

Differentiating organic carbon residues in spent oil shale

Justin E. Birdwell^{1,*}, Tim E. Ruble², Christopher D. Laughrey³, David R. Roper² & Greg Walker²

¹U.S. Geological Survey, Denver Federal Center, Box 25046 MS 977, Denver, CO 80225

²Weatherford International Ltd., 5200 N. Sam Houston Parkway West, Houston, TX 77086

³Weatherford International Ltd., 16161 Table Mountain Parkway, Golden, CO 80403

*Corresponding Author - Email: jbirdwell@usgs.gov; Tel.: (303) 236-1534; Fax: (303) 236-3202

Abstract

The organic carbon residue present in retorted oil shale and high maturity source rocks consists of a combination of recalcitrant substances including thermally degraded kerogen, char and pyrobitumen. Differentiating the relative contribution of each material is important to understanding the chemical properties of spent shale for reclamation, beneficial reuse and gas storage potential. It is also needed to facilitate the development of robust geochemical models of hydrocarbon-generating systems. Standard chemical methods used to assess residual carbon content typically cannot distinguish between these materials despite their differing origins. In this study, we apply a combination of analytical techniques to provide greater insight into the nature of the carbonaceous materials in spent oil shale. Spent shale from low temperature (360°C) open- and closed-system retorting experiments were analyzed by high temperature programmed pyrolysis (HT-PPy, up to 800°C) following different heating times in order to assess the change in the relative amount of each residual carbon type present. The HT-PPy pyrograms of the samples retorted under closed, high-pressure conditions become more complex relative to the raw shale as heating time increases. Pyrobitumen was distinguished from heavy oil residue, thermobitumen and residual kerogen by differences in degradation temperature, much like free oil and natural bitumen (S_1) are differentiated from kerogen (S_2) by the Rock-Eval method. Char content was estimated based on the carbon-13 nuclear magnetic resonance-determined aromaticity of the residue. The results are supplemented by Fourier transform infrared spectroscopy and compared to bulk analysis.

Introduction

In addition to generating oil and gas, thermal alteration of source rocks both in nature and during pyrolysis leads to the formation of carbonaceous residues that are relevant to both understanding of fossil fuel organic geochemistry and the development of energy resources. In natural systems, post-mature rocks may contain significant quantities of recalcitrant organic residues, such as spent kerogen and pyrobitumen, that can influence pore structure and gas retaining capacity of a formation and may be a source of late-stage methane generation during metagenesis (Burruss and Laughrey, 2010).

The nature of the residue(s) present in oil shale following retorting is strongly dependent on the pyrolysis method. Fast heating to high temperatures (500°C or higher) as in surface retorting systems will leave behind different amounts and distributions of carbon residues than slow heating to moderate temperatures (350-400°C) typical of *in situ* retorting. Another issue is the pressure within the retort, as higher pressure inhibits the conversion of kerogen to oil and gas and encourages oil coking (Burnham and Singleton, 1983). The composition of spent oil shale carbon residue is particularly important in the case of *in situ* retorting, as an understanding of this residual carbonaceous material is (1)

essential to proper reclamation and hazard mitigation following shale oil and gas production, and (2) may define a medium that enhances CO₂ sequestration potential in amenable formations.

Oil, gas, kerogen and bitumen have generally accepted physicochemical or operational definitions, but terms like semicoke, coke, char and pyrobitumen, which in certain fields indicate clearly defined products of specific processes, are also used to describe oil shale pyrolysis residues (see Nomenclature for a summary of definitions). For example, in Chong et al. (1989), the term pyrobitumen is used to describe the intermediate, organic solvent-soluble material generated during kerogen pyrolysis that is considered to be the dominant precursor to oil formation, whereas the more common use of the term is to describe an insoluble material derived from the thermal alteration of oil (Meyer and De Witt, 1990). The term thermobitumen, which is defined as an unexpelled, bitumen-like product of kerogen thermal degradation (Ballice, 2003) will be used in this work to indicate the "bitumen" intermediate generated during the conversion of kerogen to shale oil (McKee and Lyder, 1921; Maier and Zimmerley, 1924; Hubbard and Robinson, 1950; Allred, 1966; Miknis et al., 1985) and the term "natural bitumen" will indicate the chloroform-soluble organic matter present in raw, unretorted oil shale (Hubbard and Robinson, 1950; Allred, 1966).

Oil shale organic residues may include various forms of thermally altered kerogen (the remaining "backbone" of the original material) and an array of other hydrogen-depleted organic phases that are expected to resemble coal coke but are typically referred to simply as char. The term char is used throughout the pyrolysis and combustion literature as a catchall for chemically indistinct, carbon-rich matter left behind following thermal alteration. There is also likely to be some pyrobitumen formed from solidified heavy oil fractions (*e.g.* resins and asphaltenes), particularly in

systems operated at moderate pyrolysis temperatures and high pressure, as some of the heavy oil components are expected to remain associated with the solid phase due to low volatility. The pyrobitumen may be further degraded during long heating times to a more hydrogen-depleted substance described as graphitic-pyro-bitumen (Mossman and Thompson-Rizer, 1993).

Differentiating the organic phases expected to be present in oil shale at different points in time during pyrolysis and following exhaustion of oil-generating potential, is an important aspect of developing robust chemical models of source rock pyrolysis. Some of the most sophisticated models of oil shale pyrolysis (Burnham and Braun, 1990; Braun and Burnham, 1992) have reaction schemes including three to four chemically distinct "char" or "coke" phases participating in various processes as both products and reactants. Although it appears that in these modeling studies the indicated char phases are hypothetical, the models provide some guidance as to what the chemical differences in these materials will be. The most hydrogen-depleted structures are particularly difficult to assess, but some may be observable by programmed pyrolysis or inferred based on assessment of data from techniques like ¹³C nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectroscopy. In this paper, we report the results of a preliminary study to assess, qualitatively and quantitatively, the post-pyrolysis residues generated following laboratory-simulated retorting of oil shale.

Experimental

All experiments were conducted using oil shale collected as slabs from outcrops of the Mahogany zone of the Eocene Green River Formation at the Anvil Points Mine near Rifle, in the Piceance Basin, northwestern Colorado, in July 2007. Material from three slabs was crushed, homogenized and sieved to obtain a uniform oil shale laboratory standard with a particle

size range (-8/+35 mesh or 0.500 to 2.380 mm) consistent with the American Society for Testing and Materials (ASTM) Fischer Assay method (ASTM, 1980). Mineralogy was determined by x-ray diffraction (XRD) with Rietveld refinement and an internal standard (20 wt % corundum). Several standard source rock characterization methods were applied to the laboratory standard to determine oil yield potential and obtain information on the kerogen type and thermal maturity, including Fischer Assay, Rock-Eval Pyrolysis, total organic carbon (TOC) by the Leco method, Source-Rock Analyzer (SRA) and elemental analysis of isolated kerogen.

Weatherford International (Shenandoah, Texas) performed all source rock analyses except for kerogen isolation and elemental analysis, which were performed at the U.S. Geological Survey (USGS) in Denver, Colorado. We attempted to determine vitrinite reflectance values for the raw and spent oil shale; however, due to the lack of discernable vitrinite in these samples it was not possible to obtain viable measurements, which is common for oil shale containing significant amounts of lipid-rich kerogen (Dyner, 2005).

The lab standard oil shale is described as a dolomitic marlstone based on the XRD analysis. Mineral and organic material properties are summarized in Table 1. Rock-Eval+LECO TOC, SRA and kerogen analysis all show that the lab standard contains a type I kerogen that is thermally immature, as was expected for oil shale from this deposit.

Batch experiments to mimic *in situ* retorting conditions were conducted using a system similar to that described by Winters et al. (1983), only without the addition of water. The system, or *In Situ* Simulator (ISS), consists of two Parr non-stirred, Hastalloy or Inconel pressure vessels, one serving as the reactor (250 mL) and the other as the gas and oil collector (500 mL).

