



PII S0016-7037(02)00871-2

$\delta^{13}\text{C}$ of low-molecular-weight organic acids generated by the hydrous pyrolysis of oil-prone source rocks

ROBERT F. DIAS,^{1,2,*} KATHERINE H. FREEMAN,¹ MICHAEL D. LEWAN³ and STEPHEN G. FRANKS^{4,†}¹Department of Geosciences, Pennsylvania State University, University Park, PA 16802, USA²Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23505, USA³U.S. Geological Survey, Denver, CO, USA⁴ARCO Exploration and Production Technology, Plano, TX, USA

(Received October 13, 2000; accepted in revised form February 18, 2002)

Abstract—Low-molecular-weight (LMW) aqueous organic acids were generated from six oil-prone source rocks under hydrous-pyrolysis conditions. Differences in total organic carbon-normalized acid generation are a function of the initial thermal maturity of the source rock and the oxygen content of the kerogen (OI). Carbon-isotope analyses were used to identify potential generation mechanisms and other chemical reactions that might influence the occurrence of LMW organic acids. The generated LMW acids display increasing ^{13}C content as a function of decreasing molecular weight and increasing thermal maturity. The magnitudes of observed isotope fractionations are source-rock dependent. These data are consistent with $\delta^{13}\text{C}$ values of organic acids presented in a field study of the San Joaquin Basin and likely reflect the contributions from alkyl-carbons and carboxyl-carbons with distinct $\delta^{13}\text{C}$ values. The data do not support any particular organic acid generation mechanism. The isotopic trends observed as a function of molecular weight, thermal maturity, and rock type are not supported by either generation mechanisms or destructive decarboxylation. It is therefore proposed that organic acids experience isotopic fractionation during generation consistent with a primary kinetic isotope effect and subsequently undergo an exchange reaction between the carboxyl carbon and dissolved inorganic carbon that significantly influences the carbon isotope composition observed for the entire molecule. Although generation and decarboxylation may influence the $\delta^{13}\text{C}$ values of organic acids, in the hydrous pyrolysis system described, the nondestructive, pH-dependent exchange of carboxyl carbon with inorganic carbon appears to be the most important reaction mechanism controlling the $\delta^{13}\text{C}$ values of the organic acids. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

Organic acids occur naturally in formation waters, with the dominant species being short chain ($\text{C}_2\text{--C}_8$) aliphatic carboxylic acids (Carothers and Kharaka, 1978; Means and Hubbard, 1987). These organic species can play an important role in the primary migration of petroleum and natural gas (Cordell, 1972; Palmer and Drummond, 1986b), mineral diagenesis, and the formation of secondary porosity in sedimentary basins (MacGowan and Surdam, 1990; Barth and Riis, 1992; Giles et al., 1994). Low-molecular-weight (LMW) organic acids have been proposed as a source of natural gas and carbon dioxide (Carothers and Kharaka, 1978; Kharaka et al., 1983; Kawamura et al., 1986; Cooles et al., 1987; Andresen et al., 1994) and as indicators of thermal maturation (Carothers and Kharaka, 1978), oil proximity (Zinger and Kravchik, 1973; Kartsev, 1974; Collins, 1975; Carothers and Kharaka, 1978), migration pathways (Workman and Hanor, 1985; Palmer and Drummond, 1986b), and biodegradation (Cozzarelli et al., 1994; Manning, 1997). Although the occurrence of LMW organic acids in reservoir fluids is well documented, their generation during catagenesis and subsequent geochemistry are topics of active discussion.

Several generation mechanisms have been proposed for the

occurrence of LMW organic acids in oil-field waters. The loss of oxygen from kerogen during early catagenesis (Tissot et al., 1974) and the observation of a low activation energy required for the generation of acetic acid from oil-prone source rocks (Barth et al., 1989) prompted the hypothesis that LMW organic acids were bound in kerogen through weak, noncovalent bonds (Barth et al., 1989). However, kinetic results from Barth and Nielsen (1993) and more recently Knauss et al. (1997) suggest that organic acid generation is more consistent with C-C bond cleavage. In short, kinetic studies of organic acid generation remain inconclusive with regard to suggesting specific generation mechanisms. Additional reaction mechanisms suggested for explaining the generation of LMW organic acids include the release of acids that were trapped or incorporated in the kerogen matrix during diagenesis (Kawamura et al., 1986), generation by catalytic oxidation of suitable acid precursors (Kawamura et al., 1986; Siskin and Katritzky, 1991; Lewan and Fisher, 1994), pyrolytic reactions (Cooper and Bray, 1963; Barth et al., 1988), and the hydrolysis of hydrocarbons at the oil-water interface (Helgeson et al., 1993).

Carbon-isotope analyses of individual organic acids should provide constraints on their mechanism of generation and post-generation chemistry. Each generation reaction is potentially accompanied by a characteristic carbon-isotope fractionation. For example, reactions involving the cleavage of a C-C bond should show evidence of a primary kinetic isotope effect, whereas those involving ionic interactions may not. Previous studies on the carbon-isotope values of organic acids are scarce

* Author to whom correspondence should be addressed (rfdias@odu.edu).

† Present address: Rock Fluid Systems, Inc., 3020 Legacy Drive, Plano, TX 75023.

Table 1. Geological and geochemical information for the six source rocks used in the hydrous pyrolysis experiments.

Rock Unit	Green River	Green River	Ghareb Limestone	Ghareb Limestone	New Albany Shale	Wilcox/Calbert Bluff
Member	Mahogany shale	Black shale facies	—	—	Clegg Creek	—
Location (basin)	Utah (Uinta)	Utah (Uinta)	Jordan (Dead Sea)	Israel (Dead Sea)	Indiana (Illinois)	Texas (Gulf Coast)
Age	Eocene	Eocene	Upper Cretaceous	Upper Cretaceous	Mississippian-Devonian	Paleocene
Lithology	Marlstone	Claystone	Limestone	Limestone	Claystone	Lignite coal
TOC (mg/g rock)	15.23	5.86	18.33	14.14	15.12	57.96
T _{max} (°C)	438	427	413	403	426	418
HI (mgH/g TOC)	962	734	819	759	486	259
OI (mgO/g TOC)	27	46	20	46	6.5	2.8
Kerogen type ^a	I	I	IIS	IIS	II	III
Kerogen δ ¹³ C (‰)	-30.1	-30.4	-29.1	-28.6	-29.4	-26

^a As characterized by a modified VanKreulen diagram (Tissot et al., 1974).

and have primarily focused on either analytical technique (Vogler and Hayes, 1979; Dias and Freeman, 1997) or various biologic processes (Meinschein et al., 1974; Vogler and Hayes, 1979; Monson and Hayes, 1980, 1982; Blair et al. 1987; Gelwicks et al., 1989).

Franks et al. (2001) provided a first look at the δ¹³C composition of organic acids in formation waters from the San Joaquin Basin, California, USA. They observed apparent intramolecular fractionation in organic acids such that the carboxyl carbons were significantly ¹³C-enriched relative to the alkyl carbons and that the δ¹³C value of the alkyl carbons were isotopically similar to the parent oil, whereas the δ¹³C values of the carboxyl carbons were more similar to dissolved inorganic carbon (DIC). Previously, intramolecular isotopic fractionation in organic acids was shown to arise from various biologic processes (mentioned above), thermal decarboxylation (Kharaka et al., 1983) or as a function of thermodynamic equilibrium (Galimov, 1973). The observations of Franks et al. (2001) mark a significant departure from past proposed fractionation processes and suggest that the organic acids can react with DIC to so as to acquire a more isotopically enriched signal by incorporating the DIC at the carboxyl position. Although to our knowledge Franks et al. (2001) is the only available field study, the suggested cause of intramolecular isotopic heterogeneity of oil-associated organic acids and the potential to provide information about the parent oil through interpretation of organic acid δ¹³C values clarifies the need for a comprehensive study of the δ¹³C compositions of organic acids in petroleum-related waters. To that end, in this work, we evaluate the carbon-isotope values of LMW organic acids generated from six different source rocks during simulated catagenesis to identify possible generation mechanisms and postgeneration reactions that influence their occurrence and isotopic composition.

2. EXPERIMENTAL

2.1. Hydrous Pyrolysis

Hydrous pyrolysis was used to simulate catagenesis. This technique involves heating coarsely ground source rocks in the presence of liquid water at subcritical temperatures (T < 374°C) (Lewan et al., 1979; Lewan, 1983). Hydrous pyrolysis generates free-flowing liquid pyrolyzates that are compositionally and physically similar to natural crude oils (Lewan et al., 1979; Lewan, 1983, 1985). Additionally, hydrous pyrolysis of source rocks and kerogens generates suites of organic acids

similar to those found in petroleum-associated formation waters (Kawamura et al., 1986; Cooles et al., 1987; Eglinton et al., 1987; Lundegard and Senftle, 1987; Barth et al., 1988, 1989; Barth and Bjorlykke, 1993; Kharaka et al., 1993; Borgund and Barth, 1994).

Six thermally immature source rocks representative of kerogen types I, II, IIS, and III (Table 1) were subjected to hydrous pyrolysis conditions. Efforts were made to ensure source-rock homogeneity (Lewan, 1983). Although all source rocks used in these experiments are considered thermally immature, there are significant differences in thermal maturity between the samples as measured by T_{max} (Table 1). Typically, 200 to 300 g of crushed (0.5 to 1.5 cm in diameter), whole source rock chips and 200 to 300 mL of distilled and deionized water were loaded into a 1-L Parr reactor vessel (carburized 316-stainless steel or carburized Hastelloy-C). After sealing, the reactor was evacuated and 2.4 bar of helium was added as a headspace gas. The weighed reactor was heated to a predetermined temperature (between 200 and 360°C) for 72 h. At the end of each reaction period, the reactor and its contents were allowed to cool to room temperature (~12 to 18 h). After weighing the reactor again, all phases (gases, expelled oil, water, and thermally altered source rock) were sampled for subsequent quantitative and carbon-isotope analyses.

2.2. Organic Acid δ¹³C Analysis

The distributions and ¹³C contents of the organic acids in the pyrolysis waters were determined at Penn State University by means of methods described by Dias and Freeman (1997). A 20-mL water sample was treated with 4.6 N NaOH (until pH > 10), then extracted three times with 20 mL of dichloromethane to remove nonpolar organic compounds. A 4-mL aliquot of the extracted water was acidified to pH < 2 with 12 N hydrochloric acid to protonate the organic acids. The acidified solution was allowed to equilibrate with a Carbowax solid-phase microextraction needle (Supelco) for 15 min, where extraction of the organic acids occurred. The organic acids of interest (as well as a host of other unidentified, higher-molecular-weight compounds) were thermally desorbed from the fiber into the gas chromatography (GC) inlet of an isotope ratio-monitoring GC mass spectrometer (IRM-GCMS) system for both isotopic and quantitative analyses with a Finnigan-MAT 252 mass spectrometer (Ricci et al., 1994; Merritt et al., 1995; Leckrone and Hayes, 1997). Chromatographic conditions were as follows: J&W FFAP column, 30 m × 0.32 mm × 0.25 μm film thickness; 60°C initial temperature, hold for 1 min, then ramp to 240°C at 5°C/min and hold for 30 min; injector temperature of 240°C in a splitless mode for 1 min.

