Characterization of water dynamics in frozen soils by solid-state deuteron NMR

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ABSTRACT

The presence of unfrozen water in soils at sub-freezing temperatures is important for biogeochemical processes as well as for the genesis of landscapes and survival of life. While several mechanisms can lead to the existence of liquid water at sub-freezing temperatures, this work focuses on the dynamical (entropic) contribution stemming from motions of water molecules at water–soil or water–ice interfaces. We demonstrate the utility of solid-state ^{2}H NMR methods for characterization of water dynamics in soils on various time scales. Using a sample from McMurdo Dry Valleys, Antarctica, we show the existence of dynamics spanning a milliseconds to picoseconds time scale range. Computational modeling allows for a quantitative description of the dynamics, which involves models such as an exchange between bound and free water, and changes in effective viscosity of water in the soil matrix.

1. Introduction

Subsurface water plays an important role in the genesis of landscapes and survival and formation of life. The presence of unfrozen water in soils at sub-freezing temperatures is paramount for biogeochemical processes occurring in soils at northern latitudes. Mechanistic studies geared toward understanding of microbiological, geochemical, and landscape forming processes related to the abundance of liquid water need tools for quantification of water content and identification of the main factors responsible for the existence of liquid water at subzero temperatures. Sparrman et al. [1] have proposed a ^{2}H high-field Nuclear Magnetic Resonance (NMR) technique which allows for precise quantification of water content. This technique, based on the quadrupole echo pulse sequence [2], has led to several interesting investigations of water content at sub-freezing temperatures [3,4]. In order to predict and model the existence of phases in a multi-component system, in principle, one has to characterize several contributions to the Gibbs free energy. Several mechanisms can lead to the existence of liquid water at sub-freezing temperatures, such as melting point depression due to the presence of various solutes and the influence of interfaces on equilibrium (Gibbs–Thomson effect) [5–7]. The latter can have a dynamical (entropic) component stemming from motions of water molecules at water–soil or water–ice interfaces.

The goal of this work is to present an experimental strategy which enables focus on the dynamical component contributing to water survival in soils at subfreezing temperatures. The importance of the dynamical component is demonstrated on a soil sample from McMurdo Dry Valleys, Antarctica, which have an extremely cold and arid climate and serve as analogs of the Martian environment [8,9]. Chemical analyses of these soils point to the existence of unfrozen water in soil samples down to a depth of 1.6 m [10], when modeling freezing based on a chemical equilibrium model [10,11].

We will show that the application of ^{2}H NMR techniques using a spectrometer equipped with a solids probe allows not only for direct measurements of water content, but also for the observation and quantification of water dynamics on various time scales, spanning a range from milliseconds to picoseconds. We employ well-known experiments such as deuteron quadrupole echo line shape and longitudinal relaxation measurements, which are very sensitive to the details of molecular motions [2]. We compare the results for salt-rich samples with various hydration levels as well as for a salt-free sample.

2. Experimental section

2.1. Soil sample preparation

For this study, we have used a soil sample taken from Beacon Valley located in the McMurdo Dry Valleys region of Antarctica.

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The sample was taken at the 10 cm depth level. Its composition, while free of organic matter, is rich in various inorganic salts with a total concentration of 2 mg of salts per g of soil. Supporting Information presents detailed chemical data as well as surface areas measured by Brunauer Emmett Teller (BET) measurements.

The hydration level of the main sample used in this study was 20% by weight, which is a typical amount of water present in ice-cemented soils of Antarctic Dry Valleys soils [12]. Dry soil was sieved below 2 mm and then hydrated by pipetting the appropriate amount of solvent of 18 MΩ water enriched with 4% D_2O into the dry sample.

For hydration studies, additional samples with 30, 40, and 60 wt% hydration levels were prepared. A salt-free sample of the same soil type was prepared by a succession of 1:10 water extraction using 18 MΩ water. Extracts are checked for salt concentrations using an electrical conductivity probe. Extraction was terminated when the electrical conductivity fell below 5 μS cm^{-1}, a value typical for purified water. After hydration, all samples were equilibrated for at least 24 h at room temperature. A control sample at 20 wt% hydration level equilibrated in a refrigerator for 7 days, followed by 28 days in a −80 °C freezer.

2.2. Chemical analysis

Initial salt concentrations and composition of the soil sample was analyzed on water extracts using Inductively Coupled Plasma Mass Spectrometry (ICP MS, Agilent 7500c) and Ion Chromatograph (IC, Dionex 1000).

