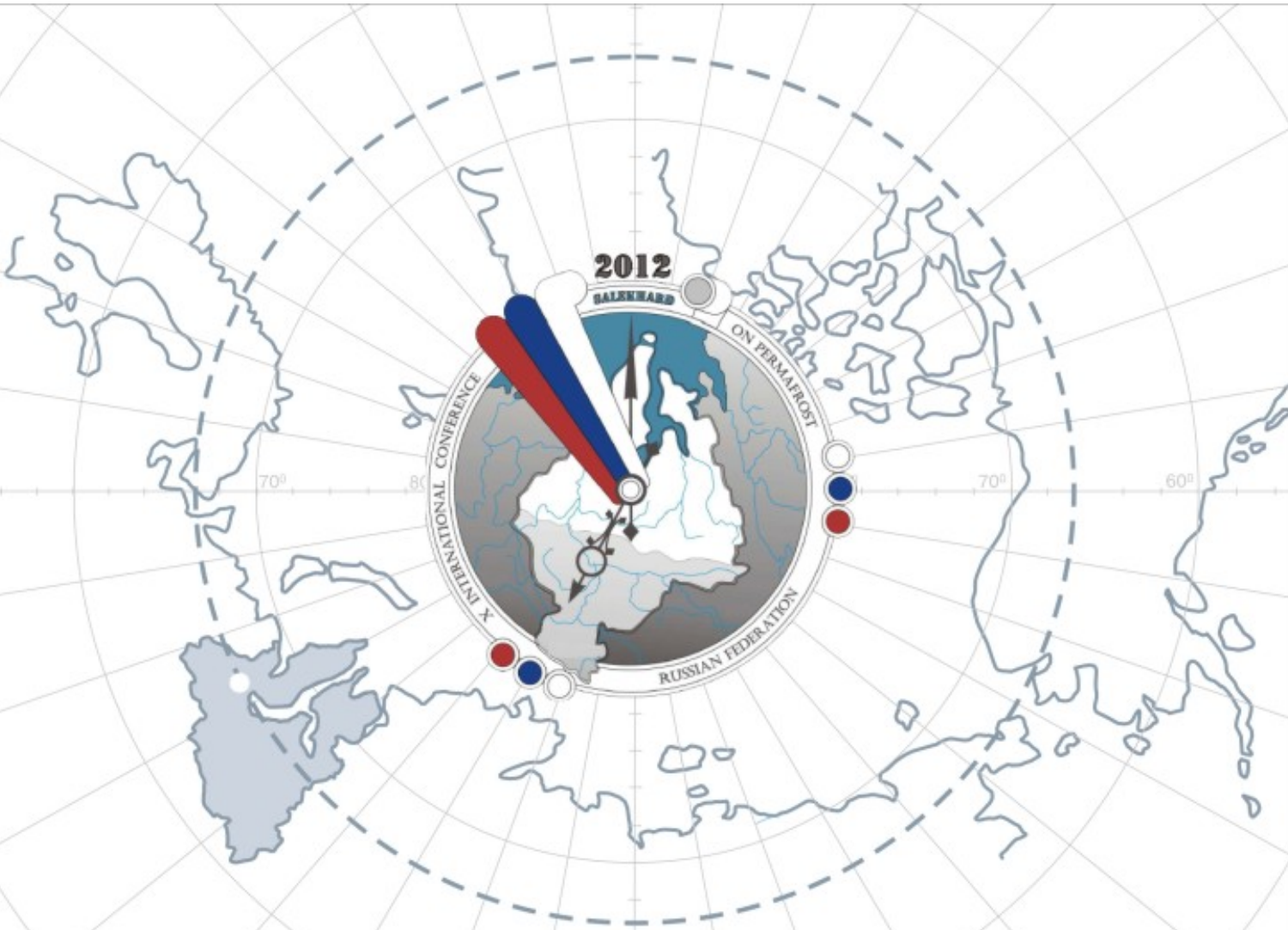


# Proceedings of the Tenth International Conference on Permafrost

Salekhard, Yamal-Nenets Autonomous District, Russia
June 25–29, 2012

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# Improvement of Pulse-NMR Technology for Determining the Unfrozen Water Content in Frozen Soils