Carbon-isotope values for the organic acids were determined relative to an in-house carbon dioxide standard that was calibrated vs. NBS-19 and are reported relative to PDB. These values were corrected to organic acid standards, the δ¹³C values of which were determined via off-line closed tube combustion techniques and used as syringe-injected external standards in separate IRM-GCMS determinations (Dias and Freeman, 1997). Organic acid δ¹³C values are single analyses,

Table 2. Amounts of organic acids generated from each of the source rocks under hydrous pyrolysis conditions.^a

Temperature (°C)	pH	Aqueous organic acids (mg/g TOC)					Total
		C ₂	C ₃	C ₄	C ₅	C ₆	
Mahogany shale							
270	7.6	1.05				0.013	1.06
285	7.7	1.65	0.330			0.031	2.01
300	7.7	1.95	0.464		0.039	0.055	2.51
315	7.6	2.87	0.633		0.073	0.105	3.68
330	7.5	4.22	0.90	0.000	0.132	0.183	5.44
345	7.6	5.08	1.07	0.228	0.186	0.260	6.82
350	7.6	7.18	1.32	0.269	0.219	0.306	9.30
355	7.1	5.58	1.27	0.290	0.246	0.343	7.73
360	7.2	5.27	1.33	0.309	0.291	0.350	7.55
Black Shale							
285	7.1	4.41	0.60	0.098	0.052	0.056	5.22
300	7.2	4.83	0.73	0.136	0.071	0.071	5.84
310	7.0	6.56	1.01	0.176	0.098	0.101	7.94
320	7.2	5.80	0.97	0.182	0.100	0.099	7.15
330	NA	6.76	1.15	0.233	0.123	0.116	8.38
340	7.2	7.53	1.38	0.283	0.145	0.139	9.48
345	7.0	6.96	1.31	0.281	0.150	0.147	8.85
350	7.1	6.43	1.31	0.333	0.191	0.184	8.45
355	7.1	6.05	1.31	0.333	0.202	0.194	8.09
360	7.1	8.49	1.45	0.325	0.167	0.135	10.56
365	7.1	11.05	2.11	0.488	0.274	0.243	14.17
New Albany Shale							
270	6.6	0.774				0.016	0.79
285	6.5	1.27	0.617		0.027	0.018	1.93
300	6.7	1.78	0.898		0.033	0.022	2.73
310	6.7	2.14	1.06	0.081	0.038	0.026	3.34
320	6.9	2.47	1.15	0.095	0.043	0.026	3.78
330	6.9	3.44	1.36	0.111	0.042	0.026	4.98
340	7.1	3.13	1.17	0.108	0.041	0.023	4.47
350	7.2	3.44	1.05	0.122	0.041	0.021	4.67
360	7.3	3.42	0.99	0.106	0.041	0.021	4.57
Ghareb—Israel							
200	7.0	2.74	0.677				3.42
240	6.9	3.37	0.659		0.045	0.046	4.12
280	7.5	8.75	1.92	0.431	0.109	0.188	11.40
300	7.4	9.60	2.13	0.515	0.217	0.218	12.68
310	6.8	16.16	3.33	0.692	0.259	0.204	20.65
320	6.8	11.79	2.83	0.000	0.376	0.377	15.36
330	6.8	11.74	2.55	0.000	0.270	0.270	14.83
340	6.8	14.84	3.37	1.04	0.505	0.504	20.26
350	7.8	13.62	3.11	1.03	0.453	0.425	18.64
360	7.5	18.38	3.13	0.705	0.232	0.169	22.62
Ghareb—Jordan							
240	6.5	1.05	0.00	0.000	0.032	0.024	1.11
280	6.5	2.39	0.00	0.115	0.077	0.065	2.65
300	6.6	3.38	1.10	0.283	0.158	0.141	5.06
310	6.7	4.06	1.34	0.223	0.131	0.106	5.86
320	6.7	4.74	1.52	0.314	0.161	0.136	6.88
330	6.7	7.27	1.82	0.421	0.221	0.179	9.91
340	6.8	8.15	2.14	0.514	0.279	0.234	11.32
350	6.8	10.63	2.59	0.647	0.340	0.274	14.48
360	6.8	11.36	2.45	0.642	0.262	0.263	14.98
Wilcox Coal							
210	6.7	0.41	0.000	0.000	0.000	0.0000	0.41
246	6.4	2.77	0.306	0.000	0.000	0.0000	3.07
280	5.1	10.76	1.13	0.086	0.016	0.0059	11.99
300	5.0	8.22	0.978	0.087	0.018	0.0067	9.31
310	5.1	7.18	0.900	0.083	0.018	0.0062	8.18
320	5.3	8.27	1.03	0.099	0.021	0.0079	9.44
330	5.5	8.63	1.06	0.102	0.021	0.0084	9.82
340	5.0	10.40	1.22	0.124	0.025	0.0091	11.78
350	5.3	11.86	1.12	0.118	0.023	0.0078	13.13
360	5.1	10.80	0.976	0.117	0.026	0.0092	11.93

^a The pH of the waters was determined at room temperature after cooling the reactor to room temperature and subsequent sampling. NA = not available.

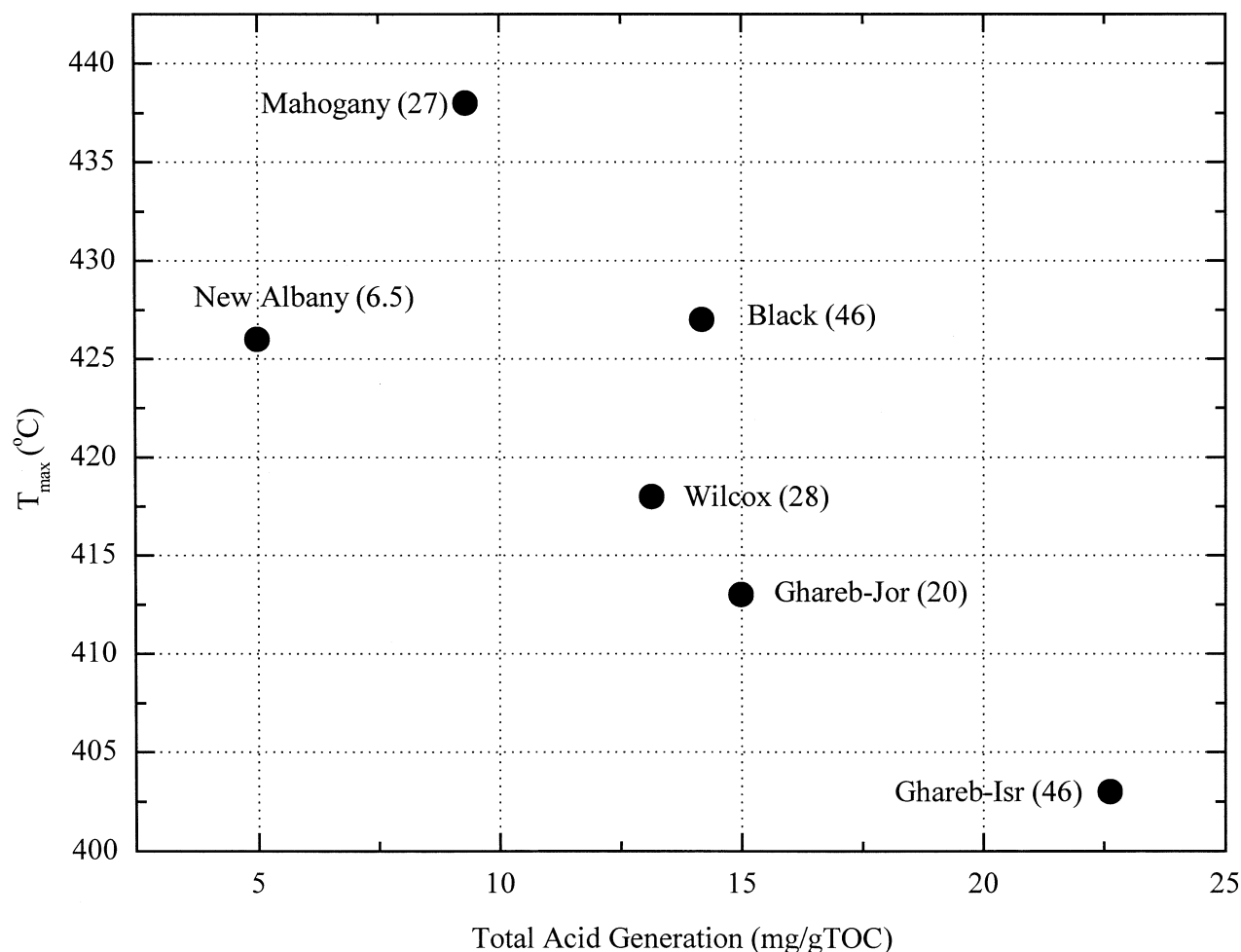


Fig. 1. Normalized acid generation (maximum) for each source rock plotted against thermal maturation parameter T_{\max} ($^{\circ}\text{C}$). The number in parentheses is the corresponding oxygen index (OI) from Table 1.

except where noted in Table 3. The error associated with single solid-phase microextraction determinations of $\delta^{13}\text{C}$ values and concentrations for organic acids are typically $\pm 0.20\%$ and $\pm 5\%$, respectively (Dias and Freeman, 1997).

2.3. Carboxyl-Carbon $\delta^{13}\text{C}$ Analysis

The ^{13}C content of organic acid carboxyl-derived carbon was determined by gas chromatography pyrolysis isotope ratio mass spectrometry (GC-Py-IRMS) (Dias et al., 2002). This is a new continuous-flow isotopic technique that uses a palladium reactor under reducing conditions that allows for the $\delta^{13}\text{C}$ analysis of just the carboxyl group of an organic acid. Chromatographic conditions were similar to those described above for the total acid $\delta^{13}\text{C}$ determinations. The ^{13}C content of the carboxyl-derived carbons are reported in standard delta notation ($\delta^{13}\text{C}$, ‰), relative to PDB.

2.4. CO_2 $\delta^{13}\text{C}$ Analysis

Carbon isotope values of the CO_2 in the headspace gas for the Ghareb limestone and the Wilcox coal samples were determined by IRM-GCMS. The $\delta^{13}\text{C}$ values were determined as described above, corrected to a natural gas standard, NGS-2A (Chevron Petroleum Technology Co.), and are reported relative to PDB. GC conditions were as follows: GS-Q column, $30\text{ m} \times 0.53\ \mu\text{m}$ (J&W Scientific); 30°C initial temperature, hold for 2 min, then ramp to 240°C at $20^{\circ}\text{C}/\text{min}$,

hold at 240 for 10 min; split mode injection at 10 to 1 to 20 to 1 split, depending on injected sample size (10 to $20\ \mu\text{L}$).

Carbon dioxide $\delta^{13}\text{C}$ values for the Mahogany, Black, and New Albany shales were determined at the U.S. Geological Survey (Denver) by conventional dual-inlet isotope ratio mass spectrometry, after separation by packed-column chromatography, combustion, and vacuum-line purification.

2.5. Kerogen $\delta^{13}\text{C}$ Analysis

Kerogen carbon-isotope values for the six source rocks were determined via off-line, closed-tube combustion techniques, and $\delta^{13}\text{C}$ values represent the average of two determinations. Weight percent total organic carbon (%TOC), hydrogen index (HI), OI, and T_{\max} were determined by Rock-Eval analyses on the original, thermally immature source rock at the U.S. Geological Survey (Denver).

3. RESULTS

3.1. Organic Acid Quantitation

The amounts of TOC-normalized $\text{C}_2\text{-C}_6$ aqueous organic acids generated from the hydrous pyrolysis experiments are summarized in Table 2. Aqueous organic acids from C_2 to C_6 were quantified; organic acids as high as C_{12} were present.

