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FIS# FI120814a

*Fluid Inclusion Technologies, Inc.*  
*Innovations in Petroleum Risk Management*

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**A Stratigraphic Reconstruction of  
Bulk Volatile Chemistry from  
Fluid Inclusions in:**

*Werner Hatch 1*

Prepared September 5, 2012 for

*Nalcor Energy*

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*Data Reduction: FITsolve-5*

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A Stratigraphic Reconstruction of Bulk Volatile  
Chemistry from Fluid Inclusions in:

*Werner Hatch 1*

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by

*Fluid Inclusion Technologies, Inc.*





## Executive Summary for well: Werner Hatch 1

### 1 FIS Summary for Werner Hatch 1

According to public information, this well is the first shale-gas/shale-oil well drilled in the Deer Lake Basin, onshore Western Newfoundland. The well targeted interbedded organic rich mudstones and turbiditic siltstones of the Brook Formation. Elevated gas readings were encountered throughout a significant part of the interval drilled. The well was continuously cored at 101-445 m. A total of 91 samples labeled 30-441 m were analyzed.

FIS data from the interval above 200 m consists of intermittent wet gas, gas condensate, and oil-like responses. Highest signals on liquid-range species occur at 65-95 m. A single sample displaying anomalous benzene without acetic acid is recorded at 45 m. In general, benzene anomalies without organic acid may be sensing nearby gas. A thin section from 80 m reveals shaly carbonate with common yellow, white, and blue-fluorescent, unknown gravity (possibly upper-low to upper-moderate) oil inclusions in matrix carbonate. High inclusion abundance suggests high petroleum saturation at some time. No petroleum inclusions are identified in another thin section from 136 m. High abundance of immature oil-prone and lesser gas-prone kerogen is noted. If correct, sub-oil-window maturity would suggest that petroleum was introduced from a more mature section of the formation.

The section at 200-441 m gives intermittent wet gas, gas condensate, and oil-like FIS responses, as above. The interval at 201-251 m shows stronger liquid signals. Thin sections from 216 m and 386 m contain common, yellow and/or white-fluorescent oil inclusions, as above, and lesser blue-fluorescent subtypes in matrix carbonate. Again, high inclusion abundance suggests high oil saturation at some time. Kerogen is abundant as in the shallower section, and may be marginally mature below 200 m.

### 2 FIS Chemical Zonation

#### 30 m to 200 m :

Wet gas: 10%

WG-GC: 5%

GC-Oil: 18%

Low hydrocarbon responses: 67%

Hydrocarbon species to C13 are found in this interval. Proximity to gas indications are rare. There are no proximity to liquid petroleum indications documented in this zone. Sulfur species are not documented.

*Slide @ 80 m:* Population 1: Common, indeterminate gravity petroleum inclusions are indicated. Population 2: Common, indeterminate gravity petroleum inclusions are present. Population 3: Common, indeterminate gravity petroleum inclusions are preserved. Inclusion abundance indicates high petroleum saturation or paleo saturation. Several occurrences of gas prone kerogen and abundant occurrences of oil prone kerogen are documented.

*Slide @ 136 m:* Several occurrences of gas prone kerogen and abundant occurrences of oil prone kerogen are documented.

**200 m to 441 m :**

Wet gas: 6%

WG-GC: 3%

GC-Oil: 10%

Low hydrocarbon responses: 80%

Hydrocarbon species to C12 are indicated in this zone. No proximity to pay signal is documented. Sulfur species are not observed.

*Slide @ 216 m:* Population 1: Rare, indeterminate gravity petroleum inclusions are indicated. Population 2: Rare, indeterminate gravity petroleum inclusions are found. Population 3: Common, indeterminate gravity petroleum inclusions are preserved. Several occurrences of gas prone kerogen and abundant occurrences of oil prone kerogen are recorded.

*Slide @ 386 m:* Population 1: Rare, indeterminate gravity petroleum inclusions are documented. Population 2: Common, indeterminate gravity petroleum inclusions are documented. Several occurrences of gas prone kerogen and abundant occurrences of oil prone kerogen are found.

### Summary of Results for well: Werner Hatch 1

This report contains Fluid Inclusion Stratigraphy and Fluid Inclusion Petrography results for Werner Hatch 1 and was prepared for Nalcor Energy by *Fluid Inclusion Technologies*, 2217 N. Yellowwood Ave., Broken Arrow, OK 74133; ph: (918) 461-8984; fax: (918) 461-2085; [www.fittulsa.com](http://www.fittulsa.com).

Table I: Logistical Information

Client:	<b>Nalcor Energy</b>	Analyzed Depth:	<b>30 - 441 Meters</b>
Well:	<b>Werner Hatch 1</b>	Sample Spacing:	<b>See Individual Spectra</b>
		Sample Total:	<b>91</b>

Table II: Fluid Inclusion Petrography from Werner Hatch 1

Well Name: Werner Hatch 1																					
Sample Depth	Rock Type		Petroleum Fluid Inclusion Populations												Kerogen (possible source rk)					Bitu- men	
			Population 1				Population 2				Population 3										
Units: (Meters)	Dominant	Subordinate	Fluorescence Color	API Gravity (estimated)	Host Mineral & occurrence	Abundance	Fluorescence Color	API Gravity (estimated)	Host Mineral & occurrence	Abundance	Fluorescence Color	API Gravity (estimated)	Host Mineral & occurrence	Abundance	Host Rock	Type	OP Fluor Color	GP Abundance	OP Abundance	Type	Abundance
80	shcb		yl		cm	c	wt		cm	c	bl		cm	c	sh	go	wt	sv	a		
136	shcb														sh	go	wt	sv	a		
216	shcb		wt		cm	r	bl		cm	r	yl		cm	c	sh	go	yl	sv	a		
386	shcb, tr ss		yl		dq	r	wt		cm	c					sh	go	yl	sv	a		

ss: sandstone	mt: metamorphic rock	m: moderate	r: rare	ds: dead petroleum stain
si: siltstone	no: none	um: upper-moderate	sv: several	po: pore-occluding bitmn
sh: shale	br: brown	h: high	c: common	pb: pyrobitumen
cb: carbonate	or: orange	dq: frac in detrital quartz	a: abundant	
sa: salt	yl: yellow	dr: quartz dust rim	xa: very abundant	Notes: shcb = shaly carbonate
an: anhydrite	wt: white	qc: quartz cement	go: oil and gas prone	
ch: chert	bl: blue	df: frac detrital feldspar	op: oil prone	
co: coal	l: low	cm: matrix carbonate	gp: gas prone	
ig: igneous rock	ul: upper-low	cc: carbonate cement	ls: live petroleum stain	

Table III: FIS Terminology: Abbreviations and Acronyms

HC Type & Quality		Anomalous HC Zones		Fluid Contacts	
<b>NHC</b>	non-hydrocarbon	<b>MP</b>	migration pathway	<b>OWC</b>	oil-water contact
<b>DG</b>	dry gas	<b>PC</b>	present day ptrlm column	<b>GWC</b>	gas-water contact
<b>WG</b>	wet gas	<b>PPC</b>	paleo-ptrlm column	<b>GOC</b>	gas-oil contact
<b>GC</b>	gas condensate	<b>RI</b>	recycled ptrlm inclusions	<b>POWC</b>	paleo-oil-water contact
<b>VO</b>	volatile oil	<b>SR</b>	source rock	<b>PGWC</b>	paleo-gas-water contact
<b>O</b>	oil	<b>GP</b>	gas prone kerogen	<b>PGOC</b>	paleo-gas-oil contact
<b>BD</b>	biodegraded	<b>OP</b>	oil prone kerogen		
<b>TA</b>	thermally altered	<b>OGP</b>	oil and gas prone kerogen		
		<b>CNT</b>	contamination		
Water-Soluble Anomalies				Miscellaneous	
<b>WS</b>	undifferentiated water-soluble anomaly			<b>SL</b>	seal
<b>WSSR</b>	source rock related water-soluble anomaly			<b>MS</b>	microseep
<b>WSTA</b>	water-soluble anomaly sourced from thermal alteration				
<b>PTPL</b>	proximity to oil or gas-condensate				
<b>PTPG</b>	proximity to gas				
Petrographic Observations					
<b>A</b>	abundant	<b>IG</b>	igneous rock	<b>SA</b>	salt
<b>AN</b>	anhydrite	<b>L</b>	low	<b>SH</b>	shale
<b>BL</b>	blue	<b>LG</b>	large	<b>SI</b>	siltstone
<b>BR</b>	brown	<b>M</b>	moderate	<b>SM</b>	small
<b>C</b>	common	<b>MD</b>	medium	<b>SS</b>	sandstone
<b>CB</b>	carbonate	<b>MT</b>	metamorphic rock	<b>ST</b>	petroleum stain
<b>CC</b>	carbonate cement	<b>NO</b>	none	<b>SV</b>	several
<b>CH</b>	chert	<b>OR</b>	orange	<b>UL</b>	upper-low
<b>CM</b>	matrix carbonate	<b>PB</b>	pyrobitumen	<b>UM</b>	upper-moderate
<b>CO</b>	coal	<b>PF</b>	pore filling bitumen	<b>V</b>	variable
<b>DF</b>	detrital feldspar	<b>PR</b>	pore rimming bitumen	<b>W</b>	weak
<b>DQ</b>	detrital quartz	<b>QC</b>	quartz cement	<b>WT</b>	white
<b>DR</b>	quartz dust rim	<b>R</b>	rare	<b>XA</b>	extremely abundant
<b>H</b>	high	<b>S</b>	strong	<b>YL</b>	yellow



