

● *Contributed Paper*

FREEZING D₂O CLAY GELS

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To obtain the T_1 surface value in smectites/D₂O diluted suspensions or gels, as was obtained on a monolayer deuterated clay, we freeze them. The broad Pake's doublets similar to ice doublets and with the same T_1 show that we can separate frozen from unfrozen D₂O. The latter exhibits a narrower line and a single T_1 and is attributed to the liquid surface water layer in rapid exchange with the nearby supercooled water, the quantity of which diminishes with the lowering of the temperature depending on the gel porosity. It is possible to measure the supercooled water quantity and to correct the T_1 measured values to extract the T_1 surface. The value extrapolated at room temperature allows the complete clay surface area measurement. The example of a montmorillonite is given and a comparison with laponite is made. © 1998 Elsevier Science Inc.

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INTRODUCTION

In a previous study, Fripiat¹ had shown how T_1 measurements could be used to determine the area S of the wetted surface in clay/water suspensions or gels. The calculation is based on the fact that, when a rapid exchange (as compared to T_1 values) exists between the water (hydrogen or deuterium) populations of the bulk a , and of the surface bound layer b , a single T_1 is observed and $R1 = T_1^{-1}$ is the average of the relaxation rates of both populations, weighted by the molar fractions:

$$R1 = (a/a + b)R1a + (b/a + b)R1b = \chi a R1a + \chi b R1b. \quad (1)$$

Eq. (1) is also valid for $R2 = T_2^{-1}$.

Adsorbed Volume and Surface Area Measurements

Thus, measuring $R1$ vs. clay concentration ($C = \text{solid mass/water mass}$), fits a straight line:

$$R1 = R1a + \chi b R1b = R1a + (\rho z SC) R1b \quad (2)$$

because we use diluted suspensions, with volume $a \cong a + b = 1$.

Eq. (2) gives access to the adsorbed volume b . From S values measured by a microcalorimetric method (Harkins and Jura²) for (te, oc), kaolinite, and (te, oc, te), hectorite and laponite, clays, it had been shown that the adsorbed water layer thickness z was about 1 nm; this layer can freeze only at very low temperature. ρ is the volumic mass of the (heavy) water.

Now knowing $z = 1$ nm, allows S determination from T_1 (or T_2) measurements. ¹H or ²H relaxation may be used; although less sensitive, ²H relaxation of clay/D₂O is preferable, since it is not much affected by paramagnetic impurities such as iron. The useful room temperature equations are given.³ For ²H, one obtains

$$R1 = 2.2 + (40.3 + F')b = 2.2 + K'C. \quad (3)$$

F' may be calculated from the iron content and repartition on or near the solid surface. It is the paramagnetic dipolar relaxation term. Generally, $F' < 40.3$. The value $T_1 b = 24.8$ ms was measured on a monolayer deuterated sample of halloysite at room temperature,⁴ and was also calculated from the minimum of the T_1 vs. $1/T$ curve (Fig. 1), using the classical quadrupolar three-dimensional equations.⁵

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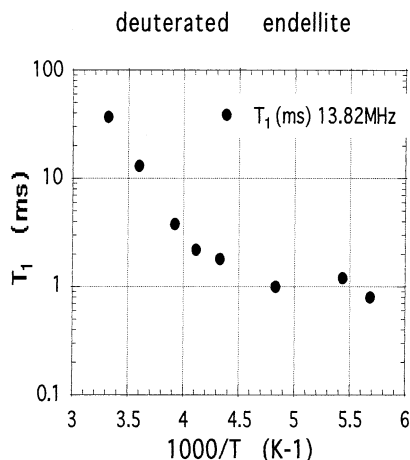


Fig. 1. T_1 vs. $1000/T$ for a monolayer hydrate of halloysite (endellite).

