Evaluating the effect of grain size and salts on liquid water content in frozen soils of Antarctica by combining NMR, chemical equilibrium modeling, and scattered diffraction analysis

Liliya Vugmeyster^{a,*}, Birgit Hagedorn^b, Matthew A. Clark^b, R.S. Sletten^c

^a University of Colorado at Denver, Denver, CO 80204, United States

^b University of Alaska Anchorage, Anchorage, AK 99508, United States

^c University of Washington, Seattle, 98195, United States

ARTICLE INFO

Article history:

Received 15 September 2016

Accepted 27 March 2017

Available online xxxx

Keywords:

Water content

NMR

FREZCHEM

Freezing curves

Antarctic soils

Grain size

Modeling

ABSTRACT

Recent studies point to the possible existence of liquid water on Mars surface. While many efforts have focused on experimental determination and modeling of liquid water content in inorganic-salt rich soils, additional factors that govern liquid water formation remain largely unexplored. The purpose of this study is to determine main soil properties that will affect unfrozen water content. We analyzed liquid water content and bulk freezing points using high field deuterium NMR measurements and compared the results to the amount of liquid water content at the same temperatures based on salt concentration and composition using an empirical chemical equilibrium model (FREZCHEM). We selected soils with a wide range of salt concentrations and composition collected from the McMurdo Dry Valleys, Antarctica. The comparison indicates that at 50% unfrozen water content the freezing temperatures deviate substantially from water content modeled based on salt composition. In particular, the NMR freezing points are lower than those calculated with FREZCHEM for all low to medium salt content samples. The results indicate that soil properties other than aqueous chemical composition add to liquid water content. Particle size does not necessarily correlate with the liquid water content, revealing that more detailed investigation including surface area and composition may be necessary to describe the dependence of unfrozen water content on soil properties. The study highlights the necessity of experimental measurements of water content due to effects of multiple factors that are difficult to take into account in simulations.

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1. Introduction

Studies indicate that transient liquid water may exist on Mars surface due to high salt concentrations and may support life (Boxe et al., 2012; Chevrier et al., 2009a; Cull et al., 2010; Davila et al., 2010; Hanley et al., 2012; Hecht et al., 2009; Marion et al., 2010; Rennó et al., 2009; Zorzano et al., 2009). In addition, deliquescence of iron sulfates and perchlorates may contribute to viscous flow and modern formation of Martian gullies (Chevrier et al., 2009b) Cull et al. (2010) interpret the occurrence of massive perchlorate as a result of salt transport through thin water films during seasonal ice covers. It is speculated that oscillation of temperatures above and below eutectic temperature may lead to the formation of excess pore ice over longer time periods (Rennó et al., 2009).

Another mechanism for liquid water survival in dry and cold environments is formation of adsorbed films on particle surfaces. It is

believed that adsorbed water was observed by the Observatoire pour la Mineralogie l'Eau, les Glaces et l'Activite (OMEGA), indicating that at the Phoenix lander site 10–11% of water is likely adsorbed to particle surfaces (Poulet et al., 2010). In soils the adsorbed water is directly related to the relative humidity in the presence of ice and salt. Models designed for high ionic strength must be used to model the phases and unfrozen water content in such a multi-component system. In addition, the influence of interfaces on unfrozen water (Gibbs-Thomson effect) must be accounted for (Anderson and Morgenstern, 1973; Dash et al., 1995; Horiguchi, 1987; Rempel, 2011). The latter can have a dynamic (entropic) component stemming from motions of water molecules at the water-soil interface (Anderson and Anderson, 2010) (Rempel et al., 2004). Interfacial water is known to be important in many surface processes including: stability of suspensions (Crocker et al., 1999; Israelachvili and Wennerstrom, 1996), protein folding and dynamics (Bergknut et al., 2011; Frauenfelder et al., 2009; Graziano, 2010; Krushelnitsky et al., 2009; Mallamace et al., 2007; Sterpone et al., 2012; Vugmeyster et al., 2011), and clay swelling (Asay and Kim, 2005; Geissbuhler et al., 2004; Goertz et al., 2007; Karaborni et al.,

* Corresponding author.

E-mail address: LILIYA.VUGMEYSTER@UCDENVER.EDU (L. Vugmeyster).

