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SOLID STATE ^{13}C NMR OF ISRAELI OIL SHALES

Tsevi Minster, Francis P. Miknis

Report GSI / 4 / 95
Jerusalem, January 1995

דו"ח מס' GSI / 4 / 95
ירושלים, שבט תשנ"ה

WESTERN RESEARCH INSTITUTE
The University of Wyoming Research Corporation

SOLID STATE ^{13}C NMR OF ISRAELI OIL SHALES

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ממצאים של בדיקות ^{13}C NMR (מצב מוצק) בפצלי שמן ישראליים ומשמעותם

תקציר

18 דוגמאות מייצגות של פצלי שמן ישראליים מ- 11 אגנים שונים , אשר גילן קמפאן עד מאאסטריכט תיכון, נבדקו בשיטת ^{13}C NMR Cross Polarization Magic-Angle Spinning (ריזוננס מגנטי אטומרי) ובמקביל גם לתכונות פיסיקליות וכימיות נוספות. מטרות העבודה היו לאמוד, באמצעות שיטה זו, את הפוטנציאל האנרגטי הגלום בפצלי השמן וכן לבחון האם ניתן להגדיר הבדלים ברי משמעות בין דוגמאות מאגנים שונים ומחלקי חתך שונים בהם.

התוצאות של בדיקות ה- Solid-state NMR מצביעות על דמיון רב המסתמן בין כל הדוגמאות שנאספו מתת הקרקע מהאגנים השונים שנבחנו וכן בין דוגמאות של תצורות מישאש וע'רב בחתך חבורת הר הצופים; כלומר, היחסים בין הפחמן האליפטי והארומטי המתקבלים בשיטה זו אינם מראים שינויים ברי משמעות בין הדוגמאות השונות. היחס הממוצע בין ערך היפק השמן (Fischer assay) לבין הערך של ההמרה לשמן (Oil conversion value) הוא סביב 59%, ערך המתאים לטווח הצר, יחסית (0.6-0.7), של מקטע הפחמן האליפטי. שיעור ההמרה (Conversion amount) של פחמן אורגני לשמן, אשר נמצא כמאפיין את הדוגמאות של פצלי השמן הישראליים אשר נבדקו, נמוך ביחס לפצלי השמן שבחתך של ה- Green River Fm. שבמערב ארה"ב אך גבוה באופן משמעותי בהשוואה לפצלי השמן ממזרח ארה"ב (Eastern oil shales). נצפתה מגמה של ערכים גבוהים יותר בפרמטרים של הארומטיות (Aromaticity) והצפיפות (Specific gravity) של השמן המופק בדוגמאות תצורת מישאש (מגיל קמפאן) ביחס לדוגמאות מתצורת ע'רב (מאאסטריכט).

בדוגמא יחידה אשר נדגמה ממחשוף (באיזור הור ההר, נחל צין) התקבל מרשם (spectrum) NMR שונה משל שאר הדוגמאות. התוצאה השונה נובעת, ככל הנראה, מחימצון מתקדם המביא לפירוק (Decomposition) חלקי של החומר האורגני. הבדל שכזה יכול להיות מוסבר גם על ידי שוני במקור החומר האורגני.

לשם השוואה מובאים מרשמי NMR אשר נתקבלו מאגנים אחרים מאיזור הים התיכון; אלה מירדן וממרוקו ובמידה מסויימת גם אלה שמספרד ומתורכיה מראים דמיון רב למרשמים שנמצאו בדוגמאות מאגנים של פצלי שמן בישראל.

Abstract

Representative samples from a wide range of oil shale occurrences in Israel, aging from Campanian to middle Maastrichtian, were analysed for their solid state ^{13}C NMR pattern and for some additional properties in an attempt to assess their energy potential and to examine if significant differentiations between various basins and strata can be determined.

The results point out on a great similarity which prevails between all subsurface samples from the different sampled basins and strata; thus, the aliphatic to aromatic carbon ratio determined by NMR does not show significant variations. The average Fischer assay to oil conversion value of all the samples is about 59%, a value which copes well with the relatively narrow range (0.6-0.7) of the aliphatic carbon fraction. The conversion amount of organic carbon to oil found in the Israeli samples is quite below that of the Green River oil shales but is considerably higher than that of the US Eastern oil shales. Higher trends of the aromaticity in the rocks and the specific gravity of the generated oils are indicated in the Mishash (Campanian) samples when compared to those of the Ghareb (Maastrichtian).

One surface sample showed a unique NMR response. It may be due to severe oxidation causing a partial decomposition of the organic material.

The generated NMR charts resembles responses of oil shales from other basins around the Mediterranean, in Jordan, Morocco, Spain and Turkey.

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^{13}C NMR Spectra of sample from the WRI archive:
I) Um Barek (= En Boqeq).
II) Ef'e (= Mishor Rotem).

Introduction

Solid-state nuclear magnetic resonance (NMR) techniques have gained a relatively wide usage during the 1980's in evaluating source rock potential (Miknis et al., 1979, 1982b; Miknis, 1982, 1992; Axelson, 1985; Wilson, 1987). In particular, the solid-state ^{13}C NMR techniques of cross polarization (CP) with magic-angle spinning (MAS), seem to be most applicable in assessing the potential of fossil fuels. Some of the advantages of this technique, as discussed by Miknis et al. (1982), are that measurements can be made on wholerock samples regardless of their non organic fraction content including mineral carbons, and are non-destructive so that limited quantity of sample material can be preserved for further research and analyses.

No data have been previously published on ^{13}C NMR properties of Israeli oil shales.

The aim of this study was to apply solid-state ^{13}C NMR techniques to examine samples from various localities and section units of oil shales from Israel, in an attempt to define properties, pinpoint differences between various basins and sequence units, and to contribute a better assessment on the potential for economical applications.