Satoshi Akagawa
*Cryosphere Engineering Laboratory, Hachioji, Tokyo, Japan*

Go Iwahana
*University of Alaska Fairbanks, USA*

Kunio Watanabe
*Mie University, Mie, Japan*

Evgeny M. Chuvilin
*Moscow State University, Moscow, Russia*

Vladimir A. Istomin
*GAZPROM VNIIGAZ LLC, Moscow, Russia*

## Abstract

Several methods are used to observe unfrozen water content in frozen soil. These include pulse-NMR (P-NMR), time domain reflectometry (TDR), differential scanning calorimetry (DSC), and the contact method. However, a preliminary study by the authors reveals that test results depend on the method. This disagreement may be caused by improper treatment of data in P-NMR analysis. In this paper, free induction decay (FID) followed by a 90° pulse of P-NMR has been reexamined with four different soils in order to confirm the validity of the analytical method. In the discussion, two different methods used to determine the appropriate time for choosing signal intensity of each specific FID, are discussed. After the appropriate method to determine the rational time for the signal intensity of FID is clarified, the effect of cooling and warming runs (hysteresis) is discussed.

**Keywords:** unfrozen water content; P-NMR; 90° pulse; FID, hysteresis.

## Introduction

The behavior of water molecules in the liquid phase in frozen soil has drawn attention for a long time. In this paper, the liquid phase $H_2O$ in frozen soil is defined as "unfrozen water." Several methods are used to measure the quantity of unfrozen water, such as pulse nuclear magnetic resonance (P-NMR) (Tice et al. 1978, Tice et al. 1981), time domain reflectometry (TDR) (Smith & Tice 1988, Hivon & Sego 1990), differential scanning calorimetry (DSC) (Smith & Tice 1988, Hivon & Sego 1990, Kozlowski 2002), and the contact method (Ershov et al. 1979, Chuvilin et al. 2008). However, results produced from these various methods are rarely identical. In order to improve consistency among these methods, the authors re-examined the data analysis procedure for the P-NMR method as an initial step. We give special attention to the free induction decay (FID) signal after a 90° pulse; in the P-NMR method, the FID signal intensity is directly proportional to water content.

## P-NMR Method

*Conventional P-NMR method*

Since the main objective of this paper is the technological improvement of the P-NMR method, the theory of P-NMR (e.g., Hornek http://www.cis.rit.edu/htbooks/nmr/) is not discussed. The conventional data analysis procedure is summarized in Figure 1. The P-NMR method utilizes free induction decay (FID) followed by a 90° pulse (Fig. 1A). During and after the 90° pulse, the receiver that monitors FID

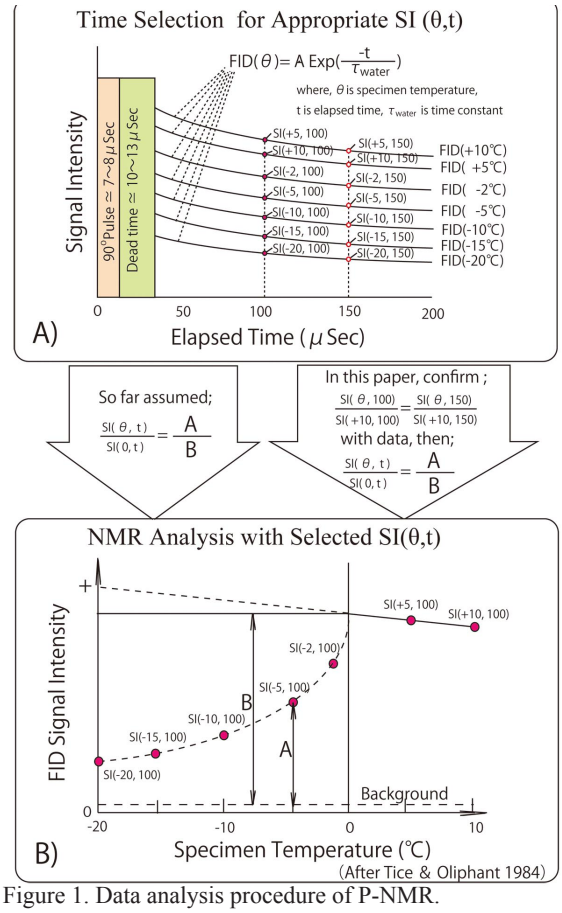



Figure 1. Data analysis procedure of P-NMR.

is turned off for a certain period to protect the receiver from the strong pulse.

