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A solid state ^{13}C -NMR study of kerogen degradation during black shale weathering

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Abstract—Solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy is used to examine kerogen composition in weathering profiles of the Monterey, Green River, Woodford, and New Albany formations. Techniques include cross polarization (CP) and Bloch decay (BD) spectral acquisition, dipolar dephasing (DD), spin counting, experiments to provide estimates of relaxation times ($T_{1\rho}\text{H}$ and $T_1\text{H}$), and proton spin relaxation editing (PSRE). It is demonstrated that CP/MAS (cross polarization/magic angle spinning) spectra obtained on isolated kerogens provide reliable characterization of kerogen composition (compared with BD spectra and whole-rock samples). Highly aliphatic (polymethylenic) kerogens are not appreciably altered during weathering. Aromatic and/or branched aliphatic kerogens accumulate oxidation products and preferentially lose aliphatic relative to aromatic carbon during weathering. No relation is observed between $T_{1\rho}\text{H}$ times and either kerogen composition or degree of weathering; $T_1\text{H}$ times correlate with aromaticity. Two distinct components within kerogens are discerned by PSRE: one highly aliphatic (largely polymethylenic) component and one mixed aliphatic/aromatic component. During weathering, the highly aliphatic component remains largely unaltered, while the mixed component loses aliphatic carbon and accumulates carbonyl oxidation products. Thus it appears that kerogen weathering is dominated by two separate processes: Linear alkyl fragments are cleaved without oxidation, and aromatic/branched alkyl fragments are oxidized while attached to the kerogen macromolecule and then cleaved. Copyright © 2001 Elsevier Science Ltd

1. INTRODUCTION

Sedimentary rocks contain the largest reservoir of organic matter (OM) on earth. Weathering of ancient OM stored in sedimentary rock, with associated release of CO_2 and consumption of O_2 , is a major process controlling the composition of earth's atmosphere (Holland, 1978; Berner, 1987; Petsch and Berner, 1998). Controls on OM remineralization during weathering are poorly understood. There is evidence that some pool of OM escapes remineralization during weathering and becomes reburied in modern sediments (Sackett et al., 1984; Barrick et al., 1980; Eglinton et al., 1997; Rowland and Maxwell, 1984). Incomplete OM weathering may result from at least two separate phenomena: (1) Rapid erosion and transport limits the time a given parcel of OM spends in oxidative, biologically active environments, in direct corollary with cumulative O_2 exposure time controlling OM preservation in sediments (Hartnett et al., 1998) and (2) Specific organic moieties may be resistant to oxidation/dissolution reactions, in analogy to selective preservation in marine sediments and soils (Goth et al., 1988; Derenne et al., 1991, 1992a,b; Flaviano et al., 1994; Kokinos et al., 1998; Lichtfouse et al., 1998; Hatcher et al., 1983; Augris et al., 1998). For example, inherent resistance of highly aliphatic OM is used to explain differences in kerogen composition between unweathered and weathered samples of the Indiana Paper coal (Nip et al., 1989).

The study presented here comprises samples from weathering profiles developed on the Monterey, Green River, Woodford, and New Albany shales. The extensive organic carbon

loss revealed in these sample sets provides a unique opportunity to examine both selective degradation of various kerogen components and accumulation of kerogen degradation products. Organic carbon loss between the most and least weathered sections of each profile range from 60% (Monterey) to nearly 95% (New Albany) (Petsch et al., 2000). Infrared (IR) spectra of these sample sets reveal preferential loss of alkyl C–H bonds and enrichment in C=C and C=O bonds; pyrolysate compositions within these sample sets remain largely unchanged with weathering except within the Green River profile, in which long linear alkyl fragments are mildly enriched with weathering (Petsch et al., 2000).

The focus of the study presented here is to use ^{13}C nuclear magnetic resonance (NMR) spectroscopy to provide a detailed description of changes that occur in kerogen composition during weathering of black shales. NMR spectroscopy complements other kerogen analytical methods in several ways. A description of the whole kerogen sample is obtained, compared with only the pyrolysable and GC-amenable fraction revealed by pyrolysis-gas chromatography (Py-GC). NMR provides greater specificity in carbon bond types and improved quantification over IR spectroscopy. In this study, we employ a variety of NMR techniques to examine oxidation and other alterations in OM structure that accompany weathering of black shales. These techniques include both Bloch decay and cross-polarization signal acquisition with magic angle spinning and high-power proton decoupling, dipolar dephasing (or interrupted decoupling) pulse sequences, variable contact time experiments, and inversion recovery experiments. Characteristic relaxation times obtained from inversion recovery experiments are used to generate subspectra of chemically distinct and

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Fig. 1. Exposure of New Albany shale near Clay City, KY. A 5 to 10 m wide zone of weathered rock developed here on the unweathered shale has been exposed by a roadcut. TOC contents in this weathering profile range from 1.5% in the soil to 9.6% in the unweathered shale.

spatially separated kerogen components using proton spin relaxation editing (PSRE). Spin counting is used to determine the degree of quantitation achieved with both cross-polarization and Bloch decay techniques.

2. EXPERIMENTAL

2.1. Sample collection and preparation

The outcrop region of each shale was surveyed to locate an exposure that revealed a complete weathering profile (soil, regolith, and unweathered shale). Usually a recent road cut into a hillside was used (Fig. 1). Soils at each site were thin to non-existent; bedding could be discerned extending from unweathered shale completely through the weathered rock. Samples were collected as profiles along single stratigraphic horizons from heavily weathered shale at the surface to unweathered shale from the hillside's original interior (i.e., before creation of the roadcut), taking care to remove any recent weathering and detritus from the face of the exposure. Macroscopic plant remains (roots) were observed only in the most weathered samples from the New Albany and Green River shale profiles; these materials were removed by hand.

Samples were crushed in a ball mill, extracted with 2 : 1 v/v $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ and air-dried. Samples were demineralized to isolate kerogens using sequential $\text{HCl}/\text{HF}/\text{HCl}$ digestions, followed by a second $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ extraction. Sample names and key geochemical parameters are listed in Table 1.