An Application: Cement Setting

An application of this wetted solid surface S , or adsorbed water volume, $b = Sz$, measurement is that of cement setting, which offers chemical reactions slow enough (in hours) to give the time necessary to a T_1 measure.⁶ As an example, the action of a superplasticizer on the setting is obvious. The proton $R1$ and $R2$ vs. time curves are delayed by 2 h when adding 1% Sikafluid in the water of a synthetic white cement.⁷

Another example is that of synthetic tricalcium silicate C3S (150 ppm iron) hydration. With curing time, the development of the hydrates (tobermorite CSH) surfaces, S , may be measured *in situ*, and at a given time the sample may be destroyed, ground, and mixed into heavy water to re-obtain S , assuming $z = 1$ nm. The T_1b value was here directly measured (25 ms).³

T_1 of the Adsorbed Layer

As we can see, the main parameter is $R1b$, and one would like to be able to directly measure it on the sample itself without preparation that could disturb the structure, and if possible study it to gain information on the surface. In a recent paper, Korb⁸ used selectively deuterated pyridine adsorbed on calibrated nanoporous silica glasses and, with the simple biphasic fast exchange model, could obtain access to the dynamic parameters of the confined layer. In the case of clay gels, however, we do not know the porosity distribution. A method of separating the surface contribution from the bulk is to freeze the suspension.

MATERIALS AND METHODS

Materials

The swelling clays used belong to the smectites family. They were purified and saturated with sodium.

The morphology of the sheets association may be obtained by micrography after having exchanged the water of the suspensions by a resin.⁹

Hectorite (Hector, CA, USA; 250 ppm iron) shows a morphology in souple 100×1000 -nm laths associated in tactoids of a few sheets. The unit formula, written to show the (te, oc, te) sheet structure and the bound water is: $(\text{Si}_2\text{O}_5)(\text{Mg}_{2.7}\text{Li}_{0.33})(\text{OH})_2(\text{Si}_2\text{O}_5)$, $(\text{Na}_{0.33}, n\text{H}_2\text{O})$.

Laponite (Laporte Industries, Widnes, Cheshire, UK; 1060 ppm iron) is a synthetic hectorite; it shows small particles with a diameter of about 30 nm: $(\text{Si}_2\text{O}_5)(\text{Mg}_{2.67}\text{Li}_{0.33})(\text{OH}_{0.75}\text{F}_{1.25})(\text{Si}_2\text{O}_5)$, $(\text{Na}_{0.33}, n\text{H}_2\text{O})$.

Montmorillonite from Wyoming (3690 ppm iron) shows large souple sheets associations of about 1000×1000 nm: $(\text{Si}_8)(\text{Al}_{4-y}\text{Mg}_y)\text{O}_{20}(\text{OH})_4, \text{Na}_y^+$.

The preparation consisted of drying the purified clay (150°C , 12 h), mixing it with D_2O , and shaking it vigorously for 2 min, then softly overnight.

In this study, montmorillonite was specially chosen for its ability to swell greatly in presence of water and for its very large sheets, allowing the detection of a possible two-dimensional relaxation effect. Gaboriau¹⁰ measured $39 \text{ m}^2/\text{g}$ with ^2N -BET, with little microporosity and no mesoporosity, but we expect a much higher surface when diluted into water.

Methods

Some measurements were performed at $\omega/2\pi = 13.8$ MHz (2.17 T) in a resistive magnet with a SXP Bruker spectrometer (Sadis Brucker Spectrospin, Wissembourg, France), but most were taken at 55.25 MHz in a broad band (1.2 MHz) probehead in an Oxford Instruments superconducting magnet (Oxford Instruments, Oxford, UK) with a MSL and DSX Bruker spectrometer. The $\pi/2$ pulse is $6.6 \mu\text{s}$, short enough to measure T_1 by inversion-recovery for lines under 50 kHz. The magnet homogeneity does not allow measuring lines under 20 Hz.

For the large ice doublets, T_1 was only estimated by saturation, and the line shape was obtained after a $\pi/4$ pulse ($4.5\text{-}\mu\text{s}$ dead time) or by an echo ($2\text{-}\mu\text{s}$ pulse and $10\text{-}\mu\text{s}$ refocusing time). The frozen bulk and liquid heavy water populations are estimated by integrating the whole spectrum (without deconvolution) and comparing the central area to the total area. The temperature was lowered to 200 K, then the spectra were recorded with increasing temperature.