The reactor temperature is regulated using an electric heater with a Parr model 4838

Table 1: Properties of the laboratory standard oil shale from the Anvil Points Mine

<i>Mineralogy by XRD (weight percent)</i>		
Dolomite	41.5	
Sanidine	18.5	
Quartz	13.3	
Muscovite	9.9	
Analcime	6.1	
Albite	5.8	
Calcite	3.9	
Pyrite	0.6	
Siderite	0.4	
<i>Fischer Assay oil yield (n = 10)</i>		
Gallons per ton	38.4 ± 1.0	
Weight percent	14.4 ± 0.4	
<i>Total Organic Carbon (mg C/g rock)</i>		
LECO	193	
SRA	185	
<i>Rock-Eval Parameters (mg/g TOC)</i>		
	Rock Eval	SRA
Hydrogen Index	1014	940
Oxygen Index	14	10
T _{max} (°C)	439	443
<i>Kerogen Isolate (n = 3)</i>		
H/C	1.43 ± 0.05	
O/C	0.13 ± 0.03	

Temperature Controller. For each run, approximately 100 g of oil shale are loaded into the reactor, which is purged and pressure tested with helium (~1,000 psia) and then evacuated to <0.6 psia prior to heating. The reactor is then heated to 360 ± 5°C (heating rate ~3°C/min) and held for 6, 24, 72, 120 or 288 h. Prior to the end of each pyrolysis experiment, the collector is evacuated to <0.6 psia and cooled to and held at an internal temperature of ≤ 5°C using a laboratory chiller. At the end of the experiment, the reactor and collec-

tor are connected using a 316 stainless steel flex-hose and the reactor is vented to the collector for ~1 minute. Both vessels are then left standing for ~24 hr to return to room temperature. Afterwards, the pressure in both vessels is determined, a gas sample is taken from the collector and the remaining products are extracted from both vessels. Spent oil shale is weighed, and then placed in a fume hood overnight to dry (typical weight change <1%).

Retorting experiments at near atmospheric pressure with continuous product removal were conducted using a Fischer Assay system at a maximum temperature of 360°C for comparison to the high-pressure batch method. Samples processed using the low-temperature Fischer Assay (It-FA) method were held for 3, 6, 10, 14 and 18 h (3- and 18-h experiments conducted in triplicate), following heat up using two different heating rates (1°C/min and 12°C/min). Because not all spent shale samples from the It-FA experiments have been fully characterized, the focus of this paper will be on the ISS samples, though relevant comparisons will be made using the available data collected on spent shale from the It-FA and standard Fischer Assay (500°C, 1 h, 12°C/min) experiments.

Bulk analysis was performed on the raw and spent oil shale samples to determine the soluble organic matter (natural bitumen and thermobitumen), insoluble organic matter (kerogen, char and pyrobitumen) and mineral content of each sample. The soluble organic matter (OM) of the raw oil shale and spent shale samples was determined by sonicating 50-mg pulverized rock aliquots in 1 mL of chloroform over 15 min intervals. Following each sonication cycle, samples were centrifuged and the chloroform was decanted into a collection vial. The process was repeated until the solvent was clear. The chloroform was then evaporated under a gentle nitrogen stream and the dried bitumen was weighed using a high precision balance (± 0.1 mg). The insoluble OM and mineral content were determined by weight difference before

and after muffling at 425°C for 24 h. Samples of raw and spent oil shale (50 mg) were placed in etched and tared glass vials, weighed, muffled overnight to remove essentially all organic matter and reweighed. The mineral content was determined directly (mass of remaining material after muffling divided by the mass of the original sample) and the insoluble OM content was determined by difference using the soluble OM and mineral contents determined by extraction and muffling.

High temperature programmed pyrolysis (HT-PPy) was conducted using a Weatherford International SRA instrument. The primary difference between HT-PPy and standard SRA or Rock-Eval is that instead of heating the sample to 650°C and stopping, samples were heated to 800°C. After the initial S_1 determination period (isothermal, 300°C for 3.5 min) a constant heating rate was used (~25°C/min) for a total of 20 min to reach the maximum temperature. In addition, Rock-Eval, Leco TOC and SRA with the routine temperature programming were also applied to the spent shale samples in order to obtain standard estimates of residual hydrocarbon generation potential and degree of thermal alteration. All TOC and hydrocarbon (HC) generation values are reported on an original rock basis (value measured on spent rock multiplied by mass of recovered rock following pyrolysis divided by mass of original rock – see Table A-2 in the Appendix).

Solid-state ^{13}C NMR spectra were collected using a Chemagnetics CMX-200 NMR spectrometer (magnetic field strength 4.7 Tesla generating a carbon resonance frequency of 50.3 MHz) with a 7.5-mm ceramic ^1H -X channel MAS probe. Proton-to-carbon cross polarization and magic angle spinning (CP/MAS) were applied. For each sample, approximately 500 mg of pulverized rock was packed into a zirconium pencil rotor. Acquisition parameters included a 30,030.0 Hz spectral window, 17.051 ms acquisition time, 2.0 ms contact time, 0.5 s pulse delay and spinning rate of 5 kHz \pm

100 Hz. A minimum of 18,000 transients were collected and averaged to generate a free induction decay, which was then baseline corrected and processed using exponential multiplication with 100 Hz line broadening prior to Fourier transformation to produce chemical shift vs. intensity plots. The spectra were area normalized to unity and then to TOC prior to plotting and integrating to determine aliphatic (0 to 70 ppm) and aromatic (70 to 180 ppm) carbon content.

FT-IR spectra were collected using a Perkin-Elmer System 2000 FT-IR spectrometer in absorbance mode. Pulverized rock samples were weighed out (0.5-2.0 mg) and mixed with 200 mg of potassium bromide (KBr) using an agate mortar and pestle to further grind and mix the sample and halide matrix. Pellets (13-mm diameter disks) were formed using a die and hydraulic press. Spectra were acquired over the 4,000 to 400 cm^{-1} range with a resolution of 4 cm^{-1} and a step size of 1 cm^{-1} . A total of 10 scans was averaged to generate the spectrum for each sample. Background and baseline corrections were performed using the instrument software (Spectrum for Windows). Any sample with a maximum absorbance below 0.5 or above 1.5 absorbance units was re-analyzed at an adjusted sample to KBr ratio to mitigate the effects of non-linear detector response.

Results and Discussion

Details regarding the quality and quantity of oil and gas generated by the ISS and It-FA experiments are not presented here, but to briefly summarize, the ISS oil quality and yield results are generally consistent with those presented by Burnham and Singleton (1983) for high pressure retorting of Colorado oil shale. Notably, no water is recovered in the ISS experiments in either the collector or reactor vessels. The It-FA generates an oil product similar to that of the normal Fischer Assay, though with a lower yield (up to 90% by weight lower after 18 h). Fischer Assay generates

more oil than either of the pyrolysis methods operating at 360°C and leaves behind essentially no residual thermobitumen and appears to generate less char than ISS or It-FA at their longest heating times. Greater than 97% of all original sample mass was recovered as products for all ISS and It-FA experiments.

Figure 1 provides a summary of the bulk analysis of raw and spent shale samples, including TOC and the soluble OM, insoluble OM and total bulk OM after different heating times in the ISS (see Table 1 in the Appendix). The total bulk OM and TOC profiles show similar trends over the range of heating times examined and appear to be approaching steady state values after 120 to 288 h. The amount of soluble OM present increases dramatically after the first 6 h of heating concomitant with a precipitous drop in the insoluble OM content, indicating a rapid conversion of kerogen to thermobitumen and oil. The soluble OM content then decreases steadily after 6 h. The amount of insoluble OM decreases slightly between 6 and 24 h and then increases with heating time. Between 24 and 120 h, the amount of soluble OM exceeds the insoluble component, but at 288 h nearly the entire bulk OM residue is represented by the insoluble fraction.