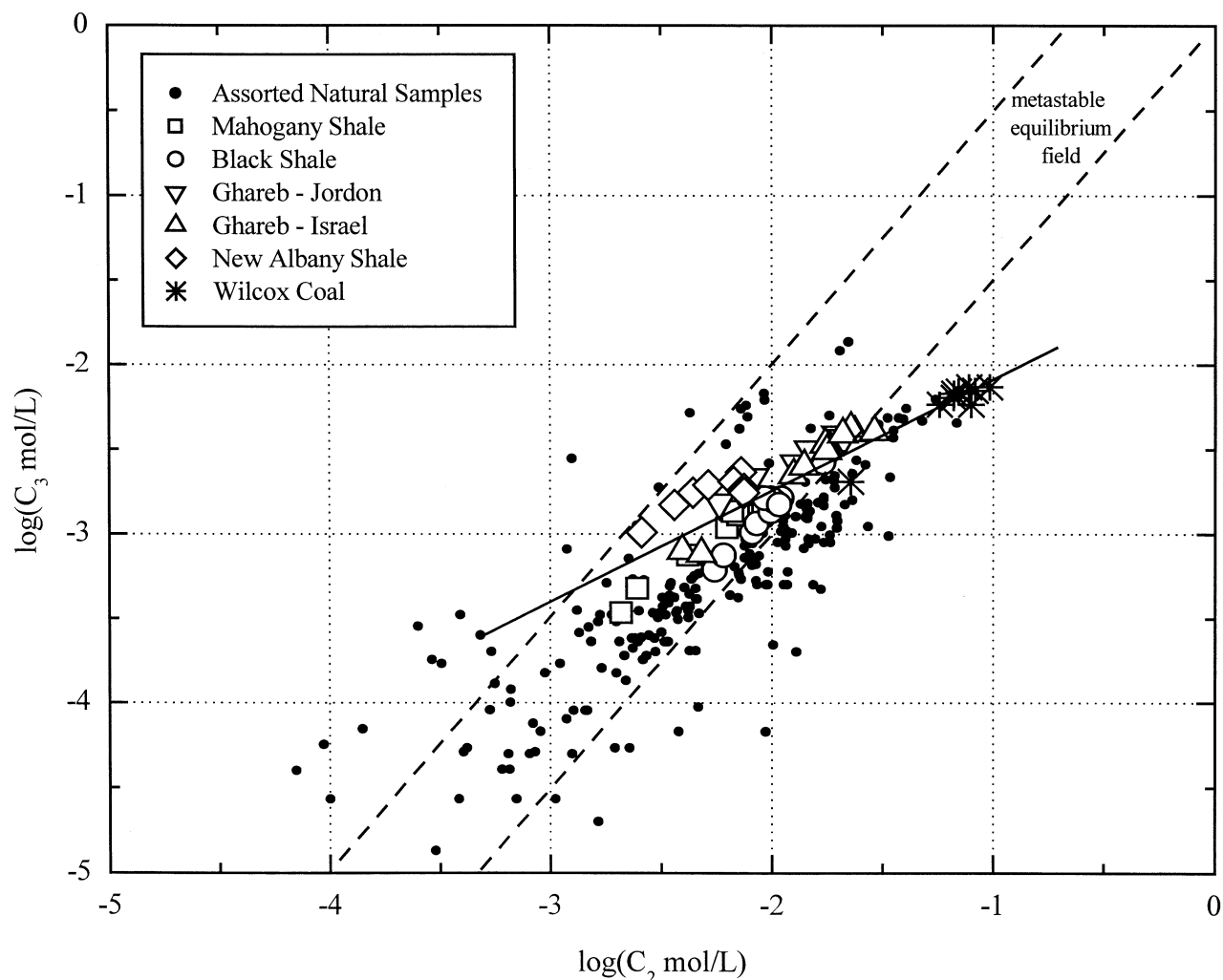


Fig. 2. Log-log plot of acetic (C_2) and propionic (C_3) acid concentrations for each source rock used in this study (after Shock, 1988). The area bounded by two dashed lines defines the range of metastable equilibrium (slope of 1.5) proposed by Shock (1988). Each point represents one set of hydrous pyrolysis conditions (time/temperature combination) for a given source rock. The solid line represents the linear regression through this data and has a slope of 0.68. The points representing natural samples are taken from the following literature: Barth and Riis (1992); Kharaka et al. (1983); Workman and Hanor (1985); MacGowan and Surdam (1990); Means and Hubbard (1987); Fisher (1987); and Hanor and Workman (1986).

Typically, acetic acid accounts for more than 70% of the total organic acids (C_2 - C_6) analyzed for any given source rock. Although TOC-normalized total organic acid concentrations are of a similar order of magnitude for each source rock regardless of kerogen type, differences in concentrations exist. The New Albany shale produced the lowest amounts of organic acid (1 to 5 mg/g TOC), whereas the Israeli-Ghareb limestone produced the highest levels of organic acid (3 to 23 mg/g TOC) over the entire thermal range. The total amount of organic acids generated shows a general correlation with initial source rock maturity as measured by T_{max} (Fig. 1).

Source rocks with lower initial maturity generate more organic acids during pyrolysis experiments than those with higher initial maturity. Notable exceptions are the type I Mahogany and Black shale samples. These two source rocks generate more organic acids than the type II New Albany shale, even though the latter has a lower starting thermal maturity. The

kerogens in these rocks do, however, have higher initial oxygen contents (OI, Table 1) than the New Albany shale. Thus, the quantity of organic acids generated is not entirely a function of %TOC and initial maturity, but is also a function of kerogen type.

The concentrations of organic acids generated in our experiments are consistent with those found in natural samples. Figure 2 plots the log of the concentration of propionic acid vs. the log of the concentration of acetic acid from each of our experiments together with data from natural systems. A slope of 1.5 is the theoretical relationship between acetic and propionic acid proposed by Shock (1988). Our concentration data show a slope of 0.68, not 1.5. However, this slope is strongly influenced by our Wilcox coal data, which lie well outside the concentration range proposed for metastable equilibrium. The data for all other samples are largely consistent with the concentration range identified for metastability.

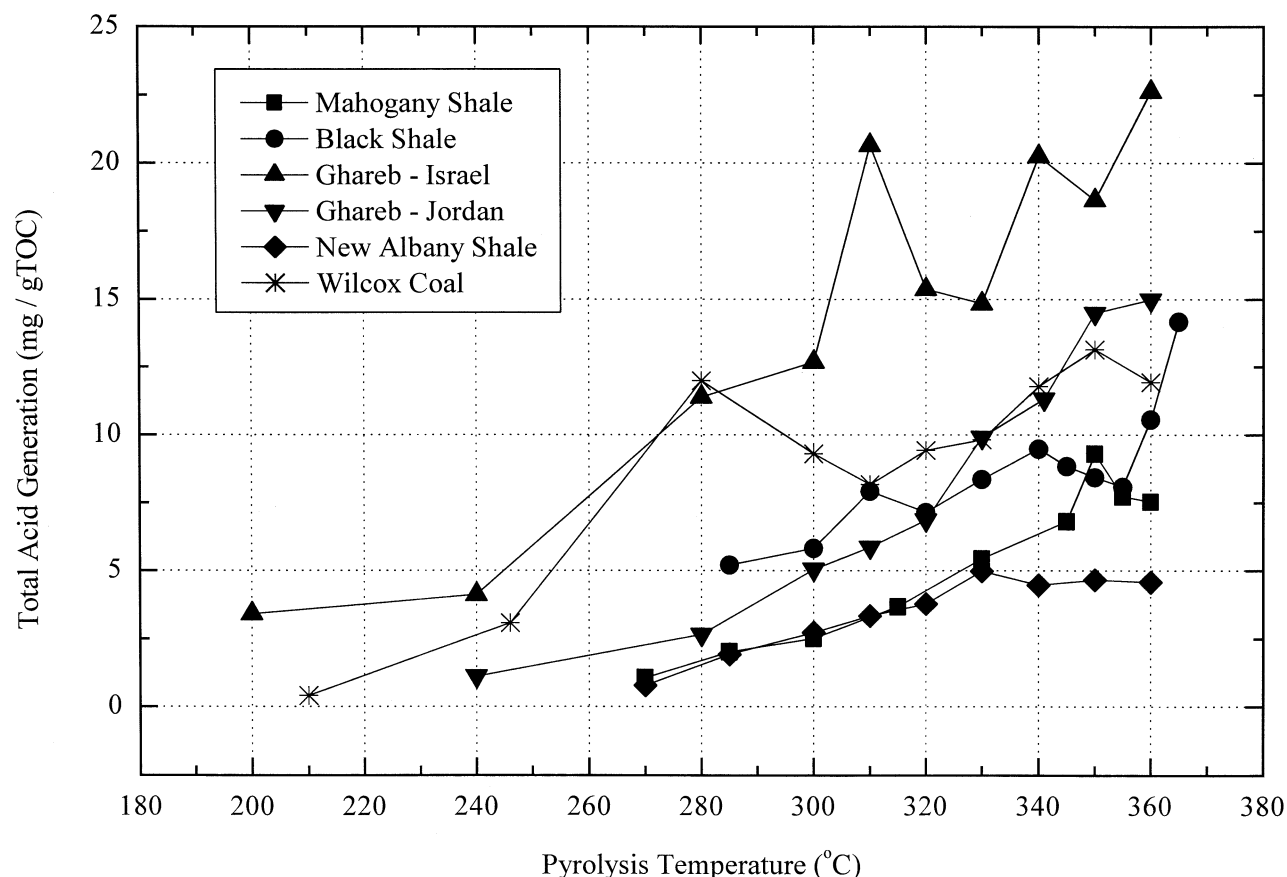


Fig. 3. Normalized total organic acid generation for each source rock plotted as a function of reaction temperature. All hydrous pyrolysis reactions were for 72 h.

In these experiments, organic acid concentrations generally increase with increasing reaction temperature. The observed increase in acid concentration (Fig. 3) concurrent with increasing total oil yields (Lewan et al., 1995; Ruble, 1996) is consistent with a model in which the generated acids migrate out of the source rock with the oil and then partition into the surrounding water phase. Lewan and Fisher (1994), who identified comigration of oil and acids as an important transport mechanism, reported similar observations for the Monterey and Phosphoria Retort shale.

3.2. Carbon-Isotope Values: Organic Acids

Carbon-isotope values for C_2 - C_6 organic acids generated under hydrous pyrolysis conditions for each source rock are shown in Table 3. In Figure 4, the effects of source-rock type and increasing thermal maturity are observed in the $\delta^{13}C$ values for acetic acid. Acetic acid carbon-isotope values span an approximate 12‰ range from -28.4‰ for the Wilcox coal to -16.7‰ for the Mahogany shale at the highest reaction temperature (360°C). At high levels of thermal maturity, the Mahogany and Black shales show the most enriched carbon-isotope values (-19 to -16.7‰), whereas the other source rocks show systematic depletion in ^{13}C relative to the kerogen type: IIS, -24 to -21‰ ; II, -28 to -26‰ ; III, -30 to -28‰ .

With the exception of the Mahogany and Black shales, the acetic acid generated at the lowest reaction temperatures (200 to 260°C) is isotopically depleted relative to the starting kerogen. Low concentrations of acetic acid at lower temperature for the Mahogany and Black shales prevented isotopic analyses. From 270°C , acetic acid becomes more enriched in ^{13}C , to various extents, with increasing reaction temperature for each source rock. For example, the New Albany shale shows a continuous 7‰ enrichment over a large temperature range (270 to 360°C). In contrast, acetic acid released from the Black shale only shows a 3‰ enrichment over a 30° temperature interval (280 to 310°C) and maintains a relatively constant $\delta^{13}C$ value from 310 to 365°C . Acetic acid from the Wilcox coal exhibits isotopic depletion relative to the kerogen from 200 to 240°C , consistent $\delta^{13}C$ values from 240 to 310°C and then increases to more ^{13}C -enriched values from 310 to 360°C . Acetic acid from the Jordanian-Ghareb limestone shows a combination of more constant $\delta^{13}C$ values relative to the kerogen at low temperatures, and increasing ^{13}C enrichment from 280 to 360°C . The Israeli-Ghareb limestone shows an initial isotopic depletion relative to the starting kerogen at 200°C , followed increasing isotopic enrichment up to 310°C , then rather consistent $\delta^{13}C$ values from 310 to 360°C . Although in general, ^{13}C enrichment of the organic acids occurs with increasing temperature, each data set displays unique structure.

Table 3. Carbon-isotope values for organic acids and CO_2 generated from the source rocks of interest under hydrous pyrolysis conditions.