Freezing D_2O . Pure D_2O freezes at $T_0 = 277.5$ K. For $T > T_0$, one observes a narrow, lorentzian line with a theoretical width $\Delta fa = 1/\pi T_2 a = 1/\pi T_1 a = 2.2/\pi = 0.7$ Hz. The curve $R1a$ vs. $1/T$ fits a straight line and shows that the classical quadrupolar relaxation law is obeyed,⁵ with the rotational correlation time $\tau \ll 1/\omega$. For $T <$

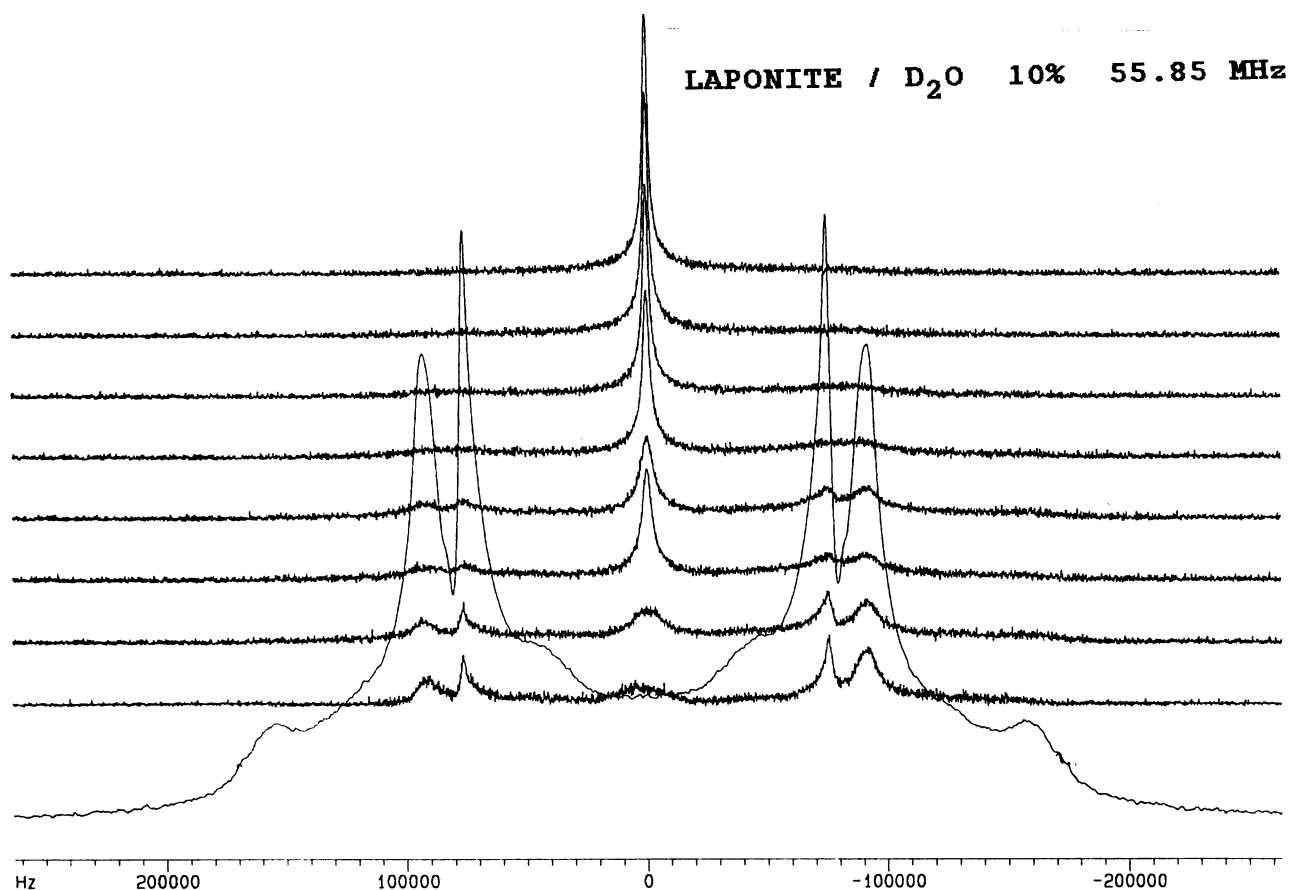


Fig. 2. Laponite/D₂O spectra recorded at 55.85 MHz with increasing temperature, from below 200 K (sixteen scans), then 222/232/244/250/256/268/272/274 K (one scan). Single pulse sequence.