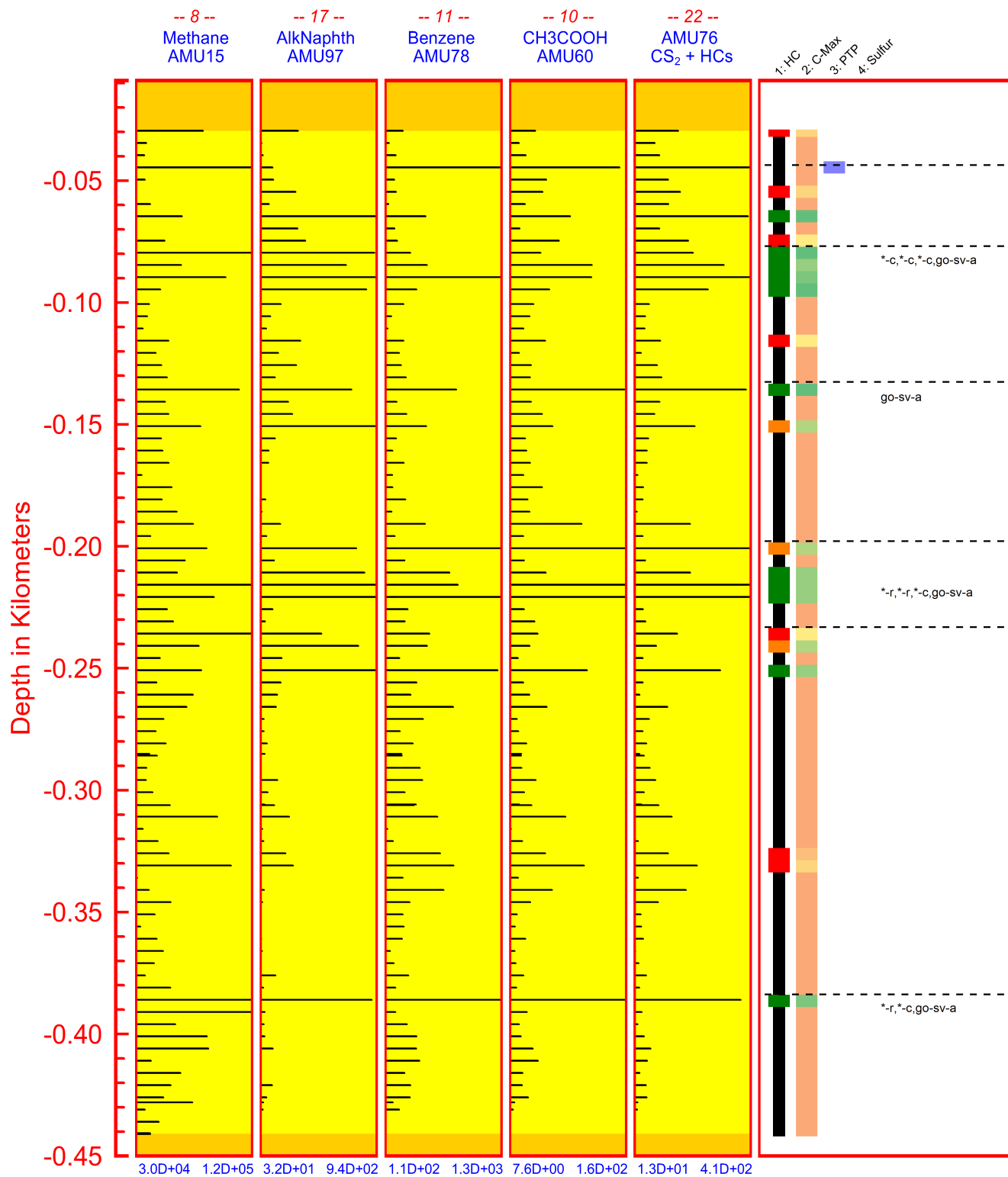


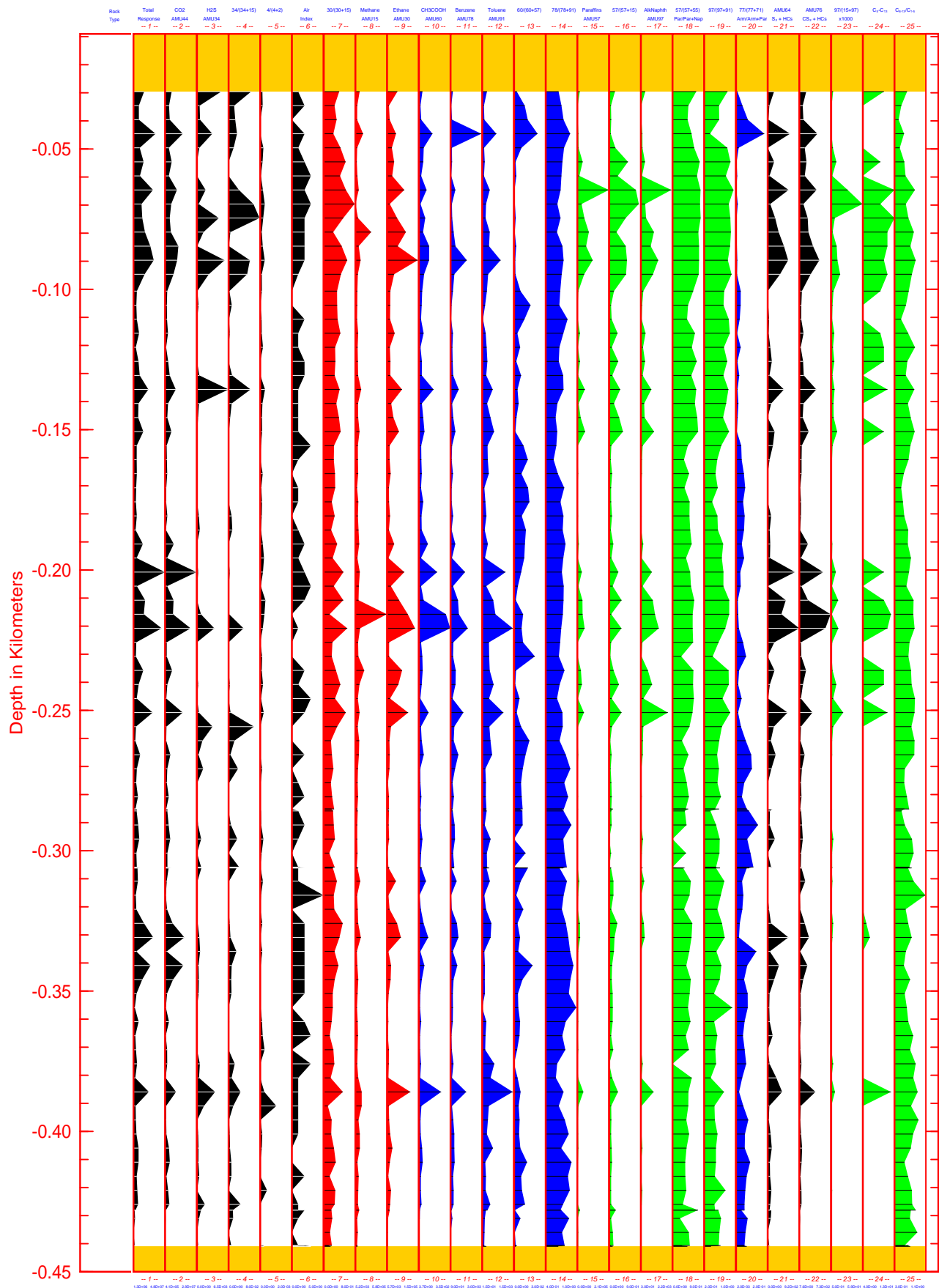
Figure 1: FIS Summary Tracks (see Sect. A for further explanation)

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1: HC				2: C-Max				3: PTP				4: Sulfur	
NH	WG	GC-Oil	C <sub>1</sub>	C <sub>3</sub>	C <sub>5</sub>	C <sub>7</sub>	C <sub>9</sub>	C <sub>11</sub>	C <sub>13</sub>	Gas	Sulfur		
DG	WG-GC		C <sub>2</sub>	C <sub>4</sub>	C <sub>6</sub>	C <sub>8</sub>	C <sub>10</sub>	C <sub>12</sub>		Liquid	S2-SO2		