Temperature ($^{\circ}\text{C}$)	Aqueous organic acids ($\delta^{13}\text{C}$)					CO_2 (g)
	C_2	C_3	C_4	C_5	C_6	
Mahogany Shale						
270	-22.3				-26.2	3.1
285 ^a	-19.3	-21.2			-26.3	
300	-17.3	-19.8		-24.4	-27.8	1.3
315	-17.4	-20.1		-25.4	-28.3	1.5
330 ^a	-17.3	-20.1	-24.6	-25.5	-27.4	1.4
345	-17.4	-20.2	-19.8	-26.8	-29.8	-0.1
350	-17.8	-20.3	-20.4	-26.5	-29.5	-3.3
355	-17.1	-20.4	-20.1	-26.2	-29.1	-1.3
360	-16.8	-21.1	-19.9	-26.9	-27.1	-4.5
Black Shale						
285 ^a	-21.2	-25.2	-23.9	-27.6	-29.1	0.2
300 ^a	-20.2	-24.7	-19.7	-26.2	-28.6	-1.1
310	-18.6	-24.0	-22.0	-25.6	-28.0	-0.8
320	-18.4	-22.1	-21.4	-25.4	-27.7	-1.3
330 ^a	-18.8	-22.5	-22.2	-24.2	-27.5	-2.0
340	-19.0	-22.3	-22.1	-25.4	-27.8	-2.5
345	-18.8	-22.2	-21.8	-25.3	-27.8	-2.1
350	-18.5	-21.6	-22.5	-25.7	-28.1	-2.3
355	-18.8	-21.2	-20.8	-25.7	-28.4	-2.4
360	-19.1	-21.2	-21.4	-25.2	-27.6	-2.1
365	-19.0	-21.9	-22.1	-25.8	-28.0	-5.1
New Albany Shale						
270 ^a	-33.3				-30.5	-11.8
285 ^a	-32.6	-30.0		-30.3	-30.4	-13.6
300	-31.1	-27.8		-30.1	-29.9	-14.6
310	-28.5	-26.3	-28.7	-27.3	-29.8	-15.5
320 ^a	-28.1	-29.0	-29.4	-28.3	-29.3	
330	-27.5	-27.2	-27.6	-27.3	-27.6	-17.2
340 ^a	-27.1	-26.4	-27.6	-28.4	-27.8	-17.2
350	-26.3	-27.0	-24.9	-24.8	-25.9	-14.7
360	-26.0	-26.3	-25.3	-25.0	-25.5	
Ghareb—Israel						
200	-31.2	-29.1				-15.1
240	-30.3	-29.1		-27.6	-32.2	-15.5
280	-28.3	-28.1	-28.8	-30.3	-30.3	-6.3
300	-23.9	-26.4	-28.0	-28.9	-29.4	-1.9
310	-21.4	-25.0		-27.4	-27.9	-3.4
320	-21.9	-25.3		-27.6	-28.2	-4.7
330	-22.6	-25.9		-27.9	-28.5	-5.8
340	-21.8	-23.8	-26.5	-26.4	-26.1	-7.2
350	-21.8	-23.1	-25.9	-25.5	-26.2	-10.4
360	-21.6	-22.6	-25.3	-24.2	-25.2	-10.4
Ghareb—Jordan						
240 ^a	-29.2	-28.5	-26.5	-30.2	-30.7	-7.9
280 ^a	-28.6	-29.4	-27.7	-29.7	-28.9	-4.5
300	-27.3	-28.2	-27.6	-28.4	-28.5	-2.1
310	-24.7	-26.7	-28.8	-27.8	-28.1	-3.7
320	-23.8	-26.1	-23.0	-27.1	-27.5	-6.5
330	-23.3	-24.8	-25.4	-26.7	-27.2	-6.9
341	-23.9	-24.9	-25.9	-26.2	-26.5	-8.0
350	-22.4	-23.1	-23.9	-25.0	-25.5	-10.9
360	-21.9	-23.9	-24.7	-24.3	-24.4	-11.6
Wilcox Coal						
210	-28.1					
246	-31.4	-26.8	-25.0			-20.9
280	-31.4	-27.0	-24.5	-25.7	-26.4	-21.5
300	-31.6	-27.6	-26.0	-24.4	-25.9	-21.2
310	-31.6	-26.9	-25.4	-25.3	-24.9	-21.9
320	-30.3	-25.4	-24.9	-25.1	-25.6	-21.7
330	-30.1	-26.6	-25.0	-25.3	-26.7	-21.8
340	-29.6	-26.0	-25.2	-25.6	-25.8	-21.2
350	-28.7	-24.8	-24.2	-24.6	-25.9	-21.3
360	-28.7	-23.6	-23.4	-24.1	-24.8	-21.4

^a Denotes the average of duplicate acid isotopic analyses.

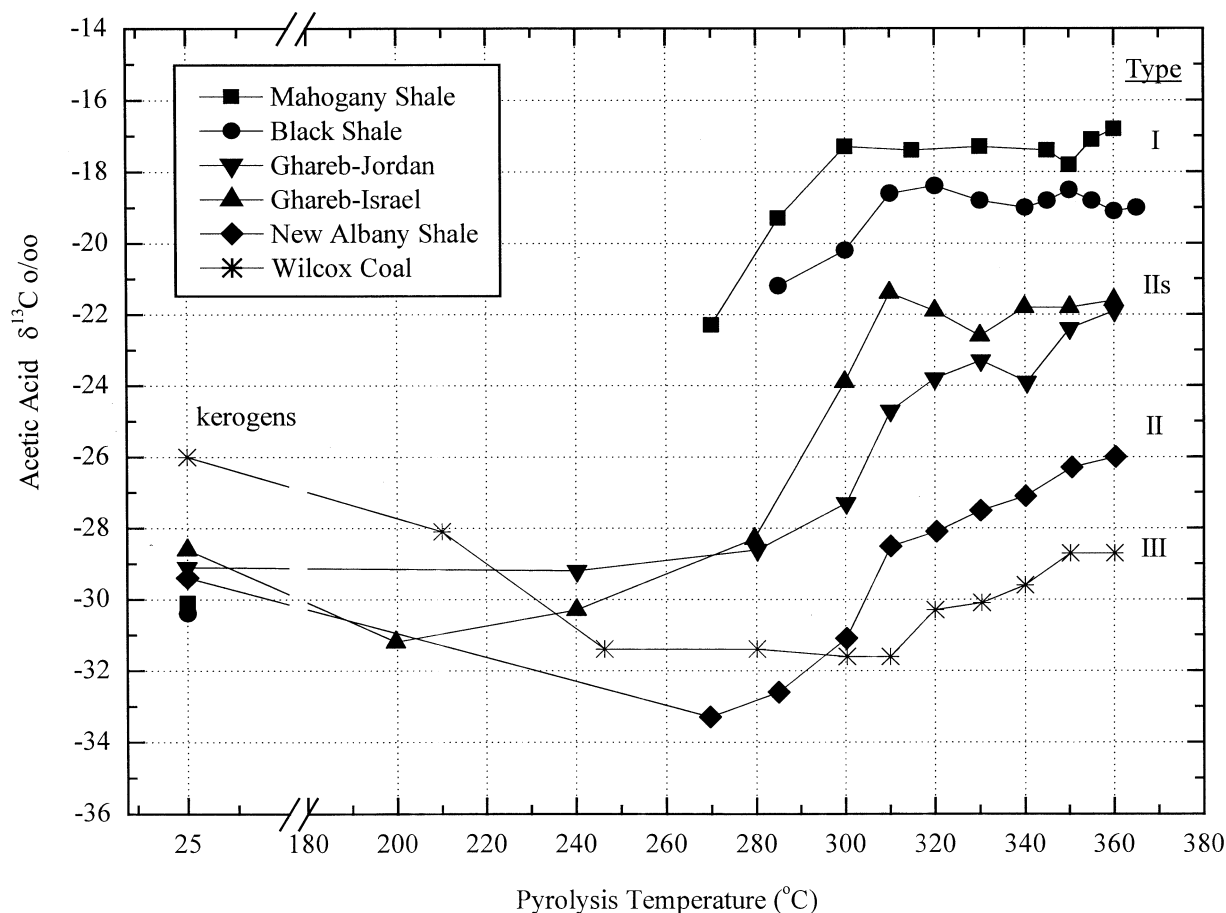


Fig. 4. The carbon-isotope values for acetic acid generated by each of the six source rocks under hydrous pyrolysis conditions.

Propanoic through hexanoic acids are also progressively enriched in ^{13}C as a function of increasing reaction temperature for all but the Mahogany and Black shales. Organic acids from the Black shale sample show relatively constant $\delta^{13}\text{C}$ values with increasing reaction temperatures, whereas C_5 and C_6 acids from the Mahogany shale become more isotopically depleted.

An important general trend in the carbon-isotope data is the tendency toward more ^{13}C -depleted values as the alkyl chain length increases from C_2 to C_6 , especially for acids liberated from the Green River and Ghareb rocks. This trend is attenuated and possibly reversed in acids from the New Albany shale and Wilcox coal samples. Figure 5 plots the $\delta^{13}\text{C}$ values of the LMW organic acids from each source rock after hydrous pyrolysis conditions of 350°C for 72 h (at or near peak oil generation for each kerogen). The $\delta^{13}\text{C}$ values of the longer alkyl-chain acids (C_5 , C_6) approach the carbon-isotope composition of the bulk kerogen, whereas the $\delta^{13}\text{C}$ values for acetic acid tend toward that of DIC (calculated from ambient headspace CO_2 below).

3.3. Carbon Isotope Values: Headspace CO_2 and DIC

The $\delta^{13}\text{C}$ value of headspace CO_2 at ambient temperature conditions after reactor cooling are shown in Table 2. These

values were used to estimate the $\delta^{13}\text{C}$ values of $\text{CO}_{2(\text{aq})}$ and HCO_3^- at reaction temperature by applying a temperature correction to the isotopic fractionation ($\epsilon_{\text{HCO}_3^--\text{CO}_{2(\text{g})}}$) between bicarbonate and gaseous CO_2 (Mook et al., 1974):

$$^{13}\epsilon_{\text{HCO}_3^--\text{CO}_{2(\text{g})}} = (-9483/T) + 23.89\%, \quad (1)$$

where T is the hydrous pyrolysis reaction temperature in Kelvin. A similar isotopic correction was made for dissolved $\text{CO}_{2(\text{aq})}$ after Vogel et al. (1970):

$$^{13}\epsilon(\text{CO}_{2(\text{g})}) = (-373/T) + 0.19\%. \quad (2)$$

Eqn. 1 was shown to be reliable to 200°C ; thus, we have a high confidence in calculating the $\delta^{13}\text{C}$ for bicarbonate at elevated temperature. However, the correction for dissolved CO_2 was based on experiments conducted at or near room temperature, and we therefore have a lower confidence in those calculated $\delta^{13}\text{C}$ values.