Only a few of the It-FA samples have been processed to determine bulk composition. The 3 h It-FA sample contained a large quantity of thermobitumen (96.9 mg/g rock), similar to the ISS samples heated for 72 h or less. Both It-FA heating rates yielded spent shale with similar quantities of soluble and insoluble OM after heating for 18 h as well as similar amounts of gas, oil and water, indicating that this difference in heating rate was insufficient to have a significant effect on the pyrolysis process. The results for the 18-h It-FA residues were comparable to those observed for ISS retorted shale heated for 288 h.

All HT-PPy, standard SRA (up to 650°C) and Rock-Eval + Leco TOC measurements were made on whole spent shale samples;

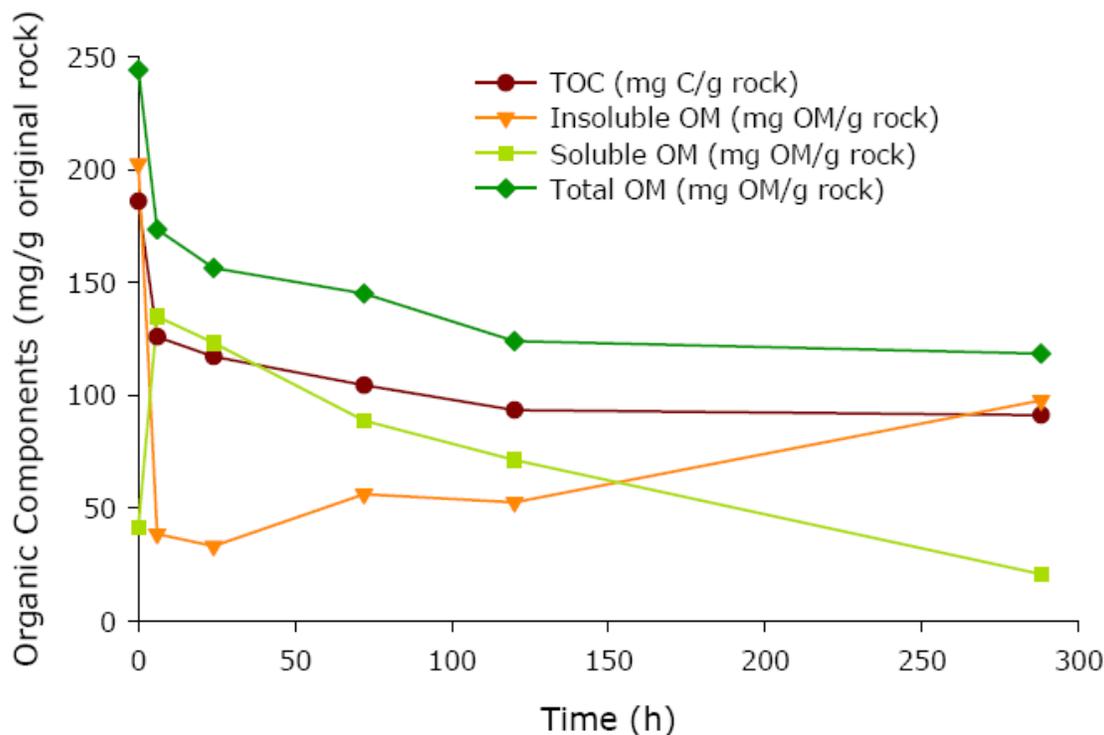


Figure 1. Bulk analysis of raw and ISS-retorted oil shale samples

therefore they include soluble organic and insoluble OM (see Tables 2 and 3 in the Appendix). The results of SRA and Rock-Eval analyses were in good agreement and are well represented by the HT-PPy data and so will only be described briefly. As expected, both methods showed decreases in the S_2 peak and HI with increasing heating time for both the ISS and It-FA samples. The OI values were essentially unchanged in all samples regardless of heating time, except for the standard Fischer Assay spent shale, which had a much higher OI value (31 mg CO_2/g TOC) than any of the other samples (~ 10 mg CO_2/g TOC). A similar result was observed in the T_{max} values determined on the spent shale samples, in that all values for the ISS and It-FA samples were similar to those of the raw shale (raw shale $T_{max} = 439^\circ C$; highest T_{max} on a spent sample = $447^\circ C$, lowest = $428^\circ C$), whereas the

standard Fischer Assay spent shale had a significantly higher T_{max} ($535^\circ C$). The high OI of the Fischer Assay sample may be due to adsorption of CO_2 from the atmosphere, and the lack of any discernable trend in T_{max} with thermal alteration is likely due to the homogeneity of OM in Mahogany zone shale and not the presence of thermobitumen (Ruble, 1996).

HT-PPy pyrograms are presented for un-retorted oil shale and ISS and It-FA ($12^\circ C/min$) spent shale in Figure 2. The $1^\circ C/min$ It-FA pyrograms (not shown) were similar to those for the samples heated at $12^\circ C/min$. Due to the bimodal nature of the S_2 peak region (between 3.5 and 17 min, corresponding to 300 to $650^\circ C$) in the ISS samples, a non-standard set of peaks was defined and used to describe the pyrograms based on guidance from the programmed pyrolysis literature (Butler and Barker, 1986; Tarafa et al., 1988; Peters,

