallow groundwater

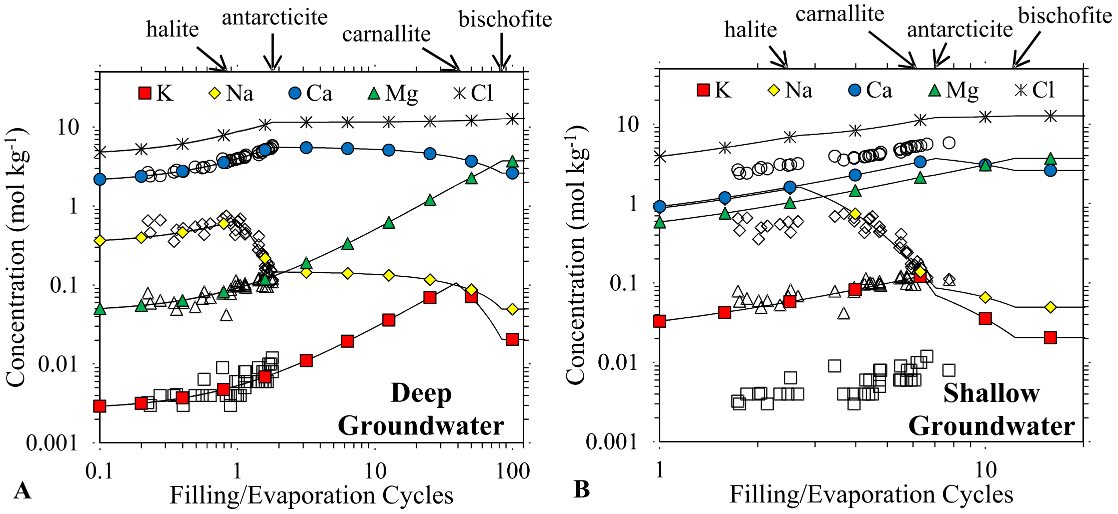

Fig. 2. The closed-basin evolution of Na^+, K^+, Ca^{2+}, Mg^{2+}, and Cl^- concentrations (mol kg^{-1}) in DJP as a function of filling/evaporation cycles at 5 °C. In panel (A) we model closed-basin evaporation assuming deep groundwater inputs to DJP to a final Mg–Ca–Cl-rich brine. In panel (B) we model closed-basin evaporation assuming shallow groundwater inputs. A filling/evaporation cycle indicates the addition of groundwater equal to the starting brine content of the pond balanced by continuous evaporation. The hollow symbols are measured ion concentrations in DJP from Marion (1997), where the filling/evaporation cycle of a measured brine is set equal to the filling/evaporation cycle of the modeled brine having the same Cl^- concentration.

models predict the redissolution of any chloride phases. This indicates that the equilibrium and fractional crystallization pathways are equivalent in our model. We also make the simplifying assumption in our model that the water content of DJP is constant over time; however, observations indicate that the volume of DJP varies due to groundwater, stream water, and evaporation fluxes (Harris and Cartwright, 1981). Such variations in pond volume will not change the overall chemical evolution of the pond, but they could affect the inferred age of the brine. For example, a steady decline in pond volume over time in our model would have the effect of making the brine appear older i.e., shift the filling/evaporation cycle towards a higher value.

Temperatures also vary in DJP over the austral year, which could affect the model results. Lower temperatures will cause minerals to precipitate out of solution sooner (i.e., at lower concentrations), with the exception of halite, which has a nearly temperature invariant solubility. In the deep groundwater model, early precipitation of antarcticite at lower temperatures limits the maximum concentration of Ca^{2+}, which is inconsistent with high Ca^{2+} concentrations found in DJP. For example, Ca^{2+} concentrations up to 5.6 mol kg^{-1} have been measured in DJP, but at −10 °C our model predicts maximum Ca^{2+} concentration of 5 mol kg^{-1}. This supports our assumption that most evaporation occurs during the austral summer at 5 °C in DJP.