3.4. Carbon-Isotope Values: Carboxyl-Derived Carbons from the Organic Acids

The $\delta^{13}\text{C}$ values of carboxyl-derived carbons for selected hydrous pyrolysis samples are listed in Table 4. Additionally,

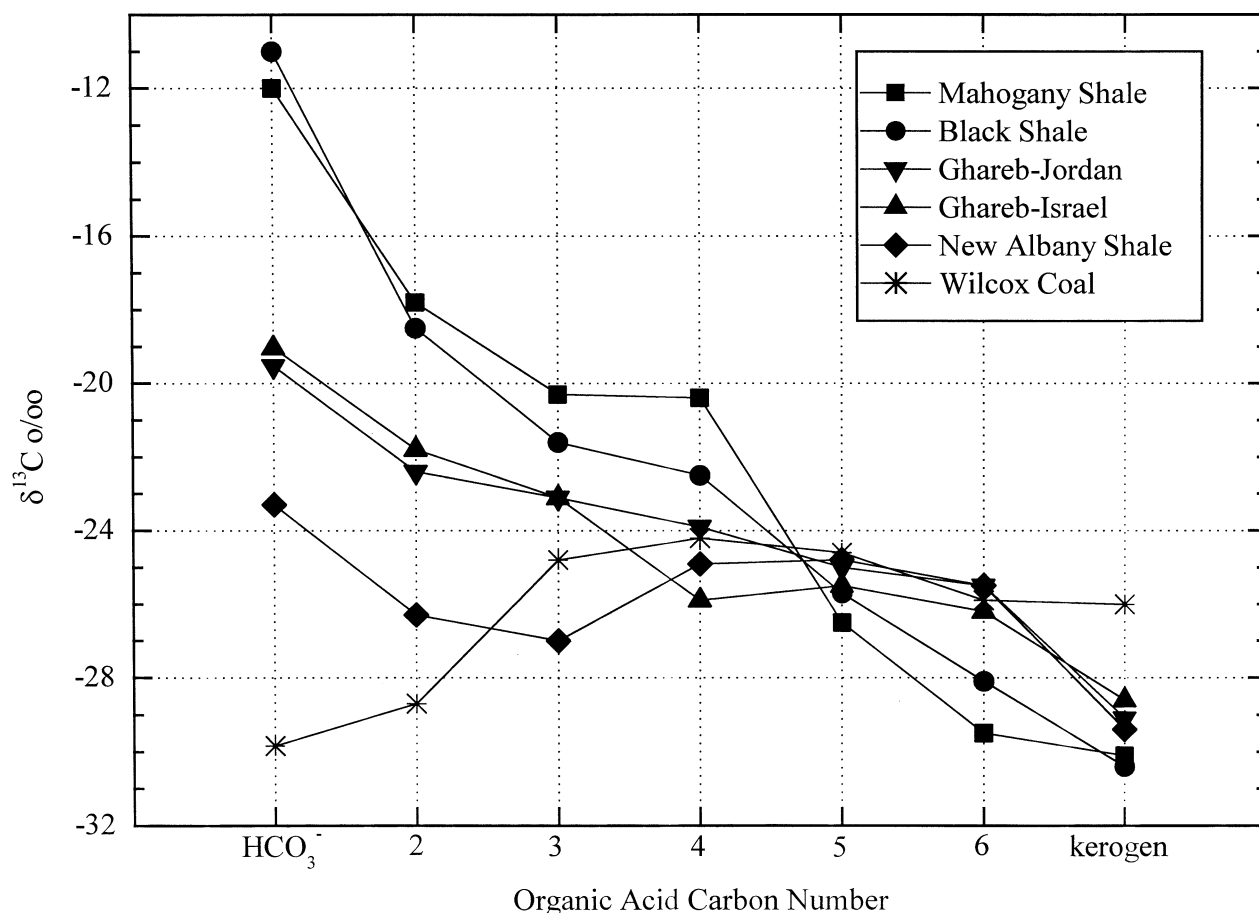


Fig. 5. Carbon-isotope values of $\text{C}_2\text{-C}_6$ organic acids generated from each source rock at hydrous pyrolysis conditions of 350°C for 72 h. Additionally, the calculated $\delta^{13}\text{C}$ values for the associated aqueous bicarbonate and the $\delta^{13}\text{C}$ value of the respective thermally immature kerogen are plotted for each sample.

the $\delta^{13}\text{C}$ values of the total organic acids and those of the alkyl-derived carbons are shown. The carbon-isotope composition of the alkyl group for each acid was calculated by means of the following mass balance equation:

$$\delta^{13}\text{C}_{\text{tot}} = \delta^{13}\text{C}_{\text{alk}}(n_{\text{alk}}/n_{\text{total}}) + \delta^{13}\text{C}_{\text{carb}}(1/n_{\text{total}}), \quad (3)$$

where n_{total} and n_{alk} are the numbers of carbon atoms in the total acid and the corresponding alkyl group, $\delta^{13}\text{C}_{\text{tot}}$, $\delta^{13}\text{C}_{\text{carb}}$, and $\delta^{13}\text{C}_{\text{alk}}$ are the isotopic compositions of the total acid, the carboxyl-derived carbon and the alkyl-derived carbons.

With the exception of the organic acids from the Wilcox coal, the $\delta^{13}\text{C}$ values of carboxyl-derived carbons are isotopically enriched relative to the $\delta^{13}\text{C}$ value of the total, parent acids by as much as 22.8‰ (hexanoic acid, Mahogany shale). And the calculated $\delta^{13}\text{C}$ values of the alkyl-derived carbons are isotopically depleted relative to the $\delta^{13}\text{C}$ values of the total acids by as much as 13.8‰ (acetic acid, Black shale). In addition, the methyl carbon of acetic acid in all samples is the most depleted of any other alkyl group by as much as 10.5‰.

Figure 6 plots the $\delta^{13}\text{C}$ values of the total acid, carboxyl-derived carbon and alkyl-derived carbon as a function of carbon number for acids from the Black shale. The carbon-isotope composition of the carboxyl-derived carbon is intermediate of

the $\delta^{13}\text{C}$ value of the aqueous carbon dioxide and bicarbonate. Additionally, the calculated $\delta^{13}\text{C}$ values for the alkyl-derived carbons are generally coincident with the measured $\delta^{13}\text{C}$ values of the thermally immature kerogen.

4. DISCUSSION

Three general isotopic trends are present in the organic acids generated from each of the source rocks: (1) $\delta^{13}\text{C}$ variation as a function of source rock, (2) ^{13}C enrichment due to increasing thermal maturity, and (3) ^{13}C enrichment as a function of decreasing molecular weight of the organic acid. Each of the trends must be considered in the context of constraining potential generation and postgeneration reactions.

4.1. Potential Organic Acid Generation Mechanisms

Proposed generation mechanisms for LMW organic acids include pyrolysis of fatty acids (Cooper and Bray, 1963), oxidation of an ester, unsaturated fatty acid or other suitable acid precursor (Kawamura et al., 1986; Siskin and Katritzky, 1991; Lewan and Fisher, 1994), the release of "caged" organic acids during early kerogen breakdown (Kawamura et al., 1986), the cleavage of ionic bonds (Barth et al., 1989), and hydrolytic

disproportionation of light hydrocarbons (Helgeson et al., 1993). Our isotope data provide no evidence that any one mechanism is more responsible than any other for the generation of organic acids by hydrous pyrolysis. In addition, the carbon-isotope data provides no evidence to suggest that a generation mechanism is solely responsible for the observed isotopic trends with thermal maturity, source-rock type and organic acid molecular weight. For example, during the oxidation of hydrocarbons or other suitable precursors, it is envisioned that ^{12}C would be more easily oxidized, leading to an isotopic depletion in organic acids with decreasing molecular weight. As for the release of caged or ionically bound acids, we would expect little or no fractionation because no covalent bonds are broken. The carbon-isotope values of the caged or

Table 4. Carbon-isotope values for measured carboxyl carbon, measured total acid, and calculated residual alkyl carbon for selected samples.

Temperature (°C)		o.a.	$\delta^{13}\text{C}_{\text{tot}}$	$\delta^{13}\text{C}_{\text{carb}}$	$\delta^{13}\text{C}_{\text{alk}}$	
Wilcox Coal						
350	C ₂		-28.7	-25.2	-32.3	
	C ₃		-24.8	-26.6	-23.9	
	C ₄		-24.2	-26.5	-23.4	
	C ₅		-24.6	-26.5	-24.2	
	C ₆		-25.9	-26.8	-25.7	
	330	C ₂		-30.1	-25.3	-35.0
C ₃			-26.6	-26.7	-26.5	
C ₄			-25.0	-26.8	-24.4	
C ₅			-25.3	-26.7	-24.9	
C ₆			-26.7	-27.4	-26.6	
310		C ₂		-31.6	-25.8	-37.3
	C ₃		-26.9	-26.9	-26.8	
	C ₄		-25.4	-26.6	-25.0	
	C ₅		-25.3	-25.5	-25.2	
	C ₆		-24.9	-25.5	-24.7	
	280	C ₂		-31.4	-25.4	-37.5
C ₃			-27.0	-26.0	-27.4	
C ₄			-24.5	-25.8	-24.1	
240		C ₂		-31.4	-25.2	-37.6
		C ₃		-26.8	-24.9	-27.8
200		C ₂		-28.1	-24.4	-31.8
Mahogany Shale						
350	C ₂		-18.8	-4.1	-33.6	
	C ₃		-22.5	-7.1	-30.2	
	C ₄		-22.2	-8.4	-26.8	
	C ₅		-24.2	-9.0	-28.0	
	C ₆		-27.5	-8.6	-31.3	
	Ghareb Limestone (Jordan)					
350	C ₂		-22.4	-14.5	-30.3	
	C ₃		-23.1	-15.3	-27.0	
	C ₄		-23.9	-14.1	-27.1	
	C ₅		-25.0	-14.9	-27.6	
	C ₆		-25.5	-14.9	-27.6	
	330	C ₂		-23.3	-11.5	-35.2
C ₃			-24.8	-13.3	-30.6	
C ₄			-25.4	-13.3	-29.4	
C ₅			-26.7	-13.4	-30.1	
C ₆			-27.2	-13.3	-30.0	
310		C ₂		-24.7	-13.3	-36.0
	C ₃		-26.7	-16.9	-31.6	
	C ₄		-28.8	-16.7	-32.9	
	C ₅		-27.8	-16.9	-30.5	
	C ₆		-28.1	-17.4	-30.2	
	280	C ₂		-28.6	-21.1	-36.1
C ₃			-29.4	-20.3	-33.9	
C ₆			-28.9	-23.4	-30.0	
240	C ₂		-29.2	-24.1	-34.2	

Table 4. (Continued).

Temperature (°C)		o.a.	$\delta^{13}\text{C}_{\text{tot}}$	$\delta^{13}\text{C}_{\text{carb}}$	$\delta^{13}\text{C}_{\text{alk}}$	
Ghareb Limestone (Israel)						
350	C ₂		-21.8	-10.9	-32.7	
	C ₃		-23.1	-12.5	-28.4	
	C ₄		-25.9	-13.0	-30.2	
	C ₅		-25.5	-14.0	-28.4	
	C ₆		-26.2	-14.7	-28.6	
	Black Shale					
350	C ₂		-18.5	-4.7	-32.3	
	C ₃		-21.6	-6.9	-29.0	
	C ₄		-22.5	-6.8	-27.8	
	C ₅		-25.7	-7.7	-30.2	
	C ₆		-28.1	-8.1	-32.1	
	330	C ₂		-18.8	-4.1	-33.6
C ₃			-22.5	-7.1	-30.2	
C ₄			-22.2	-8.4	-26.8	
C ₅			-24.2	-9.0	-28.0	
C ₆			-27.5	-8.6	-31.3	
310		C ₂		-18.6	-3.6	-33.5
	C ₃		-24.0	-7.0	-32.5	
	C ₄		-28.0	-12.0	-31.2	
	285	C ₂		-20.2	-6.4	-33.9
		C ₃		-24.7	-11.7	-31.2
		C ₆		-28.6	-12.5	-31.8
New Albany Shale						
350	C ₂		-26.3	-18.4	-34.2	
	C ₃		-27.0	-19.5	-30.7	
	330	C ₂		-27.5	-18.7	-36.4
C ₃			-27.2	-20.2	-30.7	
C ₄			-27.6	-20.6	-29.9	
C ₅			-27.3	-18.7	-29.5	
310		C ₂		-28.5	-18.7	-38.3
		C ₃		-26.3	-20.3	-29.3
	285	C ₂		-32.6	-27.7	-37.5
C ₃			-30.0	-28.1	-31.0	

ionically bound acids would primarily be controlled by sedimentary input and subsequent diagenesis. Our isotopic data could only then be explained by the unlikely release of isotopically distinct pools of organic acids at increasing temperatures.

Acetic acid $\delta^{13}\text{C}$ values for the Ghareb shales, New Albany Shale, and Wilcox coal at low reaction temperatures are generally lower than the initial $\delta^{13}\text{C}$ values of the respective parent kerogens. This suggests that acids may be covalently bound in accordance with preferential breakage of ^{12}C - ^{12}C bonds. The observed trends with initially depleted acid $\delta^{13}\text{C}$ values are also consistent with the generation of acids by oxidation and hydrolytic disproportionation. However, reactions of model compounds under similar hydrous pyrolysis conditions suggest that ester hydrolysis may be responsible for organic acid generation and the observed low apparent activation energy of acid generation (Dias, 2000).