2.2. NMR spectroscopy

Solid state ^{13}C magic angle spinning (MAS) NMR spectra were obtained at a ^{13}C frequency of 50.3 MHz on a Varian Unity200 spectrometer. Samples of known mass (20–120 mg C) were packed in a 7 mm diameter cylindrical zirconia rotor with Kel-F end caps and spun at 5000 ± 100 Hz in a Doty Scientific MAS probe. Free induction decays were acquired with a sweep width of 40 kHz; 1216 data points were collected over an acquisition time of 15 ms. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm. Table 2 lists carbon types and corresponding ^{13}C -NMR shifts common in geochemical samples.

Cross-polarization (CP) spectra were acquired using a standard CP/MAS pulse sequence (Wilson 1987). A 1 ms contact time was used for all samples except WF-467 (500 μs) and WF-370 (670 μs), with recycle delays between 300 and 500 ms for all CP spectra. Between 5000 and 50,000 transients were collected for each spectrum. CP spectra were zero filled to 8192 data points and processed with a 50 Hz Lorentzian line broadening and a 0.010 s Gaussian broadening.

Bloch decay (BD) spectra were acquired using a 6.2 μs (90°) ^{13}C pulse. A recycle delay of 90 s was used for all samples except WF-467 for which a recycle delay of 10 s was shown to be adequate from variable recycle delay experiments. Between 600 and 2500 transients were collected for each sample. BD spectra were zero filled to 2048 data points and processed with a 50 Hz Lorentzian line broadening and a 0.010 s gaussian broadening.

The Kel-F rotor end caps give rise to a significant ^{13}C signal in BD spectra, which overlap with the NMR signal of the samples. To correct

Table 1. Sample information and geochemical data. Sample name indicates abbreviated formation name and depth (cm) into weathering profile (e.g., WF-467: Woodford profile, 467 cm from the surface). Radiocarbon data are reported as the fraction of TOC that is ancient (radiocarbon-dead) and are given for sample depths, or closest depth for which data are available. (b.d.l. = below detection limit, n/d = not determined).

Sample name	Formation, location, age	Whole rock % TOC	Whole rock % pyrite S	Kerogen % TOC	Kerogen O/C	¹⁴ C-derived fraction modern OM
WF-467	Woodford, OK (Arbuckle Mtns.), Late Devonian	22.55	1.00	65.98	0.086	0.0048
WF-370	Woodford, OK (Arbuckle Mtns.), Late Devonian	15.27	0.073	59.92	0.135	n/d
WF-272	Woodford, OK (Arbuckle Mtns.), Late Devonian	6.88	0.032	46.16	0.330	n/d
WF-195	Woodford, OK (Arbuckle Mtns.), Late Devonian	4.77	0.026	34.26	0.370	0.0443 (at 165 cm depth)
WF-136	Woodford, OK (Arbuckle Mtns.), Late Devonian	3.33	0.018	18.71	0.474	n/d
WF-82	Woodford, OK (Arbuckle Mtns.), Late Devonian	0.98	0.013	7.73	0.402	0.2999 (at 29 cm depth)
NACC-315	New Albany, KY (Clay City), Late Devonian	8.96	3.310	77.97	0.057	n/d
NACC-189	New Albany, KY (Clay City), Late Devonian	7.20	0.725	48.72	0.074	0.001 (at 220 cm depth)
NACC-105	New Albany, KY (Clay City), Late Devonian	6.08	0.122	35.47	0.146	n/d
NACC-84	New Albany, KY (Clay City), Late Devonian	4.26	0.026	24.98	0.230	n/d
NACC-63	New Albany, KY (Clay City), Late Devonian	1.83	0.015	11.98	0.376	0.0088 (at 73 cm depth)
NADV-426	New Albany, KY (Deatsville), Late Devonian	7.64	1.354	46.73	0.102	0.0073 (at 284 cm depth)
NADV-28	New Albany, KY (Deatsville), Late Devonian	3.89	0.017	18.62	0.344	0.0072
MO-232	Monterey, CA (Gaviota Beach), Miocene	12.68	0.044	57.41	0.111	0.0064
MO-0	Monterey, CA (Gaviota Beach), Miocene	5.01	0.471	42.07	0.183	0.0163
GR-366	Green River, UT (Nine Mile Canyon), Eocene	17.86	0.061	74.56	0.047	0.0022 (at 307 cm depth)
GR-30	Green River, UT (Nine Mile Canyon), Eocene	1.06	0.008	6.59	0.380	0.0126 (at 35 cm depth)

for this, the end-cap spectrum was acquired separately (7000 transients) and subtracted from each BD spectrum before integration. The end-cap signal was acquired using a recycle delay of 10 s, which is adequate for complete relaxation based on prior experiments. The CP ¹³C-NMR spectrum of the Kel-F end caps is very weak due to the low ¹H content of the fluorinated polymer; CP spectra were not corrected for end-cap signal.

All spectra (CP and BD) were baseline corrected between –100 ppm and 300 ppm and integrated between –10 ppm and 300 ppm (referred to as total intensity, I). These integration limits were chosen so as to include all resonances including the first order spinning side bands of the carbonyl and aromatic resonances (see Table 2).

2.2.1. Dipolar dephasing

Dipolar dephasing (DD) experiments were carried out using the pulse sequence of Harbison et al. (1985). Acquisition parameters were identical to those used for CP spectra, with the addition of a 42 μs “dephasing delay” during which the high power proton decoupler was turned off. A 1 ms contact time was used for all samples except WF-467 (500 μs) and WF-370 (670 μs). A 300 ms recycle delay was used for each sample except GR-366, for which a 1 s recycle delay was used. Between 1600 and 50,000 transients were collected for each DD spectrum. DD spectra were zero filled to 8192 data points and processed with a 5 Hz Lorentzian line broadening and a 0.005 s Gaussian broadening.

Table 2. Carbon types and corresponding ¹³C-NMR chemical shifts observed in kerogen samples. 2° refers to secondary alkyl carbons, 3° refers to tertiary alkyl carbons.