Oil shale basins in Israel

The Upper Cretaceous - Tertiary anoxic event in Israel has been indicated from rocks of Turonian to Eocene age. It is widely developed in rocks of the Mount Scopus Group, a schematic geological section of which is presented in Figure 1. Two formations of that group have been intensively studied as having economical potential - the Campanian Mishash Formation (which in its uppermost part contains, in places, economic phosphorites) and the overlying Maastrichtian Ghareb Formation of whose organic rich sediments have been traditionally termed "oil shale" in Israel athough their inorganic fraction is dominated by carbonates (Minster et al., 1992). The term "oil shale" will be attributed here to all domestic organic rich sediments which have some outcrops, especially in the northern and eastern Negev. However, their significant horizontal and vertical distribution can be studied basically out of data gathered from the subsurface. General location of the main oil shale bodies in Israel is shown on Figure 2.

Present estimations of oil shale reserves in Israel are in the magnitude of several tens of billion tons. More than half are burried east of the central coastal plain, on the foothills of the Judea Mountains, a region known as the Shephela. Those vast resources are very significant, especially in a country where most of the energy consumption is based upon imported oil and coal. Theoretically, these resources have the potential of solving all of Israel's energy demands for several centuries. Therefore the oil shales have attracted research and development efforts, especially in the last 20 years.

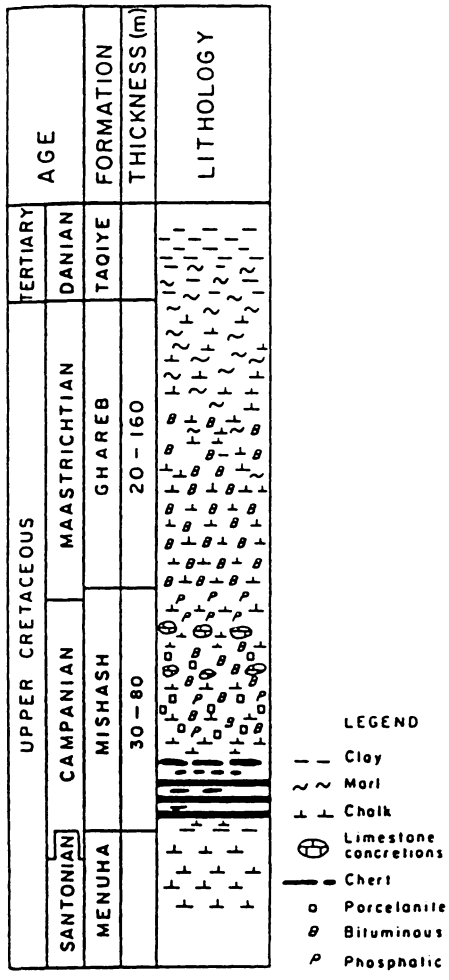
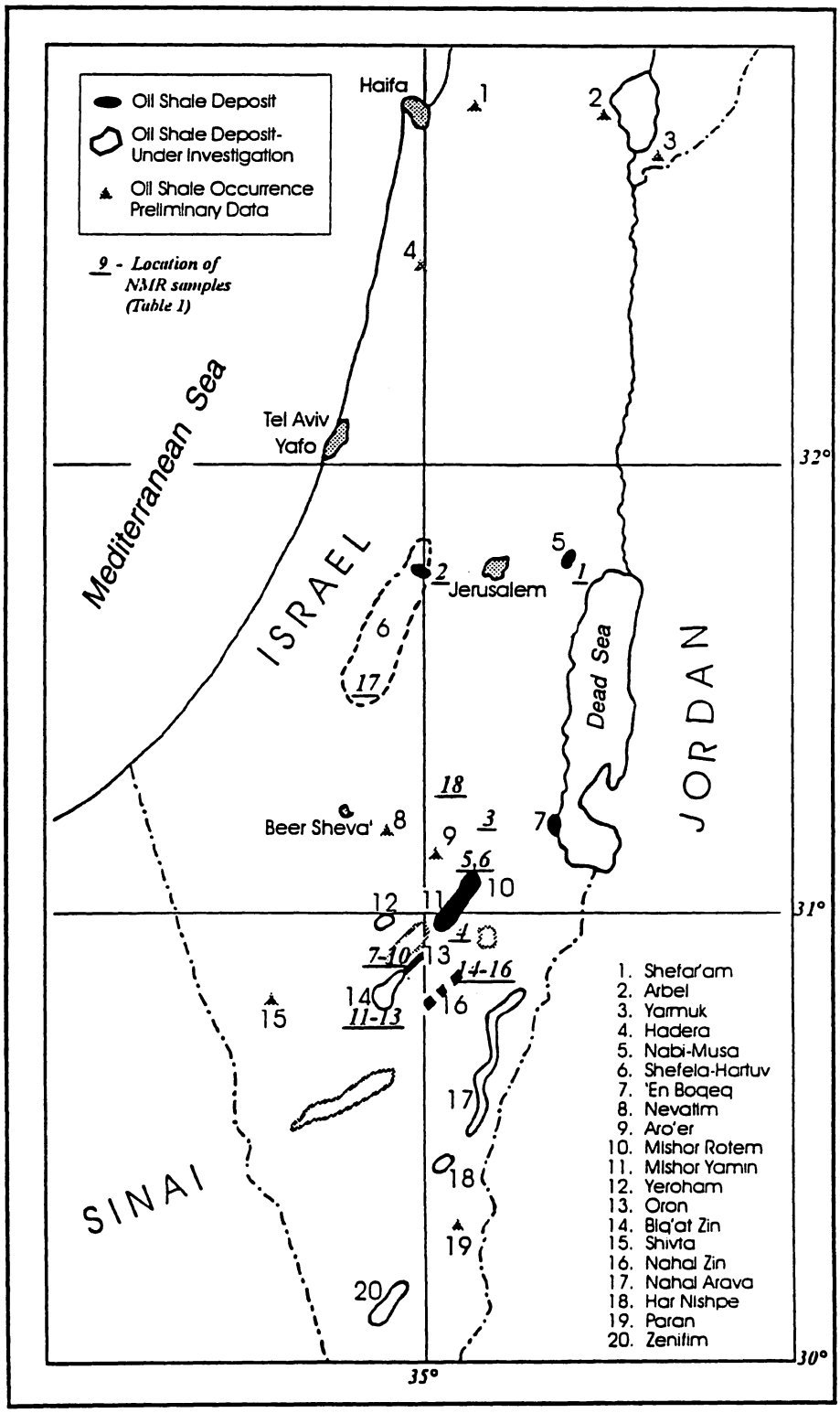