4.2. Postgeneration Reactions: Degradation

LMW organic acids undergo decarboxylation as a main degradation pathway (Jurg and Eisma, 1964; Carothers and Kharaka, 1978; Kharaka et al., 1983; Andresen et al., 1984; Kawamura et al., 1986; Palmer and Drummond, 1986a,b; Bell, 1991; Bell et al., 1994). As the reaction involves the cleavage of carbon-carbon bonds, a primary kinetic normal isotope effect

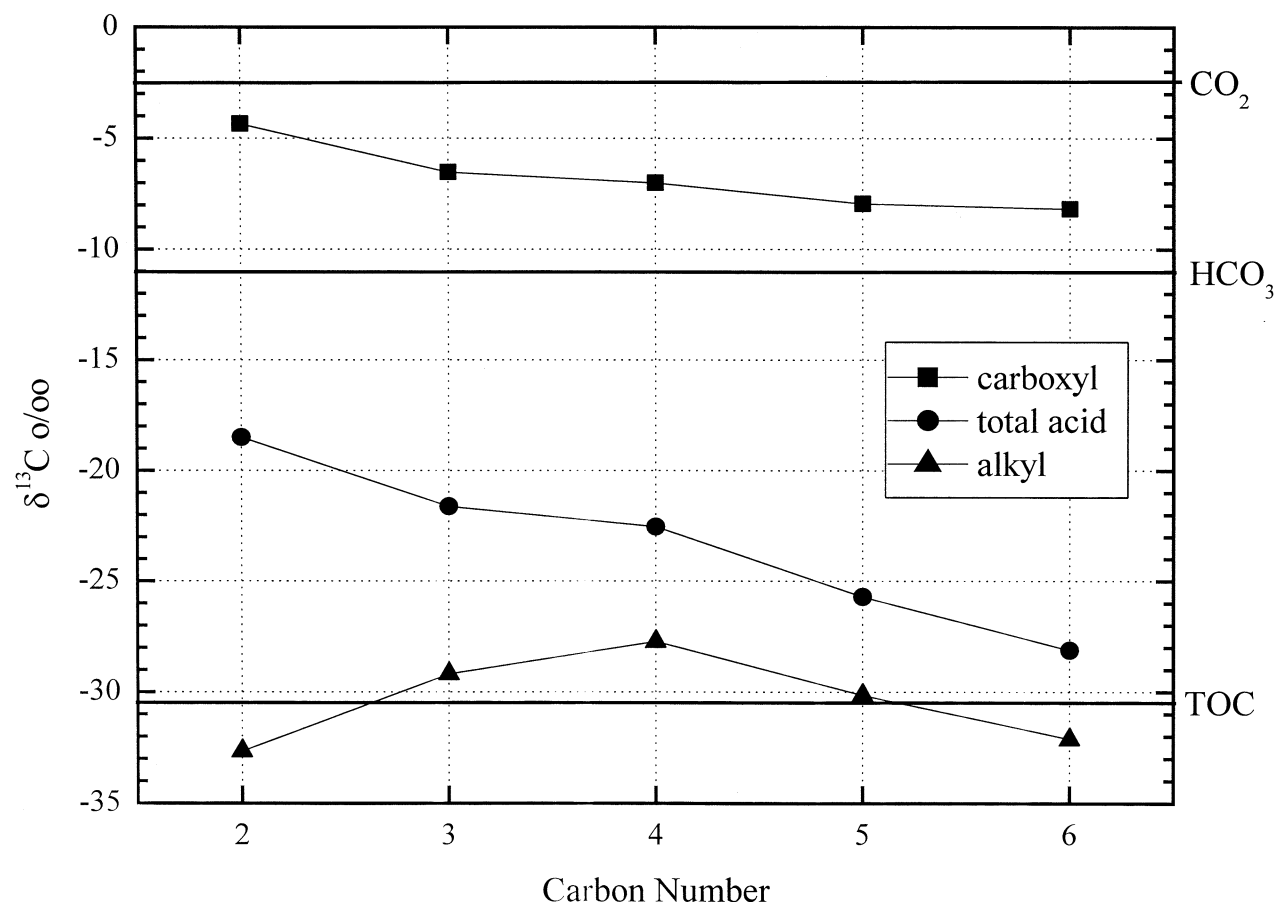


Fig. 6. Carbon-isotope values of measured carboxyl carbon, total acid, and calculated residual alkyl carbon for acids from the Black shale at 350°C for 72 h.

would result in the residual acid pool becoming enriched in ^{13}C at higher levels of thermal maturity. This effect was observed by Kharaka et al. (1983) who confirmed that ^{12}C - ^{12}C bonds were preferentially broken during acetic acid degradation and is consistent with our observation of a general increase in $\delta^{13}\text{C}$ values with increasing thermal maturity. However, we would expect to observe an equivalent isotope effect independent of source rock and kerogen type. This is inconsistent with the lack of isotopic enrichment observed in acetic acid from the Mahogany shale and Black shale (310 to 360°C) as compared with the significant enrichment observed for acetic acid generated from the New Albany shale and Wilcox coal over the same temperature range. Additionally, reaction of model organic acids at similar concentrations with bicarbonate under hydrous pyrolysis conditions (350°C/72 h) proceed with out any significant loss of organic acid (Dias, 2000). Although destructive decarboxylation likely occurs in natural systems, we believe that it does not impose a significant control on the $\delta^{13}\text{C}$ values of organic acids in our closed experimental system.

4.3. Postgeneration Reactions: Carboxyl Exchange

Shock (1988) proposed that under geologic conditions, aqueous organic acids are in a metastable equilibrium with one another and may be in equilibrium with dissolved CO_2 at

oxygen fugacities lower than those set by iron oxide mineral assemblages and that high concentrations of acids are in disequilibrium with respect to decarboxylation. Although Shock did not propose a reaction mechanism between organic acids and CO_2 , the exchange of carboxyl carbon with DIC (carboxyl exchange) is a scenario that does allow for organic acid $\delta^{13}\text{C}$ values consistent with our data and that of Franks et al. (2001). For acetic acid, carboxyl exchange was proposed to operate under acidic to neutral conditions with increasing rate of reaction as pH becomes more alkaline (Chu, 1997). More recently, Dias (2000) demonstrated using model organic acids and ^{13}C -labeled bicarbonate that carboxyl exchange occurred as a pH-dependent reaction under hydrous pyrolysis conditions similar to those employed in this work.

The effect of carboxyl exchange on organic acids from all six source rocks is demonstrated in Figure 5. Waters from the hydrous pyrolysis of the carbonate rock samples (Green River shales and the Ghareb limestones) contain significant concentrations of DIC due to the dissolution of calcium carbonate and is highly enriched in ^{13}C relative to the organic carbon in the kerogen. Incorporation of the DIC into the organic acids at the carboxyl position would result in organic acids that have distinct isotopic contributions from the organic material (alkyl carbons) and the DIC (carboxyl group). The isotopic trends

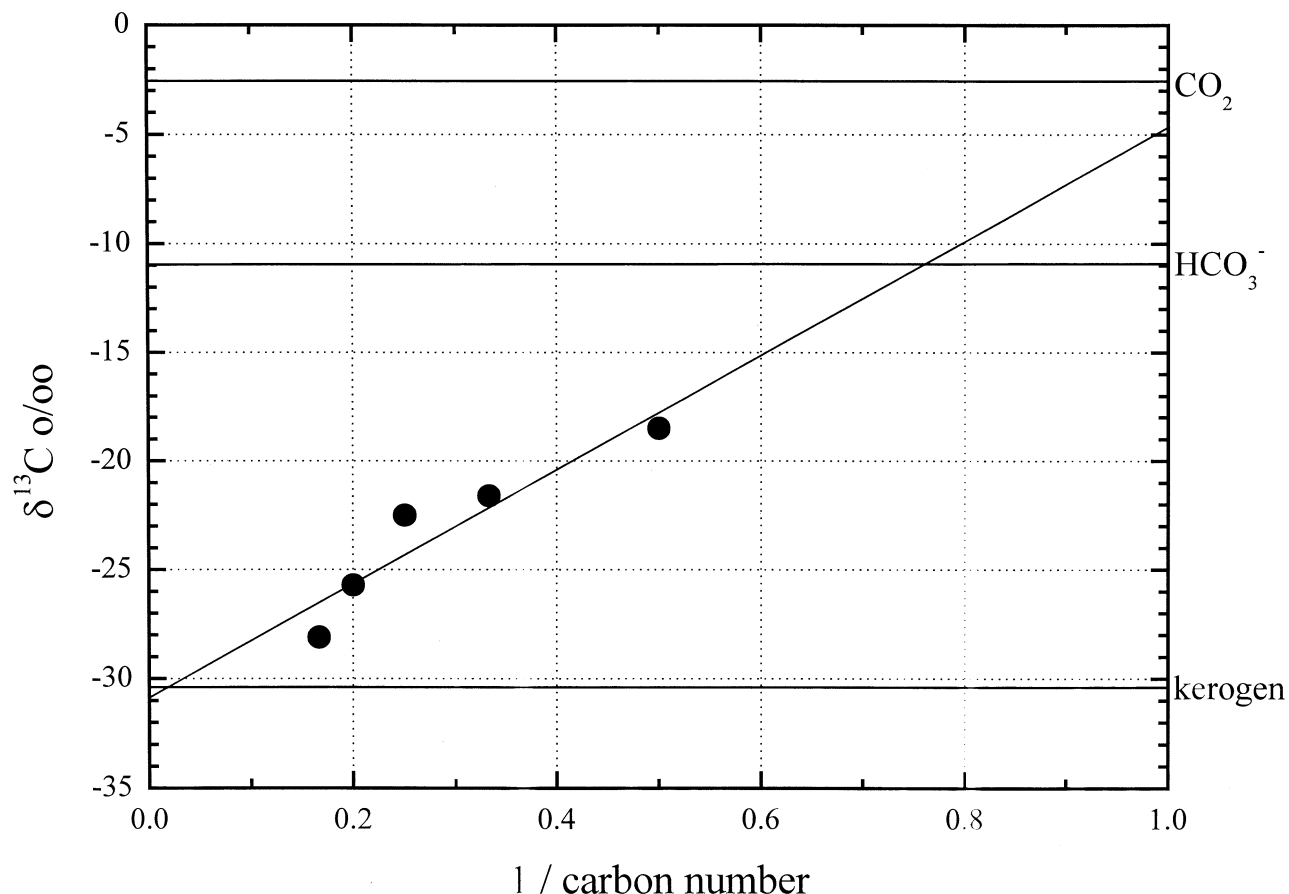


Fig. 7. Plot of $1/n$ vs. carbon-isotope value for organic acids from the Black shale at 350°C for 72 h. After Franks et al. (2001).

with molecular weight therefore represent a mixing line between the $\delta^{13}\text{C}$ of DIC and the $\delta^{13}\text{C}$ of the parent organic material. For hydrous pyrolysis conditions of 350°C for 72 h, the Green River rocks have the most enriched CO_2 values (-3.3 and -2.3%) and therefore show the most severe trend of isotopic enrichment with decreasing carbon number. The Ghareb shales have next most enriched CO_2 values (-10.4 and -10.9%) and show less pronounced trend. The New Albany shale and Wilcox coal contain no carbonate. Therefore, any CO_2 derived from these rocks must originate from the organic matter. At 350°C , these samples have $\delta^{13}\text{C}$ values for ambient CO_2 of -14.7 and -21.3% , respectively, and show flat isotopic trends with molecular weight relative to the trends for Green River and Ghareb rocks.