Carbon type	Chemical shift
<i>Aliphatic region</i>	
CH ₃ adjacent to 2°C	<15 ppm
CH ₃ adjacent to 3° and aromatic C	18–25 ppm
<i>n</i> -alkyl CH ₂	29–32 ppm
3°C; CH ₂ adjacent to 3°, aromatic, and carbonyl C; alkyl sulfides	32–40 ppm
sp ₃ C-O, i.e., ethers, alcohols and alkoxy C	50–100 ppm
<i>Aromatic and olefinic region</i>	
Unsubstituted C, thiophene C	110–130 ppm
Acid/ester substituted C and fused-ring bridgehead C	130–135 ppm
Alkyl substituted C	135–150 ppm
Alkoxy and OH substituted C	146–165 ppm
<i>Carbonyl region</i>	
Acid and ester C	165–190 ppm
Ketones and aldehydes	>190 ppm

Note: A broad spinning side band of the main aromatic resonance is often observed at ~230 ppm.

Source: Silverstein, Bassler and Morrill (1991).

2.2.2. $T_{1\rho}H$ and T_1H

$T_{1\rho}H$ values were calculated from variable contact time (VCT) experiments (Alla and Lippmaa 1976) using an array of contact times between 20 μ s and 8 ms. A recycle delay of 500 ms was used for each sample, and between 800 and 10,000 transients were collected per contact time. The free induction decay (FID) corresponding to each contact time in the array was processed in the same way as for the single contact time CP spectra. For the Green River, Monterey, and New Albany (Deatsville) samples, $T_{1\rho}H$ was calculated as the negative reciprocal of the slope ($-1/m$) of the line of best fit for the graph of $\ln(\text{total intensity})$ versus contact time for the linear decay phase of the curve. For the Woodford and New Albany (Clay City) samples, $T_{1\rho}H$ was calculated in a similar manner, but using the peak height of the alkyl resonance as a gauge of signal intensity rather than the total integral. This was required due to the presence of aromatic structures with long T_{CH} components for which $\ln(\text{total intensity})$ versus contact time was nonlinear. Upper and lower bounds of the 95% confidence interval of $T_{1\rho}H$ were calculated from the standard error of the slope (σ) as $-1/(m + 2\sigma)$ and $-1/(m - 2\sigma)$, respectively.

T_1H values were determined from inversion-recovery experiments (Wilson 1987). These experiments involved inserting a proton inversion pulse (12.8 μ s) and a variable recovery delay before the normal CP pulse sequence. An array of recovery delays between 0.1 ms and 1 s was used. A 1 ms contact time was used for all samples except WF-467 (500 μ s) and WF-370 (670 μ s). A recycle delay of 1 s was used for each sample, except WF-467 (500 ms), and between 700 and 5500 transients were collected. The free induction decay (FID) corresponding to each recovery delay in the array was processed in the same way as for the single contact time CP spectra.

Average T_1H values were calculated by fitting total (integrated) intensity (I) versus recovery delay (t) to Eqn. 1:

$$I = I_{\text{inf}} [1 - H \times e^{(-t/T_1H)}] \quad (1)$$

where I_{inf} is the total intensity of a fully relaxed (infinite recovery delay) spectrum and H is the “homogeneity factor,” which describes the efficiency of the inversion pulse.

For some samples the data fitted better to a two-component model (Eqn. 2):

$$I = I_{\text{inf, fast}} [1 - H \times e^{(-t/T_{1H_{\text{fast}}})}] + I_{\text{inf, slow}} [1 - H \times e^{(-t/T_{1H_{\text{slow}}})}] \quad (2)$$

where the subscripts “fast” and “slow” refer to parameters for a rapidly relaxing and a slowly relaxing component, respectively.

2.2.3. Proton spin relaxation editing

Proton spin relaxation editing (PSRE) was used to generate subspectra of the rapidly and slowly relaxing components identified in inversion recovery experiments, using the method of Smernik et al. (2000). PSRE involves taking linear combinations of a “normal” CP spectrum (S_{CP}) and a partially relaxed inversion recovery spectrum (S_{IR}) with recovery time (t), to generate “pure” subspectra of the rapidly relaxing (SS_{fast}) and slowly relaxing (SS_{slow}) components. The linear combinations required to generate the subspectra are:

$$SS_{\text{fast}} = -[f_b/(f_a - f_b)] \times S_{\text{CP}} + [1/(f_a - f_b)] \times S_{\text{IR}} \quad (3)$$

$$SS_{\text{slow}} = [f_a/(f_a - f_b)] \times S_{\text{CP}} - [1/(f_a - f_b)] \times S_{\text{IR}} \quad (4)$$

$$f_a = 1 - H \times e^{(-t/T_{1H_a})} \quad (5)$$

$$f_b = 1 - H \times e^{(-t/T_{1H_b})} \quad (6)$$

where T_{1H_a} and T_{1H_b} are T_1H values for the rapidly and slowly relaxing components, respectively. Note that the sum of the two subspectra ($SS_{\text{fast}} + SS_{\text{slow}}$) is exactly the “normal” CP spectrum (S_{CP}). The recovery delay (t) used for S_{IR} in generating PSRE subspectra was chosen to minimize noise in the subspectra (Smernik et al., 2000).

2.2.4. Quantification and spin counting

The degree of quantitation achieved (i.e., the proportion of potential NMR intensity that was actually observed) was determined by spin counting, using the method of Smernik and Oades (2000a,b). Glycine (AR grade, Ajax Chemicals) was used as the intensity standard.

For CP spin counting, differences in spin dynamics between the sample and the glycine standard are accounted for using the method of Smernik and Oades (2000a,b) whereby the total intensity of the CP spectrum (I) is corrected for signal loss due to $T_{1\rho}H$ relaxation using Eqn. 7:

$$I_{\text{corr}} = I/e^{(-CT/T_{1\rho}H)} \quad (7)$$

where CT , the contact time, was 1 ms for each sample except WF-467 ($CT = 500$ ms) and WF-370 ($CT = 670$ ms). For BD spin counting, the spectrum was integrated after subtraction of the end-cap signal to give I_{corr} .