1996; Skelton et al., 2011). A recent study by Boxe et al. (2012) suggests that it is particularly important to study the films of liquid water on the surfaces of ice and their potential for supporting life. The role of interfacial interactions in the presence of water in soils at sub-zero temperatures remains largely unexplored. This interstitial/interfacial water may contribute to the formation and sustainability of subsurface ice and ground flow patterns. Interfacial water has been suggested as a potential habitat on Mars (Davila et al., 2010) and may facilitate the transport and concentration of salts to the subsurface. The determination of interstitial or bulk liquid water in soils at subzero temperatures is mostly based on modeling, empirical formulas (Anderson and Morgenstern, 1973; Anderson et al., 1973) or estimates based on salt concentrations.

The McMurdo Dry Valleys (MDV) comprise a series of valleys located between the East Antarctica Ice Sheet and Ross Sea, occupying elevations from sea level to 2 km (Fig. 1). The main lithology of these Valleys is comprised of basalt, sandstone, and granitoids, which form the major parent material for soils on the Valley floors (Bockheim, 2002; Campbell and Claridge, 1987; Ugolini and Bockheim, 2008). Soils at higher elevation valleys are virtually free of organic compounds and are rich in salts such as chloride, nitrate, and sulfate (Keys and Williams, 1981); minor compounds such as perchlorate have been discovered as well (Kounaves et al., 2010). Weathering is often indicated by red staining (rubification) due to oxidation of iron rich minerals such as olivine, pyroxene, amphibole, and biotite. Weathering stage correlates well with dithionite extractable iron (Claridge and Campbell, 1984). The majority of salts in Antarctic soils are atmospherically derived (Bao and Marchant, 2006; Campbell and Claridge, 1987; Keys and Williams, 1981) and modified by in situ weathering (Faure and Felder, 1981; Jones and Faure, 1978; Ugolini, 1986) including cation exchange (Toner and Sletten, 2013; Toner et al., 2013). Although salts are deposited on top of the surface initially, they display a compositional gradient downwards that is characterized by salt solubility that implies transport by aquatic saline solutions (brine) (Dickinson and Rosen, 2003;

Hagedorn et al., 2010). Occurrence of deliquescence at low and high elevations (Levy et al., 2012; Wilson, 1979) highlights the similarity of hydrological processes to Mars. Stable isotope profiles (δD , $\delta^{18}O$) in ground ice give evidence of infiltration of brine into frozen ground (Hagedorn et al., 2010) and thus point to the occurrence of brine transport at subzero temperatures. These transport mechanisms have also been implied for salt transport in Martian soils (Cull et al., 2010). Study by Toner and Sletten (2013) further indicate that cation exchange processes in brine films may lead to high concentrations of calcium chloride in Dry Valley soils and may lead to the development of $CaCl_2$ -saturated Don Juan Pond.

This paper advances the study of liquid water molecular dynamics and content in conjunction with elevated salt concentrations. NMR experiments are employed to determine the liquid water content at sub-freezing temperatures in soils collected from McMurdo Dry Valleys, Antarctica in 2008 and 2010. We compare NMR-determined water content to prediction based on thermodynamic chemical equilibria using the program FREZCHEM (Marion and Grant, 1994). Our results indicate a difference in liquid water content at given temperatures between both approaches, thus demonstrating that unfrozen water content is affected by multiple factors that are difficult to account for using only chemical modeling.

2. Samples and methods

2.1. Soil samples and preparation

Soil samples were collected during two expeditions lead by R. Sletten, University of Washington, to MDV in 2008 and 2010 from Beacon Valley, its side valleys Mullin and Farnell, and Mount Fleming (Fig. 1). The selection of soil samples and sites was based on the goal to sample a large variation in salt concentration and composition. Samples were dried at 50 °C (which is a typical drying temperature when

Fig. 1. Location of Beacon Valley, its side valleys and soil sample collection points.

Table 1

Summary of Chemistry and bulk freezing a (T_f) based on NMR measurements and FREZCHEM modeling. T_f from NMR measurements are corrected for differences between H₂O and D₂O freezing points. Precision of NMR freezing points is 0.5°. For samples 8-18-4 and 8-22-3 FREZCHEM-based T_f values represent their upper boundaries.