Figure 1. Schematic Columnar Geological Section of the Mount Scopus Group in the Northern Negev

Figure 2. Map of the Main Oil Shale Fields in Israel (modified after Shirav & Minster, 1984) and Locations of Studied Samples.



Recently a technological breakthrough towards generating electricity from Israeli oil shale was achieved and the planning of a 75MB oil shale power station has begun (Kaiser, 1993).

With remarkable reserves indicated from neighboring countries and in particular Jordan and Syria, this energy resource may be a topic for future, mutual research and utilization.

The inorganic chemistry of some Israeli oil shales was summarized by Shirav & Ginzburg (1983).

Samples

Most of the samples chosen for the study were from the subsurface, and were prepared by combining originally collected 1 m (from core or cuttings drillhole) samples to composite samples, representing sequences of 5-20 m thick. In one case, (Borehole Sheqef-1, sample 17), in which only scattered samples were originally collected, a sample representing a section greater than 100 m was prepared. One sample (no. 15) was taken from an outcrop (Nahal Zin locality). In all, the samples were collected from 11 different localities in the central and southern parts of Israel, particularly from the basins of the northeastern Negev. Of the 18 studied samples, 8 were from the Upper Campanian sequence (Mishash Fm.) and 10 from the overlying Ghareb Fm. (Maastrichtian).

Preliminary data on the studied samples is given in table 1 and their locations are shown also on the location map (figure 2).

Analytical procedure

1) ^{13}C NMR procedure

^{13}C NMR meausurements were carried out on a JEOL FX-60Q NMR spectrometer modified for cross polarization (CP) and magic-angle spinning (MAS). CP/MAS spectra were recorded under the following conditions: 15.1 MHz ^{13}C frequency, 0.5 s pulse delay, 1 msec contact time, 32 msec acquisition time, and a spinning rate of 2.5 kHz. Typically, 40,000 to 60,000 transients were recorded, depending on the organic carbon in the sample.

Carbon aromaticity integrations covered the range of 360 to -160 ppm. This large range was required to include contributions from spinning sidebands to the aromatic carbon integrals. For all the samples the region between 340 and 100 ppm was considered as the aromatic carbon region. The region between -20 and 100 ppm was considered as the aliphatic carbon region, and the integrated sideband intensity between -20 and -80 ppm was added to the aromatic carbon integral. Aromaticity results are given in Tables 2 and 3.

Table 1. Data on the studied samples:

Sample No.	Oil Shale Basin	Borehole/ Sample Id.	From (m.)	To (m.)	TOC (%) ***	Formation *
1	Nabi-Musa	NM-4	43	62	14.5	G
2	Hartuv	ZRB-1	67	77	10.8	G
3	Hatrurim	H-1	80	101	10.5	G
4	Yamin	Bit-59	173	182	14.1	G
5	Rotem	Bit-89	53	66	3.2	M
6	Rotem	Bit-97	52	69	14.6	G
7	Oron, North	OS-17	52	65	15.6	G
8	Oron, North	OS-17	67	77	5.3	M
9	Oron, North	OS-17	85	91	14.3	M
10	Oron, South	OP-10	146	164	11.1	M
11	Sde-Boqer	NS-20	73	83	13.4	G
12	Sde-Boqer	NS-20	108	115	11.1	M
13	Biq'at Zin	NS-28	220	228	11.1	M
14	Nahal Zin	D-1	14	21	12.8	G
15	Nahal Zin	TZ	**	**	11.9	G
16	Nahal Zin	ZS-10	24	29	12.2	M
17	Shefela	Sheqef-1	445	568	12.7	G
18	Biq'at Arad	M-8	361	377	13.2	G

* - G = Ghareb Fm.; M = Mishash Fm.

** - Outcrop sample.

Table 2. Summary of results and calculations for the Ghareb Fm. samples:

		Sample No.	1	2	3	4	6	7	11	14	15	17	18	Averages
		TOC (%)	14.5	10.8	10.5	14.1	14.6	15.6	13.4	12.8	11.9	12.7	13.2	13.1
		H (%)	1.5	1.4	1.4	1.6	1.7	1.8	1.5	1.4	1.3	1.4	1.5	1.5
		H/C	1.24	1.56	1.60	1.36	1.40	1.38	1.34	1.31	1.31	1.32	1.36	1.38
		N (%)	0.26	0.34	0.26	0.36	0.40	0.33	0.29	0.35	0.45	0.3	0.31	0.33
		S (%)	0.93	2.20	2.60	0.63	3.00	2.90	2.60	2.7	2.1	2.1	2.5	2.21
Yield		Oil Yield	9.5	5.4	5.9	7.9	8.6	9.6	9.3	7.2	2.9	7.2	8.4	7.45
	Weight	Water	1.4	4.7	3.4	5.6	2.2	5.0	2.4	2.3	6.9	*	2.9	3.68
of		Spent Shale	86.0	85.8	87.4	82.0	84.1	80.2	84.2	85.3	83.7	*	84.5	84.32
	Percent	Gas + loss	3.2	4.1	3.0	4.5	5.1	5.1	4.1	5.2	6.6	*	4.2	4.5
Product	Gal	Oil	23.6	13.5	14.9	19.5	21.4	23.9	23.1	17.8	7.5	*	20.9	18.6
	p/Ton	Water	3.4	11.3	8.6	13.5	5.3	12.0	5.8	5.5	16.6	*	7.0	8.9
	Oil Specific	Gravity	0.981	0.962	0.955	0.965	0.964	0.967	0.968	0.967	*	*	0.961	0.963
	NMR	<270	0.022	0.017	0.006	0.006	0.011	0.010	0.013	0.000	0.013	0.012	0.012	0.011
	readings	270-165	0.076	0.123	0.101	0.072	0.088	0.066	0.084	0.076	0.150	0.107	0.102	0.090
	for	165-100	0.264	0.185	0.208	0.191	0.197	0.176	0.195	0.192	0.183	0.198	0.195	0.200
	each	100-50	0.134	0.172	0.148	0.167	0.169	0.169	0.143	0.151	0.147	0.159	0.110	0.152
	fraction	50-(-20)	0.471	0.464	0.499	0.519	0.486	0.538	0.539	0.543	0.461	0.480	0.544	0.508
		-20-(-100)	0.032	0.040	0.039	0.045	0.049	0.041	0.026	0.038	0.046	0.044	0.038	0.039
	Aromaticity		0.395	0.364	0.353	0.313	0.345	0.293	0.318	0.306	0.392	0.361	0.346	0.379***
	% Converted to oil		65.5	50.0	56.2	56.0	58.9	61.5	69.4	56.3	24.4	56.7 **	63.6	59.79***

* - Not analysed.

** - Calculated.

*** - Excluding sample 15.

Table 3. Summary of results and calculations for the Mishash Fm. samples:

		Sample No.	5	8	9	10	12	13	16	Averages
		TOC (%)	3.2	5.3	14.3	11.1	11.1	11.1	12.2	9.58
		H (%)	0.4	0.6	1.6	1.1	1.3	1.2	1.4	1.09
		H/C	1.50	1.36	1.34	1.19	1.41	1.30	1.38	1.35
		N (%)	0.10	0.14	0.32	0.22	0.24	0.22	0.32	0.22
		S (%)	0.17	0.22	2.80	2.40	2.30	2.10	2.50	1.78
Yield of Product	Weight Percent	Oil Yield	4.6	2.9	7.2	6.9	6.6	7.4	7.8	6.2
		Water	1.8	2.0	3.4	2.3	2.0	1.7	2.6	2.26
		Spent Shale	95.2	93.1	85.1	87.5	88.7	87.5	85.9	89.00
		Gas + loss	1.3	2.1	4.3	3.3	2.7	3.3	3.7	2.96
	Gal p/Ton	Oil	4.3	7.1	17.6	17.0	16.4	18.3	19.1	14.26
		Water	4.3	4.8	8.1	5.5	4.8	4.1	6.2	5.4
	Oil Specific Gravity		0.952	0.972	0.983	0.977	0.972	0.974	0.975	0.972
	NMR readings for each fraction	<270		0.015	0.033	0.015	0.014	0.016	0.007	0.017
		270-165		0.102	0.092	0.101	0.085	0.084	0.070	0.089
		165-100		0.197	0.220	0.233	0.214	0.220	0.196	0.213
		100-50		0.142	0.155	0.160	0.149	0.136	0.150	0.149
		50-(-20)		0.492	0.447	0.460	0.495	0.504	0.528	0.488
		-20-(-100)		0.052	0.053	0.031	0.043	0.040	0.050	0.045
	Aromaticity		*	0.366	0.398	0.380	0.356	0.360	0.322	0.364
	% Converted to oil		53.1 **	54.7	50.3	62.2	59.5	66.7	63.6	58.59

* - Not analysed (small amount).

** - Calculated.

2) Additional analyses

The traditional method for evaluating the potential oil yield of an oil shale is the Fischer assay (ASTM method D3904-80). The Fischer assay (FA) consists of heating a 100 gram samples of -8 mesh (2.38 mm) particle size oil shale to 500°C at a 12°C/min rate and maintaining this temperature for 40 min. During this heating cycle, hydrocarbon vapors are distilled from the rock and are condensed at 0°C to form a shale oil. The material is collected, its volume and weight are recorded and the specific gravity is measured. From these measurements, the potential is calculated as gallons of oil per ton of shale. Fischer assay results are given in Tables 2 and 3.

Elemental analyses (CHNS) and mineral carbon were obtained using standard instrumental methods. Carbon, hydrogen and nitrogen were determined on a Perkin Elmer Model 240C CHN Analyzer; sulfur was determined using a Fischer Model 472 analyzer, and mineral carbon was determined using a Coulometrics CO_2 analyzer. Results of the elemental analyses are given in Tables 2 and 3.

Results

Examples of CP/MAS ^{13}C NMR spectra of Israeli oil shales are presented on Figure 3 (A-D). The results are summarized also in Tables 2 (data on the Ghareb Fm. samples) and 3 (data on the Mishash Fm. samples), including the organic carbon, elemental organic results and Fisher assay data. The oil yield values (in Gal/Ton units) for those samples are also presented in relation to their organic carbon content (Fig. 4).

Discussion

The samples from the Ghareb Fm. are richer in their organic matter content than those of the Mishash Fm. (averages of 13.1% and 9.76% TOC, respectively). This is a known observation from prospection on numerous samples from both formations (T. Minster, pers. com.)