For both CP and BD spin counting, the corrected total intensity (I_{corr}) was divided by the mass (m) of material in the rotor to give the mass-corrected intensity (I^*) (Eqn. 8), which is proportional to both the percentage carbon content (%C) of the sample and the average observability of the ^{13}C nuclei in the sample (C_{obs}) (Eqn. 9). The constant (k) was determined by assuming 100% observability of the glycine sample, i.e., $C_{\text{obs}}(\text{glycine}) = 100\%$. C_{obs} for each sample was then determined using Eqn. 10.

$$I^* = I_{\text{corr}}/m \quad (8)$$

$$I^* = k \times \%C \times C_{\text{obs}} \quad (9)$$

$$C_{\text{obs}} = I^*/(k \times \%C) \quad (10)$$

Errors are estimated to be $\pm 10\%$ in $C_{\text{obs-CP}}$ and $\pm 15\%$ in $C_{\text{obs-BD}}$ (Smernik and Oades 2000a,b).

3. RESULTS

3.1. NMR comparison of whole-rock powders and kerogen isolates

^{13}C -NMR spectroscopy on whole-rock powders is often limited by low organic carbon content and the presence of paramagnetic minerals, which broaden and diminish resonances. Hence, ^{13}C -NMR spectra of whole-rock powders are often characterized by poor signal-to-noise (S/N) ratios and poor resolution. These problems can be overcome by concentration of the OM by kerogen isolation. However, it is important to ensure that the isolation procedure neither selectively removes specific OM components nor generates new artifacts.

We obtained both BD and CP spectra from selected whole-rock and kerogen isolate pairs of both unweathered and weathered shale samples. BD spectra of the whole-rock powder and the kerogen isolate from unweathered Woodford Shale (WF-467) are compared in Figure 2. Acquisition and processing parameters are identical, except that a greater number of transients were acquired for the whole-rock spectrum (7800) than for the kerogen spectrum (1296). The better S/N ratio for the kerogen sample reflects mainly a higher organic carbon content (66% compared with 22.6% for the whole rock). Both spectra are poor in resolution, but similar.

Figure 3 compares the CP spectra of whole-rock powder and kerogen isolate from a weathered sample of New Albany shale (NADV-28). The very similar distribution of resonances in each spectrum indicates a similar composition, but resolution and S/N ratio are clearly superior in the kerogen spectrum, despite the acquisition of six times as many transients for the whole-rock sample. This improvement can be attributed to

Fig. 2. Comparison of Bloch decay spectra obtained from powdered whole-rock and a kerogen isolate of unweathered Woodford shale (WF-467), revealing enhanced signal in the isolated kerogen spectrum. Spinning side bands denoted by asterisk (*).

greater carbon content in the kerogen, but also to greater NMR observability for the kerogen (90%) than for the whole rock (40%).

These results confirm that kerogen isolation generates representative ^{13}C -NMR spectra of both unweathered and weathered shale samples. For this reason, this study presents NMR spectra obtained on kerogen isolates.

3.2. Comparison of BD and CP spectra

Two different polarization methods were used in this study: Bloch decay (BD) and cross polarization (CP). Bloch decay (or direct polarization) is a more quantitatively reliable method, but generates approximately fourfold less signal per transient and requires an ~ 100 -fold longer recycle delay between transients.

Fig. 3. Comparison of cross-polarized spectra obtained from powdered whole-rock and isolated kerogen from a heavily weathered sample of New Albany Shale (NADV-28). Oxidized resonances observed in the whole-rock spectrum (carbonyl and ether/alcohol) are not lost in the kerogen isolation.

Fig. 4. Comparison of Bloch decay and cross-polarization spectral acquisition for kerogen isolated of heavily weathered Woodford Shale (WF-82) and unweathered New Albany Shale (NADV-426). Cross polarization generates improved signal-to-noise without appreciable loss of data. Spinning side bands denoted by asterisk (*).

The result is much poorer S/N ratios and/or longer acquisition times. Cross polarization is less quantitatively reliable than Bloch decay because the CP-NMR signal can be diminished for ^{13}C nuclei remote from ^1H nuclei (e.g., carbons within polyaromatic clusters) or coupled to ^1H nuclei characterized by rapid $T_{1\rho}\text{H}$ rates. However, the improved S/N ratios and shorter acquisition times make CP the preferred technique provided that there are no quantitation problems or that they can be overcome.

Spin counting is a quantitation technique that determines how much potential ^{13}C -NMR signal is actually observed. Because NMR quantitation problems involve underrepresentation of particular moieties rather than overrepresentation, observabilities near 100% ensure that the NMR spectrum quantitatively represents the distribution of ^{13}C environments present in the sample. On the other hand, spectra for which observability is substantially <100% may still quantitatively

represent the distribution of carbon types in a sample, provided that signal loss is non-selective.

Observabilities for BD and CP spectra are shown in Table 4. BD observabilities are generally higher, ranging between 61 and 98%, reflecting the more robust nature of this technique. CP observabilities vary between 23 and 92%. BD and CP spectra are very similar for each sample, even when BD and CP observabilities are significantly different. As an example, BD and CP spectra for the WF-82 sample are compared in Figure 4. Better resolution is obtained for the CP spectrum of the WF-82 sample, allowing the sharp resonances in the chemical shift range of 50 to 100 ppm to be distinguished. A comparable improvement is revealed in the CP spectrum of unweathered sample NADV-426 in Figure 4. Demonstrating that CP and BD spectra record similar carbon distributions allows confident use of CP techniques for this study.

3.3. Effects of weathering on solid state ^{13}C -NMR spectra of kerogens

The primary goal of this study was to investigate changes in kerogen structure that accompany OM loss during weathering of black shales. CP spectra of unweathered and highly weathered kerogens from five weathering profiles are compared in Figure 5, with spectra from unweathered samples shown in the left column. CP spectra were integrated to provide abundance estimates of total carbonyl (200–160 ppm), aromatic (160–100 ppm), O-alkyl (100–60 ppm), and aliphatic (60–0 ppm) carbon. Percent abundance of these carbon types (after side band correction) are shown in Table 3.