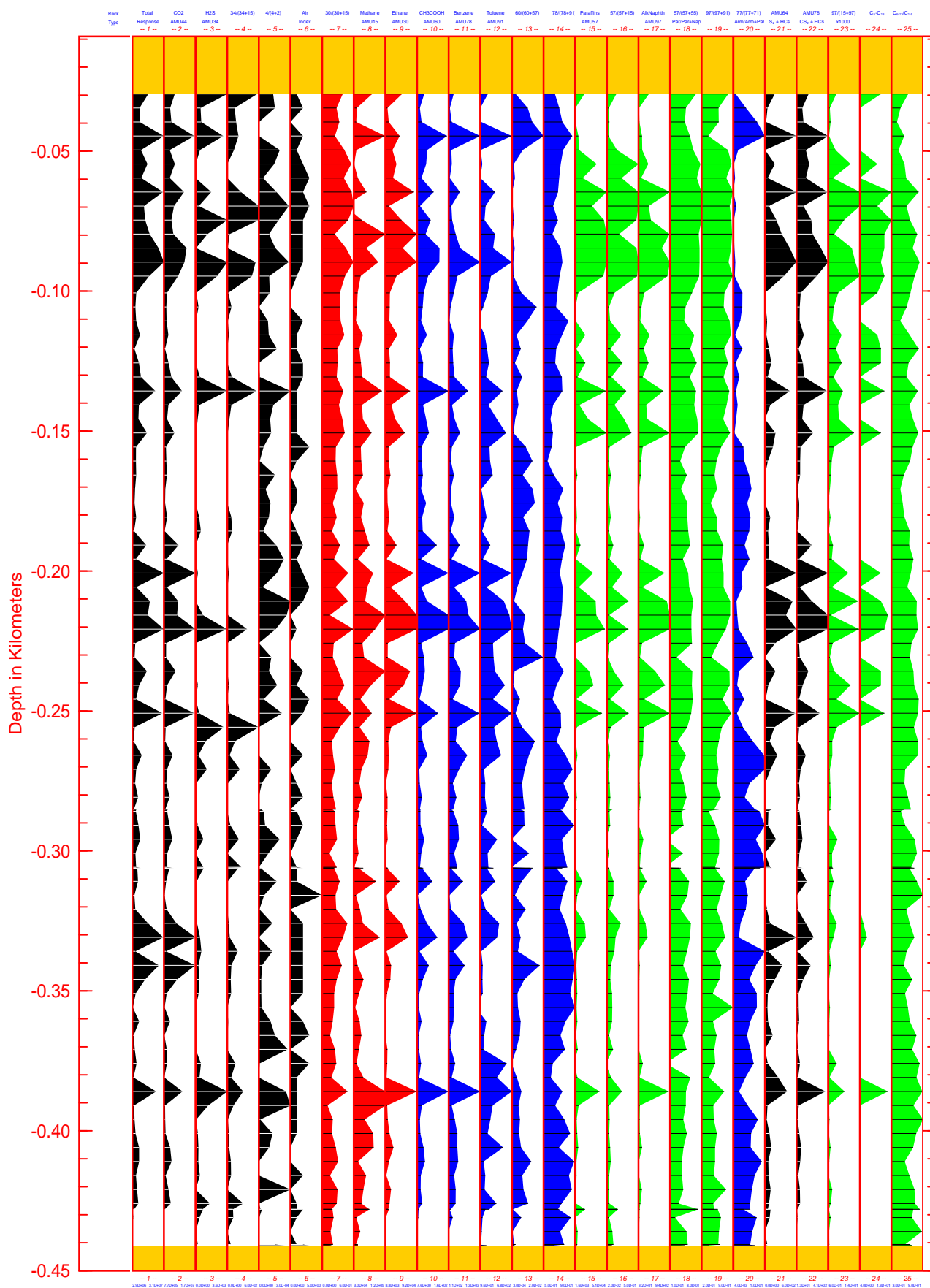


Werner Hatch 1: All FIS Data





# Werner Hatch 1 : 90% of all FIS Data





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### 3 Overview of FIT, Inc. and Fluid Inclusion Stratigraphy

**Fluid Inclusion Technologies (FIT), Inc.**, is a laboratory-based petroleum service organization established in 1997 and offering a variety of analytical services including some previously proprietary technologies. **Fluid Inclusion Stratigraphy (FIS)**, the most widely applicable of these technologies is a rapid analytical technique that involves the automated analysis of volatile compounds trapped within micron-sized cavities in rock material taken from well cuttings, core or outcrop samples. These “fluid inclusions” are representative samples of subsurface fluids, and are not subject to fractionation during sampling or evaporative loss during sample storage for any length of time. The procedure has major impact in the areas of **both Petroleum Production and Exploration Applications** providing information unattainable via more traditional methods and, has been instrumental in the discovery of significant petroleum reserves, influenced exploration and acreage acquisition decisions and provided innovative options for resource estimation, petroleum production and enhanced oil recovery operations. **Fluid Inclusion Stratigraphic Analysis**, often in combination with other patented techniques, emerging geochemical methodologies and standard microscopic methods, all available through Fluid Inclusion Technologies, Inc., provides a unique and unequaled industry product boasting an impressive list of proven applications including determination of **Product Type, Hydrocarbon Migration, Seals and Seal Integrity, Fluid Contacts, Proximity to Reservoired Petroleum, Pay Zone/By Passed Pay Delimitation, Reservoir-Scale Compartmentalization** and **Fluid Pressure Compartments**. Further information regarding the application of **FIS Analysis** and the other technical services we provide to problems in petroleum exploration and production is available elsewhere in this report and on our website: “[www.fittulsa.com](http://www.fittulsa.com)”.

#### 3.1 General Logistics of Initiating an FIS Analysis

*To Initiate an FIS Analysis:* contact FIT<sup>1</sup> directly to discuss goals of the study, sample requirements, turnaround time, pricing, and other related aspects. New clients are particularly encouraged to consult with our staff during the early stages of project development to optimize sample selection, preparation and shipment. Rock materials for FIS Analysis are shipped directly to C&M Storage<sup>2</sup>, our sample handling facility, for sample preparation including any necessary crushing/sieving, subsampling and washing. The turnaround time for a typical FIS Analysis is preliminary data in 1-2 weeks time following receipt of samples by C&M and final report 1-2 weeks following preliminary analysis. These times are approximate and depend on the amount of sample preparation required, job size and analytical backlog. At the time of issue of this report, the cost for obtaining an FIS Analysis was \$7,200 U.S. for a full-well analysis (up to 575 samples) and \$4,200 U.S. for a short-well analysis (up to 180 samples). The cost includes the automated mass spectrometric analysis, preparation of and fluid inclusion petrography on selected thin-sections sampled throughout the well, and interpretation in the form of annotated depth plots (see Figure 1).

*When sampling for FIS Analysis:* the technique is equally applicable to cuttings, core and outcrop samples, but all samples will ultimately be reduced to cuttings-sized rock material. Wells drilled with any mud system can be analyzed (including oil-based systems),

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<sup>1</sup>Fluid Inclusion Technologies, 2217 N. Yellowwood Ave., Broken Arrow, 74012, USA., phone (918) 461-8984

<sup>2</sup>Attn: FIS Analysis, C&M Storage, 3311 Hwy, 77 South, Schulenburg, TX 78956, USA

as can samples of any age (i.e., fresh cuttings or those warehoused for many years). Our suggested sampling interval for general well studies is 30 ft (10 m). Pay-delineation studies, reservoir-scale studies or other applications involving rapidly changing fluid chemistries should be sampled at the tightest possible spacing, depending on sample availability (e.g., 1-3 ft). A maximum of 575 samples can be analyzed for a given well. Approximately 1 gm of clean rock material is needed for each sample. In most cases, some amount of additional washing is required - even for “washed samples”, thus, it is best to send enough to ensure ample material after a final wash. It is further recommended that “clean lith cuts” be provided to minimize costs associated with additional sample preparation as all sample washing and preparation costs will be charged back to the client. The quoted price for an FIS Analysis is exclusive of sample preparation, handling and shipping; estimates for these project-specific services are available upon request.

### 3.2 Organization of this Report

Analytical results of the FIS analysis of Werner Hatch 1 are presented graphically in Sections 4.1 and 4.2 as a series of profiles each illustrating the variation of a particular atomic mass ( $m/z$ ) or ratio of two masses with measured depth. A general discussion of the interpretation of FIS data including the significance of particular features and trends (or their absence) is provided in Appendix A. The remaining information provided in subsequent sections includes: 1) reference spectra, collected on internal standards and used to monitor inter- and intra-analytical consistency of the quadrupole analyses which are presented and discussed in Appendix B; and 2) mass spectra from all samples which are listed individually by depth in Appendix C.

### 3.3 Output Formats

Analytical results of the present study are available in electronic format as described below.

1. FI120814a-1.las – LAS-format, 26-column file containing recorded depth and Tracks 1-25 from the *FIT Analysis* of Werner Hatch 1
2. FI120814a-1.txt – TXT-format, 26-column file containing recorded depth and Tracks 1-25 from the *FIT Analysis* of Werner Hatch 1
3. FI120814a-2.las.Z – LAS-format (compressed), 181-column file containing recorded depth and background corrected, normalized, standardized individual mass spectra ( $m/z$  2-180) from the *FIT Analysis* of Werner Hatch 1
4. FI120814a-s.pdf – PDF format, electronic file of the summary tracks and annotations from the *FIT Analysis* of Werner Hatch 1
5. FI120814a-c.pdf – PDF format, electronic file of the poster containing 90% of all FIS Data from the *FIT Analysis* of Werner Hatch 1
6. FI120814a-1.pdf – PDF format, electronic file of the final report (entire document) of the *FIT Analysis* of Werner Hatch 1

## 4 Analytical Results

### 4.1 FIS Depth Profiles Showing all Data

Millivolt responses for selected ionic species or species ratios resulting from FIS mass spectrometric analysis are displayed in Figures 2-6 (trackplots one through twenty-five). The identity of the individual ions involved in construction of the trackplots are listed in Table IV below. The tracks are organized into groups of related compounds; tracks 1-6 representing inorganic gases, tracks 7-9 representing dry organic gases, tracks 8-14 representing water soluble organic species or ratios of “more soluble” to “less soluble” species, and tracks 15-20 and 21-25 representing petroleum components of higher molecular weight and two sulfur compounds. The general interpretation of *FIS* data shown in the trackplots is discussed in Appendix A.