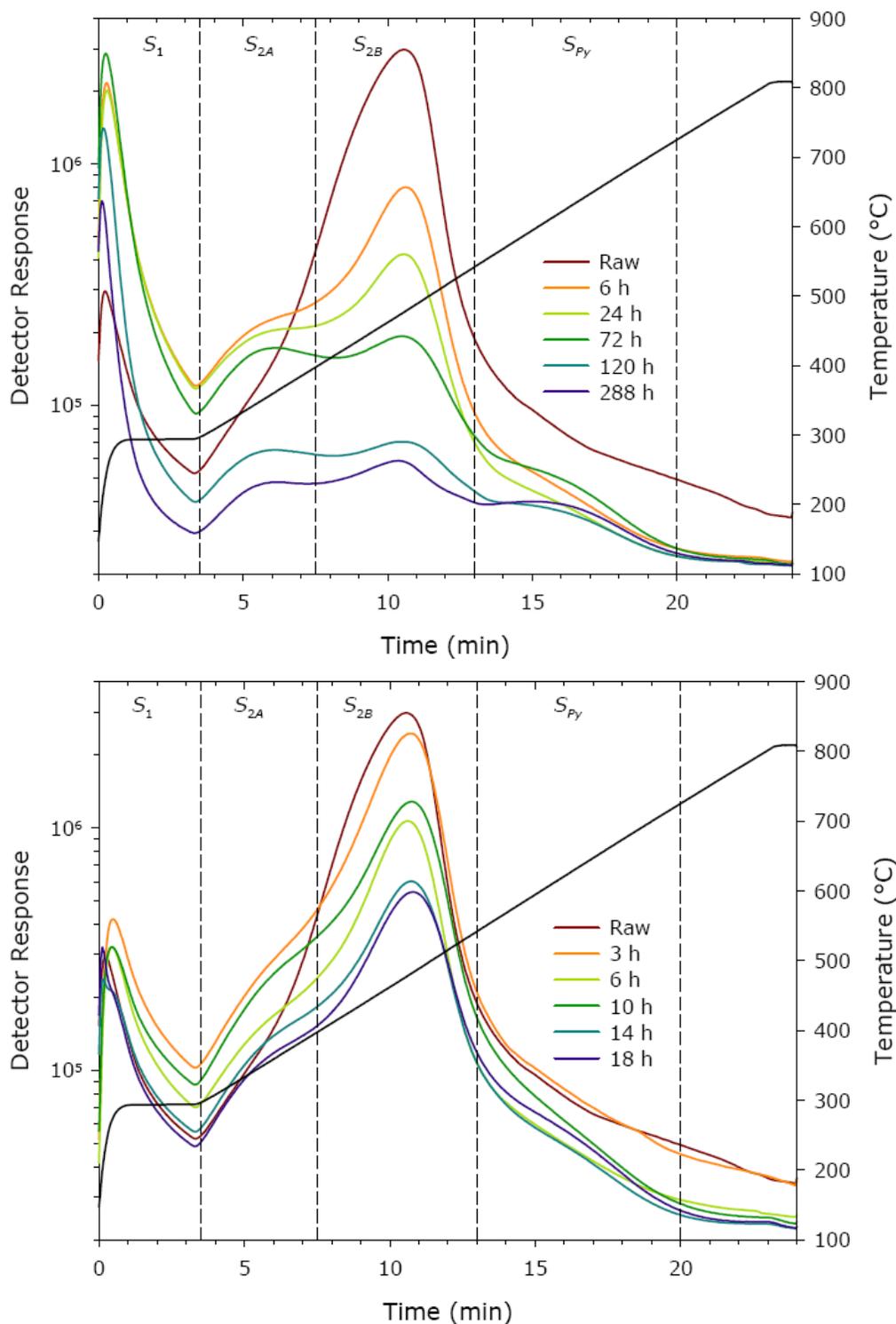


Figure 2: HT-PPy pyrograms for ISS (top) and 12°C/min It-FA (bottom) samples. Peak regions are designated S₁, S_{2A}, S_{2B} and S_{py}. Black lines represent the temperature profile (scale on the right-hand y-axis).

1986; Wilhelms et al., 1991; Everlien, 1996). The peak regions for the spent oil samples are designated as follows: S_1 = residual oil and light thermobitumen components (0-3.5 min, 300°C), S_{2A} = heavier thermobitumen components (3.5-7.5 min, 300-400°C), S_{2B} = hydrocarbon generated from kerogen (7.5-13.0 min, 400-540°C), S_{py} = pyrobitumen (13.0-20.0 min, 540-700°C) and possibly other insoluble, degraded OM containing sufficient hydrogen to be measurable using a flame ionization detector (FID).

Values of the integrated peak regions converted to mg hydrocarbon (HC) per g-rock are shown in Figure 3. Again, these peaks are only relevant to this sample set (particularly the ISS data) and differ from other normal and high-temperature programmed pyrolysis studies of source rocks, where a single S_2 peak is used and the pyrobitumen peak, S_{py} (registered trademark of Weatherford International), is integrated over a slightly different temperature range (600-800°C). True *char* and materials like graphitic-pyrobitumen are expected to be too hydrogen-depleted to be observed by HT-PPy when using a FID.

The pyrograms for the ISS samples show that the S_1 peak is a major feature and represents a significant amount of the residual generated HC, whereas in the It-FA samples this feature changes little from the raw shale following pyrolysis. This peak is attributed to residual oil components and soluble OM and the differences between the ISS and It-FA results are likely due to the way the oil product is removed from each system. In the ISS, only material present in the vapor phase is extracted from the reactor and collected, leaving behind any low volatility, heavy oil fractions, primarily resins and asphaltenes, whereas in the It-FA oil is continually removed from the reactor as liquid and vapor and less residual oil is retained by the rock.

All spent shale pyrograms show a bimodal S_2 region consisting of a shoulder between 3.5 and ~7.5 min (S_{2A}) and a peak between 7.5 and 13 min (S_{2B}) regardless of

heating time. In the ISS samples with heating times longer than 24 h the shoulder region is resolved into a separate peak. Both the ISS and It-FA samples show similar trends in the integrated peaks areas for S_{2A} and S_{2B} , with S_{2A} increasing at short heating times followed by decreasing values at longer heating times and S_{2B} decreasing with increasing heating time and appearing to approach a steady value.

The S_{py} peak is most resolved in the 120- and 288-h ISS samples, though it appears as a shoulder in the 72-h ISS and 18-h It-FA samples. It is not clear how significantly pyrobitumen contributes to this region for the spent shale samples with shorter heating times, as much of it is likely due to the long tail of the S_{2B} peak. The high S_{2A} and S_{2B} values determined for the It-FA experiments after heating for 18 h indicate that longer experimental runs are necessary to exhaust oil generation potential for this oil shale using this system, though it is unlikely to require as long as the ISS due to the lower pressure in the It-FA retort.

Comparing the ISS HT-PPy parameters in Figure 3 to the bulk analysis data shown in Figure 1, it is clear that the trend for soluble OM is similar to that of both S_1 and S_{2A} . It is also evident that S_{2B} does not account for the insoluble OM trend by itself, probably because some components of the insoluble fraction are not observed in the HT-PPy pyrogram (~25% of the OM in this oil shale does not generate FID-detectable HC under typical Rock Eval or SRA conditions). The pyrobitumen peak, S_{py} , will also contribute to the insoluble fraction, though the contribution appears to be fairly small. It should also be noted that HT-PPy pyrograms have not yet been determined on solvent-extracted samples, so it is not known how or if the S_{2B} and S_{py} peaks are affected by the presence of soluble OM like thermobitumen. Comparing the sum of the HT-PPy parameters to TOC (Figure 3) shows an increasing divergence between these values, indicating that as heating time increases, the amount of