The similarity between the NMR spectra of most of the samples, regardless of their location or age, is obvious. A very similar spectrum was encountered previously by a sample from En Boqeq locality (Appendix I). The calculated carbon aromaticity values are between 0.3 and 0.4, with a higher average characterizing the Mishash Fm. samples (0.364) than those of the Ghareb Fm. (0.344). The fraction of the aliphatic carbons for all the samples has a range of 0.6 to 0.7 and this may serve as a better conversion indicator as the aromatic carbon values may also contain contributions from carbonyl and carboxyl carbons, if present.

Figure 3. Examples of ^{13}C NMR spectra of some Oil Shale samples

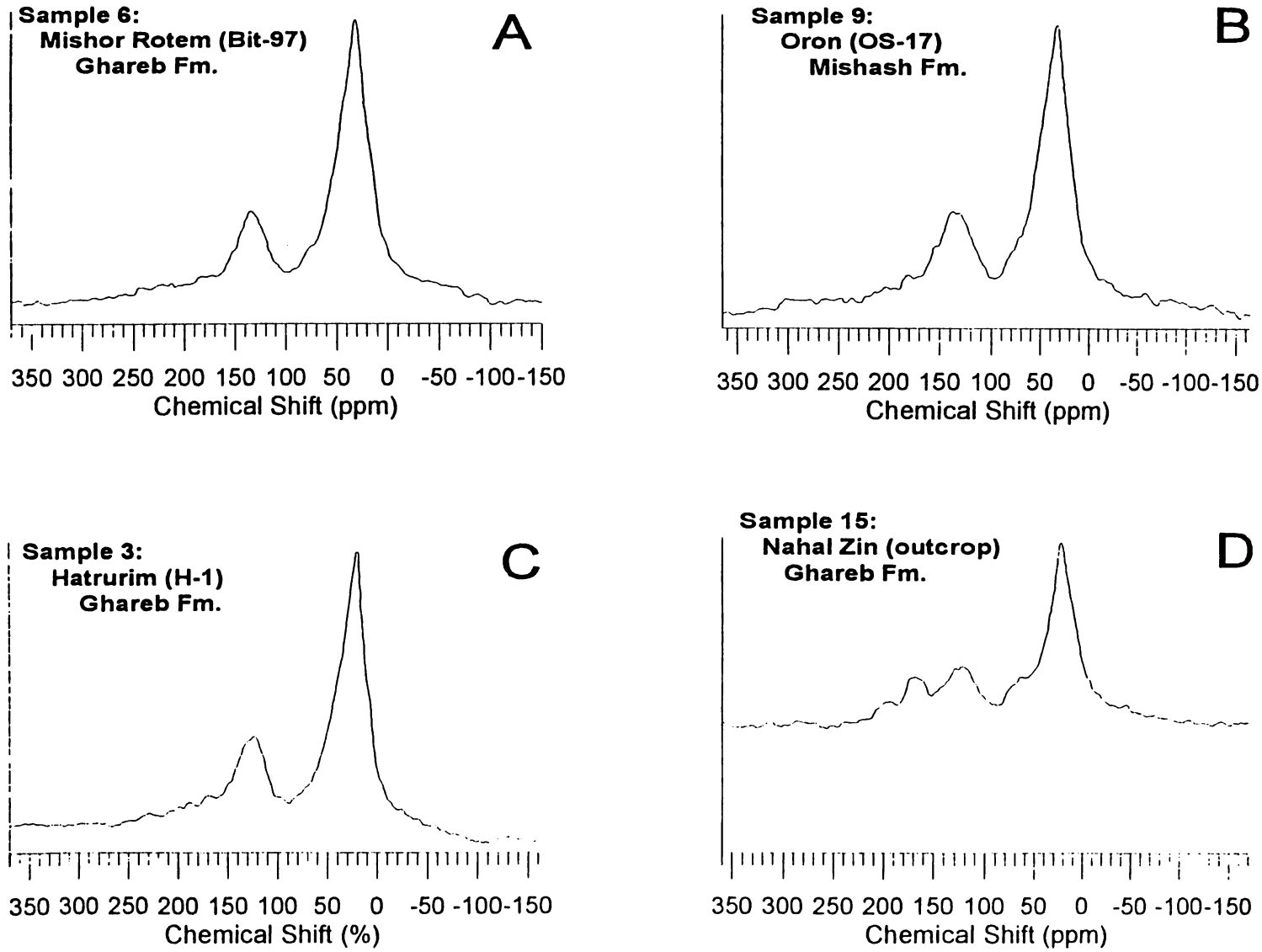
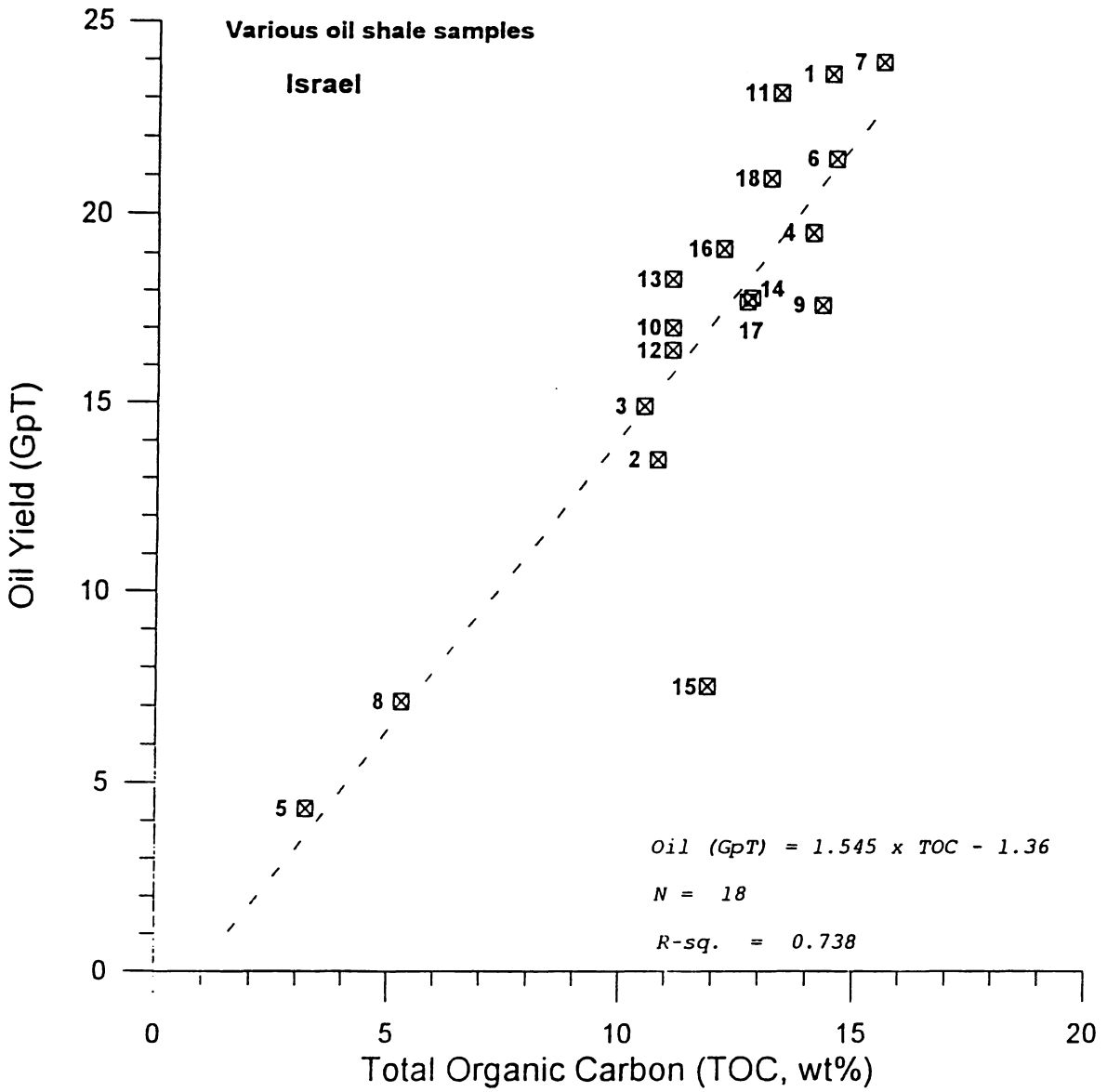


