1989 SCA Conference Paper Number 8901

DETERMINING CARBONATE CONTENT OF CORES BY ^{13}C NMR

by

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ABSTRACT

The carbonate content of cores is normally determined by wet chemical methods such as acid dissolution. Here we report a new method using natural abundance ^{13}C Nuclear Magnetic Resonance (NMR) to rapidly and nondestructively measure carbonate content.

Because of its low natural abundance and small gyromagnetic ratio, ^{13}C NMR is normally difficult to measure in small core samples. However, using a 5 1/2 in. $^{13}C/^{1}H$ coil on a General Electric CSI-2 Tesla NMR imager/spectrometer, good signal-to-noise ratio for ^{13}C is now obtained within minutes for 4 in. OD whole core.

The ^{13}C spectra of oil in rocks consist of broad aliphatic and aromatic bands. In carbonates the ^{13}C spectrum also contains a carbonate powder pattern which can be used to measure inorganic carbon. The powder pattern arises from all orientations of carbonate crystallites relative to the applied magnetic field.

The carbonate content in mixtures of dolomite/sand and limestone/sand is shown to be measured accurately by ^{13}C NMR. The ^{13}C spin-lattice relaxation time T_1 was measured for various common carbonate minerals and for single crystals of calcite as a function of crystal orientation relative to the magnetic field.

INTRODUCTION

The inorganic carbon content of cores is normally determined by acid dissolution of a small finely ground rock sample. Organic carbon is determined separately by extraction or by pyrolysis with flame ionization detection (PFID) and thermal conductivity detection of generated CO_2.[1] More recently, Core Laboratories has introduced the Minerolog which estimates mineral composition on small powdered samples by Fourier Transform Infrared Spectroscopy.[2] Here we report a new method using natural abundance ^{13}C Nuclear Magnetic Resonance (NMR) to rapidly and nondestructively measure carbonate content of whole cores. In one measurement it is now possible to determine both organic and inorganic carbon.

The only nucleus of carbon with a magnetic moment, ^{13}C has low sensitivity because of both low natural abundance (1.108%) and small gyromagnetic ratio (1.071 MHz/kilogauss). Its absolute sensitivity

relative to the proton is 1.76×10^{-4}. Because of this, where ^{13}C-enriched samples or single crystals are not available, it is difficult to measure ^{13}C NMR signals in solids where the T_1 relaxation time is also typically very long. This is the case in naturally-occurring carbonate rocks which are essentially powders with no preferred crystalline direction. The task is still more difficult because the chemical shift anisotropy in carbonates is large (75 ppm), thus spreading out the ^{13}C NMR spectrum and reducing signal-to-noise ratio.

Under these conditions, small sample analysis (~50 mg) of carbonate minerals by ^{13}C NMR cannot be performed in a practical time, even at very high magnetic field with magic angle spinning. For example, Pines et al.[1] reported an acquisition sequence in powdered $CaCO_3$ with a recycle time of 64 seconds and an accumulation time of 10 hours.

In 4 in. OD whole core, however, the quantity of material is about 70,000 times this small sample quantity. Since the RF coil sensitivity decreases only linearly as the sample dimension is increased, whereas the sample volume increases cubically, the use of whole core is an overwhelming advantage relative to small sample analysis.

In order to analyze whole core, a $^{13}C/^{1}H$ double resonance 5 1/2 in. ID NMR coil was built for a General Electric CSI-2 Tesla NMR imager/spectrometer. With 4 in. OD whole core, good signal-to-noise ratio for ^{13}C carbonate can now be obtained with a single RF pulse. The $^{13}C/^{1}H$ coil allows measurements of both water and oil saturation using ^{1}H NMR, and oil and carbonate content using ^{13}C NMR. The coil is sufficiently large that 4 in. OD whole core can be analyzed while inside a 4 3/4 in. OD fiberglass core barrel.

^{13}C NMR SPECTRA IN $CaCO_3$

The ^{13}C spectra of oil-bearing rocks consist of broad aliphatic and aromatic bands. The aliphatic band is between 10 and 40 ppm downfield relative to tetramethylsilane (TMS), whereas the aromatic band is from 120 to 140 ppm. In carbonate powders the ^{13}C spectrum also contains an axially symmetric powder pattern from 120 to 195 ppm with an average chemical shift of 170 ppm. This is useful in making separate measurements of inorganic carbon. The powder pattern is well separated from the aliphatic oil peak although there is some overlap with the smaller aromatic components in the oil.

The characteristic lineshape of the carbonate signal is due to the fact that, in the solid state, the resonant frequency of the carbonate ^{13}C spins depends upon the orientation of the carbonate group relative to the external magnetic field. Since the carbonate ion (CO_3^{--}) has a three-fold axis of symmetry, its chemical shift tensor is an axially symmetric ellipsoid of revolution:

$$D = D_1 \cos^2 \theta + D_2 \sin^2 \theta$$

where θ is the angle between the three-fold axis and the magnetic field direction, D_1 is the chemical shift when the 3-fold axis of symmetry is parallel to the field, and D_2 is the chemical shift when perpendicular.[3] Precise measurements on a single crystal by Lauterbur[3] showed D_1 = 120.0 ppm and D_2 = 195.0 ppm relative to TMS, resulting in a total anisotropy $|D_1 - D_2|$ of 75.0 ppm. The average (or isotropic) chemical shift is:

$$D_{av} = \frac{1}{3}(\text{Trace}(D)) = \frac{1}{3}(D_1 + 2D_2) = 170.0 \text{ ppm}$$

The theoretical lineshape for an axially symmetric powder pattern without broadening is[4,5]:

$$I(\omega) = \frac{1}{\sqrt{3}\ (D_1 - D_{av})\ \sqrt{(1 + 2(\omega - D_{av})/(D_1 - D_{av}))}}$$

for $\omega \geq D_1$ and $\omega \leq D_2 = -1/2\ (D_1 - 3D_{av})$, where ω is the frequency in ppm relative to TMS. The theoretical carbonate lineshape is plotted in Figure (1) along with computer-generated axially symmetric powder patterns convolved with variable amounts of Gaussian broadening.

It is clear from Figure (1) that the amount of carbonate should not be determined from the height of the peak at 195 ppm because this is dominated by line broadening at the cusp. If the oil has a strong aromatic component the total area under the curve also should not be used because of the overlap with the aromatic band between 120 and 140 ppm. The best approach is to use a least-squares fit to a composite spectrum where the amount of carbonate powder pattern and aromatic peak are fit separately.