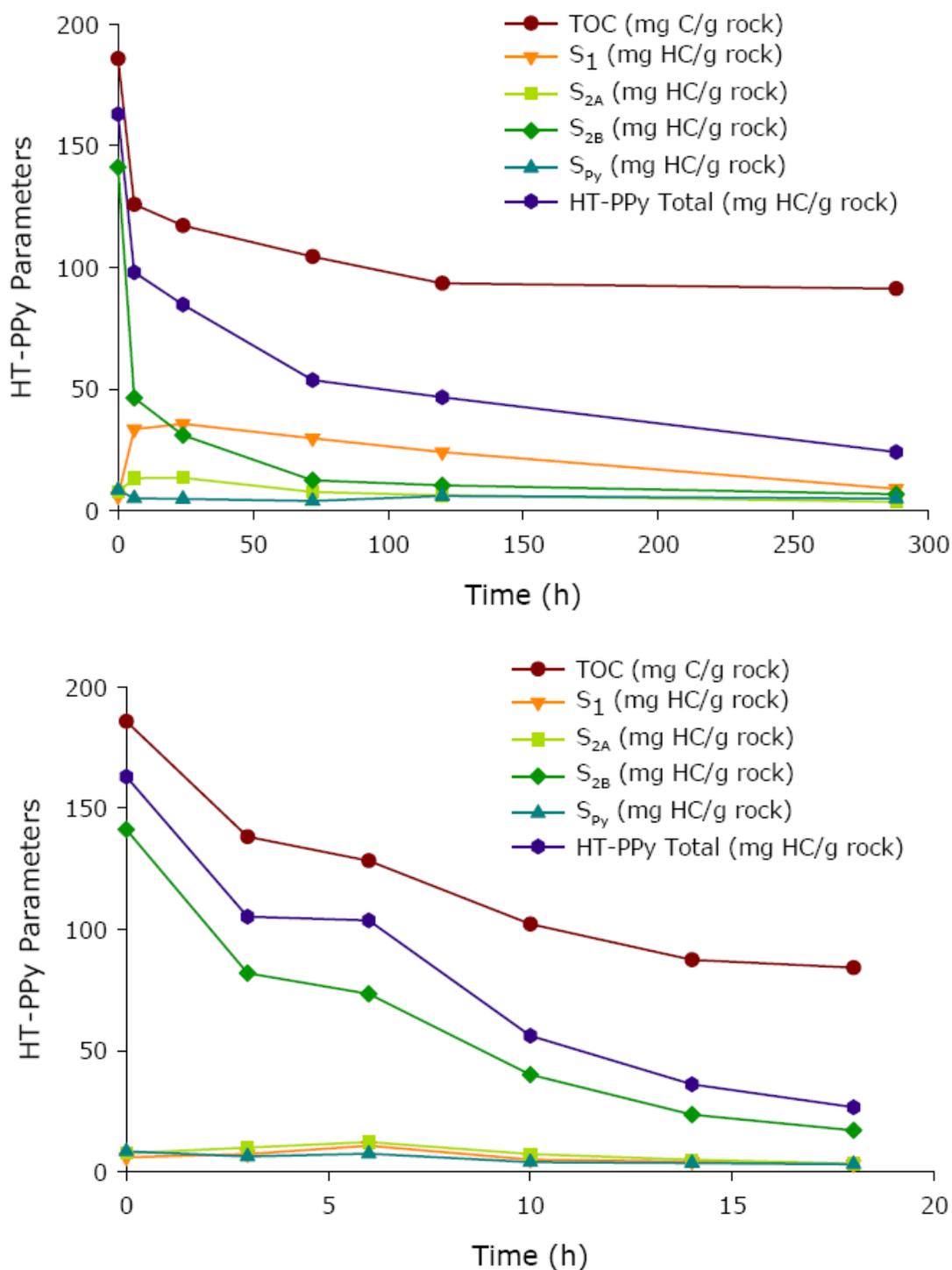


Figure 3. - HT-PPy parameters (S_1 , S_{2A} , S_{2B} , and S_{py}) as a function of time for ISS (top) and for 12°C/min It-FA (bottom) samples.

organic carbon represented by FID-detectable materials decreases, as is expected due to the depletion of hydrocarbon-generating potential and the formation of char.

The inability of HT-PPy to assess char and other hydrogen-depleted components of the spent shale residues requires the use of other methods for quantifying such materials. Many studies have shown the utility of CP/MAS ¹³C NMR for determining the distribution of carbon moieties in oil shale as well as correlations between aliphatic carbon content and oil yield (Miknis et al., 1982a; Miknis and Smith, 1984; Miknis, 1992) and aromatic carbon and char content (Miknis et al., 1982b; Miknis, 1984, 1992).

Spectra for the raw and ISS spent shale are shown in Figure 4 (see Table 3 for NMR aliphatic and aromatic content) and were collected on whole spent shale samples, so the NMR spectra represent soluble and insoluble OM present in the shale. Only the spectra shown will be discussed in detail; however, a few notes on other experiments are provided. In addition to the CP/MAS scans, direct polarization spectra were also collected for comparison (direct polarization does not require the presence of hydrogen for signal enhancement) and the integrated aliphatic and aromatic peak areas were essentially identical to those determined by CP. Spectra for the isolated kerogen were collected for comparison to the raw oil shale and the peak areas were in good agreement, as has been observed by others (e.g., Maciel and Dennis, 1982). As expected, there was a linear correlation between Rock Eval and SRA S₂ values and the ¹³C NMR aliphatic content of the raw shale, ISS spent shale, and the Fischer Assay and It-FA (3- and 18-h heating times) samples ($R^2 = 0.89$).

The intense aliphatic peak in the raw shale at 32 ppm is indicative of methylene (-CH₂-) carbon in long chains, whereas the shoulder that appears in the spectra of the ISS retorted shale at between 22-25 ppm is attributed to methylene carbons adja-

cent to methyl (-CH₃) carbons at the end of aliphatic chains and to methyl carbons attached to aromatic and heteroaromatic rings (Witte et al., 1988). The change in the aliphatic peak shape following pyrolysis has been attributed to the preferential removal of branched and cyclic aliphatic moieties (Miknis and Smith, 1984). The position of the aromatic peak shifts from 133 (raw) to 128 (288 h) ppm following retorting, indicating removal of aliphatic side chains from aromatic rings (Witte et al., 1988).

The results of several studies combining Fischer Assay and other pyrolysis techniques with solid state ¹³C NMR characterization of raw and spent shale (Miknis et al., 1982b, Miknis, 1984; Miknis, 1992) show a strong connection between the initial aromatic content, the final aromatic content and the amount of char remaining after retorting. These studies indicate that the aromatic fraction of kerogen, rather than contributing significantly to the generation of oil or gas at typical pyrolysis temperatures ($\leq 500^\circ\text{C}$), is the source of most of the char present in spent oil shale.

Miknis (1992) also reported that (1) by analyzing raw and Fischer Assay spent shale using solid state ¹³C NMR and the generated oil by liquid state ¹³C NMR, a balance on aliphatic and aromatic carbon could be obtained; and (2) the analytical results showed that 10-20% of the aliphatic carbon originally present in the raw shale kerogen is converted to aromatic char during Fischer Assay. Based on these studies, char in spent oil shale can be estimated based on the ¹³C NMR aromatic content of the sample, thereby providing a means of roughly quantifying the contribution of this component to spent shale residues. It should be noted that the contribution of heteroatom groups (polar compounds or resins) to oil generation is difficult to assess by ¹³C NMR due to the small contribution these components make to the spectra. They are obscured by the broad aliphatic and aromatic peaks.

FT-IR can be considered a comprehensive

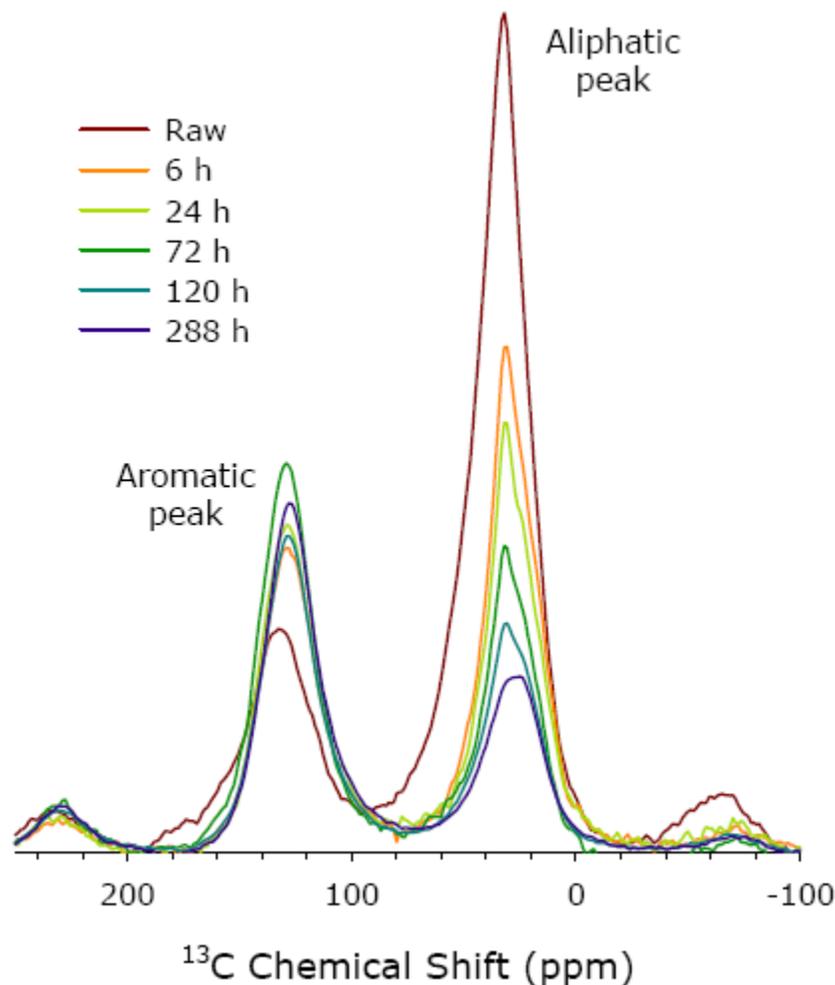


Figure 4. Solid-state CP/MAS ^{13}C NMR spectra of ISS samples. Far left (200 to 230 ppm) and far right (-40 to -90 ppm) peaks are spinning sidebands of the aromatic and aliphatic moieties, respectively.

characterization tool for oil shale because it provides information on both the organic and mineral components of source rocks. It is also a quick method relative to ^{13}C NMR, given that FT-IR spectra can be acquired in less than a minute whereas acquisition of NMR spectra generally takes many hours. The sample preparation time for both methods is similar.

