Proton Magnetic Resonance in Clay Minerals

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Nuclear magnetic resonance energy absorption line widths within the region of proton resonance were determined for a number of clays and related materials at room temperature. The line widths were calculated from the horizontal distances between the maxima and the minima of the derivative absorption curves obtained with a 1720-gauss proton-magnetic-resonance apparatus. Line widths in order of decreasing proton mobility were found to be approximately 3 gauss for pyrophyllites, 6 gauss for kaolins and halloysites, 9 gauss for a sepiolite, and 11 to 12 gauss for a bayerite and a bauxite. Illites and montmorillonites gave only narrow line widths (0.3 to 0.7 gauss) in the semi dry state, but exhibited some less mobile hydrogen (line width of 2 to 3 gauss) after drying at 200 C. Except for bayerite, bauxite, and sepiolite, the clays did not exhibit the wide lines frequently associated with either hydroxide groups or water of crystallization or as determined for brucite and gibbsite. A sample of montmorillonite frozen with liquid nitrogen and slowly thawed in the apparatus indicated that greatly increased proton mobility began at about -70 C.

● THE ROLE and position of the hydroxide groups and water in clay minerals have been the subject of extensive research for many years. Many techniques have been utilized by research workers in determining the atomic structure of the various types of clays. Grim (1), Marshall (2), Rigby (3), Hendricks (4), and many others have summarized research on the different clay minerals and presented structural arrangements. Hydroxides and water molecules are important groups in most of the proposed structures. However, the nature and position of the hydrogen of the hydroxides or the water in clay minerals are difficult to ascertain and have been the subject of much conjecture.

Nuclear magnetic resonance apparatus, tuned to the proton-resonance frequency (PMR), has been used to study the hydrogen in both organic and inorganic materials. The technique was originally developed, almost simultaneously, by Bloch, Hansen, and Packard (5) and Purcell, Torrey, and Pound (6). Comprehensive reviews of the principles involved have been presented by Andrews (7), Pake (8), Slichter (9), and others.

In the field of silicates, PMR techniques have been used by Kawachi, Murakami, and Herahara (10), French and Warder (11), Watanabe and Sasaki (12), and Blaine (13) in the study of the hydration of portland cement and related compounds. Pickett and Lemcoe (14), have reported on the use of PMR in a study of clay-water systems of rather high water content. Large quantities of free or sorbed water may, however, mask the resonance effect of the protons of the structural water or hydroxide groups which are a part of the crystal structure. It appeared desirable, therefore, to study the application of PMR techniques to semi dry clays and related materials.

APPARATUS

A Schlumberger Model 104 nuclear magnetic resonance analyzer was used for making these tests. This apparatus, which has previously been described by Rubin (15), is of the broad-band type and utilizes a 1720-gauss permanent magnet with a 2-in. gap between the 10-in. diameter pole faces. A sweep coil on the magnet varies the field strength by amounts up to 20 gauss. A crystal-activated radio frequency coil of 7.3 M

the precession frequency of the hydrogen nuclei in this particular magnetic field) is located between the pole faces of the magnet and contains the test sample in a glass vial of about 1.35-in. outside diameter. As the external field strength is varied from one side to the other of the 1720-gauss field (H_0) corresponding to the resonance frequency of protons, the instrument plots, within certain limitations, the derivative of the energy absorption of the protons in the test sample.

Smooth lines were drawn through the extraneous "noise" of the signals and measurements made of the horizontal distance between the maxima and the minima of the derivative absorption curves. These values, as obtained from the charts, were corrected in accordance with the instrument calibration previously described (13), and are termed the derivative line widths (ΔH). Tests made on a number of polycrystalline, reagent grade chemicals indicated that the ΔH values obtained with this apparatus were consistent with previously published values.

The area under an absorption curve is proportional to the energy absorbed and hence the number of protons in the sample. With the derivative curves the distance of the peaks above and below the base line is related to this area and is used to furnish a rough estimate of the number of protons involved. This value is referred to in this paper as peak signal amplitude or ΔS.

SCOPE

Measurements of nuclear magnetic energy absorption in the region of proton resonance were made on a variety of semi dry and dried clays to investigate the application of PMR to the study of water and hydroxides associated with clay minerals. Measurements were also made of clay constituents such as brucite and gibbsite. Amorphous and ground crystalline silica as well as finely divided alumina, lime, and limestone were tested to assess the effect of sorbed water on these different materials. A limited study was also made of the thawing of water in a frozen sample of semi dry montmorillonite, and a few tests were made of the effect of soil stabilizers such as $CaCl_2$ and $Ca(OH)_2$ on the water associated with a sample of montmorillonite.

TEST METHODS

Samples of some of the clays were packed into the 1.35-in. o.d. glass vials to a depth of about 2 in., whereas others were pressed into disks slightly smaller in diameter than that of the vials and placed in the vials to a $1\frac{1}{2}$- to 2-in. depth. Samples were evacuated at room temperature for various periods to remove portions of the water, after which they were dried at 100 C, then at 200 C, and finally at 350 C. After each evacuation or heat treatment the samples were allowed to remain in the stoppered vials for a few hours before weighing and testing in the PMR apparatus. Normally 3 to 5 tests were made of each sample under each condition.