T_0 , one observes Pake's doublets with peak separation, $\Delta\nu = 151.6/160.5/188.6/338$ kHz for example, at 200 K that could correspond with the asymmetry parameter $\eta = 0.1$ to a quadrupolar constant $Q_{cc} = 4\Delta\nu/3 \times 0.9 = 224.6/237.75/279.35/500.8$ kHz, to be compared to values collected by Lucken:¹¹ 213.2/216.4 kHz for D₂O ice and 318.6/649 kHz for HDO, because we may expect a certain amount of H₂O and HDO in the D₂O bottle.

Freezing D₂O gels. For $T > T_0$, the line widths are roughly proportional to the concentrations, then to b . See Table 1. For $T < T_0$ one may observe two lines, as seen in Fig. 2. 1) The broad line has exactly the shape of frozen D₂O (as an example, on montmorillonite 3.125%, one obtains at 230 K: $\Delta\nu = 151/160/189/340$ kHz), T_1 values fit D₂O curve, with $\tau \gg 1/\omega$ and the line intensity increases greatly when T is lowered. Therefore, one may attribute it to the frozen part of D₂O in the clay gel. 2) The central line is proportional to C , and its intensity and area diminish when T is lowered. The shape is a lorent-

zian (Δf the width) for the clay with small particles (laponite); for clays with large sheets (hectorite, montmorillonite), the random orientation is not possible, and the preferred orientations give a Pake's doublet (Δf the separation). In all cases, for $T \ll T_0$, $\log \Delta f$ vs. $1/T$ fits a straight line (see Fig. 3, a and b), and that is the expected relationship, since Δf is proportional to $1/T_2$. If this part of the curve represents b population only, we may extrapolate Δfb at room temperature. 3) Then at room temperature, or above T_0 , one could write:

$$\begin{aligned} \Delta f &= (a/a + b)\Delta fa + (b/a + b)\Delta fb = \Delta fa + b\Delta fb \\ &= b\Delta fb \quad (4) \end{aligned}$$

because $a \cong 1$ and $\Delta fa \cong 0$. Eq. (4) gives a measure of the bound water fraction $b = \Delta f/\Delta fb$, but accurately measuring Δf necessitates a good field homogeneity. Using Eq. (1) at room temperature gives:

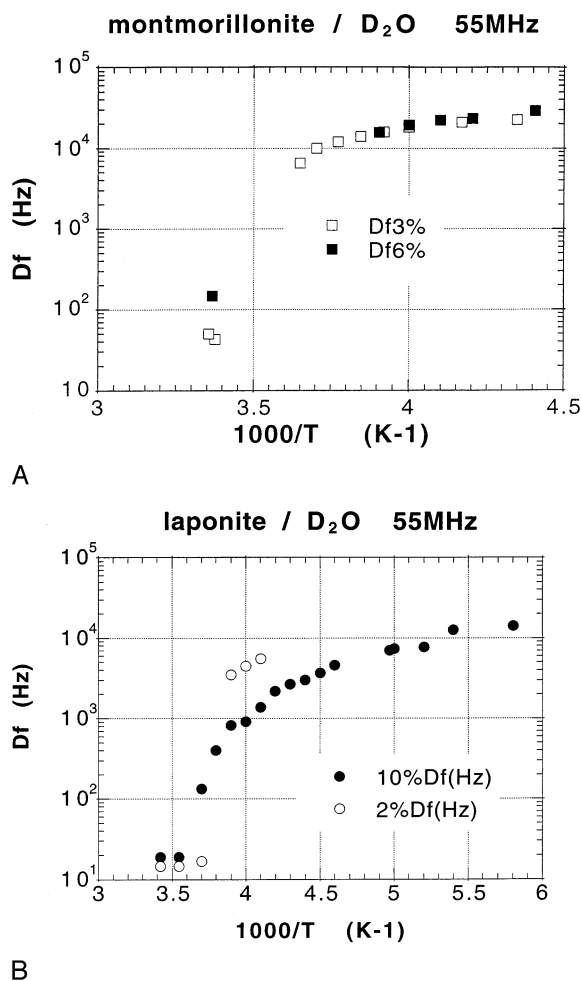


Fig. 3. (a) Central line (doublet) separation for montmorillonite. (b) Central line (lorentzian) width for laponite.

$$R1b = (R1 - R1a)/b = \Delta R/b. \quad (5)$$

Data for montmorillonite.