Figure 5 shows the FT-IR spectra measured on the whole raw and spent shale samples as well as spectra of the same samples after removal of soluble OM (solvent-extracted) and all organic materials (muffled). The spectra acquired on the

whole and extracted shale samples include prominent features in the 2800-3000, 1200-1600 and 900-1200 cm^{-1} ranges, representing aliphatic carbon moieties, carbonate minerals and silicate minerals, respectively (Snyder et al., 1983), whereas spectra of the muffled samples do not contain any aliphatic carbon peaks.

The aliphatic carbon content estimated by FT-IR is a particularly useful parameter, as it has been shown to correlate well with both Rock Eval S_2 values (Schenk et al., 1986) and Fischer Assay oil yields (Solomon and Miknis, 1980). However, due to interference from the carbonate mineral

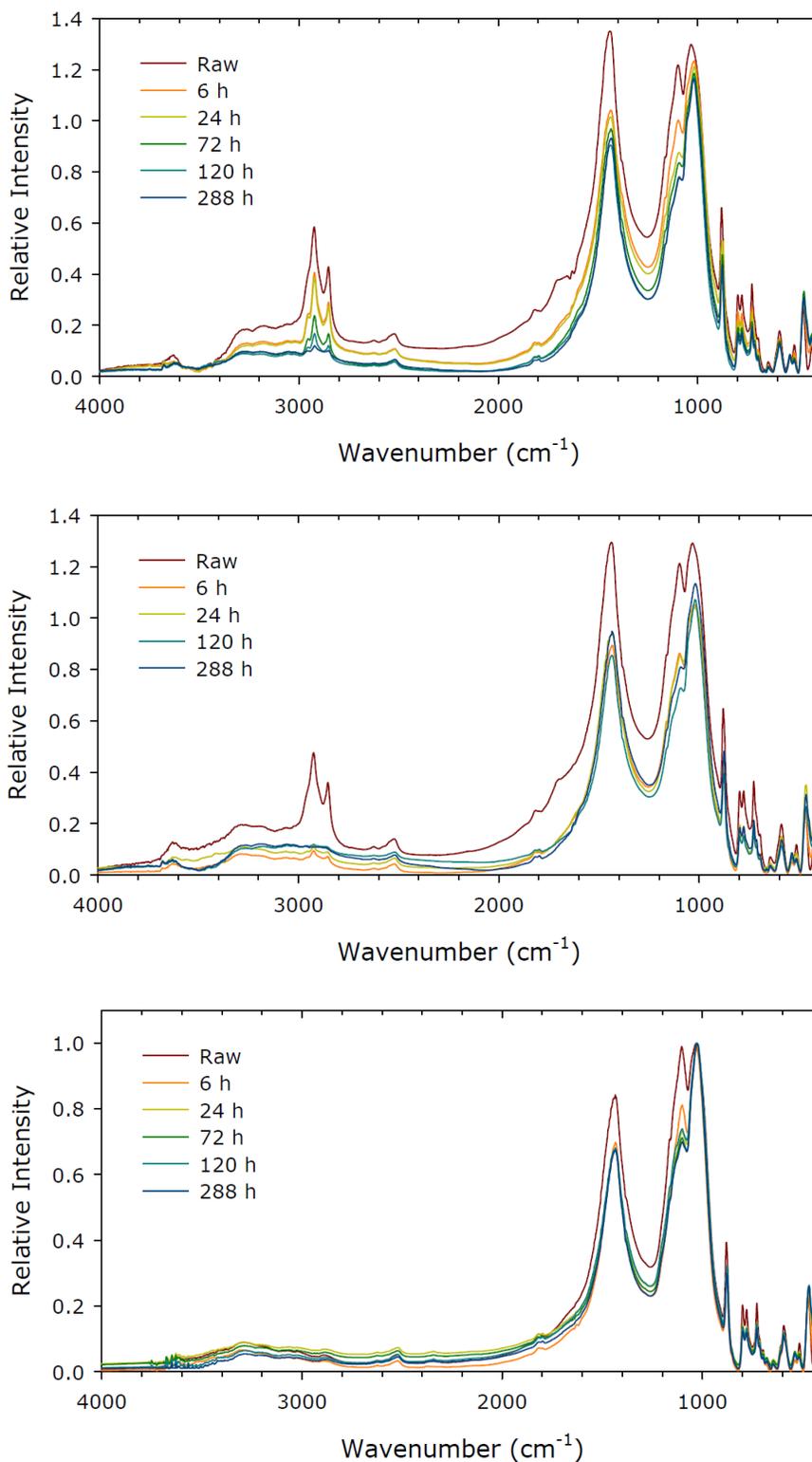


Figure 5: FT-IR spectra of (top) whole ISS raw/spent oil shale samples, (middle) ISS oil shale samples after bitumen extraction, and (bottom) ISS oil shale samples after muffling.

peak, several bands corresponding to carbonyl and carboxyl (1710 cm^{-1}) and aromatic (1630 cm^{-1}) functional groups are not discernable (Ganz and Kalkreuth, 1987).

The primary source of information on the organic component of carbonate-rich raw and spent oil shale is in the aliphatic peak region. The whole shale raw and the ISS-spent samples both show a decrease in aliphatic peak intensity with increasing heating time, which is similar to what was observed in the ^{13}C NMR spectra. However, the spectra of the solvent-extracted samples showed much lower aliphatic peak intensities, indicating that much of the aliphatic material present in the spent samples was soluble OM and not aliphatic kerogen. It appears that at some time between 24 and 120 h in the ISS (72-h sample was lost during processing), the aliphatic component of the kerogen was essentially depleted. Therefore, the aliphatic peak pre-sent in the ^{13}C NMR spectra of the ISS spent shale samples discussed previously would appear to be mainly attributable to thermobitumen and residual oil fractions present in the retorted samples. This is another indication that the conversion of kerogen to thermobitumen and oil occurs rapidly during pyrolysis at 360°C and that the conversion of thermobitumen to oil is a slower process (Allred, 1966).

Combining the results from the HT-PPy, TOC and ^{13}C NMR measurements, estimated quantities of several different carbon residues in the raw and ISS-spent shale samples were determined and the results are shown in Figure 6. The TOC values provide the total amount of organic carbon in each sample. HT-PPy provides estimates of the bitumen ($S_1 + S_{2A}$), HC-generating kerogen (S_{2B}) and pyrobitumen (S_{py}) contents, assuming the HC generated during HT-PPy was 85% carbon in order to convert from mg HC/g rock to mg TOC/g rock. The amount of char was estimated using the aromatic content determined by ^{13}C NMR and TOC (mg TOC/g rock) minus

the contribution of aromatic material from the soluble OM (assuming bitumen carbon content is 80% and 30% of that carbon is aromatic; Miknis et al., 1985). The sum of the carbon residues shows a systematic underestimation of TOC (average 23.9 mg C/g rock), likely due to issues related to instrument response factors (conversion of FID response to HC) and various other assumptions used in the analysis.

Comparison of the results of the ISS-spent oil shale bulk analysis and estimated carbon balance shows agreement in terms of general trends, but there are still important discrepancies. Soluble and inorganic OM were converted to a carbon basis assuming 80% and 75% C, respectively. Large disagreements between the soluble OM and bitumen contents and between the insoluble OM and the combined kerogen, pyrobitumen and char contents indicate that the approach must be further refined in order to accurately quantify the various carbon fractions. The combined HT-PPy and NMR analysis underpredicts soluble OM by 35-65% and overpredicts the insoluble content by as much as 130%.