In determining the over-all absorption curve, a 20-gauss field strength was traversed in 4 min, whereas, in determination of the line width of peaks near the resonance frequency field strength, only 1 or 2 gauss were traversed in 4 min. To insure a closely approximate derivative curve, the modulation amplitude employed was less than one-fifth the line width in gauss in all reported values for ΔH. Where double peaks occurred, separate determinations of ΔH were made using the required instrument parameters. The amplification of the signal was adjusted for each test sample to obtain optimum signal-to-noise ratio. Under the most unfavorable conditions reported it is estimated that the signal-to-noise ratio at the peak of the derivative curve for bound water was of the order of 4 to 1, but in most cases it was larger.

Peak signal amplitude values were determined traversing a 10-gauss field in 30 sec. Various signal amplification factors were used but, for comparative purposes the values reported have been corrected to the same arbitrary sensitivity.

The time constant of the apparatus was maintained at $\frac{1}{30}$ of the sweep time or less, a necessary requirement for quantitative measurements with the instrument used.

A sample of montmorillonite was frozen in liquid nitrogen in a special glass Dewar flask made to fit in the rf coil between the magnets. The sample was allowed to warm in the Dewar flask while in the apparatus. Alternate determinations were made of the absorption-derivative line-width and the temperature as determined by means of a
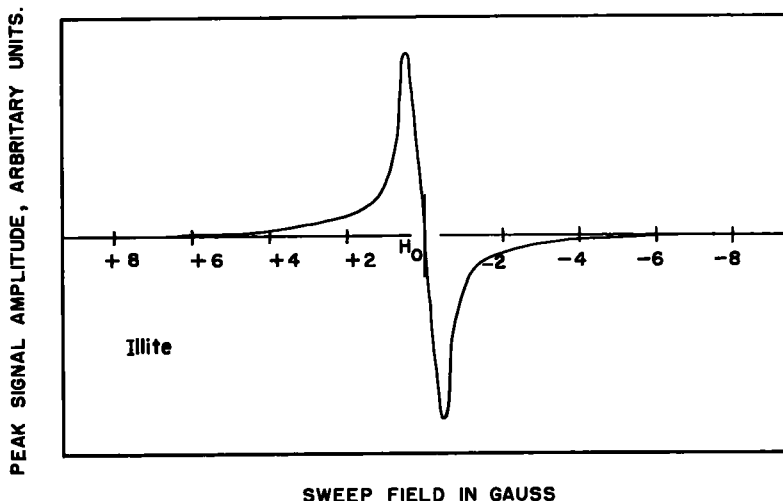
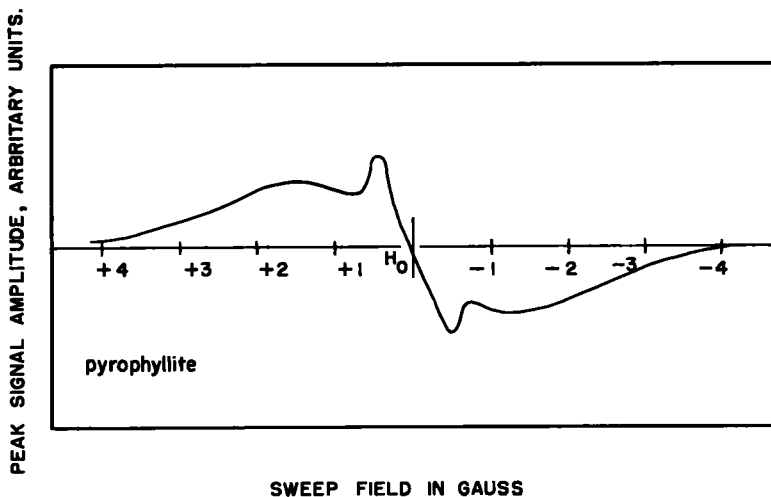Figure 1. Derivative of absorption curve obtained on illite sample.

Figure 2. Derivative of absorption curve obtained on pyrophyllite sample.

copper-constantan thermocouple inserted into the sample. Comparative measureme
were made with distilled water frozen and cooled to liquid-nitrogen temperature and
allowed to warm up in the Dewar in the apparatus.

A sample of montmorillonite was mixed with 20 percent of reagent-grade $Ca(OH)$
and water to a plastic consistency. Another sample of this same clay was mixed wi
2.5 percent of $CaCl_2$ and water. Both samples, as well as one mixed with distilled
water, were stored in stoppered vials at 50 C for one week. Measurements were th
made of the samples in the PMR apparatus after various periods of drying.

Determinations of the PMR patterns of powdered opal, gibbsite, boehmite, and b
cite were made without addition of water to the samples. The samples of quartz gr
to a surface-mean diameter of approximately 2 μ, as well as the other powdered ma
als, were compacted in the test vial containing known quantities of distilled water be
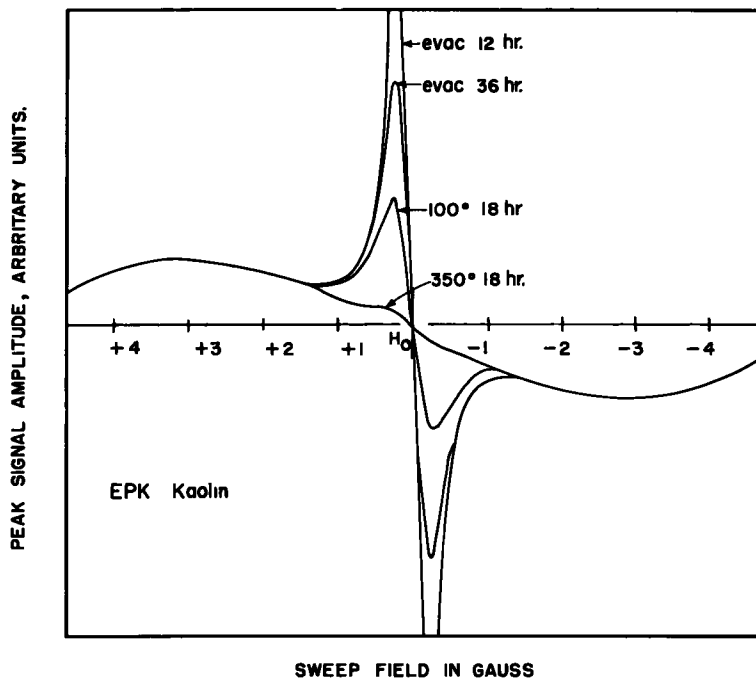the determinations.