T_1 is the same for all concentrations, and because the signal is proportional to C , one is tempted to attribute the T_1 values to the bound phase b alone. The curves T_1 vs. $1/T$ seem to fit the three-dimensional law with a minimum allowing the calculation of QCC and the branch slope, the activation energy of the dominant motion rate; see, for example, hectorite 6.7% and 20% at 13.82 and

55.25 MHz.³ The value of T_1b should be extrapolated at room temperature to about 25 ms, but the values are always too high, because we expect to find a curve similar to that in Fig. 1.

Now let us recall some general results of thermoporometry: when the temperature of a porous sample is lowered, water solidification is progressive and ends in the smallest pores. For example, Brun¹¹ gives this relationship (valid above 233 K) between ΔT , the lowering of solidification temperature and the pore radius R_p in nanometers, in a saturated porous medium: $R_p = 0.57 - 64.67/\Delta T$, with a water layer of 0.8 nm that never freezes.

Thus, if we consider that some part of D_2O bulk, @, remains unfrozen under T_0 , and that a rapid exchange exists with the nearby liquid surface layer, then Eq. (1) applies with @ instead of a , and @ tending to zero when T decreases.

The study of T_1b is directly possible only for $T \ll T_0$, but above about 230 K, one must calculate T_1b from Eq. (1) with T_1a extrapolated from liquid D_2O , @ + b measured on the central line, and frozen D_2O (a_2) measured on the broad line, with the condition @ + a_2 + $b = 1$. The ratio central area/total area = @ + $b/1$ gives @, because we know b . Then one may calculate T_1b by:

$$R1b = (R1 - @R1a)/(1 - @). \quad (6)$$

Montmorillonite. Figure 4 shows the ratio of the central line (Pake's doublet) to the total line area for $C = 3.125\%$. For $T = 250$ K, the limit is reached (also for Δf in Fig. 3a), with $b = 0.03$. From @ taken from Fig. 4, it is now possible to correct the T_1 vs. T curve and obtain T_1b of the surface.

Figure 5 shows the correction, T_1a being extrapolated at low temperature. The RT value for T_1b may be extrapolated to 26.6 ms (to be compared to an average of 20.9 ms with Eq. (5)).

Laponite. Fig. 3b shows $\Delta fb = 2200$ Hz, and because $\Delta f = 20$ Hz, we obtain $b = 0.009$. Eq. (1) for T_2^{-1} or Δf gives below T_0 :

$$@ = (\Delta fb - \Delta f)/(\Delta fb - \Delta fa). \quad (7)$$

Table 1

T (K)	C (%)	T_1 (ms)	Δf (Hz)	Δfb (kHz)	b	T_1a (ms)	ΔR (s^{-1})	$R1b$ (s^{-1})	T_1b (ms)
297	6.25	336.8	147	11	0.014	424	0.613	45.9	21.8
296	3.13	379	50	11	0.0046	415	0.227	50	20

Measured at 13.82 and 55.25 MHz, T_1^{-1} vs. C gives a slope $K' = 12.17 s^{-1}$; then Eq. (3) gives $S = 229 m^2/g$ (with T_1b average = 20.9 ms).

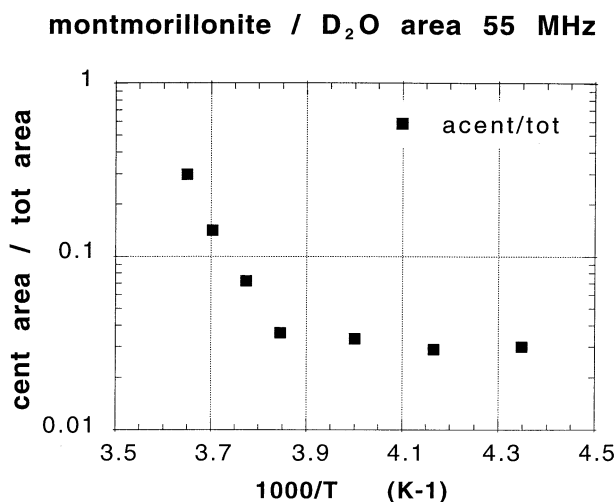


Fig. 4. Ratio of the central line (liquid) to the total line areas (liquid plus ice) for montmorillonite.

