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

J.D. Toner *, D.C. Catling, R.S. Sletten

University of Washington, Box 351310, Dept. Earth & Space Sciences, Seattle, WA 98195, USA

A B S T R A C T

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.

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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 ($-52\,°C$), 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), al-

though 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-

* Corresponding author.
  E-mail address: toner2@uw.edu (J.D. Toner).

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 × Mg^{2+}	1000 × 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·2H$_2$O), sylvite (KCl), antarcticite (CaCl$_2$·6H$_2$O), bischofite (MgCl$_2$·6H$_2$O), MgCl$_2$·8H$_2$O, MgCl$_2$·12H$_2$O, carnallite (KCl·MgCl$_2$·6H$_2$O), and tachyhydrite (CaCl$_2$·2MgCl$_2$·12H$_2$O). 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-