Figure 3. Derivatives of absorption curves of kaolin sample after removal of various amounts of water.

RESULTS OF DETERMINATIONS

Figure 1 shows a smooth tracing of a derivative absorption curve, obtained for a sample of partially dried illite where the field was traversed the nominal ±10 gauss about the H_0. Although the instrument parameters used for this test were such that the central portion of the signal was overmodulated (that is, the modulation amplitude was greater than one-fifth of the absorption line width), very little absorption was evident other than the central peaks. The values for the line widths obtained on three samples of illite are given in Table 1.

The patterns obtained with montmorillonites, conditioned in laboratory environment or partially dried, were very similar to those obtained with the illites in that the only apparent absorption occurred very close to the resonance frequency possibly associated with free water. The ΔH values obtained for a number of montmorillonites are also presented in Table 1.

A curve obtained with a pyrophyllite is shown in Figure 2, where two pairs of peaks are apparent. The peaks closest to H_0, possibly resulted from the presence of adsorbed water, whereas the other peaks are associated with structural hydrogen in the mineral. The line widths obtained with samples of pyrophyllites were approximately gauss, as given in Table 1.

Absorption curves of a kaolin evacuated and dried to remove some of the water are shown in Figure 3. The figure was traced from individual determinations after the various treatments. The sample as well as the instrument parameters were the same for each of the determinations. The broad curve with ΔH of about 6.1 gauss was common to each of the recorded patterns, whereas the height of the central peaks became smaller with evacuation or drying. Values for the line width for a number of kaolins are given in Table 1.

The halloysites gave curves very similar to those obtained with the kaolins, except that the peaks closest to H_0 indicated a slightly narrower line width than those obtained with the illites and montmorillonites.
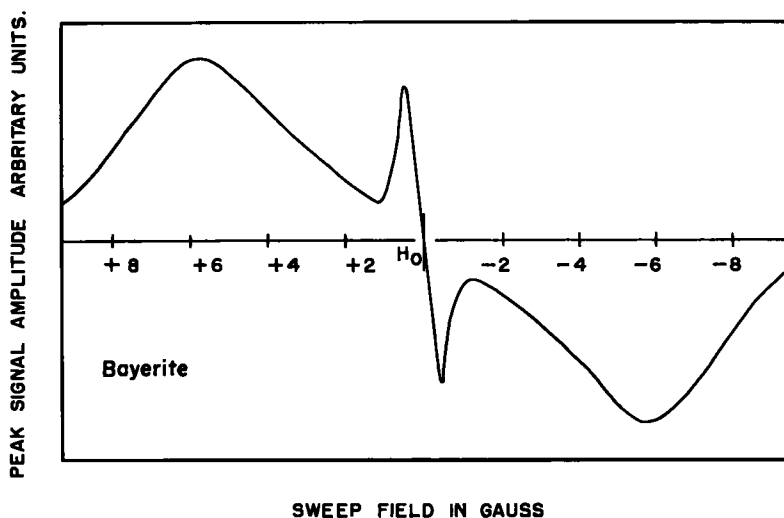
Figure 4. Derivative of absorption curve obtained on bayerite sample.

TABLE 1

ABSORPTION LINE WIDTH (ΔH) OF CLAY SAMPLES TESTED IN A SEMI DRY CONDITION

Clay Sample	ΔH (gauss)	Clay Sample	ΔH₁ (gauss)	ΔH₂ (gauss)
Illites		Kaolinites		
Oswego	0.29	Putman	6.0	0.18
McAvoy	0.50	Kamec	6.0	0.19
Fresian	0.53	EPK	5.8	0.15
Montmorillonites		Ga 600	5.9	0.20
Hectorite	0.54	Lustra	5.9	0.21
Bentonite #25 Upton	0.48	Dry Branch	5.8	0.14
Bentonite #24 Otay	0.47	(unknown)	6.2	-
Belle Fourche	0.47	Dickite	5.9	-
Belle Fourche	0.38	Georgia	6.0	0.19
Aberdeen, Miss.	0.34	Florida	5.8	0.19
Panther Creek	0.33	Mesa Alta	6.1	0.22
Chambers, Ariz.	0.67	Murfreesboro	6.2	0.16
Nontronite	0.88	Bolivia	7.5	0.10
Wyoming bentonite	0.51	Halloysite dragon	6.1	0.09
Na bentonite	0.49	Halloysite	6.0	0.10
Ca bentonite	0.62	Halloysite hydrated	6.5	-
Pyrophyllite	3.0	Sepiolite	9.1	-
Pyrophyllite 2074	2.8	Bauxite	11.0	-
Pyrophyllite 2089	2.8	Bayerite	11.4	-
Pyrophyllite 2157	2.9			

A single sample of sepiolite tested indicated a line width of 9.1 gauss, whereas bauxite and bayerite (Fig. 4) indicated line widths of about 11 gauss (Table 1).