Figure 4. Oil Yield vs. Organic Carbon Values of the Examined Samples



The aliphatic carbon values explain why the % conversion of organic carbon to wt% of generated oil ranges from about 50 to 65% (Miknis, 1992). The % conversion values obtained have almost identical averages for both studied rock formations (Mishash and Ghareb) - around 59%.

There also appears to be a trend of higher values of the specific gravity of the generated shale oils found for the Mishash Fm. samples compared to the Ghareb Fm. ones (0.972 and 0.963, respectively, average values). This difference may need explanation probably not given by the present NMR spectra.

The number of samples from each basin was too small to follow tiny differences between them in the NMR response; the small number of samples does not also provide any hints on possible variations within the Mishash (the lower unit and the Phosphorite Member) or the Ghareb (lower and upper part) formations.

The only sample which was collected from an outcrop (in Nahal Zin, no. 15, Fig. 3D) has different pattern to the rest from the subsurface and behaves in a very anomalous way. The sample was taken from an exposure in an area in which extremely high day-temperatures prevail in summer and has a unique field appearance, i.e. brown colors (which differ from all domestic exposures) and contains oil-stained chips in significant amounts. The NMR spectrum of this sample possesses much more resolution than seen in most oil shales samples, particularly in the aromatic carbon region. Significantly more oxygenated carbons (160-210 ppm) in that sample were observed than in the others.

The oxygenated carbons are mostly distinguished in two ranges - ~210 ppm carbonyl carbons as in ketones and aldehydes and 180 ppm carboxyl carbons as in carboxyl acids; also, a 70 ppm peak as in aliphatic ethers and alcohols was recorded. The higher oxygen content may explain why the sample has a low conversion to oil (~25%), given its 11.9% TOC, and reasonable aliphatic carbon value(.608). This sample also produces the most gas, which is probably CO_2 from the carboxylate carbons, and the most water. Sample from same location was found to be rich in fatty acids (Shiloni, 1988), which is compatible with the presented NMR spectra. It is suggested that this sample reflects a partial degradation of the organic matter due to oxidation rather than containing different source material which may be richer in terrestial components.

It should be also mentioned that a sample (no. 3, Fig. 3C) collected from the south Hatrurim ("Mottled Zone") basin, where most of the rocks underwent in-situ combustion and were thus metamorphosed, has the same pattern as the other subsurface samples and no changes due to substantial heating history could be detected.

NMR charts from various oil shale basins around the Mediterranean are shown on Fig. 5. and compared to the Israeli ones. The similarity between the analysed samples from Israel (fresh material), Jordan, Morroco, Spain and to some extent Turkey, is evident.