4. Discussion

4.1. *The source of salts to Don Juan Pond*

The agreement between measured and modeled ion concentrations in DJP for deep groundwater inputs strongly supports a deep groundwater source of salts that is modified by evaporation, whereas closed-basin evaporation of shallow groundwater inflows cannot form DJP brines. Even if we use different shallow groundwater compositions in our model from Cartwright and Harris (1981) (Table 1), the closed-basin evolution of such brines is similar to the Wilson (1979) brine modeled in Fig. 2B, invariably leading to Mg and K-enriched brines compared to DJP. However, many other inflowing brine compositions are possible. To investigate other possible brine sources to DJP, we compare ionic ratios in DJP to known ground and surface water compositions in Wright Valley.

Ionic ratios are useful indicators of brine origin because ions of highly soluble salts such as chlorides are conserved (i.e., remain in solution) during evaporation and freezing processes. By comparing ionic ratios relative to Cl^-, we find that DJP is distinct from all ground and surface waters in Wright Valley, with the exception of groundwaters in DVDP 13 (Table 1, Fig. 3). Na/Cl ratios in DJP average 0.056, which is much lower than the seawater ratio of 0.85. Soils, streams, and glacial ice in the MDVs typically have Na/Cl ratios near the seawater ratio, which reflects the accumulation of seawater derived aerosols (Campbell and Claridge, 1987; Toner et al., 2013). K/Cl and Mg/Cl ratios are also heavily depleted in DJP compared to other surface chemistries in Wright Valley (Fig. 3A), which is surprising because evaporative concentration of brines typically results in Mg and K-rich brines (Eugster and Jones, 1979).

Ca/Cl ratios are similar for most waters in Wright Valley, including DJP; however, this similarity is misleading because Ca^{2+} is a non-conservative ion. Upon evaporation of dilute stream, lake, and glacial waters to concentrations comparable to DJP, most of the Ca^{2+} will combine with SO_4^{2-} and HCO_3^- to precipitate from solution as insoluble calcite and/or gypsum, causing the Ca/Cl ratio to decrease far below that measured in DJP. In general, freezing and evaporation of Dry Valley surface waters results in Ca-deficient brines due to calcite and gypsum formation; however, it is possible to form $CaCl_2$-rich brines in soil solutions due to the influence of cation exchange reactions (Toner and Sletten, 2013). Toner and Sletten (2013) modeled the effects of exchange reactions on ~2000 stream and lake chemistries in the MDV and found that, although cation exchange reactions result in $CaCl_2$-rich brines, the Ca/Cl ratios are lower and the Mg/Cl ratios are higher compared to DJP. Hence, neither freezing, evaporation, nor cation exchange reactions acting on MDV surface waters can explain the chemistry of DJP or its groundwaters.

Ionic ratios in DJP are not only unique, but they have also remained remarkably stable over 30 yr of measurements, from 1961 to 1993 (Fig. 4) (Marion, 1997; Torii, 1994; Torii et al., 1977; Webster, 1994). Ca/Cl (0.46 ± 0.02), Mg/Cl (0.011 ± 0.002), and K/Cl (0.0006 ± 0.0002) ratios in DJP are all essentially constant over time within the expected experimental error, whereas Na/Cl ratios (0.06 ± 0.03) vary due to the precipitation of halite (see Fig. 2A). The tight clustering of Mg/Cl and K/Cl ratios despite wide variations in total Cl^- concentration over time (Fig. 3B) indicates that