Sample	Ca	Cl	K	Mg	NO ₃	Na	SO ₄	total	Grain size	T_f (K)	
	mmol/kg								μm	NMR	FREZ
8-26-3	157	48	15	82	2251	1995	95	4643	754	257	266
8-26-6	13	50	21	18	35	60	26	223	625	265	272
8-64-1	1832	115	8	107	128	122	1882	4194	888	266	272
8-64-3	184	75	5.1	46	51	104	222	687	576	266	272
8-14-2	29	67	11	54	122	111	50	444	573	265	272
8-14-4	62	28	7.7	27	31	69	98	323	559	265	272
8-18-2	3260	301	23	191	286	335	3337	7733	208	265	267
8-18-4	13,290	689	51	463	855	973	13,490	17,850	5	264	<240
8-22-3 ^a	511	16	159	6701	3676	4850	1170	17,083	124	252	<240

^a FREZCHEM-based freezing point for sample 8-22-3 would only converge with an additional 50% water content by weight.

mineralogy of secondary products such as salts or clay minerals, are of interest) and sieved at 2 mm for analysis. Samples with variable salt concentration were selected for the experiments (Table 1) based on their ionic concentration (see below). About 0.2–0.4 g of the selected samples were hydrated to 20% by weight with D₂O enriched water. We assume that 20% (v/w) is an average amount of water equivalent present in ice-cemented soils of MDV (Bockheim, 2002). After hydration, all samples were equilibrated for at least 48 h at room temperature, followed by at least a week in a refrigerator at 4 °C (Vugmeyster et al., 2012). This procedure allows equilibration of deuterated water throughout the entire sample.

2.2. NMR spectroscopy

NMR methodology allows for rapid determination of water content on undisturbed samples. Proton NMR is a relatively common technique in determining liquid water content (Watanabe and Wake, 2009). Deuterium NMR is much less commonly used yet offers the advantage of a better precision. We have employed a modified method previously developed by Sparrman et al. (2004) and determined liquid water content for a range of samples from different locations in the McMurdo Antarctic Dry Valleys at different depth levels (see Supplementary material). The technique relies on measuring magnetization of deuterium nuclei using the quadrupolar echo experiment (Vold and Vold, 1991; Vugmeyster et al., 2012). The only signal which is observed in this experiment is the one originating from liquid water, which can be quantified from the initial intensity of the free induction decay curve. Previous studies typically used 4% D₂O; however, incorporation of 100% D₂O greatly enhances signal intensity and allows for more precise determination of liquid water content. We have confirmed that the incorporation of 100% D₂O into the soil samples does not alter the freezing points beyond the differences between the freezing point of pure H₂O (0 °C) and D₂O (3.6 °C). All of the reported NMR data on freezing curves and freezing points are shifted by a constant offset of 3.6 °C in order to show the results for non-deuterated water. Experimental details of the NMR procedure are available in the Supplementary material.

We demonstrated previously that hysteresis of water content in the cooling/heating curves using one of the representative samples (Vugmeyster et al., 2012). The hysteresis was confirmed for all of the samples probed in this study. Since the hysteresis behavior is not the focus of this work, we choose to concentrate on the cooling curves only, for which 30 min equilibration time was used between temperature points. Based on numerous temperature-dependent NMR studies, 30 min provide generous equilibration time inside the NMR tube and account for ice-formation kinetics (Beckmann and Dybowski, 2000; Sparrman et al., 2004; Vugmeyster et al., 2012; Vugmeyster et al., 2009).

2.3. Impedance measurements

As the salt-containing water freezes, an abrupt change in conductivity is expected. The Q-factor measurements (Tooley, 2002) (Jiang, 2000)

with the sample inserted into the NMR probe is a specific approach for measuring conductivity/impedance. This approach permits for precise matching of conditions to those at which NMR measurement are performed. The Q-factor (Q_s) of the system was measured using an electrical network analyzer (i.e., a device that measures parameters of electrical networks) connected to the NMR probe. The measurements were taken at desired specific temperatures right before the NMR experiments. Thus, the conditions of the samples were identical for the NMR and Q_s measurements. Reference values Q_{ref} were recorded for each temperature by using an empty tube. The reported quantity is given by $Q = 1 - Q_s/Q_{ref}$ and corrects for temperature-dependent changes in the NMR circuit that are not related to the sample. Freezing of bulk solvent in a lossy sample causes abrupt increase in the values of Q_s , making it a convenient, robust measure of bulk solvent freezing points.