3.3.1. Unweathered kerogens

The CP spectrum of unweathered Green River kerogen (GR-366) reveals a composition of predominantly long polymethylene chains (~ 30 ppm), with minor contributions from methyl and branched alkyl groups and a modest aromatic component. The CP spectrum of the unweathered sulfur-rich type Monterey kerogen (MO-232) is quite similar to that of the Green River kerogen, but with relatively more aromatic components, the presence of acid and/or ester resonances at ~ 175 ppm, minor O-alkyl resonances between ~ 60 and 90 ppm, and a broad aliphatic carbon band between ~ 50 and 30 ppm. Sulfide-bound carbons (~ 20 –35 ppm) cannot be distinguished here from alkyl carbons, and substituted thiophenes overlap other aromatic carbons; therefore, little information about organic sulfur moieties can be discerned. The Woodford and two New Albany samples are nominally similar Late-Devonian kerogens; however, the CP spectra of unweathered samples of these shales are very different. The CP spectrum of the New Albany (Deatsville) sample (NADV-426) is similar to that of the Green River sample, but with a greater contribution from aromatic components. Aromatic carbons are even more abundant in the New Albany (Clay City) (NACC-315) and Woodford (WF-467) samples; indeed, the CP spectrum of the Woodford kerogen has roughly equal contributions from aromatic and aliphatic carbons. The broad aliphatic carbon resonance in the New Albany, Woodford, and Monterey samples indicates more abundant branched hydrocarbons, more terminal and internal methyl groups, and possibly shorter average chain lengths (which would reduce the proportion of methylene carbons) compared with the Green River sample.

3.3.2. NMR spectroscopy of weathered samples

Alteration is easily discerned in the weathered samples from each profile (right column of Fig. 5). The appearance of a carbonyl resonance from acid/ester groups at ~ 175 ppm is ubiquitous in all weathered samples, although less predominant in the Green River compared with other kerogens. Resonances corresponding to O-alkyl carbons in the range 50 to 100 ppm are only weakly present in weathered samples, with the exception of sample WF-82. The strong resonances between ~ 90 and 50 ppm in this sample indicate a significant contribution from polysaccharides to this kerogen isolate. This sample also contains the highest fraction of “modern OM” determined by ^{14}C contents (Table 1). Interestingly, no macroscopic plant remains were observed in samples from the Woodford weathering pro-

file. This material may then represent humic materials or polysaccharides that have percolated downward into the shallowest, most permeable sections of the weathering profile, either in particulate form or dissolved and then adsorbed onto the kerogen macromolecule. Why an abundance of polysaccharide is not observed in other weathering profiles remains unclear. In any case, while this modern material is apparent in normal NMR spectra, it is distinguished from true weathered kerogen by PSRE (see section 3.5).

Weathering variably affects the abundance of aliphatic and aromatic carbons. The relative abundance of aliphatic to aromatic carbons remains almost unchanged with weathering for the Green River, Monterey, and New Albany (Deatsville) profiles. In both the Woodford and New Albany (Clay City) profiles, however, a large loss in aliphatic carbon relative to aromatic is observed. Weathering also generates a mild redistribution of carbons within the broad aliphatic resonance. For example, the upfield (methyl carbon) region of the aliphatic resonance (<30 ppm) is increased in the weathered Green River sample but is diminished in the weathered Woodford sample. Also, a distinct shoulder at 55 ppm is evident for the weathered New Albany (Deatsville) sample, which was not present in the spectrum of the unweathered sample. Loss of the downfield portion of the broad aromatic resonance (substituted aromatics, $>\sim 130$ ppm) is observed in weathered New Albany and Woodford samples.

CP spectra from several depths within the New Albany (Clay City) and Woodford weathering profiles are shown in Figure 6. In the Woodford profile, weathering and TOC loss is tracked by a steady decrease in aliphatic structures and increase in carbonyl carbons. The sharp resonances in the 50 to 100 ppm region are only apparent in the most weathered samples (which contain non-fossil organic C). In the New Albany (Clay City) profile, the CP spectra appear identical from NACC-315 to NACC-105, with the carbonyl resonance only apparent in NACC-84 and, more strongly, in NACC-63. Again, the increase in carbonyl carbon is accompanied by a decrease in aliphatic to aromatic ratio.

3.3.3. Dipolar dephased spectra of unweathered and weathered kerogens

Dipolar dephasing (DD) experiments result in suppression of signal from most protonated carbons, leaving signal from both non-protonated carbon and highly mobile (methyl and polymethylene) carbons. DD spectra are shown in Figure 7 for pairs of unweathered and weathered samples from the five weathering profiles. Enhanced carbonyl resonance in weathered samples is obvious for all profiles except the Green River, which contains little carbonyl carbon. A shoulder at ~ 150 ppm (hydroxyl- or alkoxy-substituted aromatic C) becomes apparent in unweathered samples of the Monterey and both New Albany shales. However, this resonance does not increase in weathered samples. Little or no difference is observed for other specific aromatic carbons with weathering.

The aliphatic resonances in DD spectra are more revealing. Unweathered kerogens in all samples contain three resonances at approximately 30, 23, and 13 ppm. The aliphatic portion of the Green River, New Albany (Deatsville), and to a lesser extent, Monterey kerogens is dominated by the ~ 30 ppm

Fig. 5. Comparison of CP/MAS (cross polarization/magic angle spinning) ^{13}C -NMR (nuclear magnetic resonance) spectra of kerogen isolates from least and most heavily weathered samples of Green River, Monterey, New Albany, and Woodford formations. Spinning side bands denoted by asterisk (*).

Table 3. Percent relative intensity of carbon classes within kerogen samples from black shale weathering profiles derived from side band-corrected integration of CP spectra.

<i>Chemical shift span integrated (ppm)</i>	% Carbonyl 200-160 ppm	% Aromatic 160-100 ppm	% O-alkyl 100-60 ppm	% Aliphatic 60-0 ppm
Sample name				
WF-457	1.28	43.26	4.81	50.66
WF-370	6.45	47.90	6.59	39.07
WF-272	11.36	54.49	6.28	27.88
WF-195	10.65	55.88	7.35	26.12
WF-136	11.16	56.31	8.87	23.67
WF-82	16.75	59.75	10.32	13.18
NACC-315	0.00	41.98	2.70	53.81
NACC-189	0.27	40.71	3.69	55.33
NACC-105	2.60	40.79	4.76	51.85
NACC-84	5.62	45.48	5.93	42.98
NACC-63	11.26	57.91	9.15	21.59
NADV-426	0.00	30.37	2.46	67.17
NADV-28	4.10	32.27	4.94	58.69
MO-232	2.72	27.97	6.77	62.53
MO-0	4.09	26.11	7.38	62.42
GR-366	1.10	21.18	1.27	76.45
GR-30	2.62	23.13	4.93	69.32

resonance, indicating abundant “highly mobile” polymethylenic structures (see Wilson 1987). No trend is observed in relative abundance of these three resonances with weathering. Indeed, the relative proportion of total aliphatic to aromatic carbon observed in DD spectra remains approximately constant with weathering of the Green River, New Albany (Deatsville), and Monterey kerogens.