The line widths obtained on a series of clays from which water was progressively removed, first by evacuation and then by heating at 100, 200, and finally 350 C, are

TABLE 2

ABSORPTION LINE WIDTH (ΔH) OF VARIOUS CLAY SAMPLES DETERMINED AT MOISTURE CONTENT

Clay Type	Determination[1]	As Rec'd.	After Evacuation for					After Heating for 18 Hr at			After 350 C Treatment[2]
			4 Hr	8 Hr	12 Hr	18 Hr	36 Hr	100 C	200 C	350 C	
utman kaolin	Water (%)	2.06	1.76	1.61	1.54	1.50	1.42	1.17	0.63	-	14.8
	ΔH_1 (gauss)	6.00	5.90	6.10	6.00	6.00	6.00	6.10	6.10	6.10	
	ΔH_2 (gauss)	0.18	0.21	0.23	0.27	0.28	0.32	0.34	-	-	
amec kaolin	Water (%)	3.75	3.45	3.25	3.20	3.11	3.02	2.65	1.84	-	14.1
	ΔH_1 (gauss)	6.00	6.00	5.90	5.90	6.00	5.90	6.00	6.00	5.80	
	ΔH_2 (gauss)	0.20	0.20	0.19	0.22	0.22	0.23	0.17	0.11	-	
PK kaolin	Water (%)	2.73	2.27	2.09	2.02	1.87	1.78	1.45	0.66	-	14.4
	ΔH_1 (gauss)	6.00	5.70	5.80	5.80	6.10	5.70	6.00	6.00	6.10	
	ΔH_2 (gauss)	0.15	0.20	0.22	0.25	0.27	0.28	0.28	0.16	-	
600 kaolin	Water (%)	0.85	0.66	0.61	0.59	0.56	0.53	0.36	0.18	-	15.3
	ΔH_1 (gauss)	6.00	6.10	6.00	6.00	6.10	6.20	6.10	6.10	6.10	
	ΔH_2 (gauss)	0.20	0.19	0.22	0.26	0.29	0.31	-	-	-	
stra kaolin	Water (%)	0.90	0.70	0.66	0.63	0.60	0.57	0.42	0.25	-	15.3
	ΔH_1 (gauss)	5.90	5.90	6.00	6.00	6.30	6.10	6.00	6.10	6.20	
	ΔH_2 (gauss)	0.20	0.25	0.28	0.26	0.26	0.26	-	-	-	
y Branch kaolin	Water (%)	1.52	1.14	1.01	0.96	0.91	0.85	0.63	0.23	-	15.0
	ΔH_1 (gauss)	5.80	6.20	6.10	6.40	6.00	6.00	5.90	6.10	6.20	
	ΔH_2 (gauss)	0.14	0.21	0.24	0.26	0.29	0.28	0.22	-	-	
agon halloysite	Water (%)	3.36	2.58	2.27	2.12	2.02	1.79	1.25	-	-	14.8
	ΔH_1 (gauss)	6.10	6.20	6.20	6.00	6.10	6.00	6.30	6.00	6.10	
	ΔH_2 (gauss)	0.07	0.09	0.09	0.09	0.10	0.11	0.09	0.06	-	
wego illite	Water (%)	1.16	0.80	0.68	0.63	0.57	0.52	0.18	-	-	4.6
	ΔH_1 (gauss)	-	-	-	-	-	-	-	-	2.60	
	ΔH_2 (gauss)	0.28	0.26	0.14	0.14	0.14	0.11	0.10	0.09	-	
Avoy illite	Water (%)	5.21	3.98	3.42	3.22	3.02	2.78	2.39	0.71	-	4.4
	ΔH_1 (gauss)	-	-	-	-	-	-		1.10	2.40	3.00	
	ΔH_2 (gauss)	0.51	0.61	0.78	0.73	0.77	0.82	0.77	-	-	

ter that is removable by successive evacuation for 36 hr at room temperature, with 18-hr dryings at 100, 200, and
0 C, and with percentage based on weight after last drying.
sed on ignited weight at 900 C.

en in Tables 2, 3, and 4. The moisture content, based on the weight after the 350
heat treatment, for the respective determinations of line width is also given. In the
st column is the percentage moisture (or other material that may be removed) based
the 900 C ignited weight but still present after the 350 C treatment.
The ΔH_1 line width was arbitrarily assigned to the greater of the two values and ΔH_2
values of the peaks closest to the resonance frequency H_O. As previously indicated
a single sample of kaolin (Fig. 3), the broad lines for the various kaolins and the
loysite did not change appreciably with the removal of water at 350 C or below. The
line width, which is possibly associated with interlayer or adsorbed water, general-
increased slightly as water was removed, which is in accordance with published data
other materials (16).
The line widths for two of the three illites and two montmorillonites (Tables 2-4)
o increased slightly with decrease in moisture content. These materials exhibited
y narrow line widths at the higher moisture contents. However, after drying at 100
200 C, a second set of peaks became apparent on samples of the McAvoy and Fithian
tes, the two montmorillonites, and the mixtures of illite and montmorillonite of
le 3. The line widths of these peaks increased with decrease in moisture content.
example, the ΔH_1 line width for the McAvoy illite was 1.1 gauss after drying at
C, 2.4 gauss after 200 C and 3.0 gauss after the 350 C drying. The signals obtained
these dried samples were, however, very weak. Plotting line widths vs respective
sture contents for an illite (Fig. 5) and a montmorillonite (Fig. 6) indicates rather
rp breaks in both curves. On the basis of the 900 C ignited weight, the illites and
ntmorillonites have about 4 percent water remaining after the 350 C drying treatment
compared to the kaolins and halloysite which had about 15 percent. It was also ap-