T_1 RELAXATION TIME IN CARBONATES

Even with good signal-to-noise ratio, quantitative ^{13}C NMR would not be possible if the carbonate spins have excessively long T_1, the nuclear spin-lattice relaxation time. Lauterbur[3] reported a T_1 of about 40 minutes in a single crystal of calcite (clear, colorless "Iceland spa"), which would have been too long for routine NMR analysis. However, we have found that T_1 of carbonate reservoir rocks is actually much shorter, of the order of a few minutes or less in all samples measured to date.

Table 1 lists the T_1 and line broadening (half width at half maximum at the cusp) for a suite of carbonate minerals, including both limestones and dolomites. Because of the relatively long ^{13}C relaxation time, the T_1 data were obtained by the method of saturation recovery.[7] In this method a rapid series of pulses is used to saturate the spins, then after variable time delays (30, 60, 120, 240 seconds), a 90 degree pulse is used to measure the regrowth of magnetization.

The best single exponential fits for the carbonate T_1 times range from 25 to 146 seconds, with an average of 88 seconds. In general, the dolomites have the longer relaxation times, but the overlap in relaxation times between some dolomites and limestones may preclude a determination of the degree of dolomitization by simple T_1 measurement. The difference between spin lattice relaxation times for different carbonate samples is not understood. Since Lauterbur has shown that the ^{13}C spin lattice relaxation times in a pure single crystal of Icelandic spar can be very long, the shortening of T_1 in natural carbonate reservoir rocks may be caused by the presence of small amounts of impurities with magnetic moments, such as iron. This is supported by the correlation between shorter T_1 and increased line broadening shown in Table 1.

The ^{13}C T_1 was measured for an optically clear single crystal of calcite as a function of crystal orientation relative to the magnetic field. Table 2 lists the chemical shift of the ^{13}C resonance at each

crystal orientation and the associated T_1. Virtually no variation of T_1 was observed with crystal orientation. The fact that the carbonate spins in a particular sample relax at the same rate, independent of orientation, is also confirmed by Figure (2) which shows the uniform recovery of the carbonate powder pattern in Austin chalk after saturation.

NMR APPARATUS

As described elsewhere,[8] two GE 2 Tesla CSI NMR 12 in. bore imaging/analysis spectrometers have been adapted for rock studies. The high field region of the Oxford Instruments superconducting magnet (± 5% of peak field) is about 2 feet long, which allows most of a 3 ft box of core to come to thermal equilibrium at the same time. The field homogeneity can be shimmed to better than 1 part in 10^6 over a 140 mm diameter spherical volume.

As shown in Figure (3), the whole core double resonance RF coil consists of a ^{13}C birdcage[9] coil 5 1/2 in. ID by 8 in. long, concentric with a larger ID ^1H birdcage coil 5 3/4 in. ID by 6 in. long. Because of the concentric configuration, the ^{13}C coil partially shortcircuits the ^1H coil, and a loss of sensitivity of about a factor of two is observed for the proton. This is not a problem, however, because of the high proton sensitivity and the large sample size. For the 5 1/2 in. coil the 90° RF pulse length for ^{13}C and ^1H is 150 and 200 microseconds, respectively.

The RF field homogeneity in the ^{13}C coil has been mapped using a small vial of ^{13}C–enriched methanol and found to vary by less than 5% in a cylindrical region 4 in. OD by 6 in. long. The high degree of field homogeneity is also demonstrated in Figure (4) which shows the ^{13}C integrated intensity from long glass bottles of various diameters filled with Soltrol, plotted versus the square of the bottle diameters.

DATA ACQUISITION

Because of the relatively long carbonate relaxation times, the sample positioning system and NMR acquisition have been automated to allow acquisition of both ^1H and ^{13}C signals in the shortest time consistent with full spin magnetization. This is important because of the large difference in ^{13}C T_1 between the carbonate spins (minutes) and the oil spins (seconds).

A nonmagnetic programmable table has been constructed which is controlled by output pulses from the CSI console. The core is placed on a precision translational drive consisting of a drive table and a takeup table on opposite sides of the NMR magnet. The tables are connected by a 5 in. ID Pyrex tube into which the core is inserted. The drive table has a 4 ft precision screw (5 turns/in.) driven by a rotary dc motor. This allows a 3–ft core to be conveniently imaged, after subtracting the length of the trolleys. A programmable table positioner (Unidex IIIA, Aerotech) controls table movement. Table movement is initiated by interrupt pulse from the CSI console to the Unidex sent after each acquisition is completed.

The automatic table enables the following interleaved sequence of ^{13}C and ^1H data acquisition, which is necessitated by the long ^{13}C carbonate T_1. First, the core is positioned so that the first 3 in. are centered in the coil. The core is then moved in 3 in. increments until ^1H data is obtained over the full 3 ft length. For the ^1H data, four 45° tip sequences with 3 second recycle time are used (acquisition time = 12 seconds). The ^1H spectra are stored after each acquisition.

The core is then backed up so the first 6 in. are centered in the RF coil and ^{13}C oil data acquisition is begun. Several hundred 45 degree tip sequences with short recycle time (~1 second, depending on oil T_1) are used to acquire the ^{13}C signals from the oil (acquisition time ~ 5 minutes). The ^{13}C carbonate signals are highly saturated during the oil acquisition , which improves discrimination of the aromatic oil peak overlapping the tail of the carbonate spectrum.

Since the ^{13}C oil acquisition takes several minutes, the ^{13}C carbonate spins in the next 6 in. section have had time to reach thermal equilibrium ($3xT_1$). Thus, as soon as the table moves to the next position, a single 90 degree pulse is used to acquire the carbonate data at the new position before the ^{13}C oil acquisition is begun. Thus the carbonate data acquisition requires essentially no additional measurement time.

RESULTS

Figure (5a) shows the ^{1}H-coupled ^{13}C NMR spectrum of cyclohexane-saturated Indiana limestone. The carbonate powder pattern has been highly saturated. The 1:2:1 multiplicity in the cyclohexane triplet pattern at 29 ppm is due to the magnetic coupling of the ^{13}C spin to the two adjacent equivalent protons. The central resonance is twice as intense as the outer peaks because there are two possible ways of pairing up the protons in an antiparallel configuration.

Figure (6a) compares the ^{1}H-coupled ^{13}C NMR spectrum of cyclohexane-saturated Bentheim sandstone, demonstrating the absence of the carbonate peak. Figure (6b) shows the ^{1}H-decoupled spectrum, where the cyclohexane triplet is collapsed to a single more intense peak with better signal-to-noise ratio by saturating the proton resonance using the ^{1}H coil. Under ^{1}H decoupling, irradiation of the proton spins forces them to undergo frequent flips between their two allowed alignments relative to the ^{13}C spin. The net spin of each proton is effectively averaged out and the ^{13}C spin no longer experiences a net coupling to the adjacent protons (whence the single resonance under decoupling conditions).