2.4. Chemical analysis

About 2 mL of each sample was extracted with purified water in a 1:10 dilution and analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP MS, Agilent 7500c) and Ion Chromatography (IC, Dionex IC 500) for initial screening of salt content and composition. After the NMR measurements, ICPMS and IC samples were taken directly from the NMR tube and, based on previous measurements, were diluted to fit calibration of the instruments (ICP MS: 0.01 to 10 ppm; IC: 0.1 to 10 ppm). Samples were filtered through 0.2 μm syringe filters and acidified to 1% HNO₃ (v/v) for metal analysis following EPA 200.8 method. The international standard SRM 1640 was used for calibration verification. For anion analysis, samples were pipetted into 2 mL glass vials and analyzed with an AS15 column using KOH as eluent and a self-regenerating suppressor.

2.5. Grain size measurements

The grain size analysis was performed on ~1 g sample aliquot using a laser diffraction particle size analyzer (Beckman Coulter LS 13-320). Samples were dispersed by an ultrasonic probe in sodium hexametaphosphate/carbonate added to avoid agglomeration and to keep the sample in suspension during analysis. Between 2 and 7 measurements were performed for each sample to assure reproducibility.

2.6. FREZCHEM modeling

The FREZCHEM72 model is an equilibrium model that uses Pitzer model of ion interactions at high concentration (Marion and Grant, 1994) (Marion and Kargel, 2008) and is designed to track the amount of liquid water and salt precipitation during evaporation or freezing (Marion, 1999; Marion, 2001, 2002). The model assumes that equilibration occurs between the salts and solution. We chose the equilibration between solids and liquid assuming that salts and ice will be in constant contact with liquid water. FREZCHEM requires a perfect charge balance

and to achieve this we calculated the salt concentrations from the ICP MS and IC results assuming 20% water content in soils, and then modeled these with PHREEQC version 3 (Parkhurst and Appelo, 1999) (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/) and adjusted the concentration of SO_4^{2-} slightly to achieve the charge balance. The output concentrations from PHREEQC in units of $\text{mol} \cdot \text{kg}^{-1}$ was then used in the FREZCHEM model; all primary data are listed in the Supplementary material. Freezing was done in 5-degree increments from $+5^\circ\text{C}$ to -25°C . The 5° intervals are sufficient to trace out the temperature-dependence. Samples with very high salt concentrations did not converge at low temperatures, as indicated in Table 1.

3. Results and discussions

3.1. Experimental determination of liquid water content

The results of our analyses are summarized in Figs. 2 and 3, as well as in Table 1. The analyzed samples had different salt concentrations and compositions as documented in Table 1. Some soil samples were from the same soil pit, but collected at different depths, with higher salt concentrations in the upper soil profile and lower concentration lower in the profile (e.g. 8-26-3 top, 8-26-6 bottom). The freezing temperature T_f was defined as the temperature at which the liquid water content is half of its maximum value. The NMR data (Fig. 2) corresponding to low and medium salt content samples show clear pre and post-

transition regions. The pre/post transition regions refer to the relatively leveled regions of the sigmoidal freezing curves. For the high salt content samples shown in Fig. 3 (samples 8-18-4, 8-22-3, and 18-8-2) these regions are less defined.

To supplement NMR measurement, we conducted the impedance (conductivity) measurements on the same samples to check for correspondence between the two techniques. Abrupt conductivity changes due to freezing of bulk solvent in a salt-containing sample are relatively easy to detect and provide a good baseline control for more sophisticated techniques geared toward quantification of remaining liquid water content. As shown in the example below (Fig. 4), the freezing points determined by the two approaches are in good agreement. This is important in light of recent results by Buehler et al. that utilized impedance spectroscopy to analyze water content in simulated Martian soils (Buehler et al., 2007; Seshadri et al., 2008). We also note that similar freezing curves have been reported by Tice and coworkers for saline silt of Lanzhou, China and low-salt silts from Alaska (Tice, 1984). In their work, electrical conductivity was also used as an independent measure of soluble salt content.

3.2. Comparison with FREZCHEM modeling and grain size measurements

FREZCHEM simulations use chemical equilibrium to obtain the activity of liquid water and predict freezing points based on salt composition of the sample (Table 1). During freeze-back, FREZCHEM calculates the

Fig. 2. Comparison liquid water fractions as a function of temperature based on NMR measurements and FREZCHEM modeling. Soils are from two different depths in the same soil profile with higher salt concentration on top of soil (left column) and lower salt concentration deeper in the soil profile (right column). Total salt concentration of $\text{mM} \cdot \text{kg}^{-1}$ solution is calculated based on 20 wt% water content in soil.