If we use the calculated α values in Eq. (6), we obtain T_1b as shown in Fig. 6. The minimum value for T_1b is now 1.7 ms (QCC = 202 kHz), and the extrapolated room temperature value is about 15 ms, with an almost symmetrical curve, as expected for a three-dimensional relaxation.

CONCLUSION

We have seen how line width and line area measurements could give the unfrozen fraction α of the bulk water near the solid surface. An idea of the porosity may be obtained: for small particles of laponite, α tends to

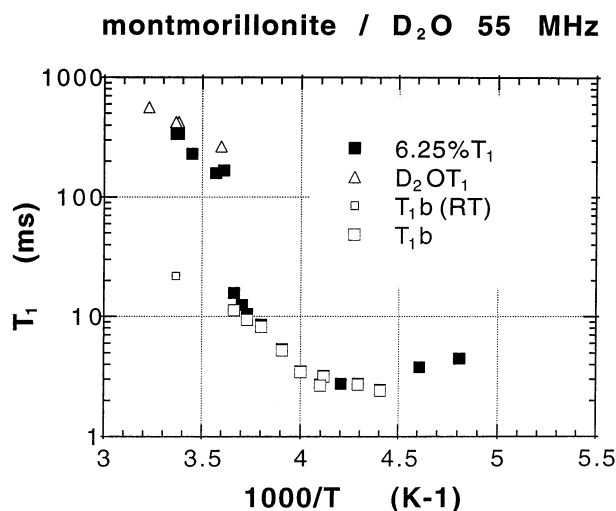


Fig. 5. T_1b (surface) corrected using Fig. 4 for α . T_1 measured for montmorillonite is in black. The T_1 value at room temperature is calculated using Eq. (5).

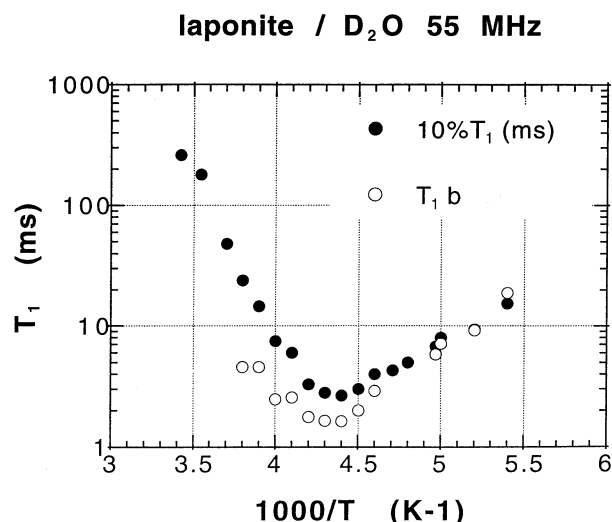


Fig. 6. T_1b (surface) corrected using line width correction by Eq. (7) for laponite.

zero toward 200 K, showing nanoporosity, and for large particles of montmorillonite, α is smaller and tends to zero at 250 K, indicating larger pores. In addition, α may be used to correct the T_1 vs. $1/T$ curve, allowing a study of the adsorbed water T_1 without destroying the sample, and to find the room temperature T_1b value necessary to determine the wetted solid surface area.

Although ^1H T_1 and $T_1\rho$ show a two-dimensional effect on the diffusion of H_2O over a scale of $1\ \mu\text{s}$ on the montmorillonite surface, the corrected ^2H T_1 's surface seem to obey a three-dimensional relaxation law, and that was verified: ^2H T_1 is almost frequency independent above 2 MHz. $T_1\rho$ results show a two-dimensional tendency, indicating a diffusional dipolar effect stronger than the quadrupolar term only at low frequencies.

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