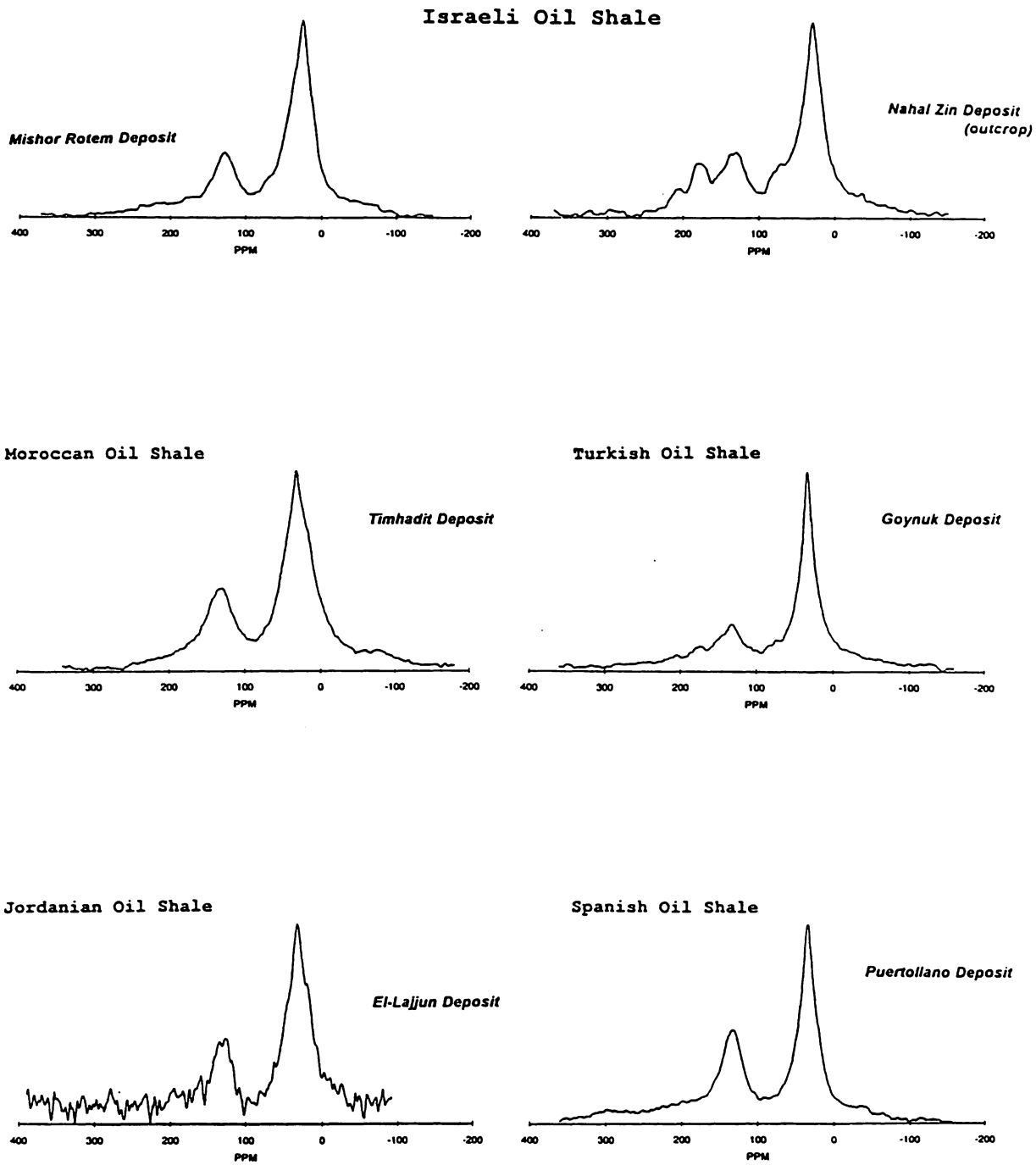


Figure 5. Comparison of ^{13}C NMR Spectra Encountered herein and Data from Various Oil Shale Basins around the Mediterranean.