Fig. 3. Comparison of fraction of liquid water as a function of temperature between NMR measurement and FREZCHEM modeling for soil samples with very high salt concentration.

precipitation of salts. Based on the different chemical compositions, different salts are precipitated for each sample and chemical composition of the remaining solution changes throughout the process. Discrepancies in measured freezing points obtained by NMR method versus modeled freezing points by FREZCHEM are shown in Fig. 5. Additionally, there are discrepancies in the shape of the freezing curves (Figs. 2 and 3). The experimentally measured NMR freezing points are lower

than those calculated with FREZCHEM for all samples with low to medium salt content. Two of the three samples with higher salt content have NMR bulk freezing points higher by 10–15° compared to those predicted by FREZCHEM (8-18-4 and 8-22-3), and only for one sample (8-18-2) the bulk freezing points are in agreement. However, the actual freezing curve for the sample 8-18-2 is still somewhat different between NMR and FREZCHEM. Discrepancies in the liquid water content at sub-freezing temperatures modeled with FREZCHEM and analyzed by NMR are not as pronounced when the fraction of liquid water is smaller than about 10%, at temperature less than -15°C . These temperatures are sustained at deeper soil horizons (e.g. Hagedorn et al., 2007), thus suggesting that modeling of freezing processes based solely on chemical equilibrium may miss certain soil properties, as well as water and solute kinetics. For example, the chemical equilibrium modeling suggests that the formation of salts such as Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), Mirabilite

Fig. 4. Comparison of freezing points determination using impedance and NMR measurements for a sample from Beacon Valley (8-26-6 sample), demonstrating agreement between bulk freezing point determined by these two techniques.

Fig. 5. Difference in T_f from NMR and FREZCHEM versus total salt concentration. T_f from NMR are corrected for differences between H_2O and D_2O freezing points.

Fig. 6. Difference in T_f from NMR and FREZCHEM (50%) versus grain size.

($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and Epsomite ($\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$) is the most common, but also that sodium and potassium nitrate and Halite hydrate $\text{NaCl} \cdot 2\text{H}_2\text{O}$ are formed. The model assumes instantaneous precipitation of these salts and re-equilibration of the solvent. However, the reaction kinetics, especially in a soil matrix with low connectivity of pore spaces, may be slower. This could lead to oversaturation that can cause higher liquid water concentration than the one modeled with FREZCHEM. This tendency seems especially true for samples with high salt concentrations. Another important soil property is the abundance and size of soil pore spaces and small pores on grain surfaces. As stated by Rempel et al. (2001), water surface curvature in small pore spaces can lower freezing points which may be a likely explanation for the deviation between NMR and FREZCHEM modeling that we observed for the samples with low salt concentration. Grain size measurements (Fig. 6) indicate moderate correlations between the grain sizes and difference in the freezing points between NMR and FREZCHEM for small grain sizes. For grain sizes larger than about 200 μm no direct correlation is seen; however NMR freezing points are always lower than the ones predicted by FREZCHEM. If pore spaces are smaller and more abundant in soils with small grain sizes, it may provide an explanation for the trend depicted in Fig. 5. Applying a more robust method to analyze pore spaces in soils and on grain surface characteristics may shed more light on the potential influence of pore space on liquid water content in frozen soils.

4. Conclusion

Our results indicate that deuterium NMR measurements provide a very precise experimental tool for determination of bulk freezing points as well as the fraction of remaining liquid water when the bulk solvent is frozen. We have observed clear deviations of the experimental freezing points from those modeled solely based on salt composition. In particular, the freezing points determined by NMR show higher liquid water content and lower freezing temperatures for salty soils versus pure solutions. Additionally, there is a lack of clear correlation of the experimental freezing points with the grain sizes. Combined analysis highlights the importance of interfacial interactions at grain/pore surfaces in sustaining liquid water. For very high salt content samples the trend is less clear and this may be due to the slower kinetics of salt precipitation. This study underlines the need of experimental measurements of liquid water content.

Acknowledgements

This research was supported by CU Denver College of Liberal Arts and Sciences award. NMR and impedance experiments were performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490, the State of Florida and the U.S. Department of Energy. We thanks Dr. Riqiang Fu and Dr. Peter Gor'kov for technical assistance.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.geoderma.2017.03.024>.

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