Table IV: Identification of Organic and Inorganic Species Represented in Track Plots

Mass #	Description
2	hydrogen ( $\text{H}_2^+$ )
4	helium ( $^4\text{He}^+$ )
15	$\text{C}_1$ fragment ( $\text{CH}_3^+$ ); largely methane
30	$\text{C}_2$ fragment ( $\text{C}_2\text{H}_6^+$ ); largely ethane
34	hydrogen sulfide ( $\text{H}_2\text{S}^+$ )
44	dominantly carbon dioxide ( $\text{CO}_2^+$ ); possible $\text{C}_3$ fragment overlap
55	contribution from $\text{C}_4$ and greater naphthenes
57	contribution from $\text{C}_4$ and greater paraffins
60	dominantly acetic acid ( $\text{CH}_3\text{COOH}^+$ ); possible dominance by carbonyl sulfide ( $\text{COS}^+$ ) in some cases
64	$\text{S}_2$ or $\text{SO}_2$ plus hydrocarbons
71	contribution from $\text{C}_5$ and greater paraffins
76	$\text{CS}_2$ plus hydrocarbons
77	contribution from aromatic species
78	benzene ( $\text{C}_6\text{H}_6^+$ ) with possible contribution by carbon disulfide ( $\text{CS}_2^+$ )
91	toluene ( $\text{C}_7\text{H}_7^+$ )
97	$\text{C}_7$ alkylated naphthene fragment

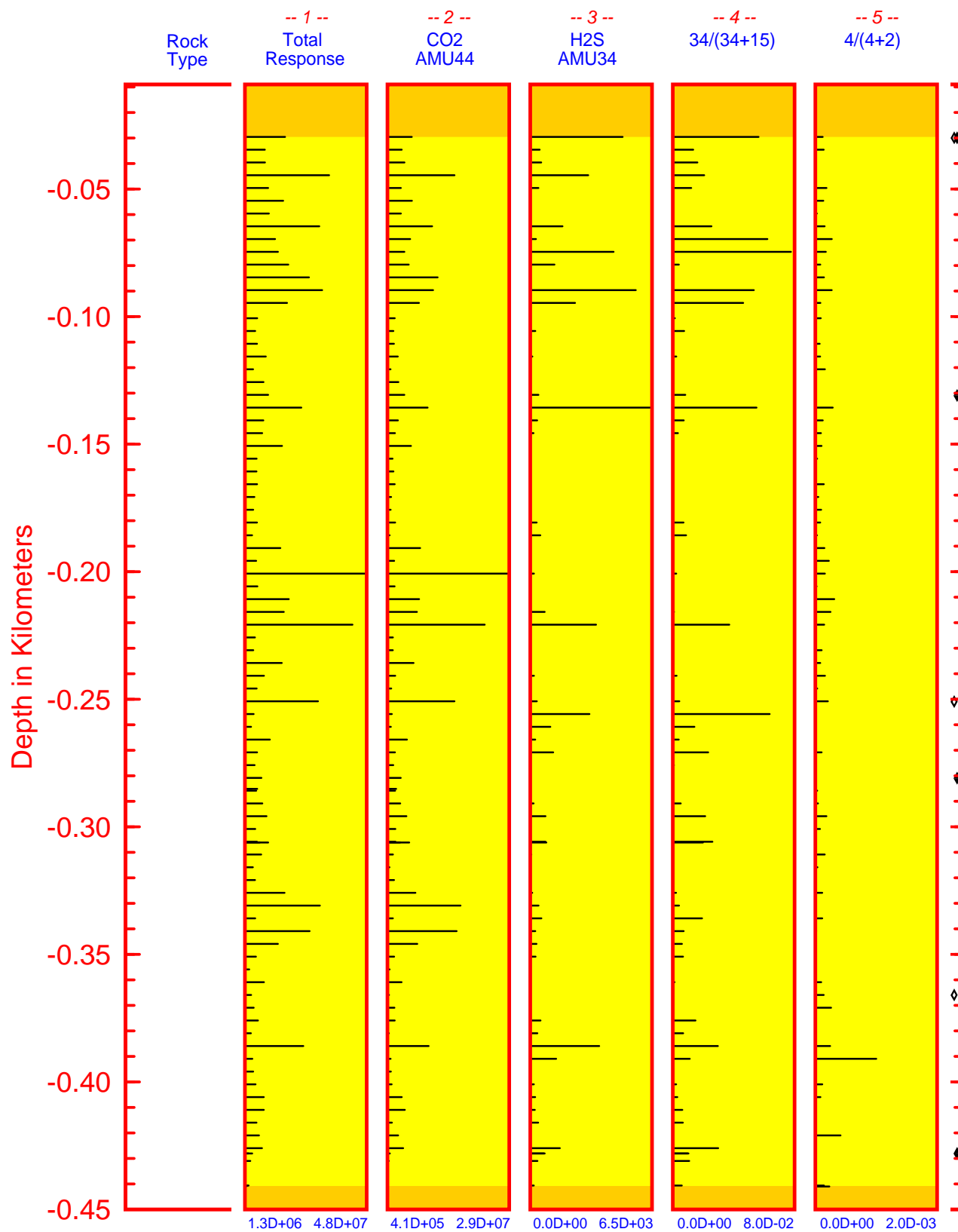


Figure 2: All FIS Data: Tracks 1 – 5 (see Sect. A.3 for explanation)

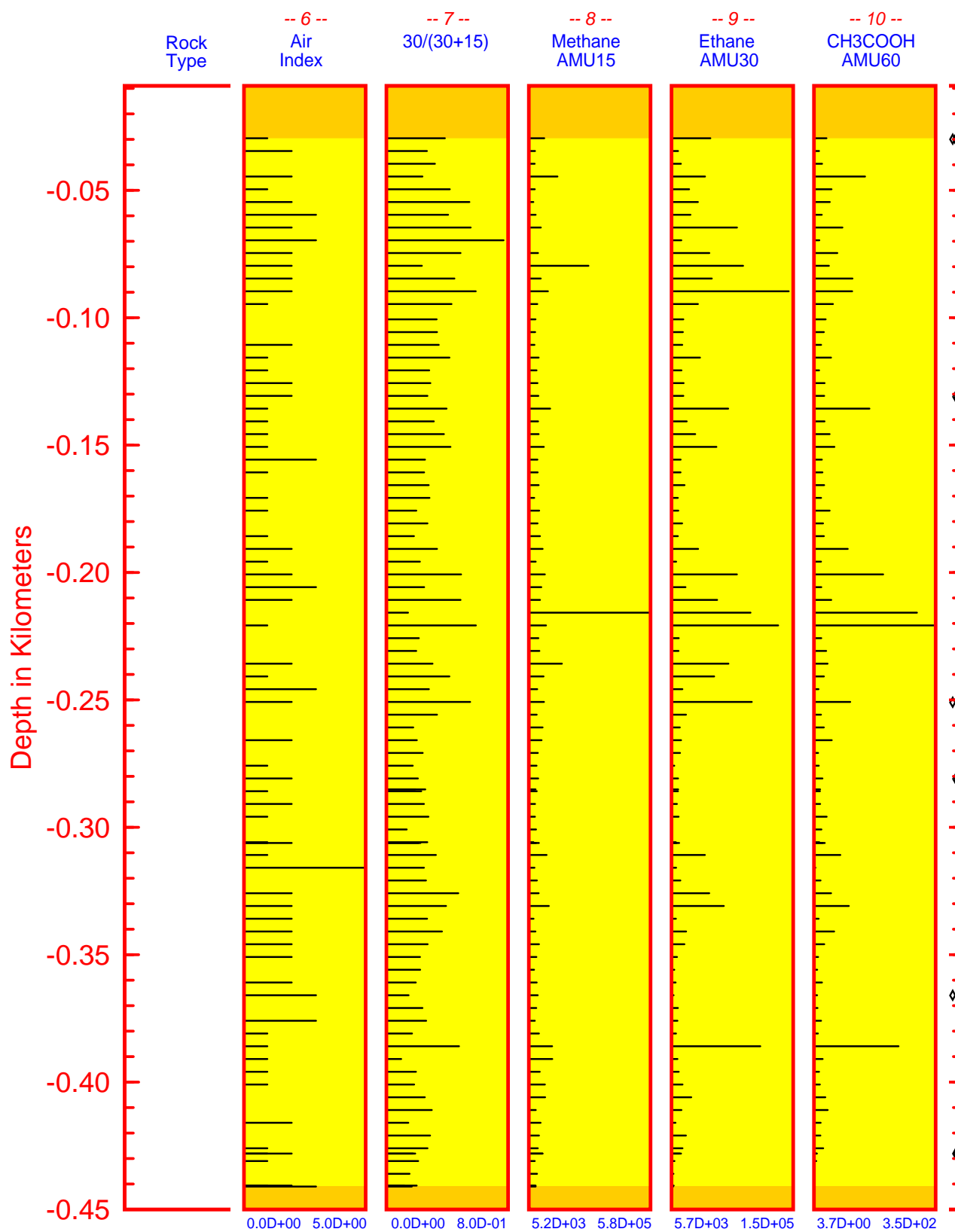


Figure 3: All FIS Data: Tracks 6 – 10 (see Sect. A.3 for explanation)