Table (3) shows the excellent agreement between prepared vs NMR-determined cyclohexane weight in 2 in. OD by 4 in. long core plugs of Indiana limestone and Bentheim and Berea sandstones using the ^{13}C aliphatic integral. The accuracy is 5% or better in each lithology.

Figure (7) shows the ^{1}H-coupled ^{13}C NMR spectrum of Indiana limestone saturated with N4RB crude. Note the small aromatic peak superimposed on the tail of the carbonate powder pattern. Broadband proton decoupling is not used with cores containing crude oils because the natural spread in chemical shifts of the different oil components (600 Hz) is considerably larger than typical carbon J-coupling (120 Hz). There is thus little narrowing of the oil bands under proton decoupling.

Figure (8a) is a single pulse ^{13}C NMR spectrum from a 4 in. OD sample of Indiana limestone saturated with N4RB crude (T_1 N4RB = 0.2 sec.). The sample was allowed to reach thermal equilibrium prior to the single pulse. In this spectrum both the carbonate and oil intensities are quantitative, but the aliphatic oil peak is very weak and the aromatic peak barely detectable relative to the carbonate. This is compared with Figure (8b) which shows the spectrum from the same sample but with 600 acquisitions, 45° partial flip and 1 second recycle time (acquisition time = 10 minutes). The aliphatic and aromatic oil peaks now dominate the spectrum, while the carbonate peak is highly saturated.

Several 500 gm mixtures were made with various fractions of reagent grade dolomite and calcite powder with Ottawa sand. Figure (9) shows the linearity of the ^{13}C carbonate integral from the mixtures versus moles of carbonate carbon. The accuracy is 5% or better except at the lowest concentration.

Figure (10) is a ^{13}C spectrum of whole core from the Monterey formation, showing the carbonate, aromatic, and aliphatic oil peaks. The heavy oil in this core is approximately 10° API gravity. The spectrum was acquired with a ten minute acquisition time with the core inside the fiberglass barrel. Dean Stark extraction for plugs from this core took approximately three months.

CONCLUSIONS

^{13}C NMR provides accurate, rapid, nondestructive measurements of inorganic and organic carbon in whole cores. Unlike the present industry practice, the organic and inorganic carbon is measured simultaneously on the entire core material. By using whole core, the measurement time has been reduced to only minutes per foot of core and includes both ^{1}H and ^{13}C NMR so that fluid-filled porosity and oil saturation are also determined.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of John Ferris and Larry Bielamowicz in performing these measurements.

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TABLES

Table 1

^{13}C Spin-Lattice Relaxation Times, T_1, and Line Broadening for Several Carbonate Minerals

Sample	T_1 (seconds)	HWHM (ppm)
Indiana Limestone	79	4.5
Leuders Limestone	40	10.0
Austin Chalk	78	4.5
Batesville Marble	25	14.5
Carthage Marble	69	4.3
Fischer Reagent-Grade Calcite Powder	90	2.7
Fossiliferous Dolomite	108	5.4
San Andres Dolomite	133	5.4
Bakers Dolomite	120	4.5
Dolomite Powder (1% Feldspar)	81	8.2

Table 2

Variation of T_1 With Angular Location For Single Calcite Crystal

Chemical Shift (ppm)	T_1 (seconds)
193.1	6.0 ± 0.8
180.4	6.3 ± 0.7
179.8	6.4 ± 0.8
161.1	6.8 ± 0.8

Table 3

Prepared vs NMR-determined Cyclohexane Weight (gm) in Various Core Plugs

Sample	Prepared	NMR-Determined	% Error
Indiana Limestone	21.98	22.4	-1.1
Bentheim Sandstone	37.11	36.7	+1.9
Berea Sandstone	33.48	31.8	-5.0