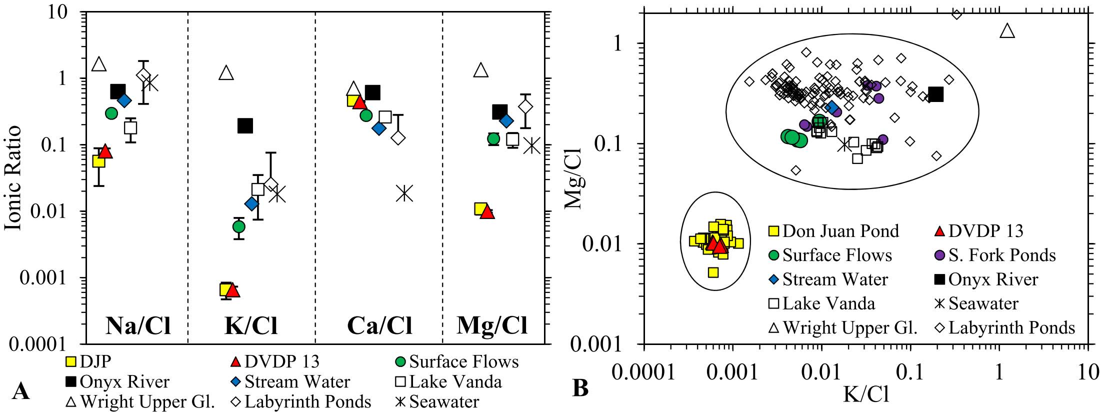

Fig. 3. Ionic ratios in DJP, groundwaters, and nearby streams, lakes, and glacial ice. In panel (A) the sample average is given, and the error bars are 1 standard deviation. In panel (B), the individual data points are shown against their K/Cl and Mg/Cl ratios with two populations. The sources of data are as follows: DJP (Marion, 1997; Torii, 1994), DVDP 13 groundwaters (Harris and Cartwright, 1981; Torii et al., 1977), shallow groundwater flows east of DJP (Cartwright and Harris, 1981; Wilson, 1979), Wright Upper Glacier ice and stream water draining into DJP from the west (Cartwright and Harris, 1981), Lake Vanda waters down to 70 m depth (Webster and Goguel, 1988), ponds in the Labyrinth region west of DJP (Torii et al., 1989), and ponds in the South Fork of Wright Valley east of DJP (Torii, 1994).

Mg^{2+} and K^+ are strongly conservative ions in DJP i.e. they do not precipitate from solution. The conservative nature of Mg^{2+} and K^+ ions, and their low concentrations in DJP compared to surface waters, further indicates that evaporation and/or freezing of surface waters cannot form DJP brines.

The unique geochemical signature of DJP and DVDP 13 groundwaters, and the stability of this chemistry over time, supports the notion that deep groundwater inputs are responsible for the salt chemistry of DJP, and not shallow groundwaters flowing into the eastern margin of the pond (or any other near-surface water). This implies that if discharges observed on the eastern margin of DJP are from shallow groundwater, as proposed by Dickson et al. (2013), then these flows must have insufficient salt content or volume to perturb chemical ratios in DJP. Alternatively, these discharges may be deep groundwater outflows, as was originally proposed by Harris and Cartwright (1981). In support of this, we note that the groundwater discharges observed by Dickson et al. (2013) are similar in frequency to sharp spikes in water level recorded in DVDP 13 (up to 30 cm in height) (Harris and Cartwright, 1981), which suggests that the observed discharges may be caused by the groundwater level spikes. Harris et al. (1982) speculated that the water level spikes in DVDP 13, which are highly unusual in groundwater systems, may be caused by movements of the rock glacier abutting DJP to the west.

Although our model indicates that salts in DJP can be solely explained by evaporative concentration of deep groundwater inputs, our results do not preclude significant freshwater or shallow groundwater inflows to DJP. Past observations (Harris and Cartwright, 1981) and recent time-lapse photography (Dickson et al., 2013) clearly show that surface flows regularly discharge into DJP, particularly from a seasonal meltwater stream that forms on the rock glacier west of DJP. Stream inflows will dilute the brine in DJP, but they will not significantly alter relative salt compositions in DJP because measured salt fluxes from meltwater streams are negligible (Harris and Cartwright, 1981).