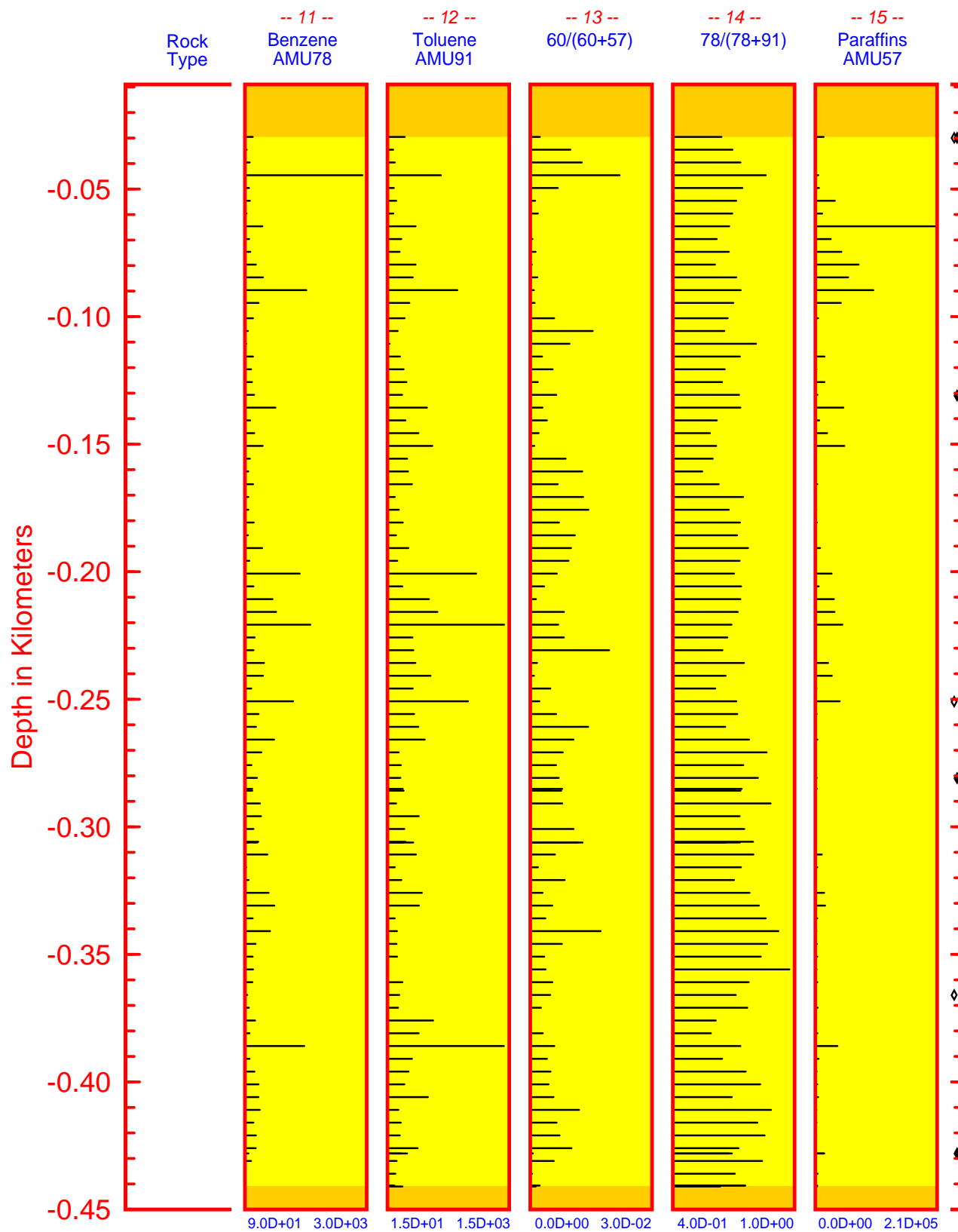


Figure 4: All FIS Data: Tracks 11 – 15 (see Sect. A.3 for explanation)

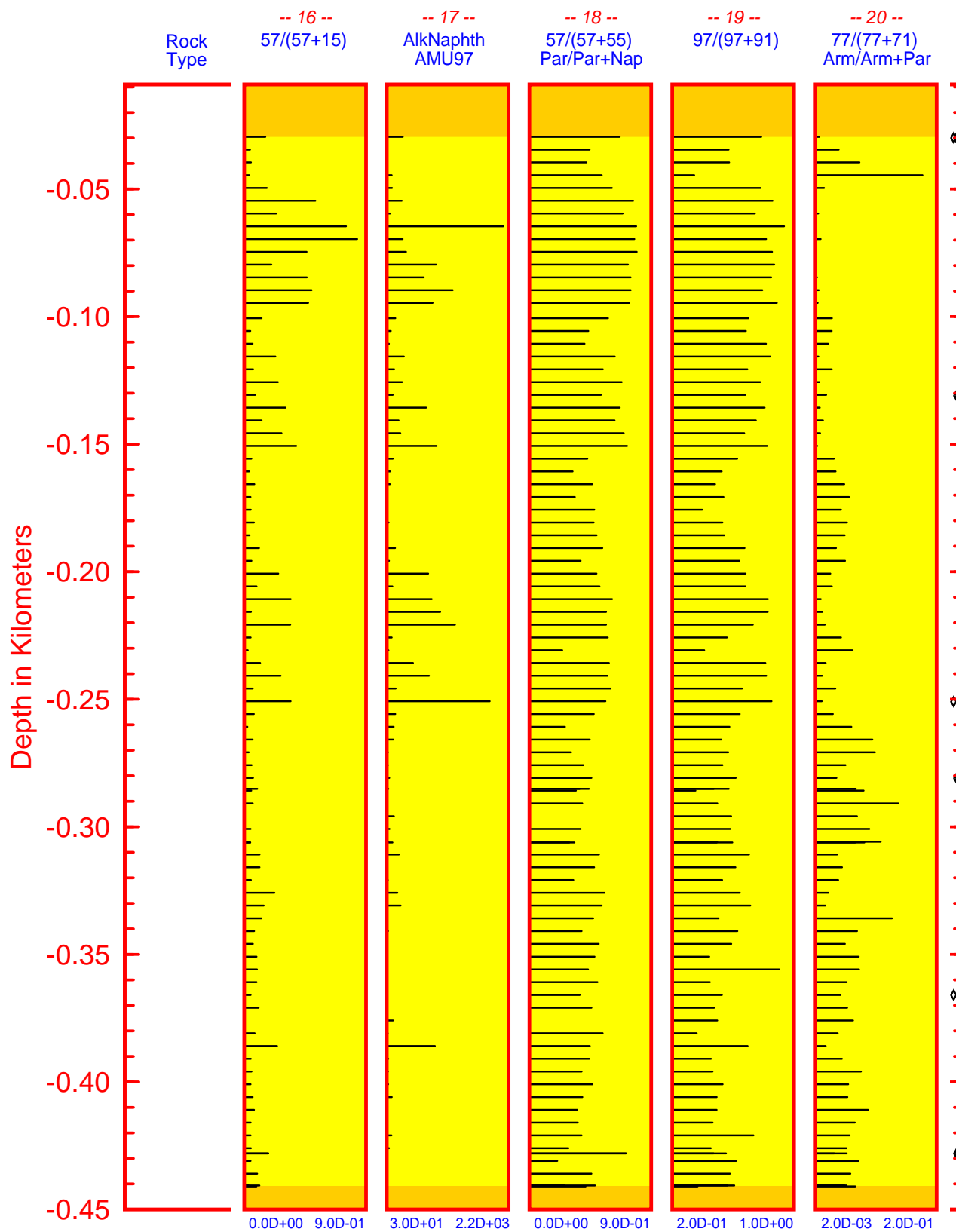


Figure 5: All FIS Data: Tracks 16 – 20 (see Sect. A.3 for explanation)

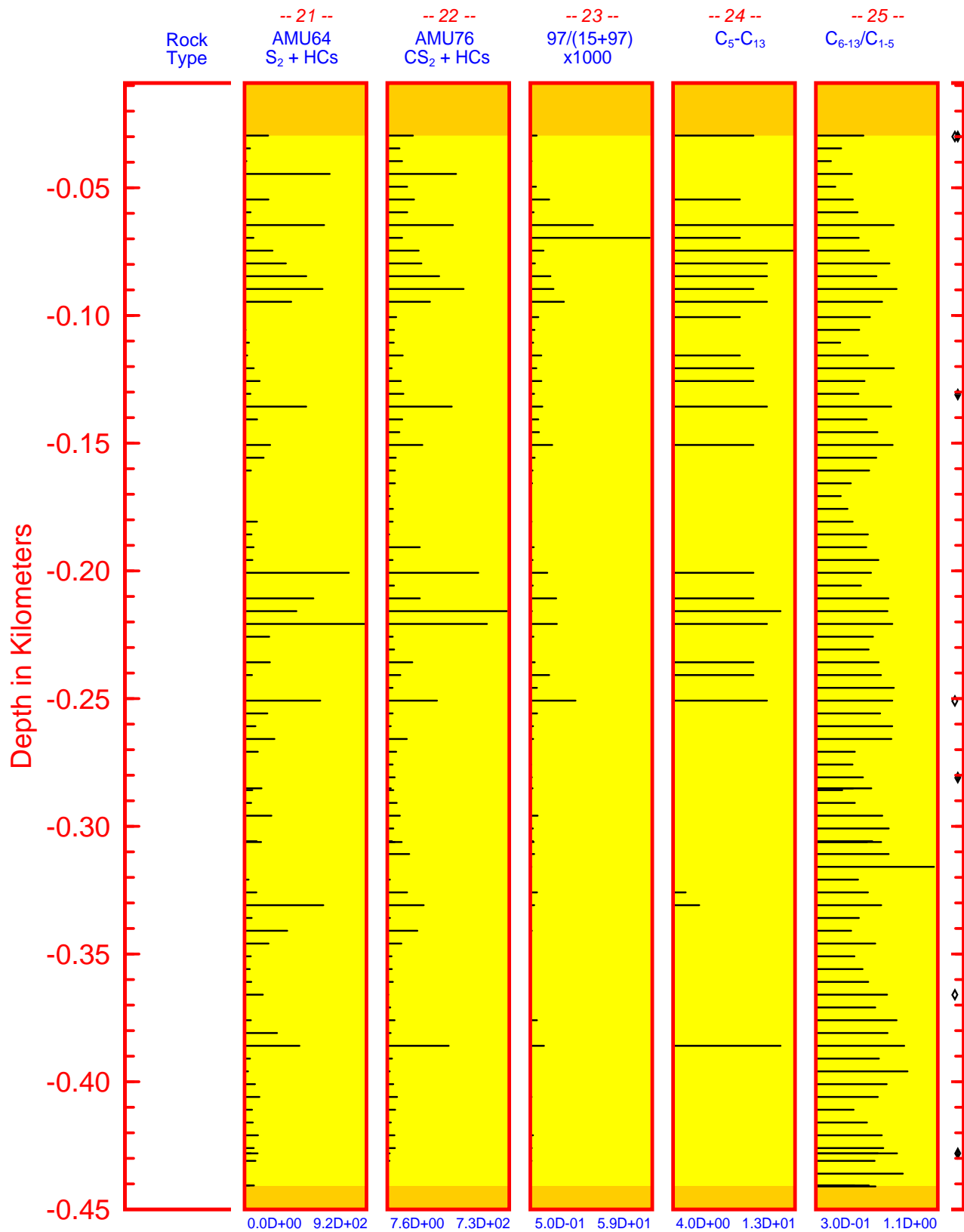


Figure 6: All FIS Data: Tracks 21 – 25 (see Sect. A.3 for explanation)