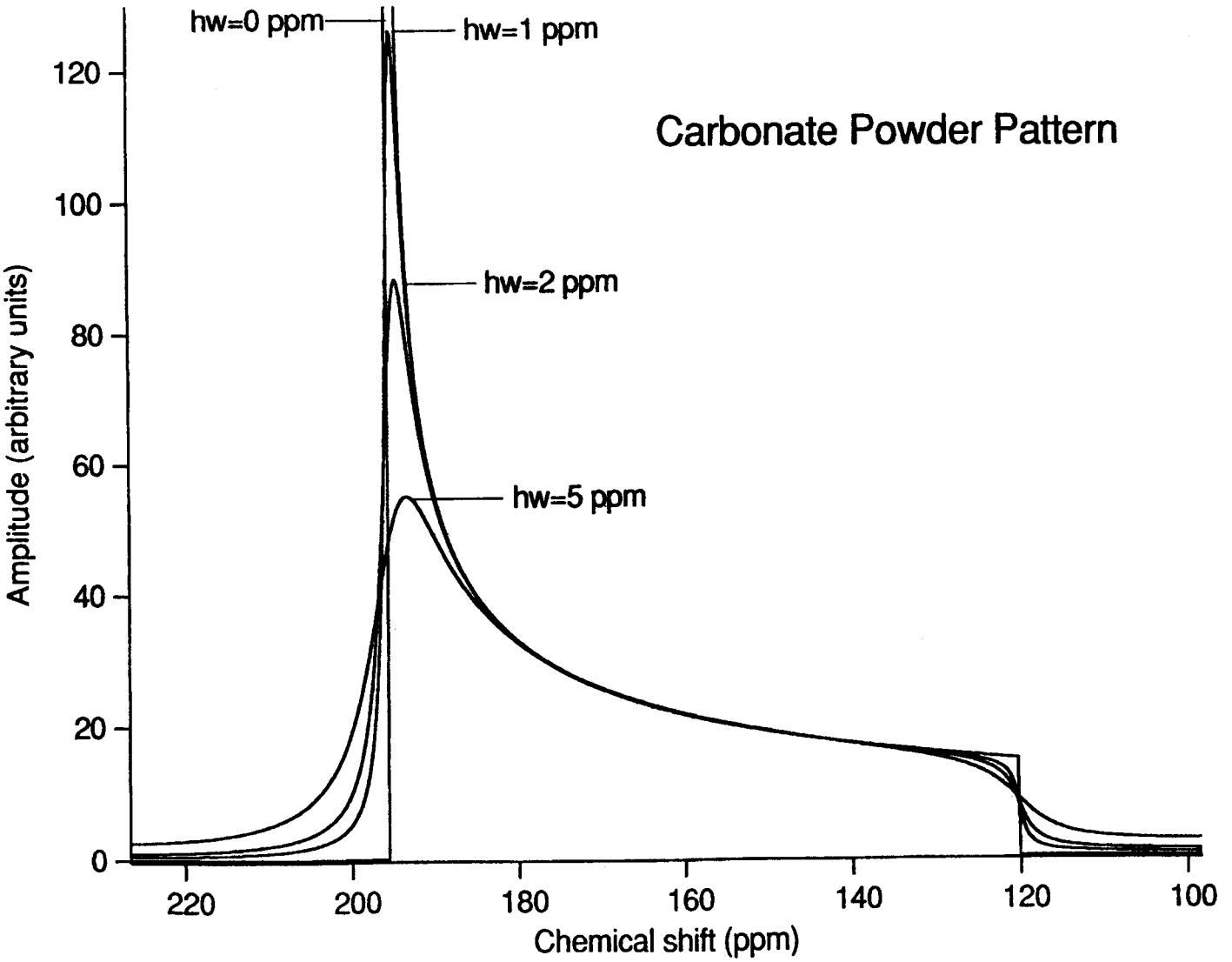

Figure 1: Powder patterns for axially-symmetric chemical shift tensor with different amounts of line broadening (half width at half maximum).

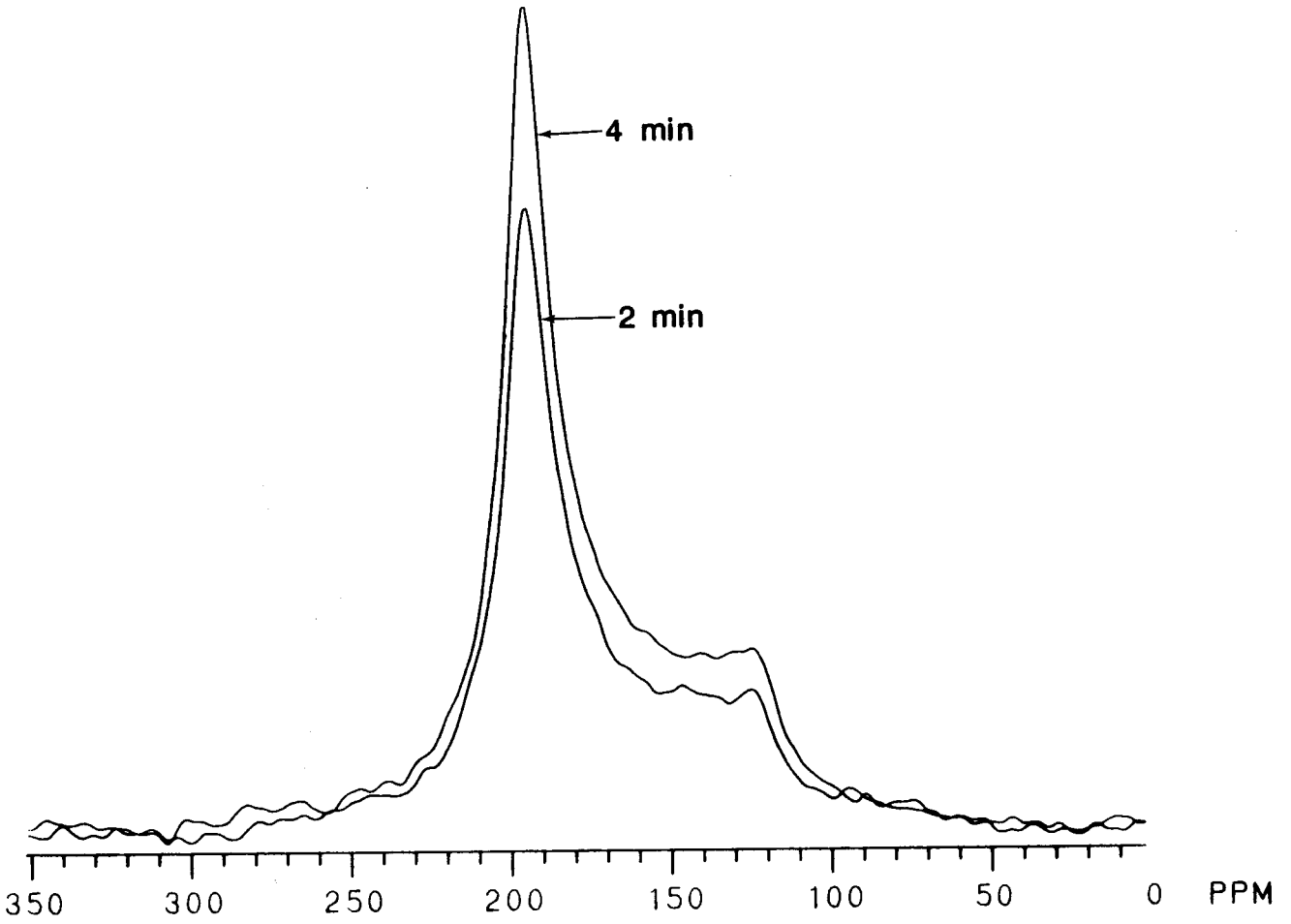

Figure 2: Recovery of carbonate powder pattern after saturation.

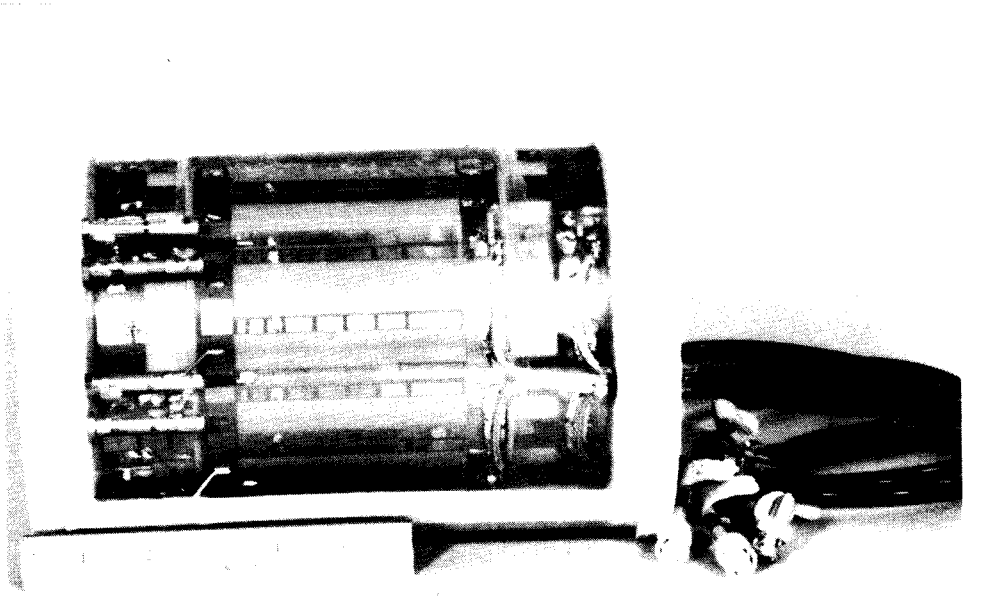

Figure 3: Photograph of double resonance 13C/1H 5 1/2 in. RF coil.