Shallow groundwater inflows are also possible, but our model indicates that such inflows have a negligible influence on the salt chemistry of DJP. The magnitude of the shallow groundwater flux to DJP is poorly constrained, but we can use a simple mixing model to estimate how much shallow groundwater is needed relative to deep groundwater to perturb ionic ratios in DJP above average measured values (Table 2). We use Mg/Cl and K/Cl ratios for this analysis because Mg^{2+} and K^+ ions are conservative in DJP, and we assume only shallow and deep groundwater inputs, noting that dilute meltwater inflows will not appreciably affect ionic ratios.

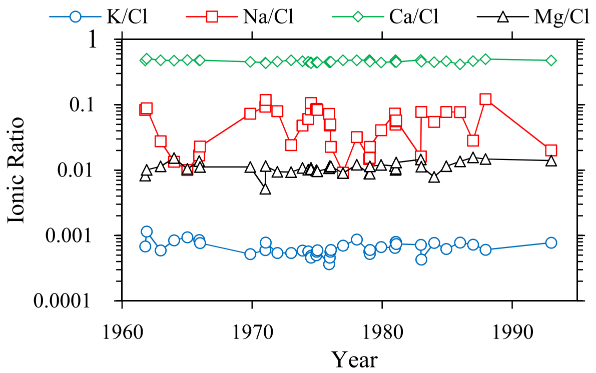

Fig. 4. Ca/Cl, Na/Cl, Mg/Cl, and K/Cl ratios in DJP vs. sampling year, from the aqueous analyses compiled in Marion (1997) and Torii (1994).

Table 2

Results from a simple mixing model indicating the relative influx of shallow groundwater relative to deep groundwater (wt.%) needed to perturb Mg/Cl and K/Cl ratios in DJP above $+1\sigma$ of average measured values in DJP ($Mg/Cl = 0.011 \pm 0.002$; $K/Cl = 0.0006 \pm 0.0002$). For deep groundwater, we use the DVDP 13 composition measured at 58 m depth. For shallow groundwaters, we use compositions given in Table 1.

Shallow groundwater brine	Shallow Groundwater (wt.%)	
	Mg/Cl	K/Cl
Wilson (1979)	3.0	6.0
Harris and Cartwright (1981)	17.4–38.3	31.0–56.9

Our simple mixing model indicates that the Wilson (1979) brine needs to comprise at least 3–6 wt.% of the total groundwater influx to perturb ionic ratios in DJP above $+1\sigma$ of the measured average. Other shallow groundwater inflows measured by Harris and Cartwright (1981) are much more dilute and must inflow at much higher proportions relative to deep groundwater to significantly affect the chemistry of DJP. These mixing model results place upper limits on the relative contribution of shallow groundwater flows to DJP, but the problem is poorly constrained because of uncertainties in the shallow groundwater influx rate and composition.

4.2. A flow-through groundwater system beneath Don Juan Pond

Our deep groundwater model of closed-basin evaporation in DJP (Fig. 2A) suggests that DJP experiences relatively limited evaporation (up to two filling/evaporation cycles). Furthermore, mea-