The DD spectrum of the unweathered New Albany (Clay City) sample contains relatively more of the high field aliphatic resonance at ~ 13 ppm (methyl carbons), and less of the ~ 30 ppm mobile methylene resonance. The abundance of the entire aliphatic region is so reduced in the weathered New Albany (Clay City) sample that specific aliphatic carbons cannot be resolved. The aliphatic region of the unweathered Woodford DD spectrum contains a broad resonance extending downfield of ~ 30 ppm, indicating various branched/methylated carbons. In the weathered Woodford kerogen, much of this aliphatic structure has been lost, and only the 30 ppm (methylene C) resonance is retained. The sharp resonances observed in the CP spectrum of WF-82 in the range 50 to 100 ppm are not present in the DD spectrum, indicating that these structures are protonated and non-mobile. Other features enhanced by DD include the O-alkyl carbons in weathered samples of the Monterey and New Albany (Deatsville) shales.

3.4. NMR relaxation rates

NMR relaxation rates provide another parameter to probe differences in kerogen from different sources and at different stages of weathering. Relaxation rates are dependent on a number of aspects of kerogen composition, such as the presence of paramagnetic centers (either organic or inorganic) and molecular mobility. Two different types of relaxation rate were determined, $T_{1\rho}\text{H}$ and $T_1\text{H}$.

$T_{1\rho}\text{H}$, the ^1H relaxation rate in the rotating NMR frame, was

determined from variable contact time experiments (Wilson, 1987). These experiments probed the dynamics of ^{13}C signal build up (characterized by the rate constant T_{CH}) and decay (characterized by $T_{1\rho}\text{H}$) during the “contact time” of the cross-polarization technique. $T_{1\rho}\text{H}$ varied between 0.56 and 5.85 ms for the unweathered kerogen samples (Table 4). Weathering did not influence $T_{1\rho}\text{H}$ for any of the profiles except the Woodford profile, for which $T_{1\rho}\text{H}$ was very short for the deepest two samples (0.56 and 0.66 ms for WF-467 and WF-370, respectively), but increased to ~ 4 ms for the three most weathered Woodford samples. The very short $T_{1\rho}\text{H}$ values for WF-467 and WF-370 indicate the presence of paramagnetic species (most likely organic free radicals) and necessitated shorter contact times in the corresponding CP spectra to optimize quantitation between protonated and non-protonated carbons. Because the Woodford is the most thermally mature of the shales examined in this study, it is not unexpected that Woodford kerogens would exhibit a strong free radical content. EPR studies have shown a strong correlation between free radical content, vitrinite reflectance, and NMR-determined kerogen aromaticity (Dickneider et al. 1995). For all other samples, $T_{1\rho}\text{H}$ was in the range where adequate quantitation is achieved using a 1 ms contact time (Smernik and Oades 2000a,b). Variable contact time experiments were also carried out on two whole-rock samples (WF-467 and NADV-28) and there was no significant difference in $T_{1\rho}\text{H}$ between whole-rock and kerogen samples.

In experiments to measure $T_1\text{H}$, proton magnetization is inverted then allowed to relax for a variable period before cross polarization. The process of proton magnetization relaxation through a null and back towards its equilibrium value is reflected in the intensities of the resultant array of spectra. $T_1\text{H}$ values are shown in Table 4. Average $T_1\text{H}$ values for the unweathered kerogen samples ranged between 12.5 ms (Woodford) and 46.1 ms (Green River). The short $T_1\text{H}$ value for the Woodford sample is consistent with its short $T_{1\rho}\text{H}$ value. There was no consistent trend in the effect of weathering on average $T_1\text{H}$. The large decrease in average $T_1\text{H}$ for the Green River kerogen is significant only in that it is the single NMR property to significantly change with weathering of this shale.

Average $T_1\text{H}$ values appear to be somewhat correlated with aromaticity, but with opposite trends for the weathered compared to the unweathered samples. For the unweathered samples, the more aromatic kerogens tend to have shorter $T_1\text{H}$ values. This trend may reflect the increasing ability of more aromatic kerogens to stabilize organic free radicals. For the weathered samples, the less aromatic kerogens tend to have shorter $T_1\text{H}$ values, with $T_1\text{H}$ decreasing in the order: New Albany (Clay City) > Monterey > New Albany (Deatsville) > Green River. It appears that weathering may quench the organic free radicals present in the unweathered kerogens. Decreases in $T_1\text{H}$ for the highly aliphatic kerogens may reflect greater molecular mobility and a “looser” packing of the long-chain polymethylene structures. The intermediate samples in the Woodford profile all had similar $T_1\text{H}$ values in the range 39.7 to 52.5 ms, which are substantially longer than for the deepest sample (WF-467), suggesting that organic free radicals are quenched early in the weathering process.

Fig. 6. Succession of CP/MAS ^{13}C -NMR spectra of kerogens isolated from the weathering profiles developed on the Woodford and New Albany (Clay City) shales, revealing that relative loss of aliphatic carbon precedes addition of carbonyl carbon during kerogen weathering. Spinning side bands denoted by asterisk (*).