TABLE 3

ABSORPTION LINE WIDTH (ΔH) OF MONTMORILLONITE AND ILLITE AND MIXTURES OF THESE
DETERMINED AT MOISTURE CONTENT

Type	Determination[1]	As Rec'd.	After Evacuation for					After Heating for 18 Hr at			After 350 C Treatment[2]
			4 Hr	8 Hr	12 Hr	18 Hr	36 Hr	100 C	200 C	350 C	
Montmorillonite (Wyoming bentonite)	Water (%)	6.67	6.16	5.35	4.82	4.21	2.98	2.03	0.28	-	4.8
	ΔH₁ (gauss)	-	-	-	-	-	-	-	3.10	3.60	
	ΔH₂ (gauss)	0.51	0.55	0.56	0.51	0.54	0.57	0.49	0.29	-	
75 M 25 I	Water (%)	6.23	5.60	5.00	4.56	3.93	2.64	1.81	0.54	-	5.1
	ΔH₁ (gauss)	-	-	-	-	-	-	-	2.70	2.90	
	ΔH₂ (gauss)	0.47	0.51	0.57	0.54	0.59	0.59	0.54	-	-	
50 M 50 I	Water (%)	5.75	5.05	4.47	4.11	3.65	2.65	2.05	0.79	-	4.8
	ΔH₁ (gauss)	-	-	-	-	-	-	-	2.60	2.90	
	ΔH₂ (gauss)	0.43	0.51	0.57	0.58	0.55	0.59	0.58	-	-	
25 M 75 I	Water (%)	5.12	4.59	4.05	3.71	3.40	2.76	2.35	0.98	-	4.8
	ΔH₁ (gauss)	-	-	-	-	-	-	-	2.60	2.50	
	ΔH₂ (gauss)	0.38	0.42	0.51	0.52	0.54	0.66	0.64	-	-	
Illite (Fithian)	Water (%)	4.88	4.26	3.83	3.68	3.50	3.28	2.70	1.43	-	4.7
	ΔH₁ (gauss)	-	-	-	-	-	-	1.00	2.10	2.50	
	ΔH₂ (gauss)	0.42	0.55	0.58	0.58	0.64	0.67	0.72	-	-	

[1]Water that is removable by successive evacuation for 36 hr at room temperature, with 18-hr dryings at 100, 200, and
350 C, and with percentage based on weight after last drying.
[2]Based on ignited weight at 900 C.

TABLE 4

ABSORPTION LINE WIDTH (ΔH) OF A MONTMORILLONITE WITH AND WITHOUT CHEMICAL
TREATMENT DETERMINED AT MOISTURE CONTENT

Type	Determination[1]	As Rec'd.	After Evacuation for					After Heating for 18 Hr		
			4 Hr	8 Hr	12 Hr	18 Hr	36 Hr	100 C	200 C	350 C
Montmorillonite as received	Water (%)	8.06	6.22	4.57	3.61	2.55	1.54	0.71	0.27	-
	ΔH₁ (gauss)	-	-	-	-	-	-	-	2.80	3.6
	ΔH₂ (gauss)	0.44	0.47	0.49	0.43	0.39	0.42	0.31	-	-
Montmorillonite[2]	Water (%)	8.92	7.37	5.22	3.92	2.54	1.45	0.67	0.31	-
	ΔH₁ (gauss)	-	-	-	-	-	-	-	2.70	
	ΔH₂ (gauss)	0.46	0.51	0.54	0.47	0.39	0.38	0.37	-	-
Mont + Ca(OH)₂[3]	Water (%)	13.82	8.89	5.85	4.79	4.30	3.59	2.63	0.81	-
	ΔH₁ (gauss)	-	-	-	-	-	-	-	2.50	2.2
	ΔH₂ (gauss)	0.15	0.20	0.32	0.40	0.42	0.46	0.50	-	-
Mont + CaCl₂[4]	Water (%)	11.72	10.75	8.90	7.70	6.48	5.44	3.35	0.52	-
	ΔH₁ (gauss)	-	-	-	-	-	-	-	2.80	2.9
	ΔH₂ (gauss)	0.37	0.38	0.34	0.38	0.41	0.47	0.68	-	-

[1]Water that is removable by successive evacuation for 36 hr at room temperature, with 18-hr dryings at
100, 200, and 350 C, and with percentage based on weight after last drying.
[2]Water added stored one week at 50 C.
[3]20 percent Ca(OH)₂ and water added, stored one week at 50 C.
[4]5 percent CaCl₂ and water added, stored one week at 50 C.

parent from the weak signals of the test patterns that fewer protons were present in
the illites and montmorillonites after drying at 200 or 350 C than were present in the
kaolins and halloysites.