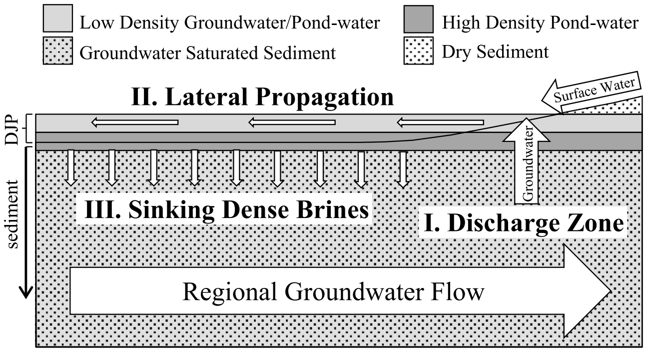

Fig. 5. A conceptual model of groundwater flow and discharge in DJP, oriented W–E. (I) Deep groundwater, shallow groundwater from east of DJP, and/or stream water periodically discharges at the pond margin. (II) Low density groundwater and/or surface water migrates laterally across the surface of DJP, on top of older, denser evaporated brines. (III) This surface loading causes denser, evaporated brines to subside into the subsurface, where they reenter the regional groundwater flow system. Continued cycles of groundwater discharge and dense brine sinking would flush salts from DJP, preventing the accumulation of Mg^{2+} and K^{+} ions. We show groundwater discharge occurring at the eastern end of DJP in this figure, but groundwater discharge and surface inflows are also found on the western end of DJP (Harris and Cartwright, 1981).

sured compositions in DJP never approach the high Mg^{2+} and K^{+} concentrations predicted by our model after 100 filling/evaporation cycles. This implies a relatively young age for DJP. To determine the timescale for closed-basin evaporation in our model, we estimate the time required for one filling/evaporation cycle using a groundwater discharge rate of 30 $m^3\,day^{-1}$ from Harris and Cartwright (1981), an average pond area of 20,000 m^2 from Torii (1994), and a nominal pond depth of 0.1 m. Our calculated age indicates a filling/evaporation cycle of ~66 days (66 days = 20,000 m^2 × 0.1 m/30 $m^3\,day^{-1}$), or that 100 filling/evaporation cycles occur every 18 yr, which would result in the Mg–Ca–Cl-rich brine in our model. At the most, brines in DJP appear to be only ~130 days old (two filling/evaporation cycles). Note that the brine "age" in this case is a measure of how long deep groundwater inputs have undergone closed-basin evaporation. This age may be subject to significant error because DJP varies in depth and extent, and the deep groundwater flux likely varies over time. Regardless, our calculated age is several orders of magnitude less than the time elapsed since DJP was first discovered in 1961.

The surprisingly young age of brines in DJP can be explained if DJP is an open system, i.e. if brines flow out of DJP as well as in. An outflow from DJP would continually flush evaporated brines from DJP, preventing the formation of late-stage closed-basin brines enriched in Mg^{2+} and K^{+}. Because DJP is topographically a closed-basin, any outflow must occur as groundwater, which suggests the existence of a flow-through groundwater system beneath DJP (Fig. 5). We propose that surface water compositions in DJP can be explained by (1) recharge due to upwelling deep groundwater, (2) evaporative concentration of brines and precipitation of salts, and (3) outflow to the groundwater system. Based on the estimated timescale for closed-basin evolution in our model, the residence time for surface waters in DJP is on the order of a year.

The process of brine reentry into the subsurface could be driven by density differences between freshly discharged groundwater and older, evaporated brine. The most highly concentrated brines in DJP have densities up to 1.39 $g\,cm^{-3}$ (Torii et al., 1977), whereas groundwater in DVDP 13 has a density of 1.18 $g\,cm^{-3}$ (Harris and Cartwright, 1981). Dickson et al. (2013, 2016) observed fluids discharging from discrete locations at the eastern and western margins of DJP, and from stream water inputs on the western margins of DJP, which then propagate across the entire pond surface. Assuming that discharged flows are comprised of either low density deep groundwater, dilute stream water, or shallow groundwater, these outflows would flow on top of denser, evaporated brine in the pond, increasing the hydraulic pressure on underlying brines and forcing them into the subsurface. Repeated cycles of lower-density groundwater discharge and dense brine infiltration into the subsurface would recycle salts in DJP.