3.5. Proton spin relaxation editing (PSRE)

Proton relaxation rates (both $T_{1\rho}\text{H}$ and $T_1\text{H}$) for individual nuclei are homogenized to a common value in most molecules

by the process of spin diffusion, by which relaxation of one ^1H nucleus causes the relaxation of nearby ^1H nuclei. However, spin diffusion is only efficient on the <100 nm scale (Zumbul-

Fig. 7. Comparison of dipolar dephased spectra of isolated kerogens from unweathered and weathered pairs of the Green River, Monterey, New Albany, and Woodford formations, with strong enhancement of carbonyl, aromatic, and polymethylenic resonances. Spinning side bands denoted by asterisk (*).

yadis 1983), so heterogeneity at larger scales can result in non-uniform proton relaxation rates. Non-uniformity in $T_1\rho$ was apparent in inversion recovery experiments for some of the kerogen samples. This can be seen quite clearly in the inversion recovery sequence for the NADV-426 sample shown in Figure 8. A rapidly relaxing component progresses through a null signal at a recovery delay of 10 ms revealing a residual,

inverted spectrum of the slowly relaxing component. This slowly relaxing component progresses through a null between recycle delay times of 20 to 35 ms, revealing the spectrum of the rapidly relaxing component. $T_1\rho$ values for the rapidly and slowly relaxing components, and their relative abundances, are shown in Table 4.

PSRE was most informative for the New Albany samples.

Table 4. CP and BD carbon %C observabilities, $T_{1\rho}H$, average T_1H , fast and slow T_1H , and relative abundance of rapidly and slowly relaxing components.

Sample	%C _{obs} -CP	%C _{obs} -BD	$T_{1\rho}H$ (ms)	T_1H_{AVG} (ms)	T_1H_{fast} (ms)	T_1H_{slow} (ms)	Fast:slow
WF-457	23	61	0.56	12.5			
WF-370	30	n/d	1.33	49.5			
WF-272	34	n/d	3.96	39.7			
WF-195	46	n/d	4.64	45.2			
WF-136	66	n/d	4.90	52.5			
WF-82	45	91	6.42	24.9	20.3	803	77:23
NACC-314	68	93	4.46	36.9	17.2	101	53:47
NACC-189	49	n/d	3.87	17.1	12.4	115	79:21
NACC-105	63	n/d	4.52	19.4	14.2	82.3	78:22
NACC-84	54	n/d	4.29	32.7	23.0	98.3	71:29
NACC-63	47	69	5.09	55.2	28.2	86.7	44:56
NADV-426	73	98	3.57	32.3	9.8	73.1	41:59
NADV-28	76	90	3.80	20.1	8.8	37.1	44:56
MO-232	54	n/d	3.02	28.9	21.5	72.3	73:27
MO-0	60	n/d	3.32	30.9	28.2	183	92:8
GR-366	92	n/d	5.85	46.1	23.0	92.7	47:53
GR-30	69	n/d	4.82	12.3			

GR-30 and most Woodford samples conform better to a one-component PSRE model than a two-component model; fast and slow subspectra were not generated for these samples. Not determined = n/d.

The slowly relaxing subspectrum of NADV-426 (Fig. 9) is highly aliphatic, resembling the spectrum of the Green River kerogen. The rapidly relaxing subspectrum of NADV-426 contains broad aliphatic and aromatic resonances, and is not unlike the spectrum of the unweathered Woodford kerogen. The PSRE subspectra of NADV-28 are very similar to those of NADV-426, indicating that weathering has little effect on the nature of these components. The relative amounts of the two components also alter little on weathering (Table 4), although T_1H for the slowly relaxing components decreases significantly, in line with the decrease in average T_1H observed for the highly aliphatic Green River kerogen on weathering.

The slowly relaxing subspectrum of NACC-315 is less aliphatic than the corresponding subspectrum of NADV-426, but the rapidly relaxing subspectra for the two unweathered New Albany kerogens are very similar (Fig. 9). Thus the greater aromaticity of the bulk New Albany (Clay City) kerogen is due less to the slowly relaxing component and more to the rapidly relaxing component compared with the New Albany (Deatsville) kerogen. The weathered New Albany (Clay City) sample also contains two components. The slowly relaxing component contains a broad aromatic resonance and a slightly less-intense broad aliphatic resonance. The rapidly relaxing component is dominated by a broad aromatic resonance and contains little aliphatic signal. The carbonyl resonance appears to be associated solely with the rapidly relaxing component.

The two-component model did not improve the fit of the inversion-recovery data for all Woodford samples except one, the heavily weathered WF-82 sample. The slowly relaxing component of the WF-82 sample (~22% of the total spectrum) contains essentially all of the O-alkyl carbon presumably derived from modern OM. This value of ~22% is fairly consistent with the ~30% modern OM derived from radiocarbon analyses (Table 1). The rapidly relaxing component may thus represent the "true" weathering products of Woodford kerogen not contaminated by modern OM. This component reveals loss of aliphatic carbon and gain of carbonyl carbon with weathering similar to the New Albany (Clay City) profile.

4. DISCUSSION

4.1. Links between OM composition and weathering characteristics

Specific morphologically distinct clasts of organic matter (macerals) in sedimentary rocks have long been recognized and assigned origins and precursors, and developments in separation techniques have allowed chemical variability among macerals also to be determined (Nip et al., 1988; 1989; Schenk et al., 1990; Senftle et al., 1991; Han et al., 1995; Stankiewicz et al., 1996). However, much organic matter in sedimentary rocks is still characterized as amorphous. Ultralaminae (thin microscopic layers within amorphous organic matter believed to derive from high aliphatic algae cell walls) have been recognized by some researchers as a major component of many kerogens (Flaviano et al., 1994; Derenne et al., 1991; 1992a,b; Largeau et al., 1990a,b). In many cases, however, light and even electron microscopy are insufficient to resolve any fine scale structure in organic matter samples (Largeau et al., 1990a,b). Thus the origin of amorphous organic matter and associations with defined macerals and their precursors remain undetermined.