This period is called "dead time" and masks the early portion of FID. Generally speaking, the length of the dead time is chosen to mask the FID of the solid phase.

According to the pioneering work by Tice and Oliphant (1984), the basis of P-NMR is that the FID signal intensity is directly proportional to the amount of unfrozen water in the frozen soil sample. This means that we can calculate the unfrozen water content of the soil shown in Figure 1B if we compare the signal intensity at a positive temperature to the water content of the soil. In other words:

$$SI\ (0,t) : w\ (0) = SI\ (\theta : t) : w_n(\theta) \quad (1)$$

where SI (0,t) is the signal intensity at 0°C and time t, w(0) is water content of the soil, SI($\theta$,t) is the signal intensity at the negative temperature $\theta$°C, and $w_n(\theta)$ is the unfrozen water content by weight (i.e., weight of unfrozen water / weight of soil particles, in percent) at the negative temperature $\theta$°C. Based on the principle demonstrated by Tice and Oliphant (1984), equation 1 is valid.

*A question on the conventional P-NMR method*

The validity of equation 1 requires the following FID relationship, as depicted in Figure 1A:

$$R(\theta,t) = \frac{SI(\theta,t)}{SI(0,t)} \quad (2)$$

$$R(\theta,t) = Const(\theta). \quad (3)$$

where $R(\theta,t)$ is a ratio at the temperature $\theta$ and the time t. The relationships shown in equations 2 and 3 suggest that the FID curves shown in Figure 1A should be converted into horizontally parallel lines. This conversion is necessary in order to apply equation 1. We examined the FIDs of four different soils using this procedure.

*P-NMR system used*

The P-NMR system we used (see Fig. 2) consists of a P-NMR machine (MARAN Ultra) and a temperature bath housed within a walk-in type cold room held at a temperature of +1°C. The operating frequency of the P-NMR is 23MHz. The 90° pulse length is 7.6 $\mu$Sec followed by a dead time of 10 $\mu$Sec. For one FID measurement, 90° pulses are applied 10 times so as to improve the signal-to-noise ratio.

The temperature of the samples is controlled within the temperature bath. The temperature control function of the P-NMR probe is not used so as to avoid shifts in resonant frequency due to changing temperature. Instead, for a reading, the temperature controlled soil samples are moved into the P-NMR probe, in which the temperature is maintained at about +1°C by the temperature of the cold room.

Since the time required for a P-NMR measurement is less than 30 seconds, the effect of sample temperature on the probe temperature is negligible and vice versa.

Figure 2. P-NMR System (MARAN Ultra with temperature bath).

*Soil samples tested*

The properties of the FID signal acquired from a soil and water mixture is not completely understood. In order to generalize the result of this study, we selected four different soils. MZ Kaolin is a typical clay sample, predominantly consisting of the clay mineral Kaolinite. NSF Clay is unique clay with Pyrophyllite as the predominant mineral. We examined a volcanic ash that contains no clay minerals but instead consists primarily of quartz and plagioclase. Finally, we tested the soft mudstone called Dotan in Japan. This soil is caked Diluvium silt and the predominant clay minerals are illite and chlorite.

Some physical properties of these soils are listed in Table 1. All of the specimens were saturated with water and then consolidated with an oedometer. The water content and wet density reported in Table 1 were measured after the specimens were consolidated.

## Measurement

*Soil sample freezing*

The focus of this experiment is the measurement method of unfrozen water content. If ice lenses form in the specimen while it is freezing, the unfrozen water content may decrease. In order to inhibit ice lens formation, samples were frozen rapidly with liquid nitrogen. Then frozen samples were placed into the bottom of the sample holder, which was made of a non-magnetic material such as Teflon.