Substantial evidence supports the existence of regional groundwater systems in the MDV. Deep groundwater systems have been inferred throughout both Wright and adjacent Taylor Valley based on electrical depth soundings (McGinnis and Jensen, 1971; McGinnis et al., 1973) and helicopter-borne electromagnetic surveys (Mikucki et al., 2015). Furthermore, Lake Vanda, located ~10 km NE of DJP, is enriched in $CaCl_2$, which has led many authors to speculate that Lake Vanda is hydrologically connected to $CaCl_2$ groundwaters beneath DJP (e.g. Cartwright and Harris, 1981; Green and Canfield, 1984; Webster, 1994; Webster and Goguel, 1988). The current elevation of Lake Vanda is lower than DJP (83 vs. 117 m), and the lake bottom, the lowest point in Wright Valley, lies at 13 m elevation. This suggests that Lake Vanda is a natural discharge point for a regional groundwater flow system.

Lake Vanda is a closed-basin lake containing ~60 m of relatively fresh water that transitions at depth (via a mixed layer) to ~10 m of brine. Surface waters in Lake Vanda are slightly enriched in $CaCl_2$, suggesting that $CaCl_2$ groundwaters are presently discharging into Lake Vanda (Toner and Sletten, 2013). The saline bottom waters are thought to be a remnant from a period of desiccation (Wilson, 1964) and are strongly enriched in $CaCl_2$ (Table 1). The $CaCl_2$-rich brine in lower Lake Vanda has relatively high Mg/Cl and K/Cl ratios (Mg/Cl = 0.13 and K/Cl = 0.01), which is consistent with the highly evaporated closed-basin brines modeled in Fig. 2. This suggests that, in contrast to the flow-through system in DJP, Lake Vanda represents a true closed-basin system lacking a significant groundwater outflow. However, the chemistry of lower Lake Vanda is not predicted at any point in our model, primarily because Na^{+} concentrations in Lake Vanda are relatively high. This is probably because our model assumes DJP groundwater as the discharging groundwater brine, which may not apply to Lake Vanda. If groundwaters discharging into Lake Vanda ultimately originate from near DJP, then the composition of these groundwaters would likely be modified after ~10 km of subsurface flow towards Lake Vanda.

4.3. The role of water–rock interactions in Don Juan Pond

Our results constrain the source and evolution of upwelling groundwater in DJP, but we do not address the original formation of the brine. Despite decades of study, the ultimate origin of the unique chemistry in DJP and its groundwater remains controversial (Lyons and Mayewski, 1993). Several authors have noted that DJP is similar in composition to deep groundwaters found in other locations (Webster and Goguel, 1988). These deep groundwaters sometimes have extreme $CaCl_2$ enrichments, nearly saturated Cl^{-} concentrations, and large depletions in Na^{+}, Mg^{2+}, and K^{+} (Garrett, 2004). The origin of these brines is uncertain, but it is generally accepted that deep $CaCl_2$-rich brines are seawater-derived brines that have been heavily modified by water–rock interactions such as albitization, chloritization of mafic rock minerals, and dolomitization. DJP may also be a modified seawater brine, as suggested by many authors; however, DJP contains relatively high NO_3^- concentrations (~5 mM) (Samarkin et al., 2010). This anion occurs in trace amounts in seawater, but is common in high elevation MDV soils (Campbell and Claridge, 1987) due to atmospheric chemical production and deposition (Michalski et al., 2005). The presence of NO_3^- in DJP implies a surface source for the brine from high-elevation soils, as suggested by Toner and Sletten (2013).

The extreme Mg^{2+} and K^{+} depletion in DJP suggests extensive modification by water–rock interactions, and that Mg and K-rich secondary phases should be associated with the brine origin (Toner and Sletten, 2013). The DVDP 13 core has been analyzed for secondary minerals (Nishiyama, 1979). Possible secondary minerals found in the borehole include the zeolites chabazite and laumonite, fluorite, gypsum, abundant calcite, and one recorded instance of chlorite at 62 m depth. Most of these minerals are calcium-rich phases, consistent with the Ca-rich composition of groundwaters, although chabazite can substitute a variety of cations. Chlorite is a Mg-rich phase that could act as a sink for aqueous Mg^{2+}, but a single identification of this mineral, which may or may not actually be secondary, does not provide compelling evidence for a Mg^{2+} sink. If groundwaters beneath DJP have been modified by water–rock interactions, then the dearth of Mg and K-rich secondary phases in DVDP 13 suggests that the water–rock interactions must have occurred elsewhere.