The relationship of peak signal amplitude to moisture content as determined on two
samples of kaolin, a sample of illite, and a sample of montmorillonite is shown in Fig-
ure 7. The moisture content was based on the weight of samples after drying at 350 C.
In these tests a 10-gauss sweep field was scanned in 30 sec using an overmodulated
signal of 5 gauss. This procedure has been used for determining moisture content of
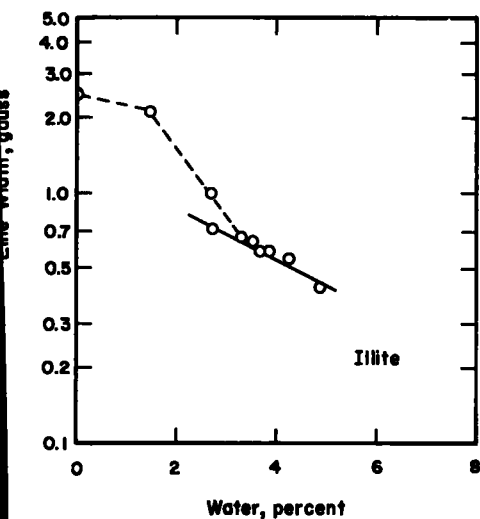
Figure 5. Absorption line width vs mois-
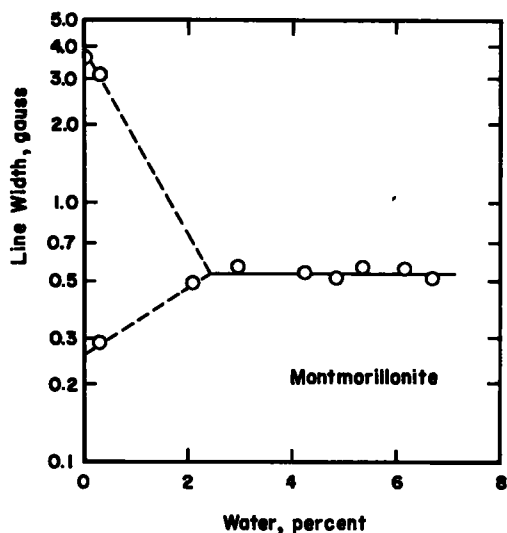ture content of illite sample.

Figure 6. Absorption line width vs mois-
ture content of montmorillonite sample.

various organic materials (15). However, structural hydrogen as well as adsorbed
water is included under these conditions. Plotting the signal amplitude vs the moisture
content based on the 900 C ignited weight places the kaolins to the right of the illite and
montmorillonite but does not remove the curvature of the lines nor bring them together.

When samples of montmorillonite were
mixed with $Ca(OH)_2$ or $CaCl_2$ and allowed
to react at 50 C for a week, the ΔH values
were not greatly different from those ob-
tained with this clay as received or with
water added before the determination and
then dried. In every instance, a line width
at 2 to 3 gauss became apparent after the
200 C drying treatment. It was noted that
the clay treated with the $Ca(OH)_2$ was fairly
hard or set after the 50 C curing period,
whereas the $CaCl_2$-treated clay and that
with water added were still plastic.

The curves obtained with brucite crys-
tals that had been pulverized are shown in
Figure 8. The line widths of both the blue
and the white crystalline material were ap-
proximately 12 gauss. The curve obtained
on gibbsite is also shown in this figure.

The ΔH values obtained with gibbsite,
boehmite, opal, silica gel, ground quartz,
hydrated lime, precipitated calcium car-
bonate, pulverized limestone, and a finely
divided Al_2O_3 are given in Table 5. The
line widths of the materials containing
sorbed water were sensitive to the amount
of water present. With silica gel, for ex-
ample, the values for line width increased
markedly with lower moisture content, as
shown in Figure 9.

TABLE 5

ABSORPTION LINE WIDTH (ΔH) OF MINERALS AND PARTICULATE MATERIALS ASSOCIATED WITH CLAY MINERALS

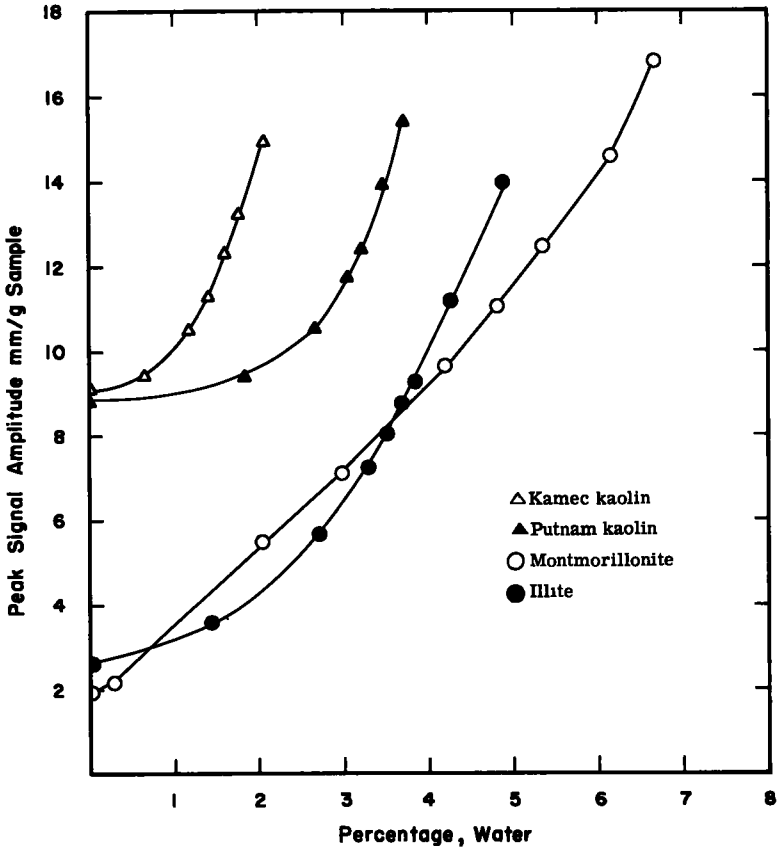| Material	Water on Dry Basis (%)	ΔH (gauss)
Brucite:		
White	-	12.6
Blue	-	13.7
Gibbsite	-	11.6
Boehmite	-	11.0
Quartz	30	0.26
Opal	10	0.075
Silica gel	13	0.036
Al_2O_3	200	0.019
Hydrated lime:		
Nonplastic	50	0.038
Plastic	50	0.030
Ppt., calcium carbonate	32	0.025
Ground Limestone:		
E	15	0.038
	15	0.10