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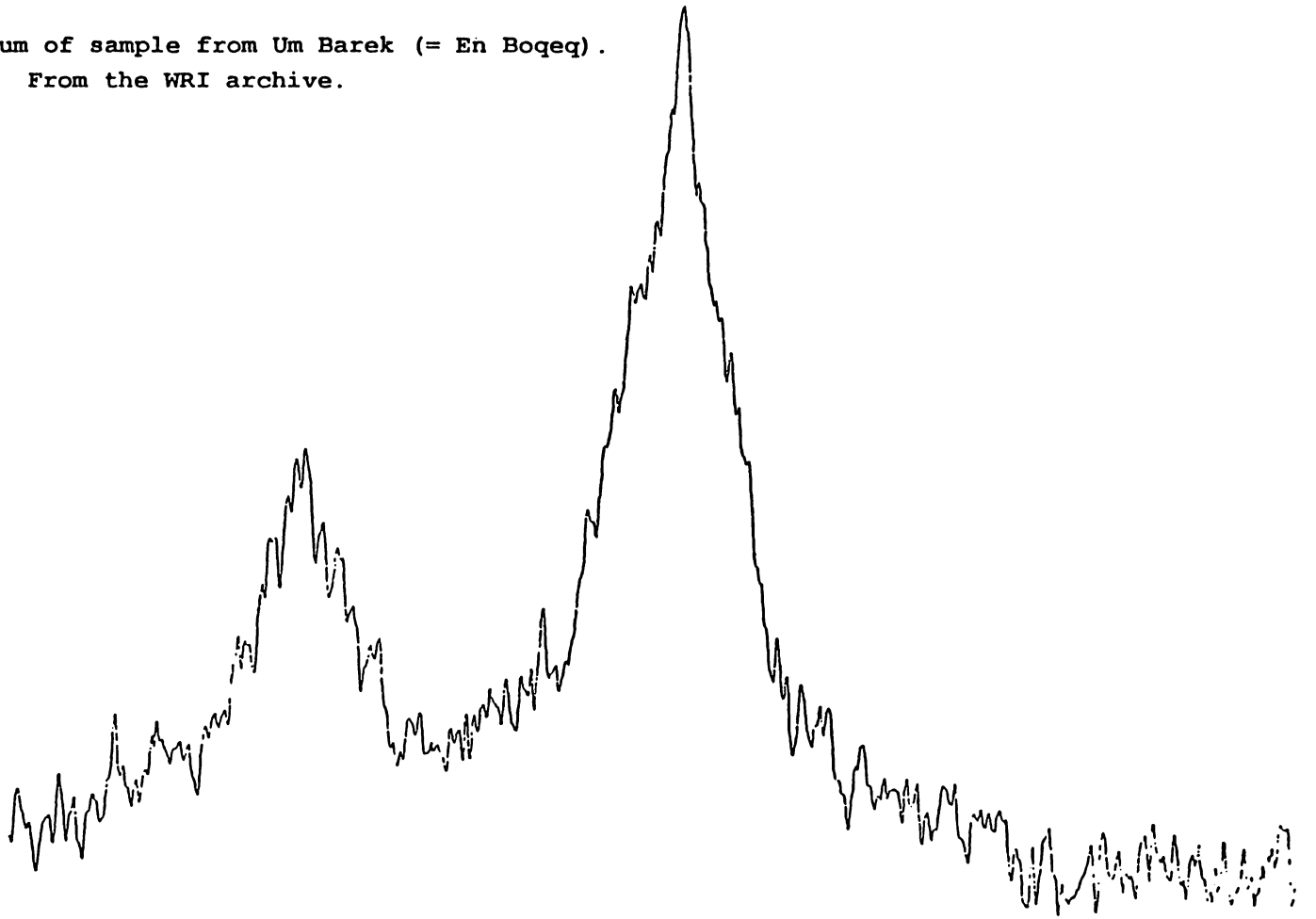
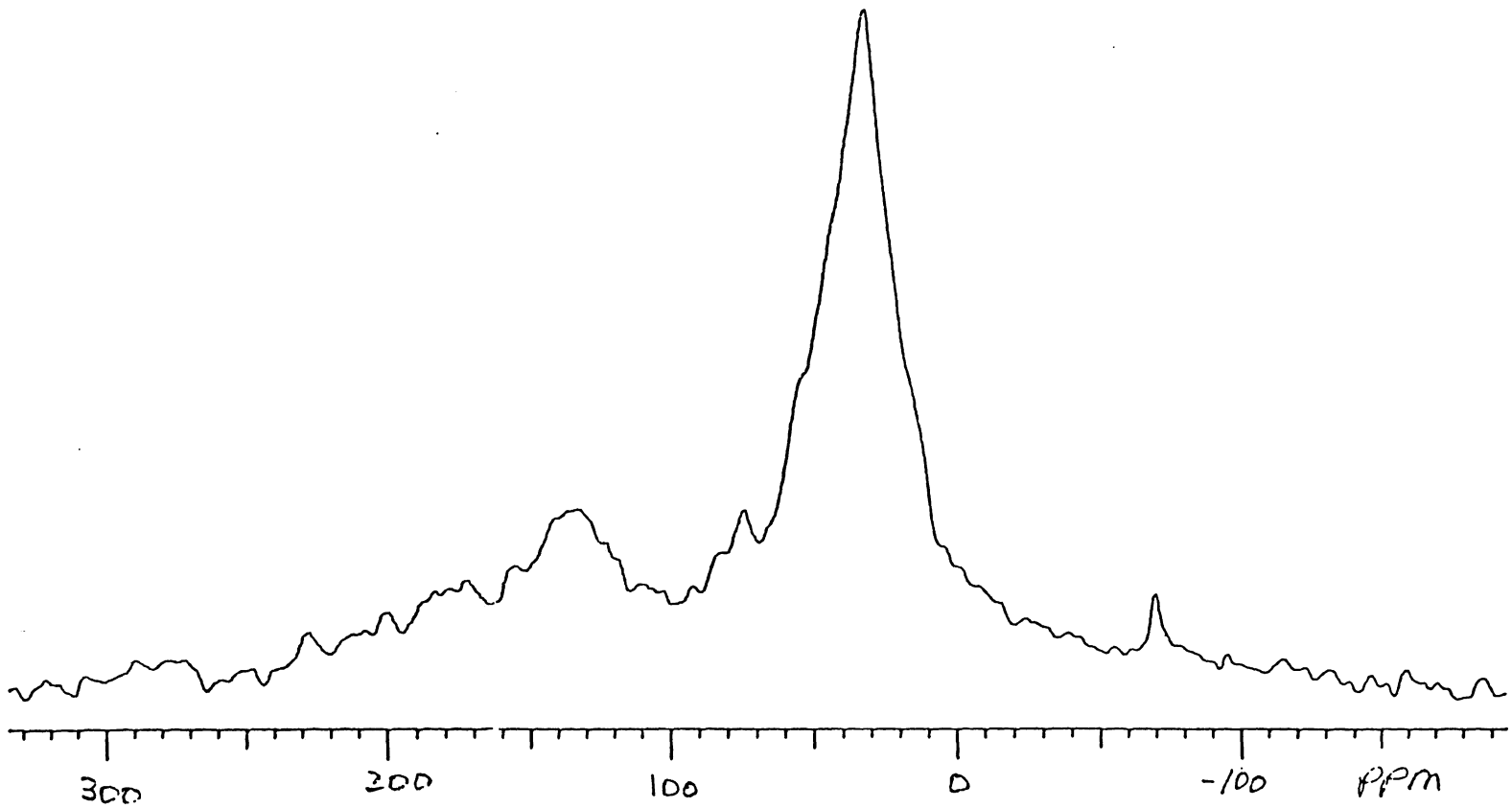
Appendix I

^{13}C NMR Spectrum of sample from Um Barek (= En Boqeq).
From the WRI archive.



Appendix II

^{13}C NMR Spectrum of sample from Ef'e (= Mishor Rotem).
From the WRI archive.



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