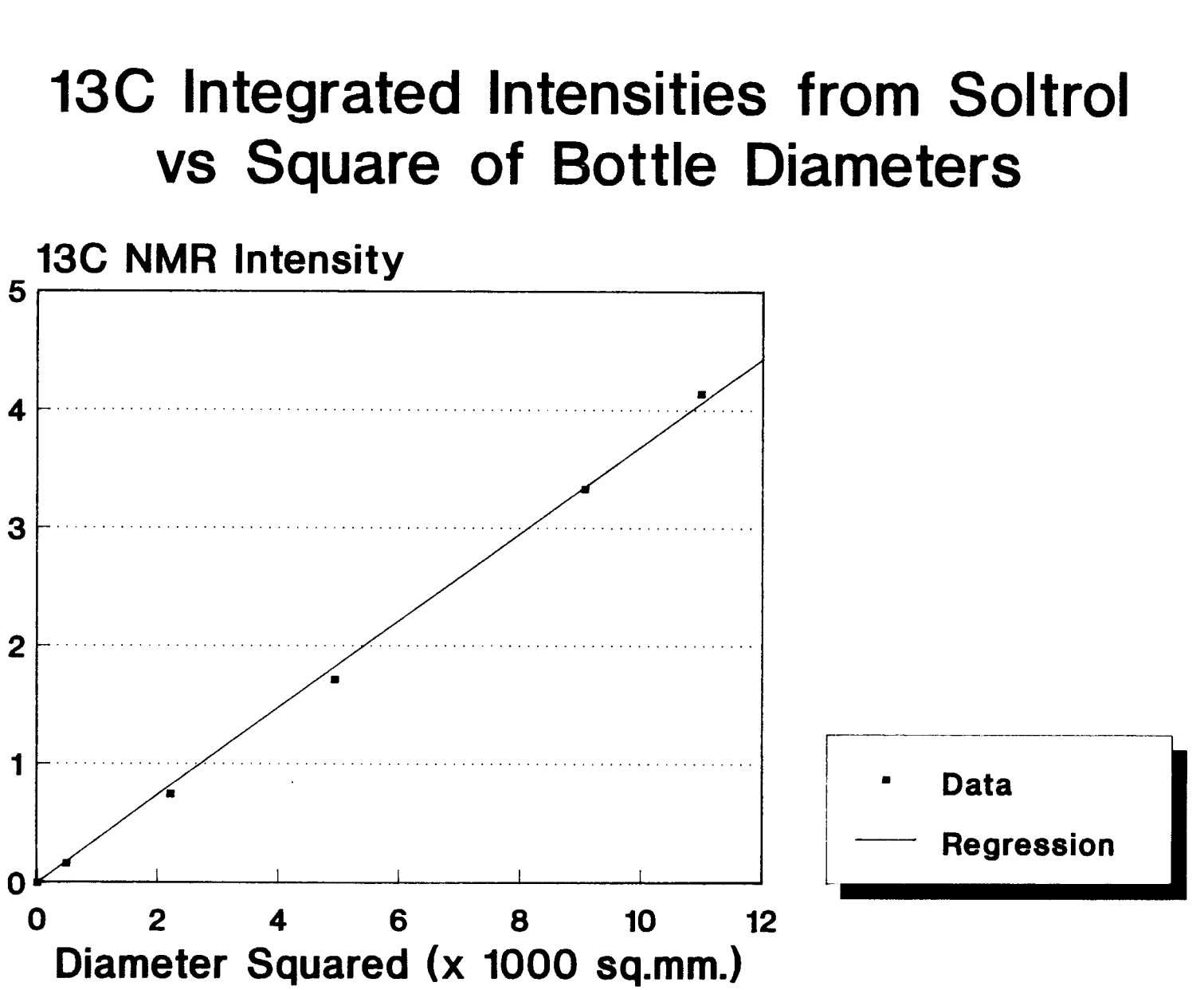

Figure 4: 13C integrated intensity from Soltrol-filled glass bottles vs square of diameters.