This indicates that, although the HT-PPy and NMR data may be able to qualitatively describe trends in the amounts of various residues in spent shale, more work is needed to obtain better quantitative agreement between bulk analysis and the analytical methods applied here for each type of material. We attribute the discrepancies to the following unresolved issues: (1) overlap of the S_{2A} and S_{2B} peaks leading to an underestimation of soluble OM by HT-PPy, (2) invalid assumptions regarding time independence of the values of the carbon content for the different residue types, (3) the lack of specific response factors for each type of carbon residue to convert FID response from the HT-PPy pyrograms to HC content, and (4) inaccuracy of the estimation of char content by ^{13}C NMR. We anticipate that future work will address these problems.

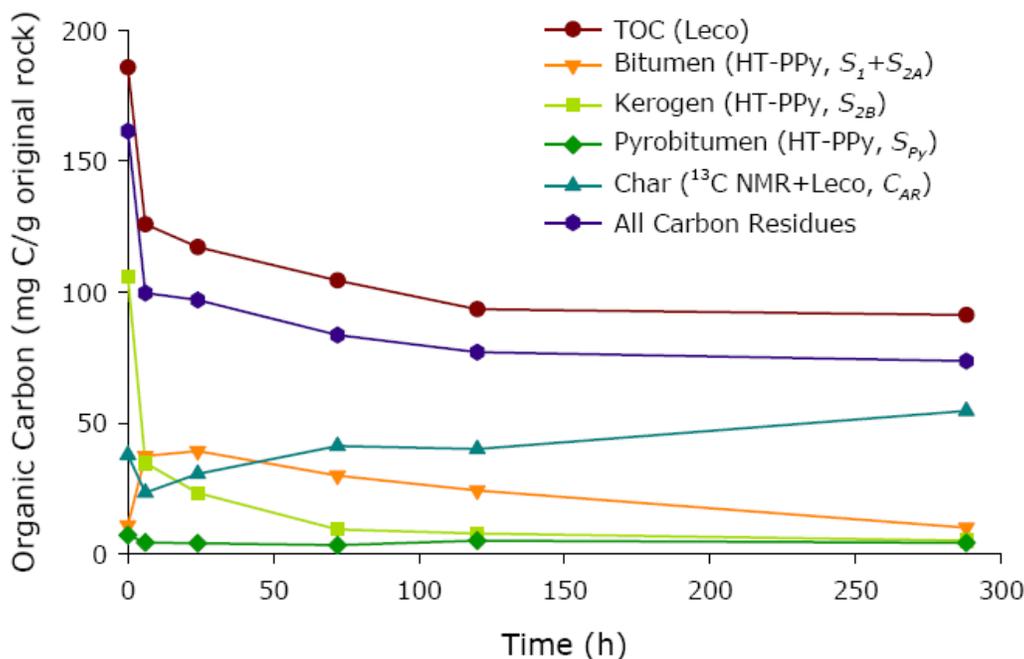


Figure 6: Estimated contribution of each carbon residue to the TOC of raw and spent oil shale samples (method used to estimate each type indicated in legend).

Conclusions

The composition of the OM in oil shale changes considerably during a laboratory-simulated *in situ* retorting process, as demonstrated using a combination of analytical methods. The results show that (1) HT-PPy can be used to identify a mixture of materials, distinguished by their pyrolysis characteristics; and (2) the amount of each of the materials can be roughly quantified in general agreement with results from bulk analysis. In addition to the anticipated degraded kerogen, bitumen and char phases, the presence of an organic phase with pyrolysis characteristics similar to the pyrobitumen in spent oil shale samples that have been heated for an extended period of time represents a potentially important finding.

The composition of post-retorting organic residue in spent oil shale is expected to be an important factor in determining the feasibility of reclamation processes and potential reuse scenarios, such as hot water

leaching and CO₂ sequestration, respectively. Hot water leaching is the reclamation approach proposed by Shell for *in situ* retorts and involves flushing water through rock that remains at pyrolysis temperatures following retorting (Shell Frontier Oil and Gas Inc., 2006). The conditions that will exist in the retort during the early stages of hot water flushing are expected to resemble those of hydrous pyrolysis (Winters et al., 1983). This may lead to additional generation or release of residual oil and bitumen from the spent oil shale in addition to extraction of volatile and semi-volatile organic compounds and metals. The potential for the reuse of spent *in situ* retorts as storage for CO₂ generated by power plants and other operations will be dependent on a wide range of characteristics, including the chemical and physical properties of the spent shale. The porosity generated by conversion of oil shale kerogen to shale oil and gas has been proposed as a CO₂ sink using *in situ* mineralization of CO₂ mixed with brine, and the microporos-

ity of the char residue may facilitate the sequestration process (Burnham, 2008).

In addition to the refinement of methods to obtain better estimates of the nature and quantity of the carbon residues present in spent oil shale, other factors need to be investigated in order to obtain laboratory results that are relevant to real world systems. For example, two important factors related to proposed *in situ* retorting methods are not addressed using the ISS pyrolysis system. These are the effects of overburden stress and of lengthy heating times on the composition of the spent shale organic residue. Meurer et al. (2008) concluded that overburden stress leads to generation of lighter oil products, but no information regarding the effect on charring was presented. Additional experiments using an overburden simulation device similar to the one described by Meurer et al. (2008) are planned for cores cut from the slabs used to generate the lab standard described in this work.

At the low heating rates proposed for *in situ* production methods like the Shell *In Situ* Conversion Process (Vinegar, 2006), the long heating period is expected to have a significant effect both on the quality of the oil and gas produced and the nature of the spent shale residues. Raley and Braun (1976) observed that preheating oil shale at sub-pyrolysis temperatures for long periods of time had the effect of reducing oil yield and increasing char content in spent shale. *In situ* heating rates as low as 0.5°C/day have been proposed and will expose targeted oil shale resources to long preheating periods that may lead to a markedly different distribution of carbon residues than was observed in the ISS-spent samples. Practical limitations on the heating times that can be applied in the laboratory make simulation of the exact thermal history of *in situ* retorts impractical. Experiments using lower heating rates than those described in this paper have been conducted in previous studies (Burnham and Singleton, 1983), and may be required to better assess the nature of

spent oil shale organic residues generated under field conditions.

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Nomenclature

In this section, definitions for many of the terms used in this manuscript are provided. In some cases, multiple similar or dissimilar definitions are given and the specific meaning applied in this study is indicated. References are provided for some terms (including direct quotes), while others with more nebulous and varied definitions are only described as “general”. This list is not comprehensive and is provided only as a guide to the reader.

Bitumen: “An organic random-molecular substance, which is mobile as a viscous fluid, or was once a mobile fluid, but which has since solidified” (Mossman and Thompson-Rizer, 1993); ***this study***, chloroform soluble organic matter residing in raw (natural bitumen) and spent (thermобitumen) oil shale; this material may be an unexpelled intermediate product of kerogen conversion to shale oil or recondensed heavy petroleum components (resins and asphaltenes) not recovered as liquid pyrolysate.

Char: *general*, commonly used term for organic residue following combustion or pyrolysis; **this study**, the non-hydrocarbon generating fraction of the organic residue left after primary pyrolysis of kerogen.

Coke: organic component remaining following coal combustion; the solid residue remaining following pyrolysis of oil or bitumen (Braun and Burnham, 1992); **not used in this study**.

Kerogen: "That fraction of particulate macromolecular organic matter dispersed in sediments, and which is insoluble in common organic solvents at STP" (Mossman and Thompson-Rizer, 1993); **this study**, organic matter residing in raw and spent oil shale that has hydrocarbon-generating potential and is insoluble in chloroform.

Natural bitumen: The organic matter present in raw oil shale that is soluble in common organic solvents such as benzene, carbon disulfide or carbon tetrachloride (Hubbard and Robinson, 1950; Allred, 1966); **this study**, the chloroform-soluble organic matter present in oil shale that has not been exposed to pyrolysis conditions.