3. H NMR spectroscopy

Quadrupole echo and longitudinal relaxation time measurements were performed on a 9.4 T spectrometer equipped with a static deuterium-tunable probe suitable for solid samples. The quadrupolar echo pulse sequence was based on an eight-step phase cycle [2]. 90 degree pulses of 2.7 μs and an echo delay time of 30 μs were employed. For longitudinal relaxation time measurements, an inversion recovery pulse sequence with a quadrupole echo acquisition scheme and 6 to 8 relaxation delays was employed. The inter-scan delays were at least 3 times the relaxation time for the quadrupole echo experiments and at least 5 times the relaxation time for the inversion recovery experiments. The number of scans was set to 1024 for the quadrupole echo experiments and 256 for the relaxation measurements, except for −8 °C, in which the number of scans was increased fifteen-fold.

Temperature calibration was performed using lead nitrate as a standard and a freezing point of water (enriched with 4% D_2O) as a fixed point [13]. To get to a set point, a manual ramp of 2° per 4–5 min was used. The cooling curve was collected first, followed by the heating curve. The temperature range spanned from +8 °C to −8 °C. The cooling-heating cycle was performed with 30 min equilibration times between all points. Another cycle, with equilibration time of 75 min between all points for the heating part of the cycle, was performed to check the stability of the hysteresis.

3.1. Data analysis

Signal intensity used in the quantification of the amount of unfrozen water was taken from the first point of the free induction decay and corrected for the Boltzmann factor of the magnetization temperature-dependence, as well as the Q-factor of the probe. The errors were calculated from the noise levels of the free-induction decays.

All free induction decays for line shape analysis were processed with 1 kHz exponential broadening for signal-to-noise enhancement and zero-filled once. The free induction decays for the determination of the relaxation times were processed with 500 Hz line broadening and zero filled once. T_{1Z} relaxation times were obtained by fitting the signal intensities taken at 0 kHz frequency to the inversion recovery function.

3.2. Computational modeling

Theoretical discussions and computational approaches for computing deuteron line shapes have been presented elsewhere [2,14,15]. In this work we utilize EXPRESS program [16], which is ideally suited for computation of the deuteron line shapes and relaxation times for a great variety of motional models. EXPRESS can simulate a line shape based on a selected model of motion and the values of its parameters. Motional model is specified by setting appropriate geometries, given by the Euler angles, for sites describing the motions of deuteron nuclei. Any chemical or conformational exchange between the sites is specified by a matrix of rate constants connecting different sites. Additional parameters include populations of each site and the description of the quadrupole coupling tensors at each site.

Line shape simulations were performed by assuming a quadrupole coupling constant of 210 kHz in the bound state and 0 kHz in the free state of water [17]. A quadrupole constant of 0 kHz corresponds to averaging of the quadrupole interaction due to rapid overall isotropic tumbling. A two-site exchange matrix was set up with variable parameters given by the population of the bound state and the rate constant for the chemical exchange between the two states. Resulting modeled spectra were obtained using the same processing parameters as the experimental ones. χ^2 minimization of the modeled spectra against the experimental data in the range of frequencies between ± 100 kHz was used to obtain the populations and rate constants for the exchange process. Errors in fitted parameters were obtained by Monte Carlo simulations and represent one standard deviation.

The effective viscosity change in the soil samples compared to free water was calculated by taking the weighted average of the relaxation rates in the bound and free states. In the bound state, the relaxation rate was assumed to be zero. The free state was modeled by an isotropic molecular tumbling mechanism [18] with the effective rotational correlation time reflecting the properties of the soil matrix. We have assumed the fast motional limit in which the relaxation rate is directly proportional to the rotational correlation time. This limit holds when the product of the rotational correlation time and the Larmor frequency is much smaller than unity [18], which is a good assumption for the whole range of the correlation times in this work. The population of the bound state p_{bound} was taken from the line shape measurements. Under these assumptions, the ratio of viscosities of water in the soil sample η_{soil} and water in the absence of soil $\eta_{pure\ water}$ is given by

$$\frac{\eta_{soil}}{\eta_{pure\ water}} = \frac{R_{1Z}^{soil}}{(1-p_{bound})R_{1Z}^{pure\ water}}, \tag{1}$$

in which $R_{1Z}^{soil} = 1/T_{1Z}^{soil}$ is the deuteron relaxation rate measured for water in the soil sample and $R_{1Z}^{pure\ water}$ is the rate measured for pure water.

Similarly, the effective viscosity change in the soil sample at a sub-freezing temperature (denoted by indices "frozen") at which there is an existence of ice interfaces is related to the viscosity at non-freezing temperatures (denoted by indices "non-frozen") by

$$\frac{\eta_{soil}^{frozen}}{\eta_{soil}^{non-frozen}} = \frac{(1-p_{bound}^{non-frozen})R_{1Z}^{soil,\ frozen}}{(1-p_{bound}^{frozen})R_{1Z}^{soil,\ non-frozen}} \tag{2}$$