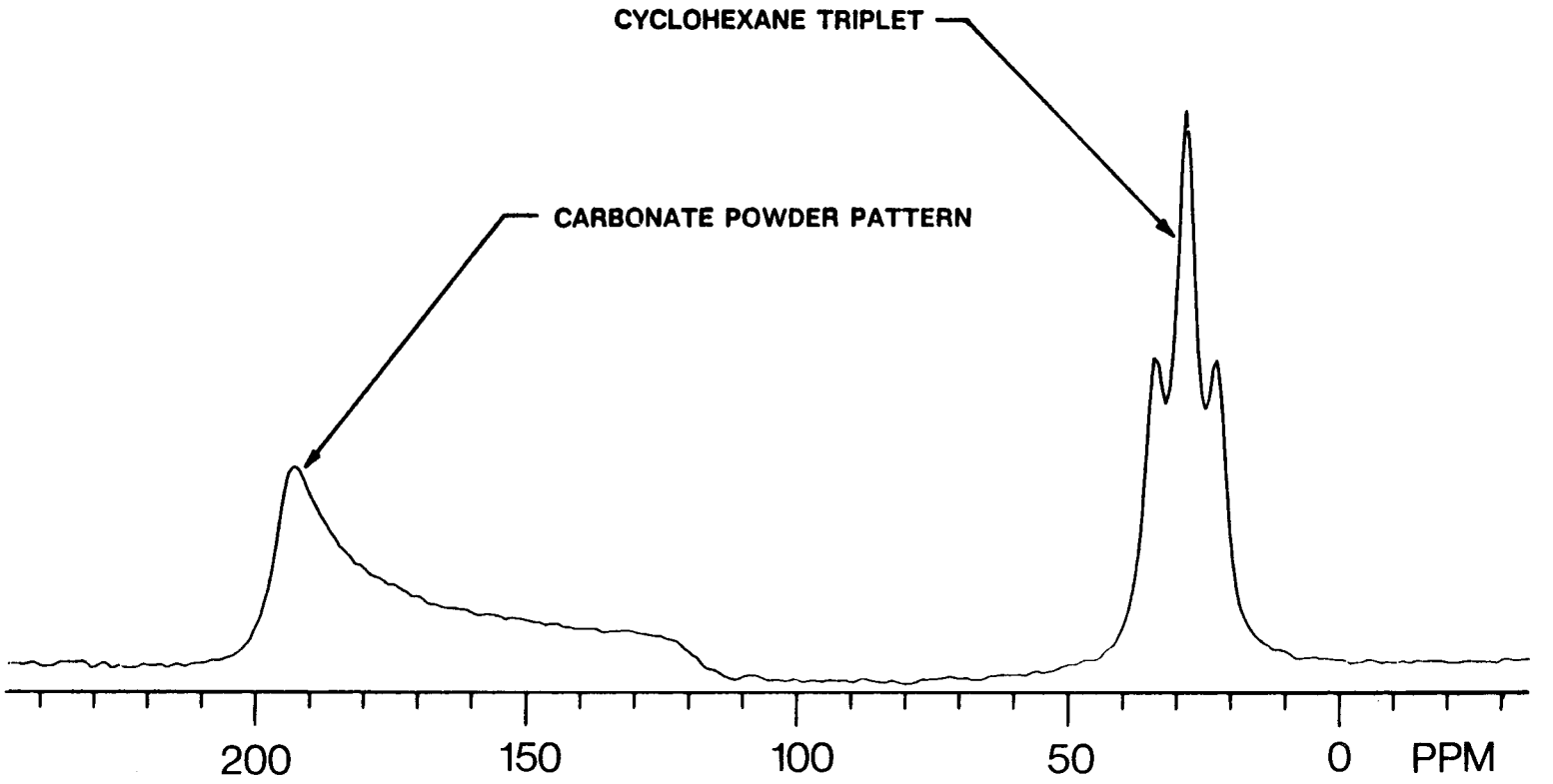

Figure 5: 13C spectrum of cyclohexane–saturated Indiana Limestone.

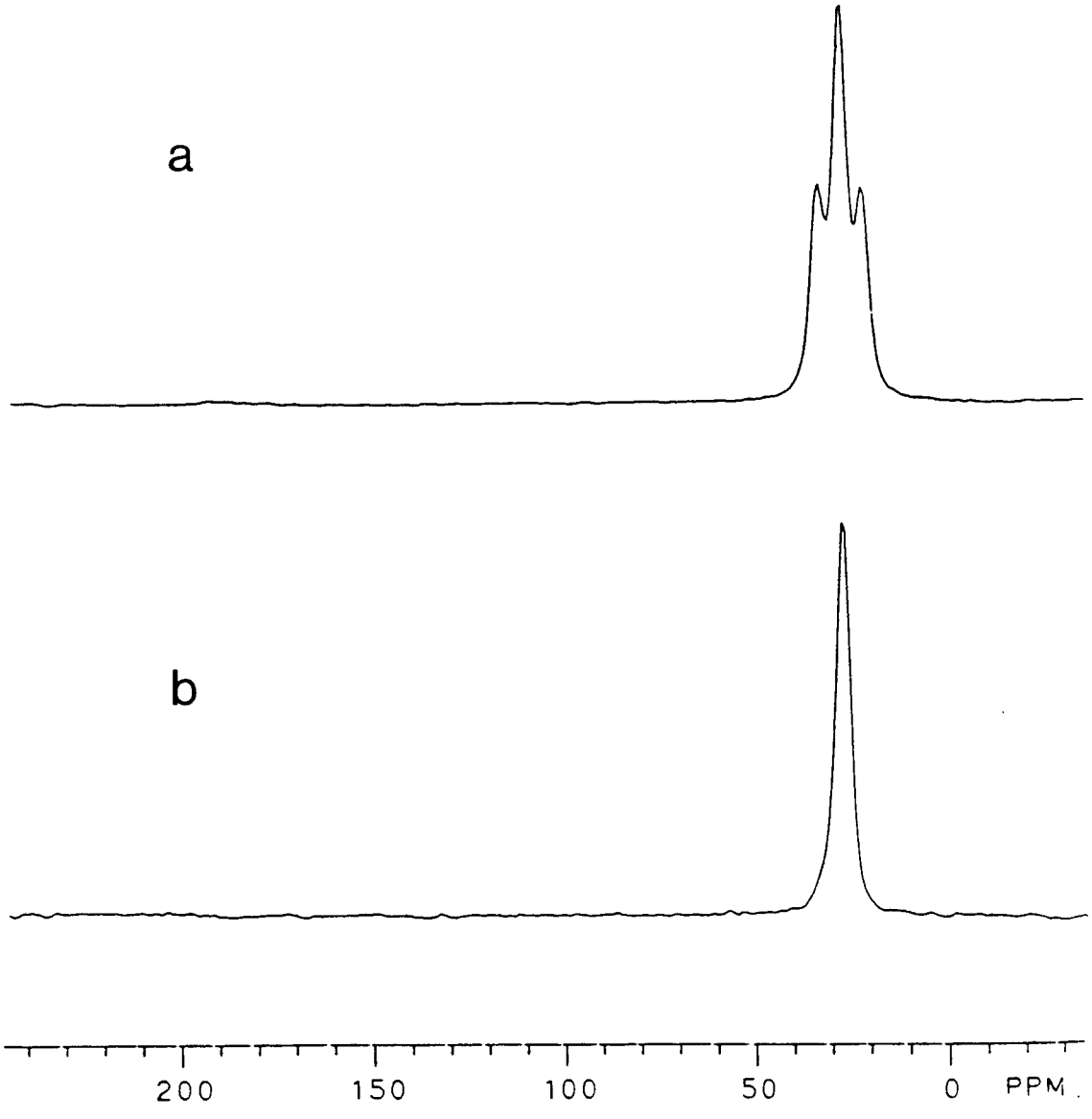

Figure 6: 13C spectrum of cyclohexane-saturated Bentheim Sandstone: (a) 1H-coupled, 256 scans; (b) 1H-decoupled, 128 scans.