Pyrobitumen: "Any dark, hard, non-volatile native substance composed of hydrocarbon complexes, which may or may not contain oxygenated substances, and are often associated with mineral matter. The non-mineral constituents are infusible, insoluble in water, and relatively insoluble in carbon disulfide. On heating, pyrobitumens generally yield bitumens, i.e. decompose rather than melt." (Mossman and Thompson-Rizer, 1993); a hydrocarbon mineraloid formed by polymerization of petroleum over geological time periods (Ralph and Chau, 2011); **this study**, an insoluble organic residue present in retorted oil shale and post-mature source rocks, formed by polymerization of petroleum and bitumen (Meyer and De Witt, 1990); the organic solvent-soluble organic matter remaining in spent oil shale following retorting (Chong et al., 1989).

Thermobitumen: **this study**, chloroform-soluble organic component generated during pyrolysis of oil shale or isolated kerogen but not expelled as a free petroleum-like pyrolysate (Ballice, 2003).

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Appendix

Table A-1: Composition determined by bulk analysis

Sample (processing conditions)	Orig. Rock (g)	Rec. Rock (g)	Mineral (g)	Soluble Residue (g)	Insoluble Residue (g)	Oil (g)	Water (g)	Gas (g)
Raw 0 hr	100.0	100.0	74.1	4.2	20.3	0.0	0.0	0.0
ISS 6 hr	100.2	91.6	74.3	13.5	3.9	5.5	0.0	2.2
ISS 24 hr	100.2	89.7	74.0	12.3	3.3	6.3	0.0	2.8
ISS 72 hr	105.4	92.4	77.7	8.9	5.6	6.8	0.0	3.1
ISS 120 hr	100.3	86.2	73.8	7.1	5.3	9.6	0.0	3.4
ISS 288 hr	100.6	85.0	73.1	2.1	9.8	9.1	0.0	4.6
12°C/min, 3 hr	100.0	87.3	71.5	9.7	6.1	8.9	1.7	2.1**
12°C/min, 18 hr	100.0	82.9	71.5	1.9	9.5	12.2	2.3	2.6**
1°C/min, 18 hr	100.0	82.6	72.7	0.9	9.0	13.0	1.8	2.5**
MFA* 500°C	100.0	80.0	72.9	0.0	7.0	14.4	1.8	3.9**

*Modified Fischer Assay (500°C, 12°C/min, 1 h)

**Indicates Gas+Loss determined by Fischer Assay procedure.

Table A-2: Parameters determined by standard programmed pyrolysis methods

<i>Rock Eval + LECO TOC Data</i>					
Sample (raw or spent rock)	TOC (mg/g orig. rock)	T_{Max} (°C)	S_1 (mg HC/g-orig. rock)	S_2 (mg HC/g-orig. rock)	S_3 (mg CO ₂ /g-orig. rock)
Raw 0 hr	193.0	439	6.2	195.8	2.8
ISS 6 hr	130.8	436	35.4	60.5	2.0
ISS 24 hr	129.7	437	40.6	48.7	2.1
ISS 72 hr	109.5	436	34.1	19.6	1.8
ISS 120 hr	98.5	429	36.0	17.6	2.1
ISS 288 hr	94.7	428	13.2	8.4	0.8
12°C/min, 3 hr	140.1	438	7.1	93.0	1.4
12°C/min, 18 hr	90.4	439	2.8	27.5	0.9
1°C/min, 18 hr	87.0	439	2.3	24.4	1.0
MFA 500°C	48.9	534	0.0	0.3	1.3
<i>Source Rock Analyzer Data</i>					
Sample (raw or spent rock)	TOC (mg/g orig. rock)	T_{Max} (°C)	S_1 (mg HC/g-orig. rock)	S_2 (mg HC/g-orig. rock)	S_3 (mg CO ₂ /g-orig. rock)
Raw 0 hr	185.9	443	4.0	174.7	1.9
ISS 6 hr	125.9	441	36.3	52.7	1.0
ISS 24 hr	117.2	445	42.8	47.3	0.7
ISS 72 hr	102.7	440	32.7	18.8	0.5
ISS 120 hr	93.5	437	21.8	15.0	0.5
ISS 288 hr	91.3	434	6.8	7.2	0.6
12°C/min, 3 hr	135.4	443	7.9	100.7	1.1
12°C/min, 18 hr	86.1	447	3.1	23.0	0.7
1°C/min, 18 hr	87.3	447	3.4	24.1	0.7
MFA 500°C	ND	ND	ND	ND	ND

Table A-3: Parameters determined using ¹³C NMR and High Temperature Programmed Pyrolysis

Sample	Aliphatic C (mg/g orig. rock)	Aromatic C (mg/g orig. rock)	S ₁ (mg HC/g orig. rock)	S _{2A} (mg HC/g orig. rock)	S _{2B} (mg HC/g orig. rock)	S _{Py} (mg HC/g orig. rock)
Raw 0 hr	139.4	46.5	5.9	7.6	141.2	8.4
ISS 6 hr	74.3	51.6	33.4	13.3	46.3	5.0
ISS 24 hr	60.9	56.4	35.6	13.4	31.0	4.7
ISS 72 hr	45.6	58.9	29.7	7.7	12.4	3.9
ISS 120 hr	38.5	55.0	24.0	6.2	10.4	6.0
ISS 288 hr	32.4	58.9	8.9	3.6	6.7	4.9
ItFA 12,3*	108.0	27.4	7.3	9.9	81.9	6.2
ItFA 12,6	ND	ND	10.7	12.2	73.4	7.4
ItFA 12,10	ND	ND	4.9	7.2	40.0	3.9
ItFA 12,14	ND	ND	4.1	4.9	23.5	3.5
ItFA 12,18	44.8	41.4	3.1	3.3	17.0	3.1
ItFA 1,3	ND	ND	7.9	10.3	95.2	8.0
ItFA 1,6	ND	ND	7.7	10.6	78.9	6.4
ItFA 1,10	ND	ND	4.9	6.9	36.8	3.6
ItFA 1,14	ND	ND	3.6	4.0	18.9	3.5
ItFA 1,18	45.2	42.1	3.6	4.0	18.4	3.6
MFA 500°C	11.9	37.0	ND	ND	ND	ND

* ItFA 12,3 indicates low temperature (360°C) Fischer Assay experiment with a heating rate of 12°C/min and soak time of 3 h.

ND: Value not determined

Table A-4: Estimated carbon balance determined using LECO TOC, HT-PPy, ¹³C NMR and bulk analysis data (all parameters reported in mg C/g original rock).

Sample	TOC	Bitumen ¹	Kerogen ²	Pyrobitumen ³	Char ⁴	Total Residue C
Raw 0 hr	193.0	11.5	120.0	7.1	36.5	175.1
ISS 6 hr	130.8	39.7	39.4	4.3	19.3	102.6
ISS 24 hr	129.7	41.7	26.3	4.0	26.8	98.9
ISS 72 hr	109.5	31.7	10.6	3.3	38.6	84.2
ISS 120 hr	98.5	25.7	8.8	5.1	37.9	77.5
ISS 288 hr	94.7	10.6	5.7	4.2	53.9	74.4

¹ Estimated using the S_1 and S_{2A} parameters determined by HT-PPy assuming bitumen-generated HC is 85% C.

² Estimated using the S_{2B} parameter determined by HT-PPy assuming kerogen-generated HC is 85% C.

³ Estimated using the S_{Py} parameter determined by HT-PPy assuming pyrobitumen-generated HC is 85% carbon.

⁴ Estimated using the aromatic C concentration determined by ¹³C NMR (calculated using the area fraction of the aromatic peak multiplied by TOC) and the soluble organic matter content (natural and thermobitumen) determined by bulk analysis with the following assumptions and formula – bitumen 80% C by weight and 30% of the carbon is aromatic (based on data for retorted Colorado oil shale reported in Miknis et al., 1985):

$$Char = Aromatic\ C - (Soluble\ OM \times 0.80 \times 0.30).$$