The carbon-isotope data for measured carboxyl-derived carbon, measured total organic acid and calculated alkyl-derived carbon presented in Table 4 shows clearly that significant intramolecular isotopic variability exists in organic acids generated from source rocks under hydrous pyrolysis conditions. As a representative example, Figure 6 plots the $\delta^{13}\text{C}$ value for the carboxyl-derived carbon, alkyl-derived carbon, and total organic acid for the Black shale ($350^{\circ}\text{C}/72$ h). The $\delta^{13}\text{C}$ value of the carboxyl carbon is intermediate of values calculated for $\text{CO}_{2(\text{aq})}$ and bicarbonate at reaction temperature from Eqn. 1 and 2, whereas the residual alkyl carbons have $\delta^{13}\text{C}$ values

(from Eqn. 2) that are similar to the $\delta^{13}\text{C}$ value for the initial kerogen. In addition to showing the intramolecular variability within the acids, it also implies ambiguity as to whether bicarbonate or $\text{CO}_{2(\text{aq})}$ is exchanging with the carboxyl carbons.

Because bicarbonate, carbonate, and $\text{CO}_{2(\text{aq})}$ exist in our experiments under all conditions, it is unclear which inorganic carbon species is the main reactant. By use of SOLMINEQ88 (Kharaka and Barnes, 1973), $\text{CO}_{2(\text{aq})}$ and bicarbonate were calculated to be the dominant inorganic carbon species under representative hydrous pyrolysis conditions with relative abundances of 60 to 70% and 30 to 40%, respectively. The amount of carbonate ion (CO_3^{2-}) was negligible. Given the $\delta^{13}\text{C}$ values of carboxyl-derived carbon and their systematic occurrence between the calculated $\delta^{13}\text{C}$ values of $\text{CO}_{2(\text{aq})}$ and HCO_3^- , it is reasonable to propose at this point that organic acids undergo carboxyl exchange with both bicarbonate and aqueous carbon dioxide under hydrous pyrolysis conditions.

4.4. Implications

As proposed by Franks et al. (2001), for a given suite of acids, a plot of the $\delta^{13}\text{C}$ values of organic acid vs. the inverse of the carbon number ($1/n$, after Eqn. 3) should yield the $\delta^{13}\text{C}$ of the organic source ($1/n = 0$) and the associated inorganic

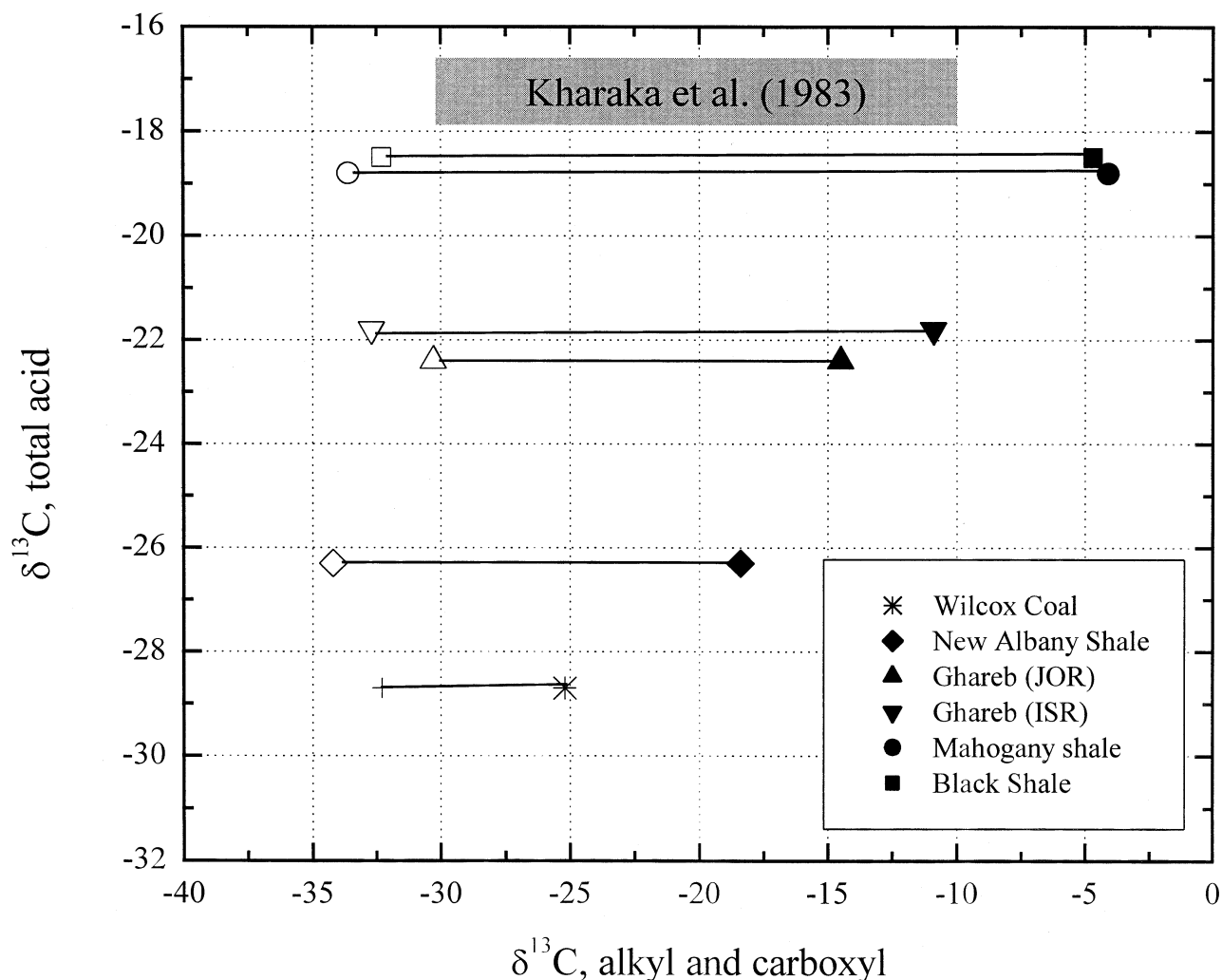


Fig. 8. Plot of total acid $\delta^{13}\text{C}$ vs. the $\delta^{13}\text{C}$ for alkyl methyl (open symbols) and carboxyl carbon (solid symbols) for acetic acids generated from each of the six source rocks at 350°C for 72 h. The shaded bar represents the 20‰ fractionation proposed by Kharaka et al. (1983), and the tie lines serve to emphasize the isotopic spread between methyl and carboxyl carbons in acetic acid.

carbon ($1/n = 1$). This model was able to delineate the two main oil sources in the San Joaquin Basin (Monterey vs. Kreyenhagen; Franks et al., 2001). Our hydrous pyrolysis data are consistent with this model. As exemplified in Figure 7 for the Black shale, at $1/n = 0$, the intercept corresponds to the $\delta^{13}\text{C}$ value observed for the original kerogen, whereas at $1/n = 1$, the best fit line falls in between $\delta^{13}\text{C}$ values for $\text{CO}_{2(\text{aq})}$ and bicarbonate. Our laboratory data validate this model for oil-associated organic acids, and it should prove a valuable reconnaissance and diagnostic tool for the exploration and reservoir management of petroleum systems.

The large variability of the intramolecular isotopic distributions between carboxyl and alkyl carbon observed in this work has implications for the formation of natural gas from the decomposition of organic acids. Kharaka et al. (1983) observed that carbon dioxide produced from acetate pyrolysis was 20‰ enriched in ^{13}C relative to the coproduced methane. This led the authors to conclude that a 20‰ fractionation occurred between the carboxyl and methyl carbon during pyrolytic deg-

radation. Although not explicitly stated, that was based on the assumption that the carboxyl and methyl carbons initially had the same $\delta^{13}\text{C}$ composition. Our observations suggest that the results of Kharaka et al. (1983) reflect, at least in part, a significant intramolecular isotopic difference between carboxyl and alkyl carbons. For example, the $\Delta\delta^{13}\text{C}_{\text{carboxyl-alkyl}}$ for acetic acid generated under hydrous pyrolysis conditions simulating maximum oil generation range from 27.6‰ for the Black shale to 7.1‰ for the Wilcox coal (Fig. 8). If the acetic acid generated from the Black Shale (or any of the other source rocks) at 350°C was allowed to pyrolyze to CO_2 and methane, the $\delta^{13}\text{C}$ values of the gases could be similar to those as shown in Table 4 for the carboxyl-derived and alkyl derived carbon. Although natural gas may form from the degradation of LMW organic acids, the isotopic differences between CO_2 and hydrocarbon gases in natural gas formed from the pyrolysis of organic acids may bear the overprint of the intramolecular fractionation between carboxyl and alkyl carbons in addition to kinetic fractionation during pyrolytic gas formation.

5. CONCLUSIONS

LMW, aqueous organic acids were generated from six different source rocks under hydrous pyrolysis conditions. Despite differences in their mineralogy and organic matter abundance and composition, TOC-normalized acetic acid generation is on the same order of magnitude for each source rock. However, significant differences in the absolute abundances of generated organic acids exist between the source rocks. Acid concentration data are consistent with a model that organic acids migrate out of the source rock with the expelled oil and then partition into the surrounding water. LMW organic acids display increasing ^{13}C content as a function of decreasing molecular weight and increasing thermal maturity. The magnitudes of the observed isotope enrichments vary with different source-rock lithologies. Our data are consistent with $\delta^{13}\text{C}$ values of organic acids presented by Franks et al. (2001) and therefore reflect the duality of distinct alkyl-carbon and carboxyl-carbon $\delta^{13}\text{C}$ values.

Our data do not support a single mechanism for the generation of organic acids. Further, the isotopic trends we observe as a function of molecular weight, thermal maturity, and rock type are not supported by either generation mechanisms or destructive decarboxylation. We therefore propose that organic acids experience isotopic fractionation during generation and subsequently undergo postgeneration reaction with DIC. Although generation and decarboxylation may influence the $\delta^{13}\text{C}$ values of organic acids, in our hydrous pyrolysis system, the nondestructive, pH-dependent exchange of carboxyl carbon with inorganic carbon appears to be the most important reaction mechanism controlling the $\delta^{13}\text{C}$ values of the organic acids.

Acknowledgments—These hydrous pyrolysis experiments represent the work of several researchers, of which this isotopic study is but one part. Hydrous pyrolysis of the Green River source rocks was performed by Tim Ruble in conjunction with the U.S. Geological Survey as part of his doctoral research (Ruble, 1996). Hydrous pyrolysis of the Ghareb limestones was performed with Eli Tannenbaum (Kimron Oil and Minerals, Israel) and Hazem Ramini (Jordanian Geological Survey, Jordan) as part of a collaborative basin evaluation project with the U.S. Geological Survey. Hydrous pyrolysis of the New Albany shale was performed for a basin evaluation project headed by Dr. Michael Lewan (Lewan et al., 1995). We thank Tanja Barth, Martin Schoell, and an anonymous reviewer for their thoughtful, constructive reviews. Funding for this work was provided by the ACS-PRF, the Atlantic-Richfield Corporation, and the U.S. Geological Survey.