## 4.2 FIS Depth Profiles Showing 90% of all Data

Figures 7-11 show the same data as that given in Figures 2-6 of Section 4.1 *except* the upper and lower 5% of the data have been removed in each track and the scale along the abscissa adjusted accordingly in order to accentuate small deviations from background and reduce attenuation effects associated with scale-dominating responses. The identity of the individual ions involved in construction of the trackplots are listed in Table IV. The tracks are organized into groups of related compounds; tracks 1-6 representing inorganic gases, tracks 7-9 representing dry organic gases, tracks 8-14 representing water soluble organic species or ratios of “more soluble” to “less soluble” species, and tracks 15-20 and 21-25 representing petroleum components of higher molecular weight and two sulfur compounds. The general interpretation of *FIS* data shown in the trackplots is discussed in Appendix A.

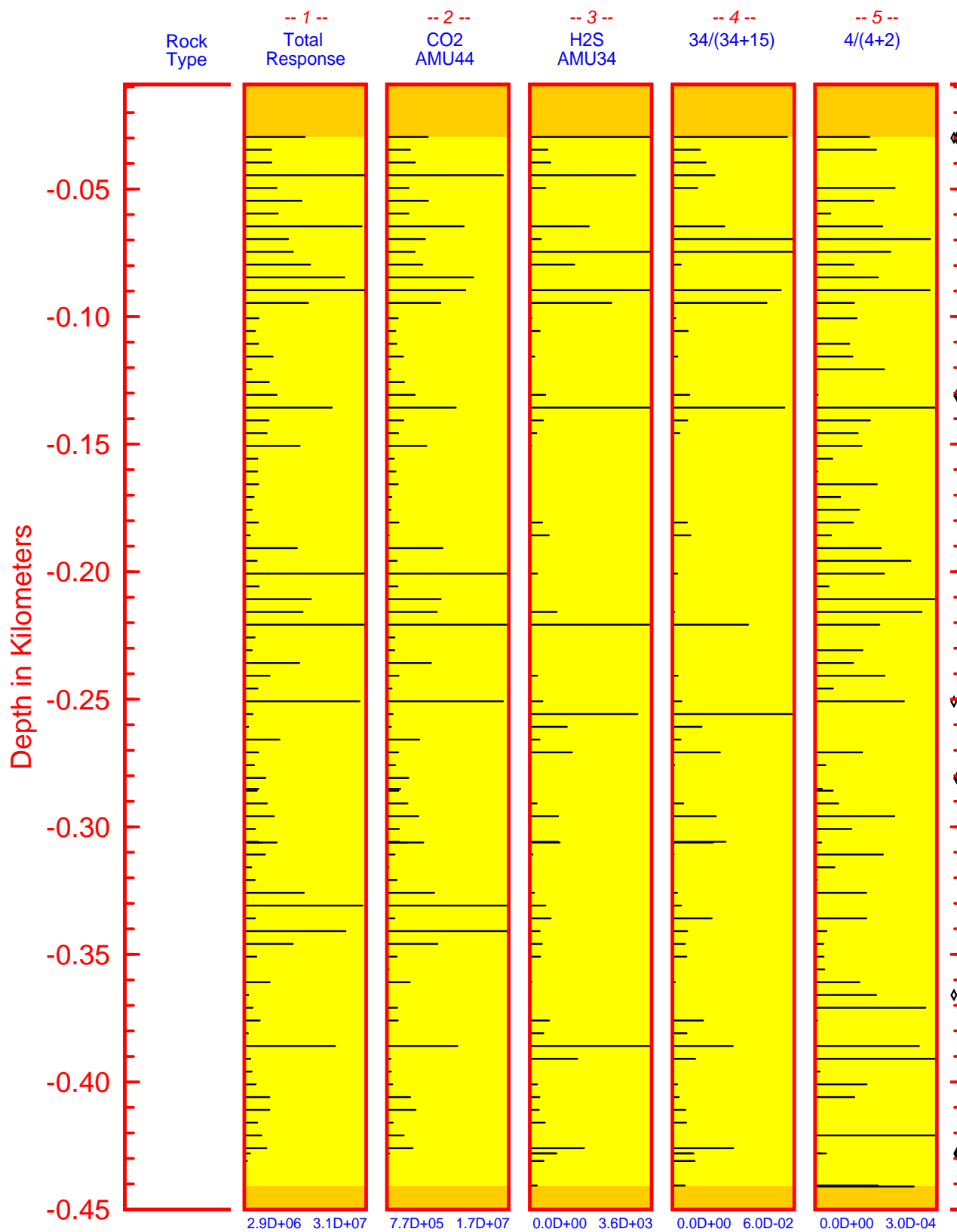


Figure 7: 90% of all FIS Data: Tracks 1 – 5 (see Sect. A.3 for explanation)

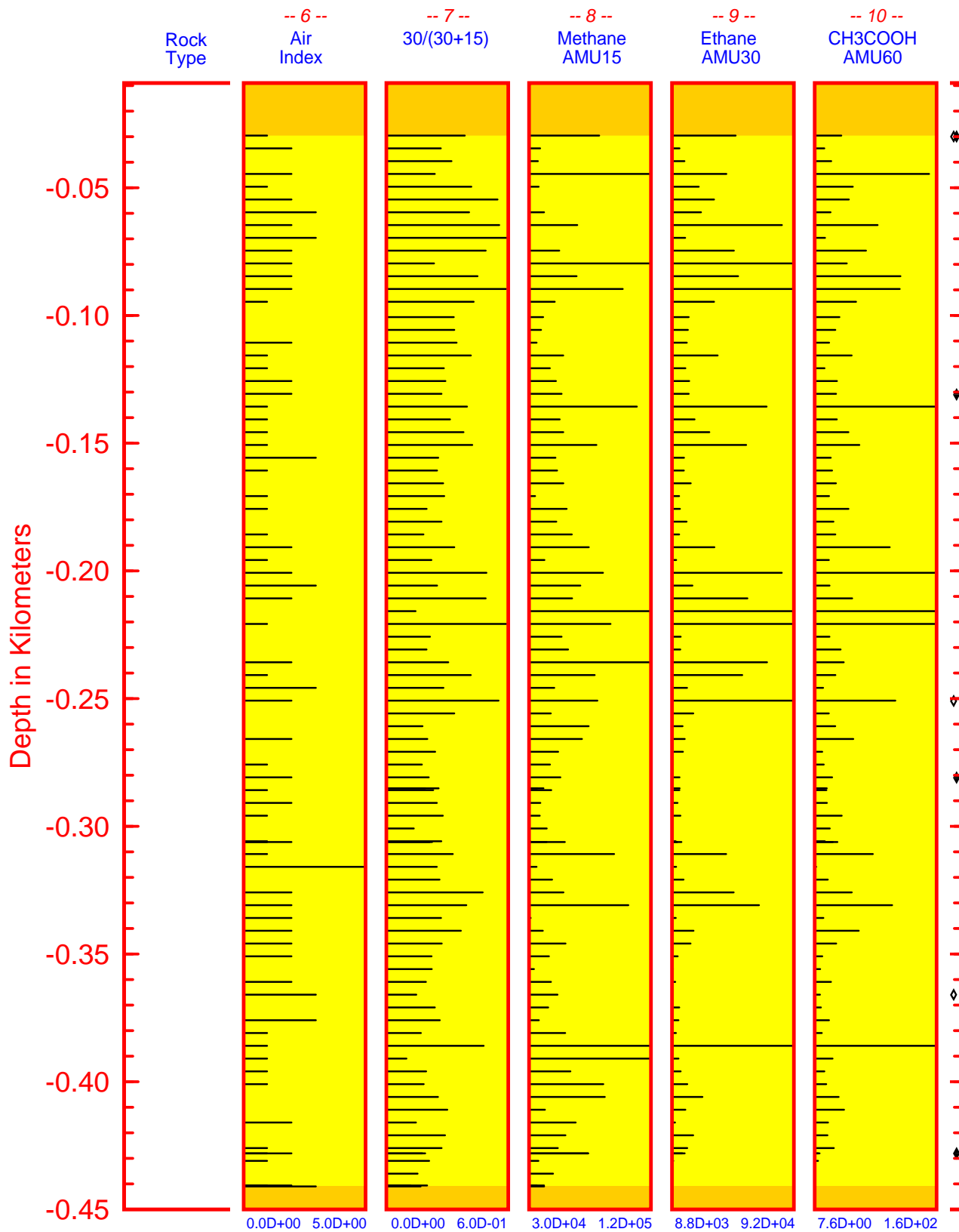


Figure 8: 90% of all FIS Data: Tracks 6 – 10 (see Sect. A.3 for explanation)