4.4. Implications for Mars

The formation of $CaCl_2$-rich groundwaters in the MDV suggests that $CaCl_2$ brines are possible in the Martian subsurface (Burt and Knauth, 2003; Dickson et al., 2013). Toner and Sletten (2013) and Toner et al. (2013) found that $CaCl_2$ brines form in subsurface sediments throughout the MDV due to the influence of cation exchange reactions in frozen soils as brine films migrate downwards into soils along temperature and water activity gradients. Similar processes may occur in Martian soils, which suggests that $CaCl_2$ brines may be widespread on Mars. Furthermore, the occurrence of deep $CaCl_2$ groundwaters on Earth suggests their possible occurrence on Mars. Outflows of either shallow or deep $CaCl_2$-rich brines could potentially explain the formation and persistence of RSL on Martian slopes despite generally cold and dry conditions (Stillman et al., 2016), although other brine compositions are possible.

The formation of $CaCl_2$ brines on Mars and the MDV could provide a potentially habitable source of water that is stable against evaporation and freezing. A water activity of 0.6 is considered to be the lower limit that terrestrial life can tolerate (Grant, 2004). The water activity of $CaCl_2$ brine saturated with antarcticite is 0.28 at 25 °C but increases to 0.61 at -50 °C. $CaCl_2$-rich brines also have ion specific effects on habitability (Oren, 2013); however, few studies have evaluated microbial activity in naturally occurring $CaCl_2$ brines. In DJP, microbial activity is so far undetectable in the most saline brines, but the total absence of microbial activity has not been ruled out (Mikucki et al., 2010). Tregoning et al. (2015) investigated microbial growth in the $CaCl_2$ brine at the bottom of Lake Vanda and found evidence of microbial growth, although the brine concentration is much lower than in DJP ($\sim$1 mol kg^{-1} $CaCl_2$) and temperatures are near 25 °C.

5. Conclusions

To test hypotheses of deep vs. shallow groundwater sources to DJP, we used a model of closed-basin evaporative brine formation in DJP, and compared the geochemistry of DJP to deep groundwaters, shallow groundwaters, and other surface waters in Wright Valley. We find that the closed-basin evolution of deep groundwater in DVDP 13 matches DJP, whereas the closed-basin evolution of shallow groundwater differs from DJP. Furthermore, ionic ratios in DJP are distinct from all surface and groundwater compositions in Wright Valley, with the exception of groundwaters beneath DJP. This provides compelling evidence that deep groundwaters are responsible for the chemistry of DJP, as opposed to shallow groundwaters. The ultimate origin of the groundwater beneath DJP is uncertain, but relatively high nitrate concentrations point to surface derived brines altered by water–rock interactions.

The modeled closed-basin evolution of deep groundwater predicts that DJP should evolve to a Mg–Ca–Cl-rich composition and eventually precipitate Mg–K-rich salts (carnallite and bischofite), but these brine compositions and salts do not occur. Furthermore, less than a year of closed-basin evaporation is needed to form brines in DJP, i.e. DJP appears to be perpetually young. The lack of Mg^{2+} and K^+ accumulation over time and the surprisingly young age of DJP is explained if DJP is an open system with respect to groundwater. We suggest that groundwaters beneath DJP are part of a regional flow-through system, and that pond waters are recycled back into this groundwater system over yearly timescales. This flow-through system may ultimately discharge into Ca–Cl-rich Lake Vanda. Recent surveys of nearby Taylor Valley have revealed extensive, possibly connected saline groundwater systems, and the results of this study suggest that a connected groundwater system is present in Wright Valley.

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