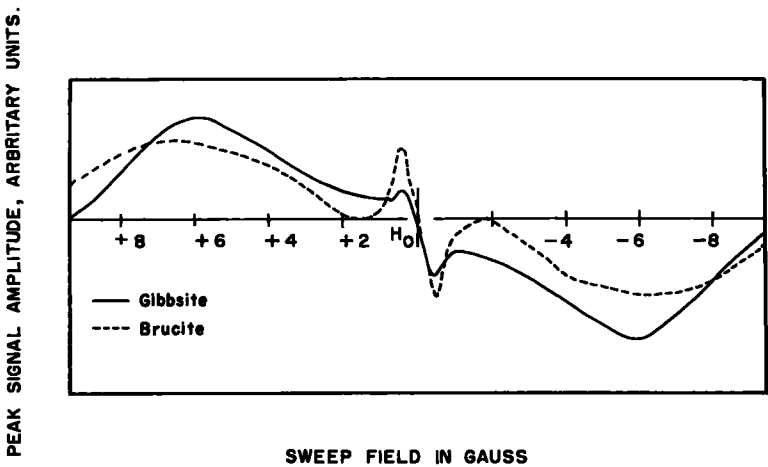Figure 7. Peak signal amplitude vs moisture content of samples.

Figure 8. Derivatives of absorption curves for samples of brucite and gibbsite.

A graph showing the line widths ob-
tained on a sample of montmorillonite
frozen with liquid nitrogen and allowed to
warm up in the apparatus is shown in Fig-
ure 10. In this figure is shown also the
peak signal amplitude as calculated from
the recorder chart values and instrument
parameters. It may be noted that a break
was obtained in each of these curves at
about -70 C, but that the change in line
width with temperature was fairly gradual.
Smooth curves were obtained in each de-
termination with no evidence of any sec-
ondary peak as would be obtained with free
water. Presented also in this graph are
tests obtained with ice frozen in liquid
nitrogen and permitted to thaw under simi-
lar conditions. A sharp break in the curve
is apparent in the -10 C region. The tem-
perature of both the ice and the montmoril-
lonite were measured near the center of

Figure 9. Relationship between derivative
line width and moisture content of silica
gel sample.

the sample, and the material near the edges may have been considerably warmer and
contributed to the apparent line width. It may be noted, however, that the ΔH value for
montmorillonite at liquid nitrogen temperature was less than half that of ice.

DISCUSSION

Many of the structures proposed for clay minerals include, in addition to interlayer
water, brucite and gibbsite layers and hydroxide groups as well as water of crystalli-
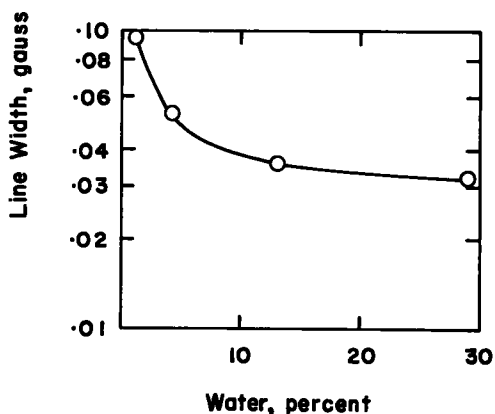zation. The line widths of both brucite and gibbsite were found to be about 11 to 12
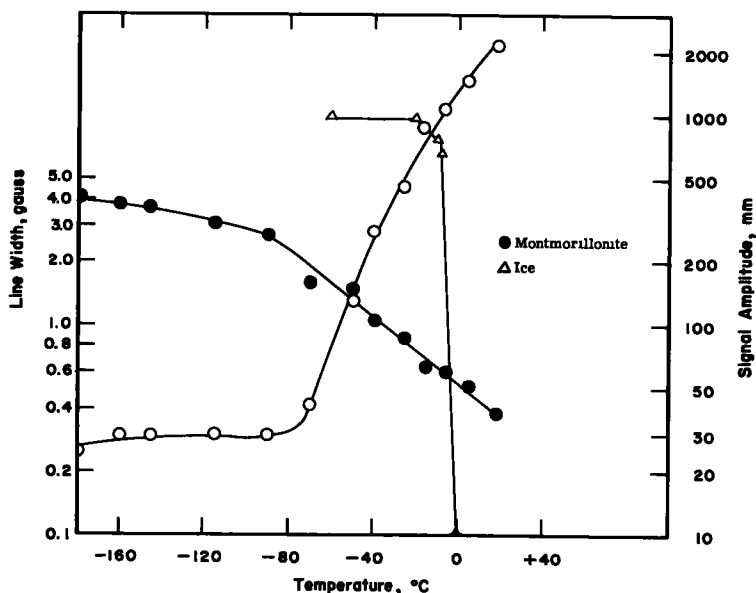gauss.

Figure 10. Relationship between derivative line widths and temperature and relationship
between signal amplitude on montmorillonite sample and temperature.