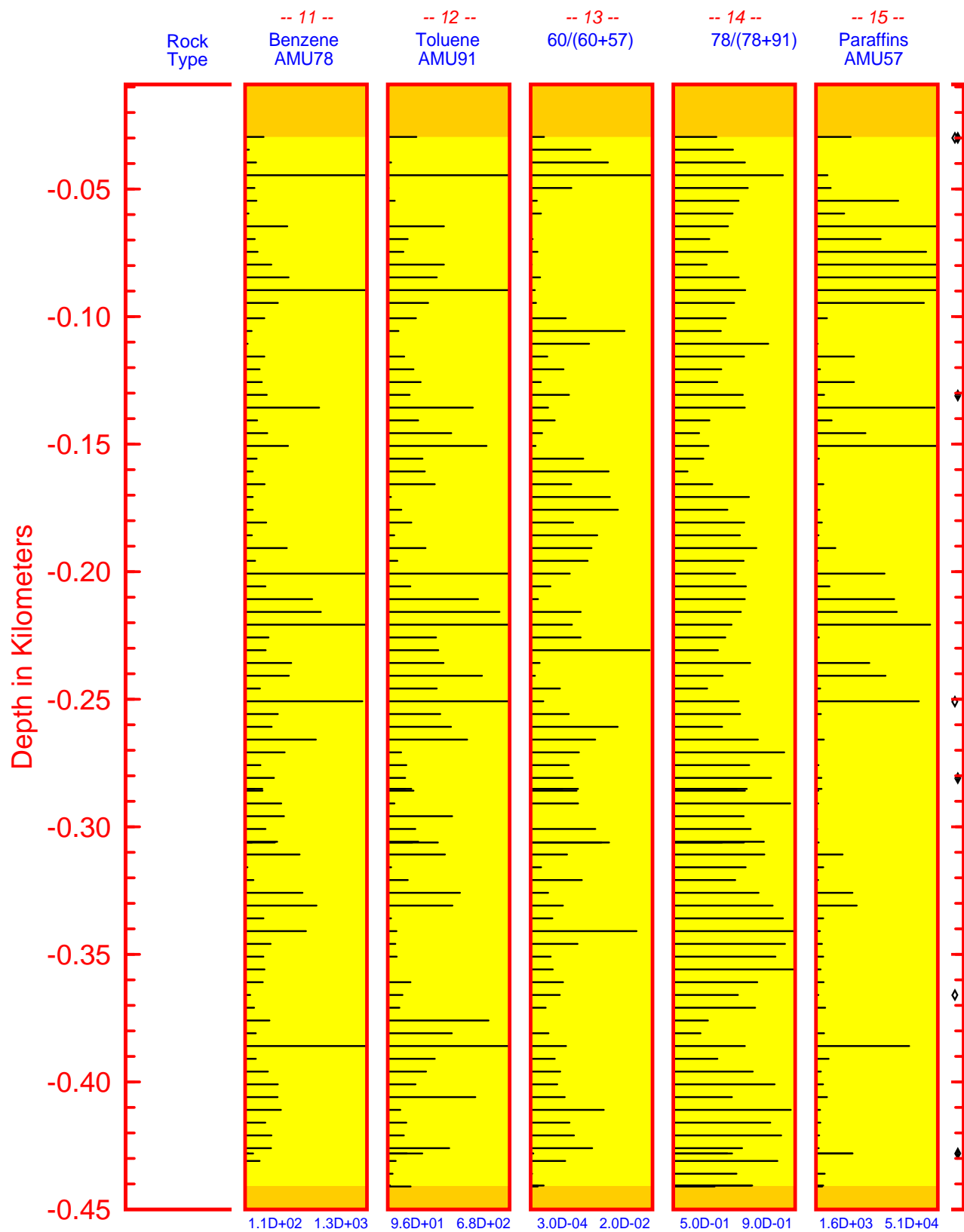


Figure 9: 90% of all FIS Data: Tracks 11 – 15 (see Sect. A.3 for explanation)

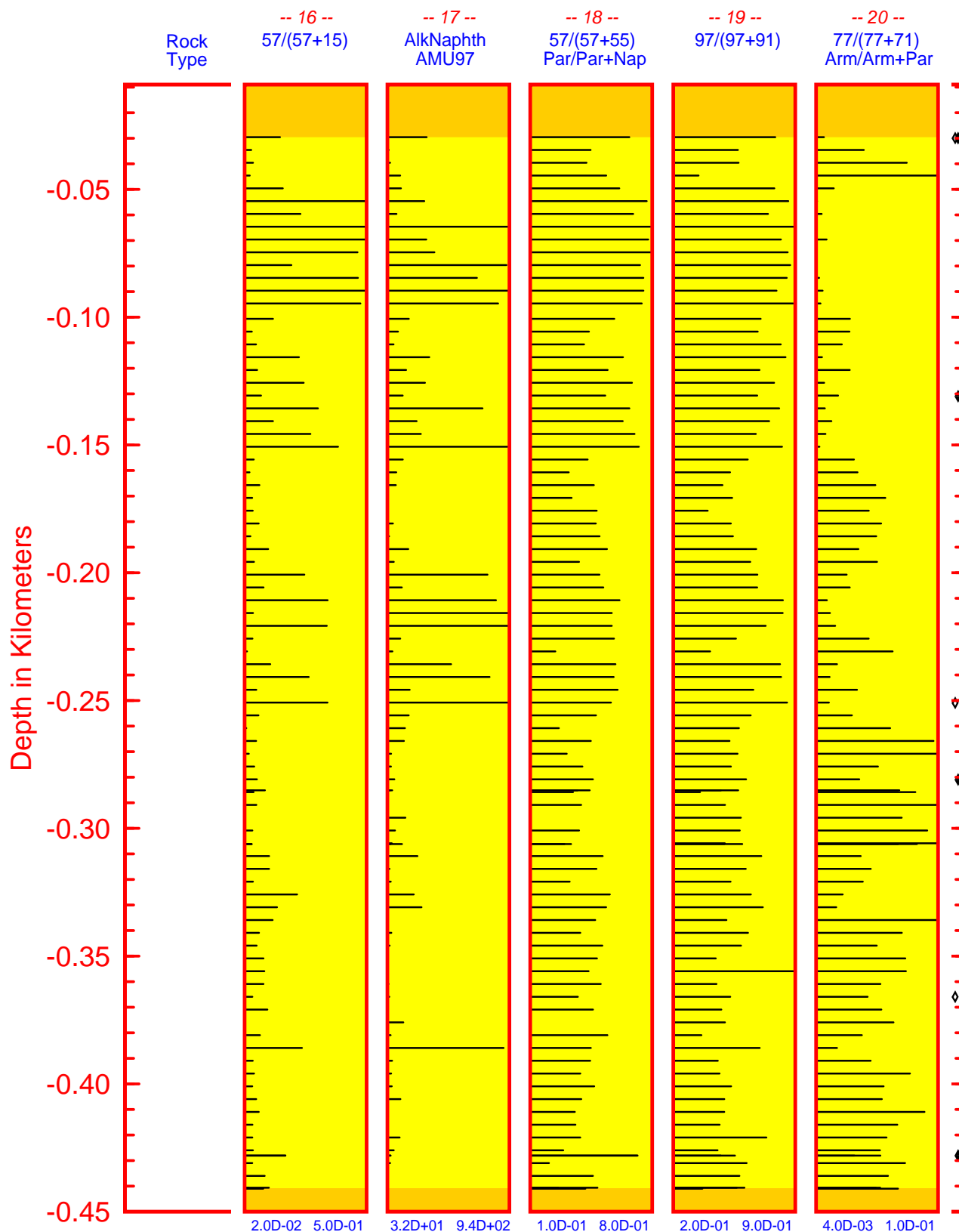


Figure 10: 90% of all FIS Data: Tracks 16 – 20 (see Sect. A.3 for explanation)