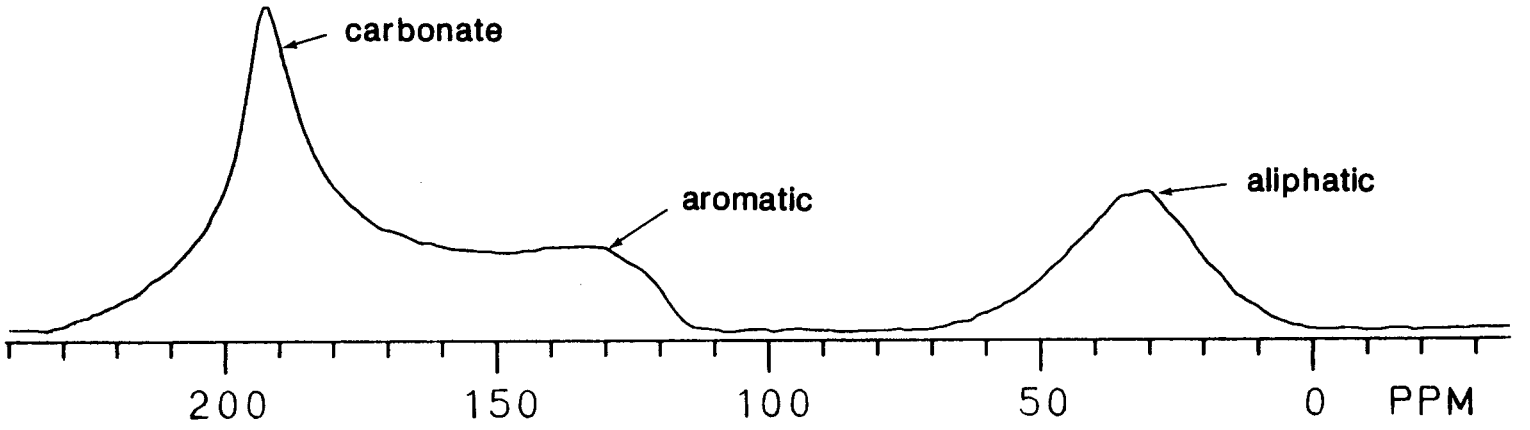

Figure 7: 13C spectrum of Indiana Limestone saturated with N4RB crude oil.

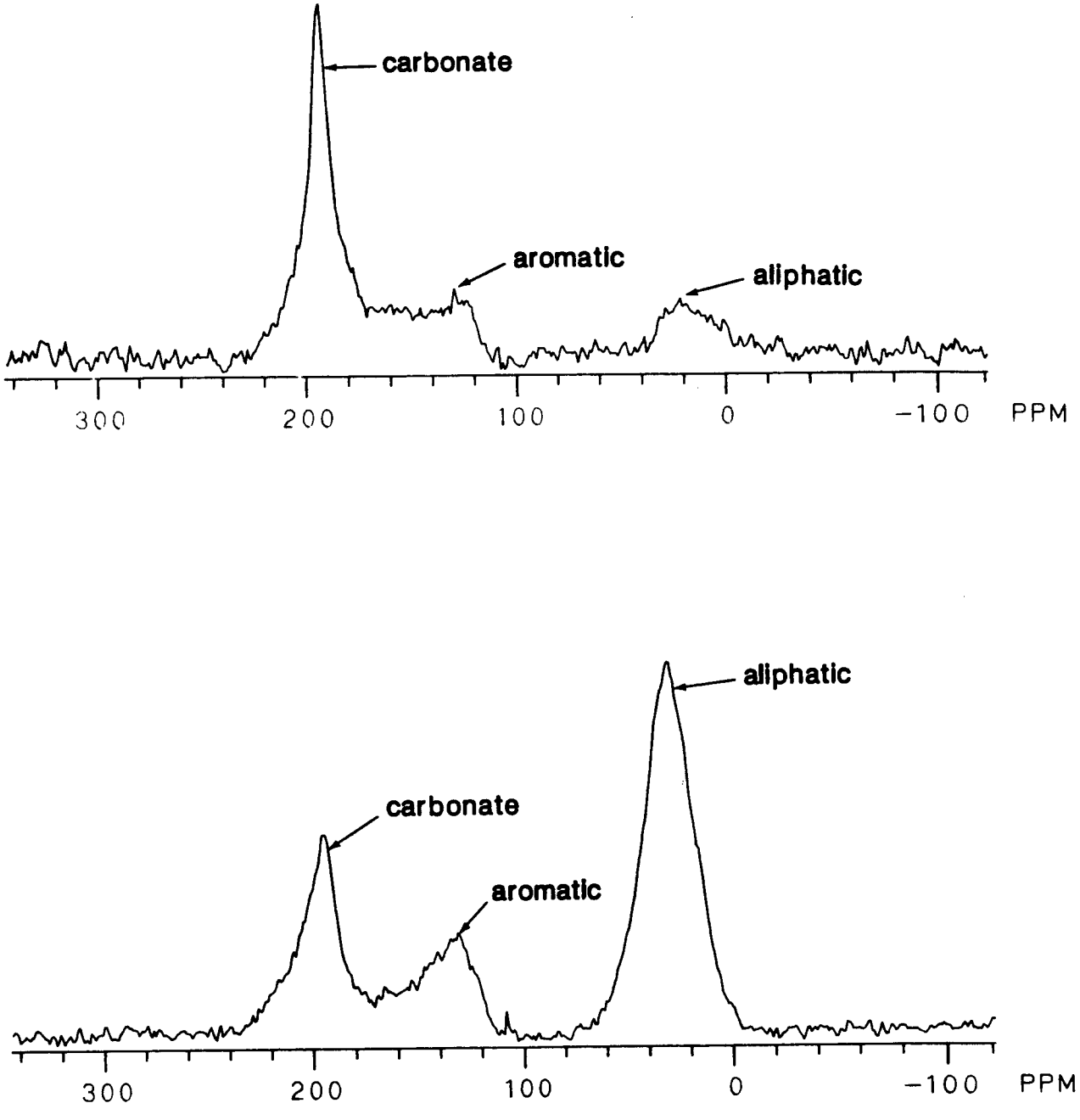

Figure 8: 13C spectrum of Indiana Limestone saturated with N4RB crude oil:
(a) single 90° pulse after reaching thermal equilibrium;
(b) 600 acquisitions, 45° partial flip, 1 second recycle time.