The results of this study suggest that the weathering characteristics of each profile fall along a continuum between two endmember patterns that are linked to two broad OM types and structures. One endmember is represented by the Green River kerogen. Weathering results in significant TOC loss from this profile; the unweathered sample contains ~18% TOC while the weathered sample contains ~1% TOC. Despite this, CP spectra of the Green River samples reveal remarkable similarity between weathered and unweathered kerogens. OM loss is largely non-selective. The highly aliphatic, dominantly methylenic nature of this kerogen is preserved with weathering, with no significant change in aromatic/aliphatic abundance and only minor addition of oxidized carbons (acids/esters and O-alkyl). Any oxidation products formed during weathering must either be rapidly removed (either in solution or suspension) or be

Fig. 8. Partial inversion recovery sequence for kerogen isolate from a sample of unweathered New Albany Shale (NADV-426), showing the partial spectra at recovery delay of 0.1 ms through 1 s. Note that at 20 ms, the more rapidly relaxing aromatic + broad aliphatic component has a positive signal (relaxed through a null), whereas the more slowly relaxing highly aliphatic component retains a negative signal (not yet fully relaxed). This difference is used to separate these chemically distinct subspectra via PSRE (proton spin relaxation editing).

much more reactive than kerogen and rapidly oxidized to CO_2 because they do not appreciably accumulate on or in this kerogen. Dipolar dephasing experiments suggest little variation in non-protonated carbon abundance.

The other endmember is the Woodford kerogen. Again, OM

loss is large; the unweathered sample contains $\sim 22\%$ TOC while the weathered sample contains $\sim 1\%$ TOC. The mixed aliphatic/aromatic carbon distribution in unweathered kerogen is altered upon weathering to reveal a large loss of aliphatic C. Weathered Woodford kerogen exhibits abundant oxidized carbons (acid/esters and O-alkyl). Thus weathering of this endmember is selective, and oxidation products are retained in the kerogen matrix. The patterns of weathering for the Monterey and two New Albany profiles can readily be seen as mixing of variable contributions from these two endmembers.

PSRE analyses indicate that these two endmember weathering patterns are actually linked to two chemically and spatially distinct types of OM structure. It will be recalled that neither the Green River nor Woodford kerogens were readily separated into chemically distinct fast and slow relaxing components based on $T_1\rho$ data. The unweathered Green River kerogen is composed entirely of highly aliphatic OM characterized by a long average $T_1\rho$, while unweathered Woodford kerogen contains broad aliphatic and aromatic carbon characterized by a short average $T_1\rho$. It is observed consistently that in the other three profiles, the rapidly relaxing component resembles the Woodford kerogen and the slowly relaxing component resembles the Green River kerogen. Furthermore, upon weathering, the rapidly relaxing component generally loses aliphatic carbon and accumulated oxidation products, while the slowly relaxing component is preserved relatively intact. This is shown schematically in Figure 10.

These observations lead to two remarkable conclusions: (1) PSRE analysis may be used to distinguish, if not individual macerals, then certainly broad divisions in OM composition. The highly aliphatic material observed in the Green River kerogen and in the slowly relaxing components of the New Albany and Monterey shales may be linked to macerals rich in aliphatic carbon such as alginite and cutinite. The more mixed alkyl/aromatic material found in the Woodford and fast relaxing components of the New Albany and Monterey kerogens may indicate a greater contribution from maceral groups rich in aromatic and more highly branched aliphatic carbon. (2) These two materials exhibit distinct weathering patterns. The aliphatic material weathers non-selectively and accumulates little or no oxidation products. The broadly aliphatic + aromatic material accumulates oxidation products and may selectively lose aliphatic carbon. Perhaps the generally non-reactive nature of *n*-alkyl chains suggests that cleavage may be the more active degradation mechanism for highly aliphatic OM during weathering, while oxidation of the more reactive branched alkyl and substituted aromatic groups may dominate weathering of this type of OM.

4.2. Non-selectivity during OM weathering

Regardless of the differences in weathering patterns observed in these profiles, it does not appear that either endmember OM structure weathers appreciably faster than the other. If rates were not similar, a significant change in the relative proportion of these two components within a given kerogen would be observed upon weathering. Likewise, a significant difference in TOC loss would be expected between the Green River and Woodford profiles for which the macroscale variables that control physical and chemical weathering (such as

Fig. 9. Comparison of rapidly and slowly relaxing components of both weathered and unweathered kerogens.

climate, hydrology and relief) are roughly similar. Instead, neither a selective enrichment is observed in samples that contain both rapidly and slowly relaxing components, nor is there any real disparity in TOC loss between the two endmember-type weathering profiles. Thus despite different OM compositions, different weathering patterns, and different underlying degradation mechanisms, TOC loss is not closely related to OM type during black shale weathering.

5. CONCLUSIONS

This study presents an investigation of black shale weathering through a variety of complementary solid state ^{13}C -NMR techniques, which reveal that weathering of black shales results in varying degrees of alkyl carbon loss and carbon oxidation. Kerogen compositions vary among unweathered samples of the five profiles, but are consistent with a model of variable degrees

Fig. 10. . Schematic representation of kerogen weathering separating slowly and rapidly relaxing components. Height of column indicates relative abundance of each component (carbonyl, aromatic, or aliphatic). PSRE based on inversion recovery experiments reveals that the examined kerogens can be separated into chemically distinct slowly and rapidly relaxing components (based on separate $T_1\rho$). The NMR spectrum of the bulk kerogen can be understood as a linear combination of these two components. Weathering of the slowly relaxing component generates little chemical alteration of the kerogen structure, whereas weathering of the rapidly relaxing component generates substantial loss of aliphatic carbon and gain of carbonyl carbon relative to aromatic carbon.

of mixing of two broad OM structures: a highly aliphatic, predominantly methylenic component, and a more condensed and branched alkyl-rich component. These compositions are resolved by considering the Green River and Woodford as representative endmembers and using PSRE analysis to determine the contributions of these endmembers to the other three kerogens. Weathering is seen to affect these two components differently. The highly aliphatic component is lost with no significant alteration or addition of oxidation products upon weathering, while the aromatic + broad aliphatic component accumulates oxidation products and selectively loses aliphatic carbon.

It does not appear that OM type or the relative abundance of these chemically distinct components strongly influences the rate of OM loss during weathering. Both components are readily removed during weathering and OM loss from profiles of the two endmembers are approximately equal. If selectivity in OM types does not control OM loss and remineralization, then other factors must be limiting. One pair of factors may be erosion rate and cumulative exposure to oxygen. The Green River and Woodford exposures, which exhibit greatest TOC loss, have slow erosion rates and thus long periods of exposure to oxygen-containing downward percolating surface waters. The Monterey exposure has limited TOC loss and very rapid rates of erosion. Other factors will be considered as research on the oxidative degradation of kerogen during weathering of shales develops further.

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