Associate editor: R. C. Burruss

REFERENCES

- Andresen B., Torbjorn T., Barth T., and Bolstad J. (1984) Thermal generation of carbon dioxide and organic acids from different source rocks. *Org. Geochem.* **21**, (12) 1229–1242.
- Barth T., Borgund A. E., Hopland A. L., and Graue A. (1988) Volatile organic acids produced during kerogen maturation—Amounts, composition and role in migration of oils. *Org. Geochem.* **13**, (1–3) 461–465.
- Barth T., Borgund A. E., and Hopland A. L. (1989) Generation of organic compounds by hydrous pyrolysis of Kimmeridge oil shale—Bulk results and activation energy calculations. *Org. Geochem.* **14**, (1) 69–76.
- Barth T. and Riis M. (1992) Interactions between organic acid anions in formation waters and reservoir mineral phases. *Org. Geochem.* **19**, (4–6) 455–482.
- Barth T. and Bjorlykke K. (1993) Organic acids from source rock maturation: Generation potentials, transport mechanisms and relevance for mineral diagenesis. *Appl. Geochem.* **8**, 325–337.
- Barth T. and Nielsen S. B. (1993) Estimating kinetic parameters for generation of petroleum and single compounds from hydrous pyrolysis of source rocks. *Energy Fuels* **7**, 100–110.
- Bell J. L. (1991) Acetate decomposition in hydrothermal fluids. Ph.D. dissertation. Pennsylvania State University.
- Bell J. L., Palmer D. A., Barnes H. L., and Drummond S. E. (1994) Thermal decomposition of acetate, III: Catalysis by mineral surfaces. *Geochim. Cosmochim. Acta* **58**, (19) 4155–4177.
- Blair N. E., Martens C. S., and Des Marais D. J. (1987) Natural abundances of carbon isotopes in acetate from a coastal marine sediment. *Science* **236**, 66–68.
- Borgund A. E. and Barth T. (1994) Generation of short-chain organic acids from crude oil by hydrous pyrolysis. *Org. Geochem.* **21**, (8–9) 943–952.
- Carothers W. W. and Kharaka Y. K. (1978) Aliphatic acid anions in oilfield waters: Implications for the origin of natural gases. *AAPG Bull.* **62**, 2441–2453.
- Chu X. (1997) Kinetics of isotope exchange reactions involving thio-sulfate and acetate intermediaries in hydrothermal systems. Ph.D. dissertation. Tohoku University, Japan.
- Collins A. G. (1975) *Geochemistry of Oil Field Waters*. Elsevier.
- Cooler G. P., MacKenzie A. S., and Parkes R. J. (1987) Non-hydrocarbons of significance in petroleum exploration: Volatile fatty acids and non-hydrocarbon gases. *Miner. Mag.* **51**, 483–493.
- Cooper J. E. and Bray E. E. (1963) A postulated role of fatty acids in petroleum formation. *Geochim. Cosmochim. Acta* **27**, 1113–1127.
- Cordell R. J. (1972) Depths of oil origin and primary migration. *AAPG Bull.* **56**, 2029–2067.
- Cozzarelli I. M., Beadecker M. J., Eaganhouse R. P., and Goerlitz D. F. (1994) The geochemical evolution of low-molecular weight organic acids derived from the degradation of petroleum contaminants in groundwater. *Geochim. Cosmochim. Acta* **58**, (2) 863–877.
- Dias R. F. (2000) Stable carbon-isotope geochemistry of low-molecular weight organic acids in oil associated waters. Ph.D. dissertation. Penn State University.
- Dias R. F. and Freeman K. H. (1997) Carbon isotope analysis of semivolatiles organic compounds in aqueous media using solid-phase microextraction and isotope ratio monitoring GCMS. *Anal. Chem.* **69**, (5) 944–950.
- Dias R. F., Freeman K. H., Lewan M. D., and Franks S. G. (2002) Gas chromatography–pyrolysis–isotope ratio mass spectrometry: A new method for investigating intramolecular isotopic variation in low molecular weight organic acids. *Org. Geochem.* **33**, (2) 161–168.
- Eglinton T. I., Curtis C. D., and Rowland S. J. (1987) Generation of water-soluble organic acids from kerogen during hydrous pyrolysis: Implications for porosity development. *Miner. Mag.* **51**, 495–503.
- Fisher J. B. (1987) Distribution and occurrence of aliphatic acid anions in deep subsurface waters. *Geochim. Cosmochim. Acta* **31**, 2459–2468.
- Franks S. G., Dias R. F., Freeman K. H., Boles J. R., Fincannon A. L., Holba A., and Jordan E. A. (2001) Carbon isotopic composition of organic acids in oil field waters, San Joaquin Basin, California, USA. *Geochim. Cosmo. Acta* **65**, (8) 1301–1310.
- Galimov E. M. (1973) *Carbon Isotopes in Oil–Gas Geology*. NASA TT F-682. National Aeronautics and Space Administration.
- Gelwicks J. T., Risatti J. B., and Hayes J. M. (1989) Carbon-isotope effects associated with autotrophic acetogenesis. *Org. Geochem.* **14**, (4) 441–446.
- Giles M. R., DeBoer R. B., and Marshall J. D. (1994) How important are organic acids in generating secondary porosity in the subsurface? In *Organic Acids in Geological Processes* (eds. E. D. Pittman and M. D. Lewan), pp. 449–470. Springer-Verlag.
- Hanor J. S. and Workman A. L. (1986) Distribution of dissolved volatile fatty acids in some Louisiana oil-field brines. *Appl. Geochem.* **1**, 37–46.
- Helgeson H. C., Knox A. M., Owens C. E., and Shock E. L. (1993) Petroleum oil field waters and authigenic mineral assemblages: Are they in metastable equilibrium in hydrocarbon reservoirs? *Geochim. Cosmochim. Acta* **57**, 3295–3339.

- Jurg J. W. and Eisma E. (1964) Petroleum hydrocarbons: Generation from fatty acid. *Science* **144**, 1451–1452.
- Kartsev A. A. (1974) Hydrology of Oil and Gas Deposits. *Natl. Tech. Inf. Service Report TT73-58022*.
- Kawamura K., Tannenbaum E., Huizinga B. J., and Kaplan I. R. (1986) Volatile organic acids generated from kerogen during laboratory heating. *Geochem. J.* **20**, 51–59.
- Kharaka Y. K. and Barnes I. (1973) SOLMINEQ: Solution–mineral equilibrium computations. USGS Computer Contributions, National Technical Information Service, PB215-899. [An updated version, SOLMINEQ88, was provided to us by Y. Kharaka, U.S Geological Survey, Open File Report 89-616.
- Kharaka Y. K., Carothers W. W., and Rosenbauer R. J. (1983) Thermal decarboxylation of acetic acid: Implications for the origin of natural gas. *Geochim. Cosmochim. Acta* **47**, 397–402.
- Kharaka Y. K., Lundegard P. D., Ambats G., Evans W. C., and Bischoff J. L. (1993) Generation of aliphatic acid anions and carbon dioxide by the hydrous pyrolysis of crude oils. *Appl. Geochem.* **8**, 317–324.
- Knauss K. G., Copenhaver S. A., Braun R. L., and Burnham A. K. (1997) Hydrous pyrolysis of New Albany and phosphoria shales: Production kinetics of carboxylic acids and light hydrocarbons and interactions between the inorganic and organic chemical systems. *Org. Geochem.* **27**, (7–8) 477–496.
- Lekrone K. J. and Hayes J. M. (1997) Efficiency and temperature dependence of water removal by membrane dryers. *Anal. Chem.* **69**, (5) 911–918.
- Lewan M. D. (1983) Effects of thermal maturation on the stable organic carbon isotopes as determined by hydrous pyrolysis of Woodford Shale. *Geochim. Cosmochim. Acta* **46**, 1471–1479.
- Lewan M. D. (1985) Evaluation of petroleum generation by hydrous pyrolysis experimentation. *Phil. Trans. R. Soc. Lond. Ser. A* **315**, 123–134.
- Lewan M. D., Winters J. C., and McDonald J. H. (1979) Generation of oil-like pyrolyzates from organic rich shales. *Science* **203**, 869–899.
- Lewan M. D. and Fisher J. B. (1994) Organic acids from petroleum source rocks. In *Organic Acids in Geological Processes* (eds. E. D. Pittman and M. D. Lewan), pp. 70–114. Springer Verlag Berlin, Germany.
- Lewan M. D., Comer J. B., Hamilton-Smith T., Hasenmueller N. R., Gutherie J. M., Hatch D. L., Gautier D. L., and Frankie W. T. (1995) *Feasibility Study of Material-Balance Assessment of Petroleum Formation from the New Albany Shale in the Illinois Basin*. U.S. Geological Survey Government Printing Office Washington, D.C. Bulletin 2137, U.S.
- Lundegard P. D. and Senftle J. T. (1987) Hydrous Pyrolysis: A tool for the study of organic acid synthesis. *Appl. Geochem.* **2**, 605–612.
- MacGowan D. B. and Surdam R. S. (1990) Carboxylic acid anions in formation waters, San Joaquin Basin and Louisiana Gulf Coast, USA—Implications for clastic diagenesis. *Appl. Geochem.* **5**, 687–701.
- Manning D. A. C. (1997) Acetate and propionate in landfill leachates: Implications for the recognition of microbial influences on the composition of water in sedimentary systems. *Geology* **25**, (3) 279–281.
- Means J. L. and Hubbard N. (1987) Short chain aliphatic acid anions in deep subsurface brines: A review of their origin, occurrence, properties and importance and new data on their distribution and geochemical implications in the Palo Duro Basin, TX. *Org. Geochem.* **11**, 177–191.
- Meinschein W. G., Rinaldi G. L., Hayes J. M., and Schoeller D. A. (1974) Intramolecular isotopic order in biologically produced acetic acid. *Biomed. Mass Spec.* **1**, 172–174.
- Merritt D. A., Freeman K. H., Ricci M. P., Studley S. A., and Hayes J. M. (1995) Performance and optimization of a combustion interface for isotope-ratio monitoring gas chromatograph/mass spectrometer. *Anal. Chem.* **67**, (14) 2461–2473.
- Monson K. D. and Hayes J. M. (1980) Biosynthetic control of the natural abundance of carbon 13 at specific positions within fatty acids in *Escherichia coli*. *J. Biol. Chem.* **262**, 8159–8164.
- Monson K. D. and Hayes J. M. (1982) Carbon isotopic fractionation in the biosynthesis of bacterial fatty acids. Ozonolysis of unsaturated fatty acids as a means of determining the intramolecular distribution of carbon isotopes. *Geochim. Cosmochim. Acta* **46**, 139–149.
- Mook W. G., Bommerson J. C., and Staverman W. H. (1974) Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. *Earth Planet. Sci. Lett.* **22**, 169–176.
- Palmer D. A. and Drummond S. E. (1986a) Thermal decarboxylation of acetate. Part 1. The kinetics and mechanism of reaction in aqueous solution. *Geochim. Cosmochim. Acta* **50**, 813–823.
- Palmer D. A. and Drummond S. E. (1986b) Thermal decarboxylation of acetate. Part 2. Boundary conditions for the role of acetate in the primary migration of natural gas and transportation of metals in hydrothermal systems. *Geochim. Cosmochim. Acta* **50**, 825–833.
- Ricci M. P., Merritt D. A., Freeman K. H., and Hayes J. M. (1994) Acquisition and processing of data for isotope-ratio monitoring mass spectrometry. *Org. Geochem.* **21**, (6/7) 561–571.
- Ruble T. E. (1996) Geochemical investigation of the mechanisms of hydrocarbon generation and accumulation in the Uinta Basin, Utah. Ph.D. dissertation. University of Oklahoma.
- Shock E. L. (1988) Organic acid metastability in sedimentary basins. *Geology* **16**, 886–890.
- Siskin M. and Katritzky A. R. (1991) Reactivity of organic compounds in hot water: Geochemical and technological implications. *Science* **25**, 231–237.
- Tissot B., Durand B., Espitalie J., and Combaz A. (1974) Influences of nature and diagenesis of organic matter in the formation of petroleum. *AAPG Bull.* **58**, 499–506.
- Vogel J. C., Grootes P. M., and Mook W. G. (1970) Isotopic fractionation between gaseous and dissolved carbon dioxide. *Z. Phys.* **230**, 225–238.
- Vogler E. A. and Hayes J. M. (1979) Carbon isotope fractionation in the Schmidt decarboxylation: Evidence for two pathways to products. *J. Org. Chem.* **44**, (21) 3682–3686.
- Workman A. L. and Hanor J. S. (1985) Evidence for large-scale vertical migration of dissolved fatty acids in Louisiana oil-field brines: Iberia field, south-central Louisiana. *Trans. Gulf Coast Geol. Soc.* **35**, 293–300.
- Zinger A. S. and Kravchik T. E. (1973) Simple organic acids in ground water in the lower Volga region (genesis and possible use in prospecting for oil). *Akad. Nauk SSSR Doklady* **202**, 218–221.