*Test temperatures and measurement*

The sample holders were inserted into the temperature bath, set at -20°C, and brought to thermal equilibrium. For the first measurement following thermal equilibration, the sample holders were sequentially removed from the bath, wiped dry, measured in the P-NMR analyzer, and then reinserted into the bath. After all samples were measured, the bath temperature was adjusted to the next measurement temperature. In our

Table 1. Soil physical properties.

| | MZ Kaolin | NSF Clay | Volcanic Ash | Soft Mudstone |
|---|---|---|---|---|
| Soil particle density(g/cm³) | 2.64 | 2.75 | 2.65 | 2.60 |
| Dry density (g/cm³) | 1.02 | 1.08 | 1.48 | 1,26 |
| Wet density(g/cm³) | 1.63 | 1.65 | 1.78 | 1.76 |
| Water content (%) | 60.1 | 53.2 | 20.3 | 39.2 |
| Liquid limit(%) | 70.2 | 55.0 | 28.6 | 62.3 |
| Plastic limit (%) | 35.3 | 29.0 | 17.7 | 41.9 |
| Plasticity index (-) | 34.9 | 26.0 | 10.9 | 20.4 |

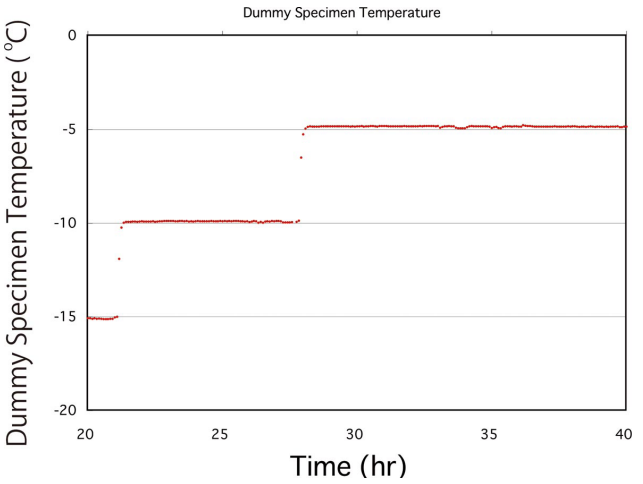



Figure 3. Temperature response in the dummy specimen.

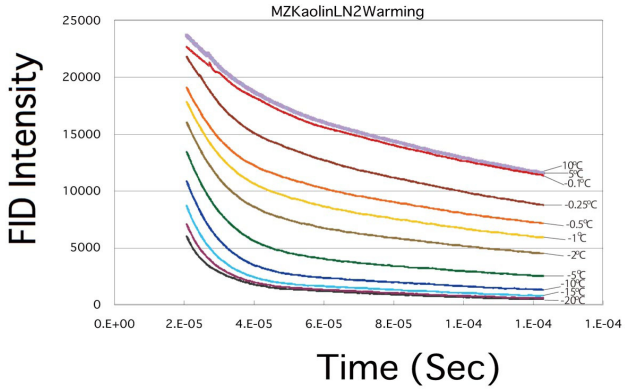



Figure 4. Typical FID curves after 90° pulse.

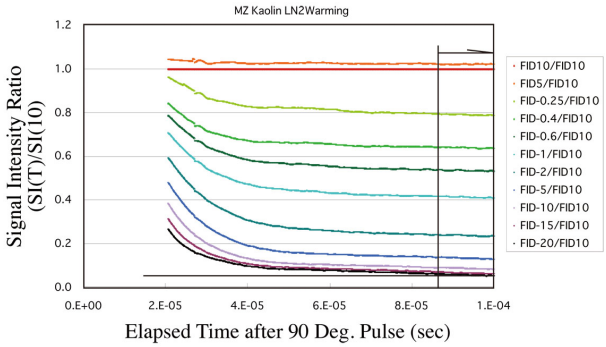



Figure 5. Normalized FID curves with SI(10).

case, the suite of measurement temperatures were -20, -15, -10, -5, -2, -1, -0.5, -0.2, -0.1 -0.2, -0.5, -1, -2, -5, -15, -20, +5, and +10°C. The time between measurements at two different temperatures was set for at least three hours to ensure thermal equilibrium. The monitored temperature in a dummy sample is shown in Figure 3. Thermal equilibrium is reached well within the three-hour period. Using this suite of temperature measurements, we also investigated hysteresis between cooling and warming runs.