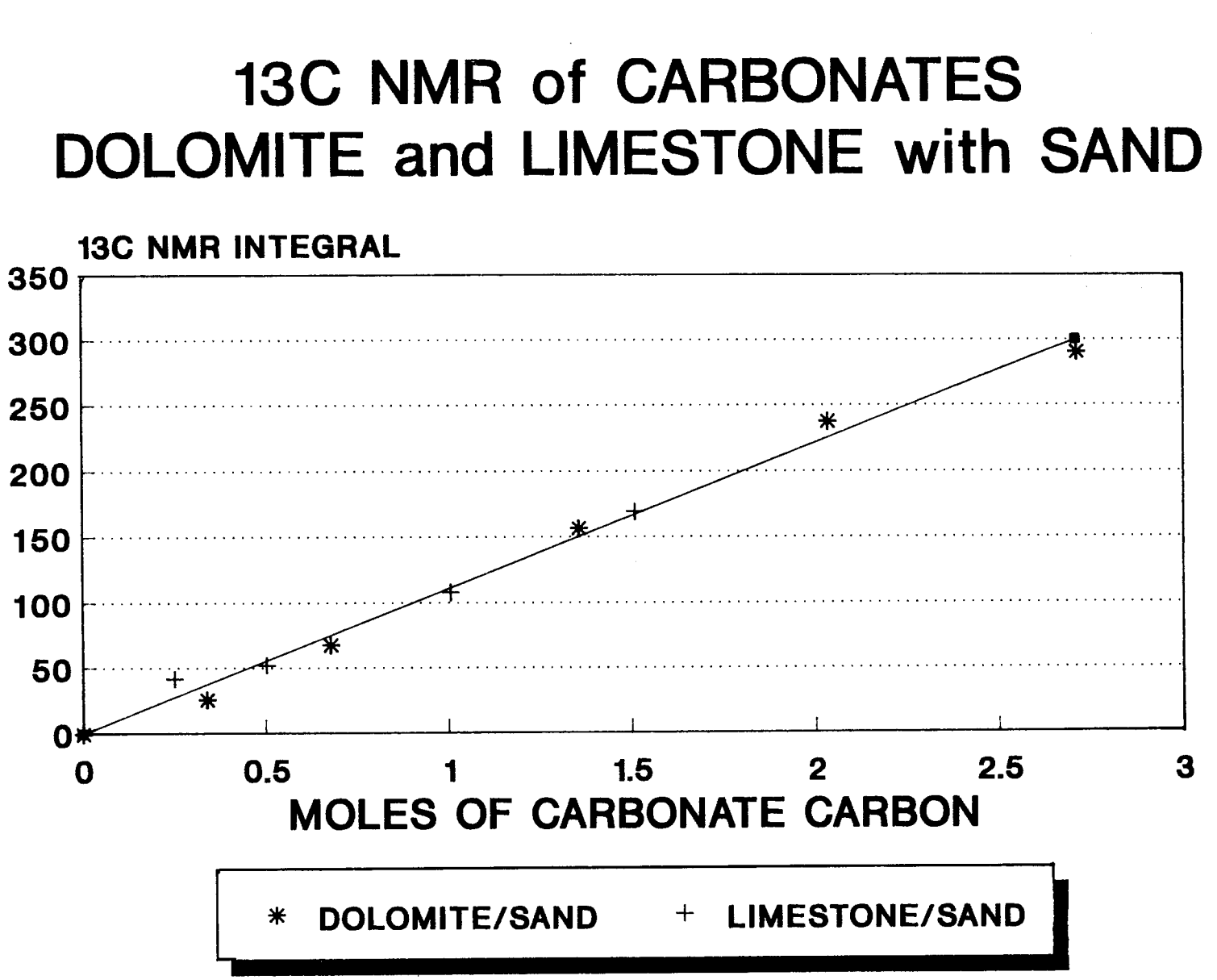

Figure 9: 13C integral verses moles of carbonate carbon for various fractions of dolomite and calcite powder with Ottawa sand.

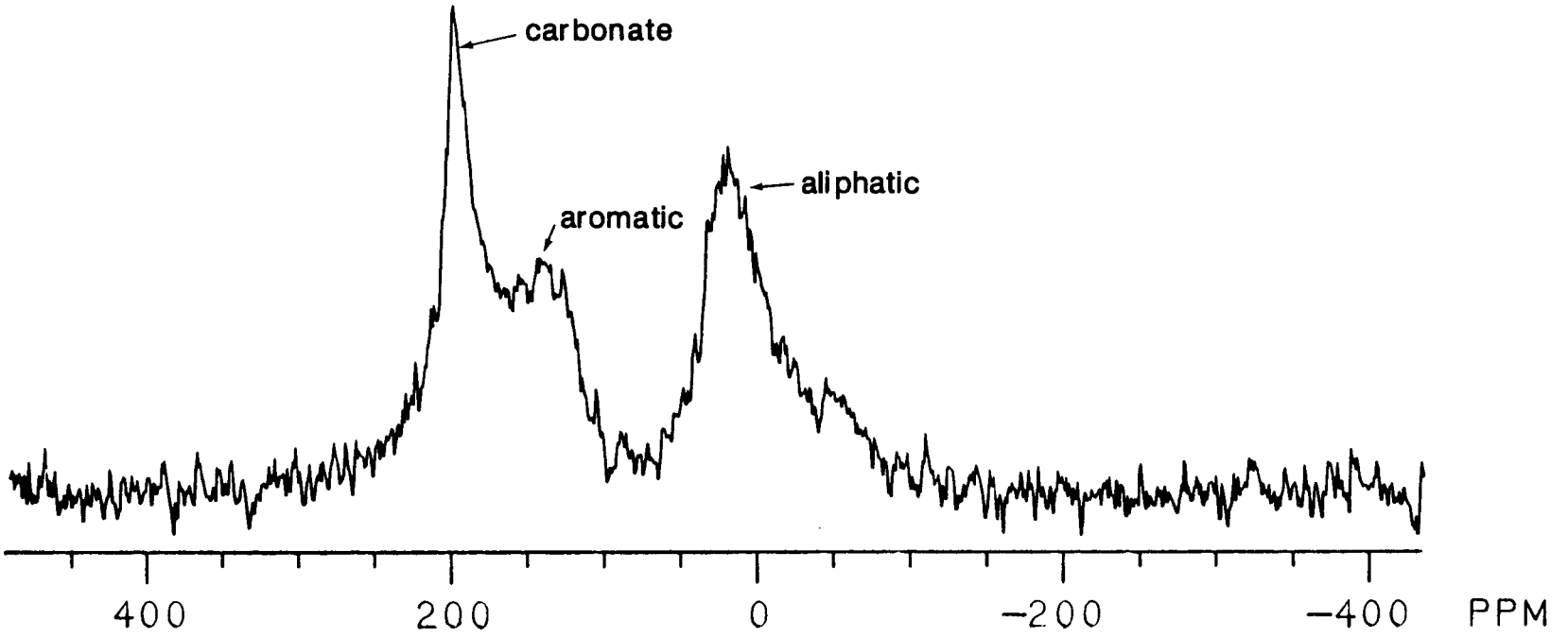

Figure 10: 13C spectrum of whole core from the Monterey formation.