Tests made with this apparatus on a large number of reagent grade inorganic poly-
crystalline hydroxides and compounds with water of crystallization indicated line width
for a great majority of the compounds in the 10- to 16-gauss range when tested at room
temperature. The ΔH values for bayerite and bauxite were within this range. Howeve
measurements on illites, montmorillonites, pyrophyllites, kaolins, and halloysites did
not exhibit any peaks in the curves with line widths in the 10- to 16-gauss range. It is
recognized that in interpretation of PMR data, many unknown factors are involved. It
appears, however, that for these clays, the apparatus used was not sensitive enough to
determine the presence of any structural hydrogen held either as hydroxides or as wat
of crystallization in the quantities present.

Nakamoto, Margoshes, and Rundle (17), in a paper on stretching frequencies as a
function of distance in hydrogen bonds, reported the bond distance of a number of com-
pounds. A few of these compounds (reagent grade) were tested in some preliminary
work with this apparatus and ΔH line widths of 2 to 10 gauss were obtained—the small
values for ΔH being obtained for those compounds reported as having low values for th
O-H-O distance.

The ΔH values for pyrophyllites, kaolins, halloysites, and sepiolite fall within this
2- to 10-gauss range as do the ΔH values for the montmorillonites and illites after dr
ing at 200 C. However, the signals for the montmorillonites and illites were very we
in this region compared to those of the other clays.

The explanation of the role of sorbed water or interlayer water associated with cla
minerals also presents some interesting problems. Water adsorbed on amorphous si
ca such as gel or opal exhibited a relatively small ΔH value, whereas powdered cryst
line quartz with a water content of 30 percent indicated a larger line-width value. Th
fact that rather narrow line widths were obtained with the very fine materials such as
silica gel, fine Al_2O_3 powder, lime, and precipitated calcium carbonate would seem t
indicate that a large surface area as such is not a major factor in contributing to the
ΔH value. Crystalline silica appears to immobilize the water to a greater extent than
amorphous silica and may be responsible for the strong adsorption of water leading to
ΔH values in the range of 0.3 to 0.7 gauss as found for the illites and montmorillonite
and the ΔH values of 0.1 to 0.2 gauss for the kaolins. The ΔH values obtained for the
interlayer adsorbed water on halloysite were appreciably lower than those obtained fo
the previously mentioned clays. These lower values may indicate a different type of
surface adsorbing the water or a surface with a different energy.

Although samples of montmorillonite tested at room temperature had only small Δ
values which suggested highly mobile protons, the sample tested at liquid nitrogen te
perature exibited a ΔH value less than half that determined for ice similarly tested.
Tests of frozen samples of other clays may furnish further information of the nature
of the water in these materials. The results obtained with the broad-band proton-magn
resonance apparatus are relatively insensitive with polycrystalline materials and ave
the effect of the different types of bonding of the hydrogen nuclei. For example, Pak
(8) has reported that $CaSO_4 \times 2H_2O$, which has two types of water molecules, exhibits
double derivative peaks with a single crystal but only one set of peaks in the powder
form. It cannot, therefore, be definitely stated that the ΔH values of 2 to 10 gauss o
tained with these clays are caused by hydrogen bonding. Further tests with highly or
ented silicate minerals appear necessary to the study of water and hydroxides in clay

It may be noted that the line widths obtained on the clay minerals appear to fall int
a pattern of multiples of 3 gauss; namely, approximately 0, 3, 6, 9, and 12 for illite
pyrophyllites, kaolins, sepiolite, and bayerite, respectively. Minor constituents, im
purities, instrumental variations, and inaccuracy of measurements may have accoun
for the different ΔH values that occurred within each group, but the differences betw
the groups appear real.

SUMMARY

Determinations were made at room temperature of the proton magnetic resonance
absorption derivative line widths of a variety of clays and related minerals.

The line widths of illites and montmorillonites were in the 0.3- to 0.7-gauss range w
tested in a semi dry condition. These values correspond to line widths associated w

strongly adsorbed water. When these materials were dried at 200 C or higher, line widths of about 3 gauss became apparent, but no absorptions corresponding to those normally obtained with hydroxides or with water of crystallization were obtained with this apparatus. The line widths of samples of pyrophyllite were also about 3 gauss, whereas ΔH values of about 6 gauss were obtained with kaolins and halloysites. Smaller ΔH values normally associated with adsorbed or interlayer water were also obtained with these clays. Line widths in the 2- to 8-gauss range are similar to those obtained on reagent chemicals having various O-H-O distances and are considerably lower than those obtained with brucite or gibbsite or with most other hydroxides or salts with water of crystallization. A sample of sepiolite gave a line width of 9.1 gauss, and samples of bayerite and a bauxite gave line widths of 11.4 and 11.0 gauss, respectively, which fall within the range normally associated with hydroxides or water of crystallization.

Removal of water by evacuation or by heating up to 350 C did not affect the line width attributed to structural water in kaolins but tended to increase the line width associated with the adsorbed water. The interlayer water or that adsorbed on different clays exhibited different degrees of line broadening and also greater line widths than were obtained with other finely divided minerals such as silica gel, ground quartz, or precipitated calcium carbonate. Adsorbed water on crystalline silica exhibited a greater absorption line width than that sorbed on either amorphous opal or silica gel.

A sample of montmorillonite frozen with liquid nitrogen and allowed to thaw in the apparatus indicated a decrease in line width (that is, an increase in proton mobility) at about -70 C. Samples of a montmorillonite clay mixed with calcium hydroxide or with calcium chloride and stored at 50 C for one week did not exhibit line widths greatly different from clay samples without the chemical treatment.

Although the results reported in this study may not be considered quantitative with respect to either structure or possible hydrogen bonding of the clay minerals, the use of proton magnetic resonance techniques appears to offer possibilities for a better understanding of these materials.

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