*Analysis method*

1) Misgivings with the analysis

The main assumption of the P-NMR method is that the FID signal intensity is directly proportional to the water content (or unfrozen water content of a frozen soil sample) as shown in equation 1. Another assumption is that the signal from the water phase in a soil sample follows the exponential curve. The FID curves acquired from MZ Kaolin (shown in Fig. 4), however, appear to demonstrate characteristics that differ from these assumptions.

The important point is that the signal intensity ratio between any two FID curves at any time should be constant, as indicated by equation 2 and equation 3. In the following, two different methods will be demonstrated and verified with FID data.

2) Method A

Equation 2 and equation 3 are the necessary conditions to satisfy equation 1. Thus the rationale behind the use of equation 2 and equation 3 should be first verified.

As is shown in equation 2, $R(\theta,t)$ is calculated using FID data. In other words, all the FID curves were compared with the FID acquired at the sample temperature of +10°C by taking the fraction of each FID over the FID of +10°C. The results are shown in Figure 5.

If all the lines in Figure 5 are horizontally parallel, as is restricted by equation 3, the assumption is applicable at any specific time during the acquisition of the FIDs. However, the horizontally parallel section becomes shorter as the sample temperature becomes lower. The time for which the assumption is true is later than 80 $\mu Sec$ in this case, as indicated by the vertical line in Figure 5.

By completing this procedure, one can determine the time range that will satisfy the assumption. Therefore, by selecting the suitable time after the 90° pulse for unfrozen water content analysis, equation 1 is applicable as the conventional data analysis procedure.

3) Method B

Generally speaking, water and ice in soil have longer FIDs (Quinn et al. 1991), with the FID of water longer than that of ice. From this it follows that the dead time after the 90° pulse in the conventional method is not long enough to mask the FID from the ice. Assuming that the disorder that is seen in the early part of the FID curves in Figure 5 is due to the overlapping of FIDs of unfrozen water and ice:

$$FID(measured) = FID(water) + FID(ice) \quad (4)$$

$$FID(water) = A \bullet Exp\left(\frac{-t}{T_{water}}\right) \quad (5)$$

$$FID(ice) = B \bullet Exp\left(\frac{-t^2}{T_{ice}}\right) \quad (6)$$

where, A, B, $T_{water,}$ and $T_{ice}$ are constants. The measured FID was discriminated into FID(water) and FID(ice) with the SOLVER function in Excel.

The typical result is shown in Figure 6. As is seen in the figure, FID(water) and FID(ice) are well discriminated using SOLVER. The FID(water)s of MZ Kaolin are shown in Figure 7. If these straight lines satisfy equation 2 and equation 3, then equation 1 is applicable.

$T_{water}$ is the time constant of the decay function of equation 5, and the values of $T_{water}$ of the each FID(water) acquired from FIDs at different temperatures are shown in Figure 8. The shape of the FID curves of each soil sample indicates that the $T_{water}$ of the four soils tested has temperature dependence.

Mathematically, a condition required by equation 3 is that $T_{water}$ is constant over the specimen temperature range. Therefore, it will be difficult to determine the appropriate time t which fulfills the requirement. However, Method B is applicable for the soils in cases where the temperature dependence of $T_{water}$ is negligible.

*4) Comparison of Method A and Method B*

Method A and Method B were applied to the soils summarized in Table 1, and the results are shown in Figures 9-1 to 9-4.

For Method A, 100 $\mu$Sec was selected as the time t required to fulfill equation 3. For Method B, $T_{water}$ in equation 5 of different FIDs were assumed to be equal. With this assumption, the requirement is fulfilled at any time t. So t=0 was chosen for equation 5, resulting in SI( $\theta$,0)=A.

As shown in Figure 9, Method A and Method B provide the same trends in unfrozen water content versus temperature (i.e., unfrozen water content decreases with temperature). However, the difference between the two methods increases as temperature decreases. The differences between Method A and Method B in the low temperature range, such as below -1°C, in the four soil samples are considerably large.

According to the data shown in Figure 5, Method A fulfills the requirement to choose the appropriate time t for FID signal intensity analysis. The data shown in Figure 9 indicates that Method B consistently provides higher unfrozen water content per soil sample. Therefore, the authors recommend Method A for finding the appropriate time t for the unfrozen water content analysis using FID signal intensity data.

*Hysteresis*

Unfrozen water content curves of warming and cooling temperature runs are shown in Figure 9. Hysteresis is clearly visible in each of these figures. All of the cooling curves demonstrate higher unfrozen water content than warming curves. It is noteworthy that the predominant temperature range of the hysteresis depends on soil type. Therefore, it is important to indicate which process (either the cooling or warming process) is used when discussing unfrozen water content curves.

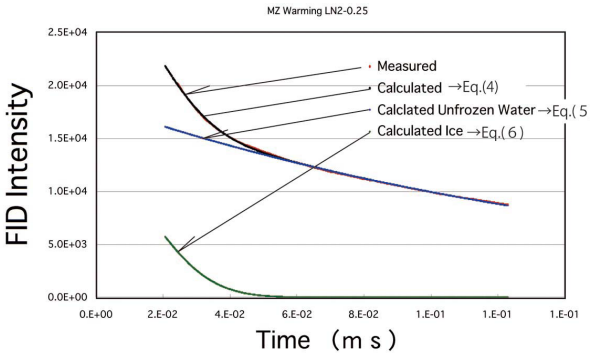



Figure 6. Discriminated FID(water) and FID(ice).

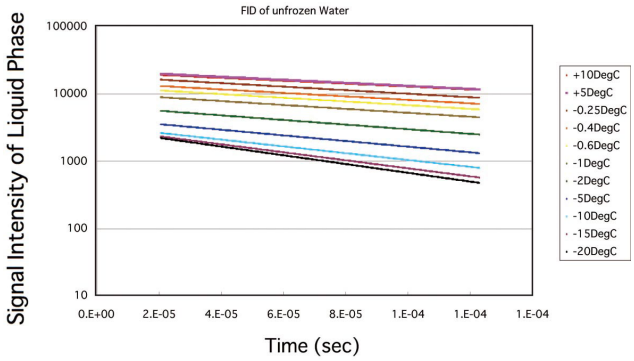



Figure 7. Typical FID(water)s at different temperatures.

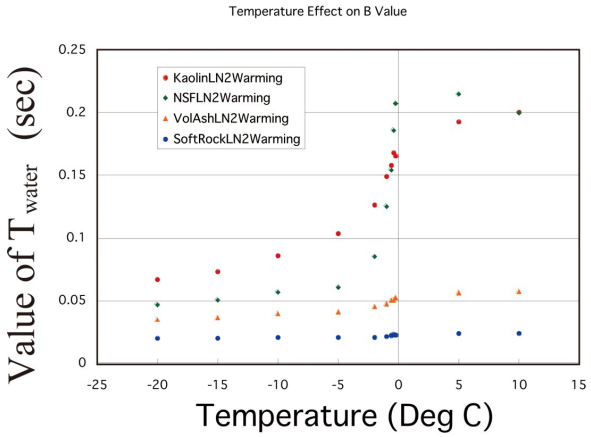
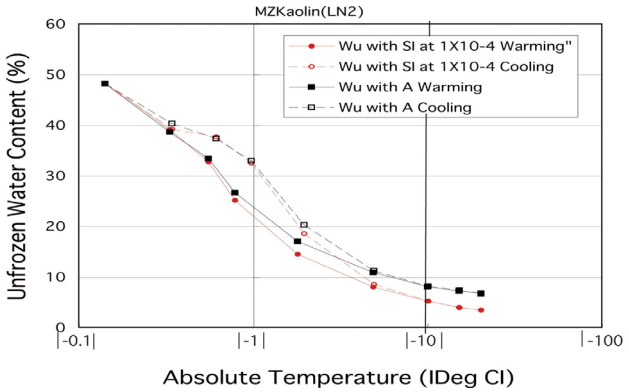


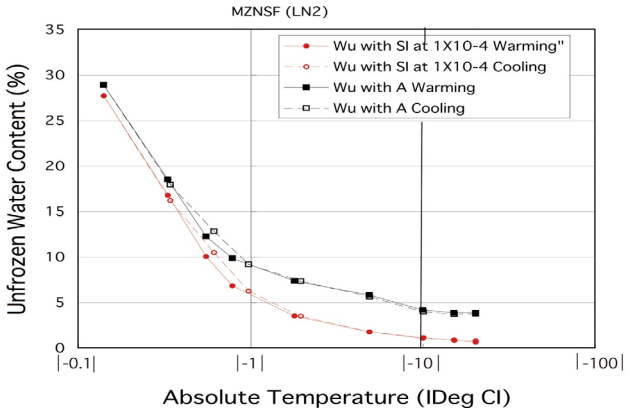

Figure 8. Temperature dependence of $T_{water}$ .

## Conclusions

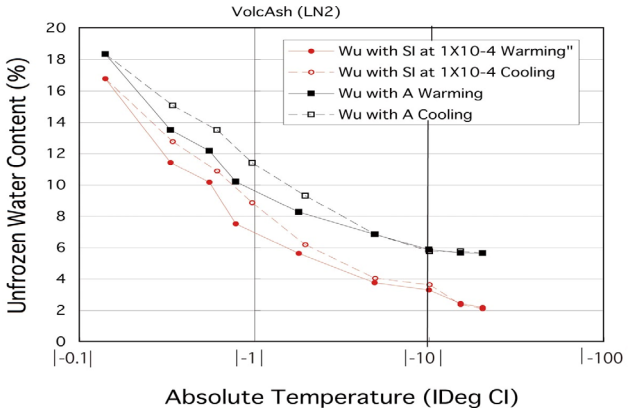
1) None of the FID curves that were acquired from the four different soils follow a simple exponential curve.
2) The early part of the FID curves especially demonstrate the tendency mentioned in conclusion 1.
3) Therefore, it is important to choose the appropriate time "t" for the analysis of unfrozen water content.
4) Method A is a simple and effective technique.



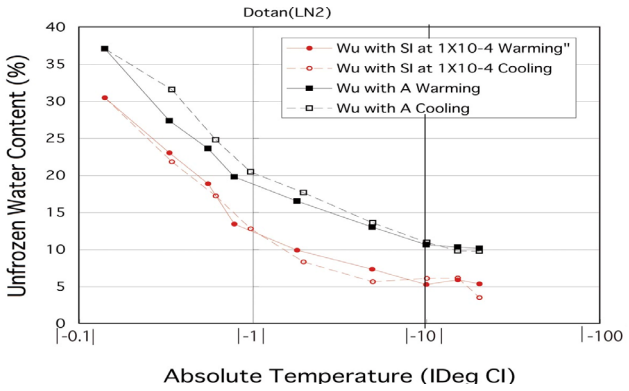

1) Comparison of Method A and Method B with MZ Kaolin frozen by LN2




2) Comparison of Method A and Method B with NSF Clay frozen by LN2




3) Comparison of Method A and Method B with volcanic ash frozen by LN2




4) Comparison of Method A and Method B with Dotan frozen by LN2

Figure 9. Comparison of Method A and Method B for different soils (data also show hysteresis).

5) Method B may discriminate between the FIDs from ice and water, assuming equation 5 and equation 6 are applicable.
6) Since the time constant, $T_{water}$, of four soils demonstrates temperature dependency, equation 2 and equation 3 may not be satisfied.
7) Therefore, Method B may not be the universal technique for the unfrozen water analysis.
8) The predominant temperature range of hysteresis depends on soil type. The description of cooling or warming processes is important when discussing unfrozen water curves.
9) An appropriate data analysis procedure for the P-NMR method is demonstrated in this paper. The consistency of the P-NMR method with other methods such as TDR, DSC, the contact method, and so forth can now be studied further.

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