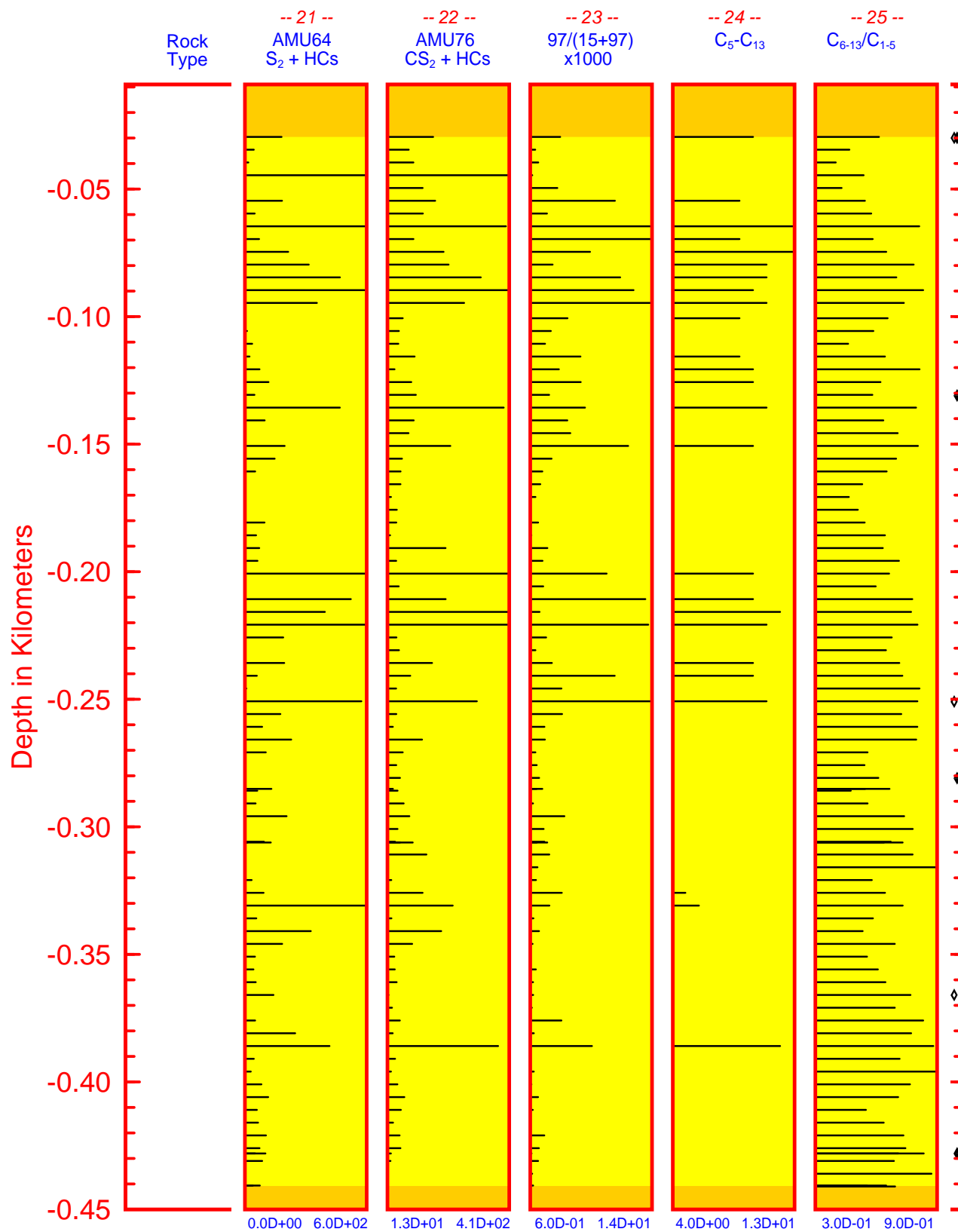


Figure 11: 90% of all FIS Data: Tracks 21 – 25 (see Sect. A.3 for explanation)

## 5 Photomicroscopy

Thin sections were prepared from Werner Hatch 1 samples at depths warranting further examination following preliminary assessment of the *FIS* analytical results. The sections were then examined under a petrographic microscope using a variety of fluid inclusion techniques (e.g., UV-fluorescence, microthermometry, etc.) in order to verify the presence of petroleum-bearing inclusions in the rock samples and to explore textural relationships that may yield additional information on the timing of hydrocarbon migration or generation. Petrographic examination is also necessary to verify that petroleum-bearing fluid inclusions present in the samples and responsible for the observed mass spectra are not relict features (i.e., that they were not already present in the mineral grains prior to deposition). The following figures contain photomicrographs representative of samples from Werner Hatch 1 at the depths indicated.

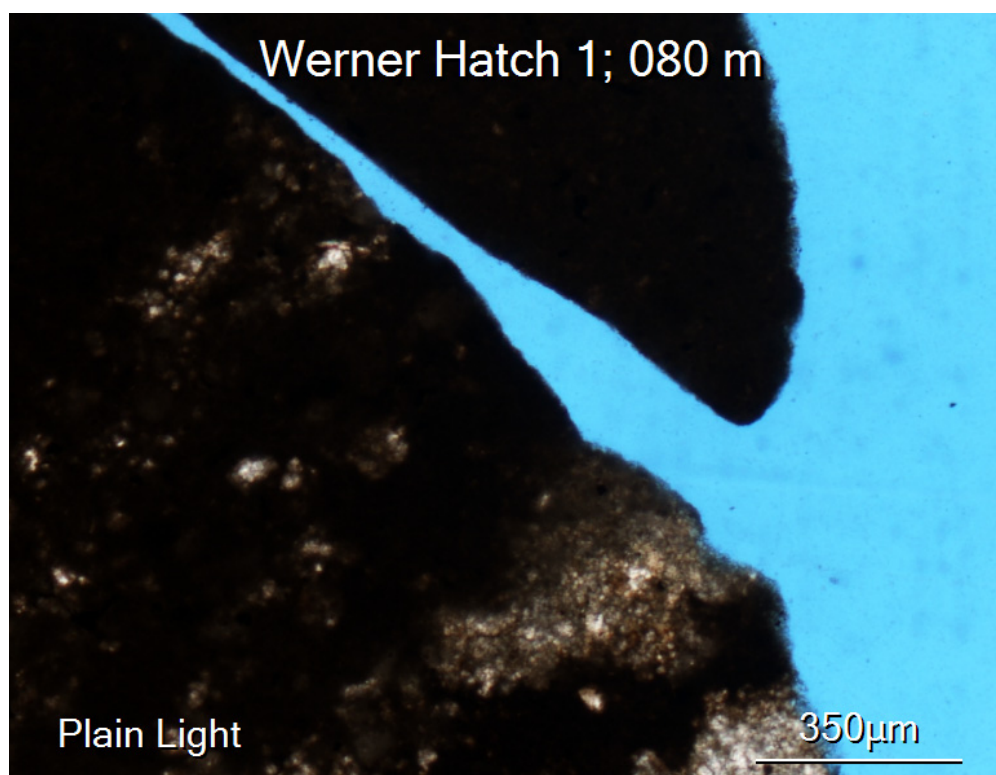


Figure 12: Photomicroscopy from Werner Hatch 1

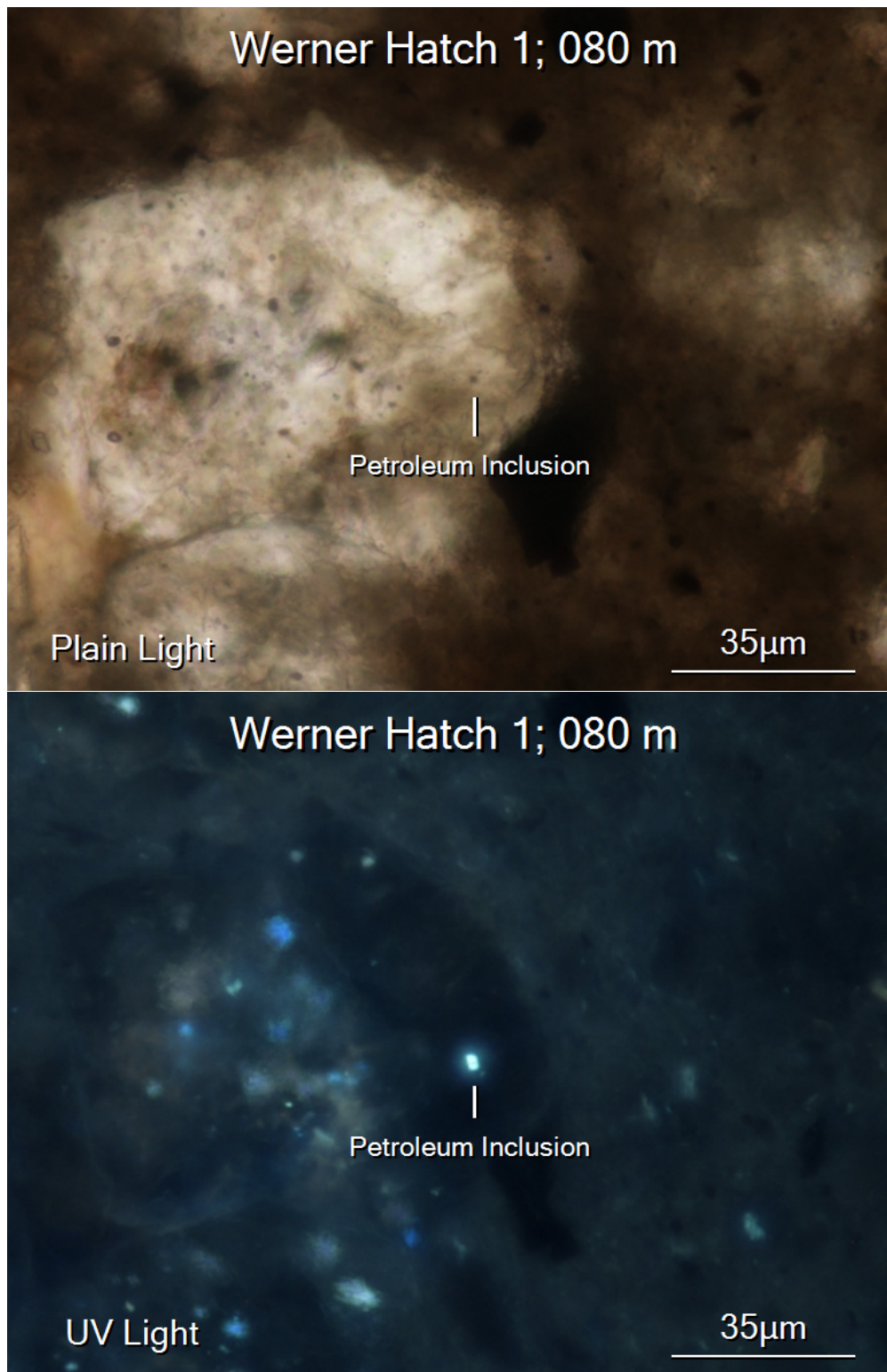


Figure 13: Photomicroscopy from Werner Hatch 1



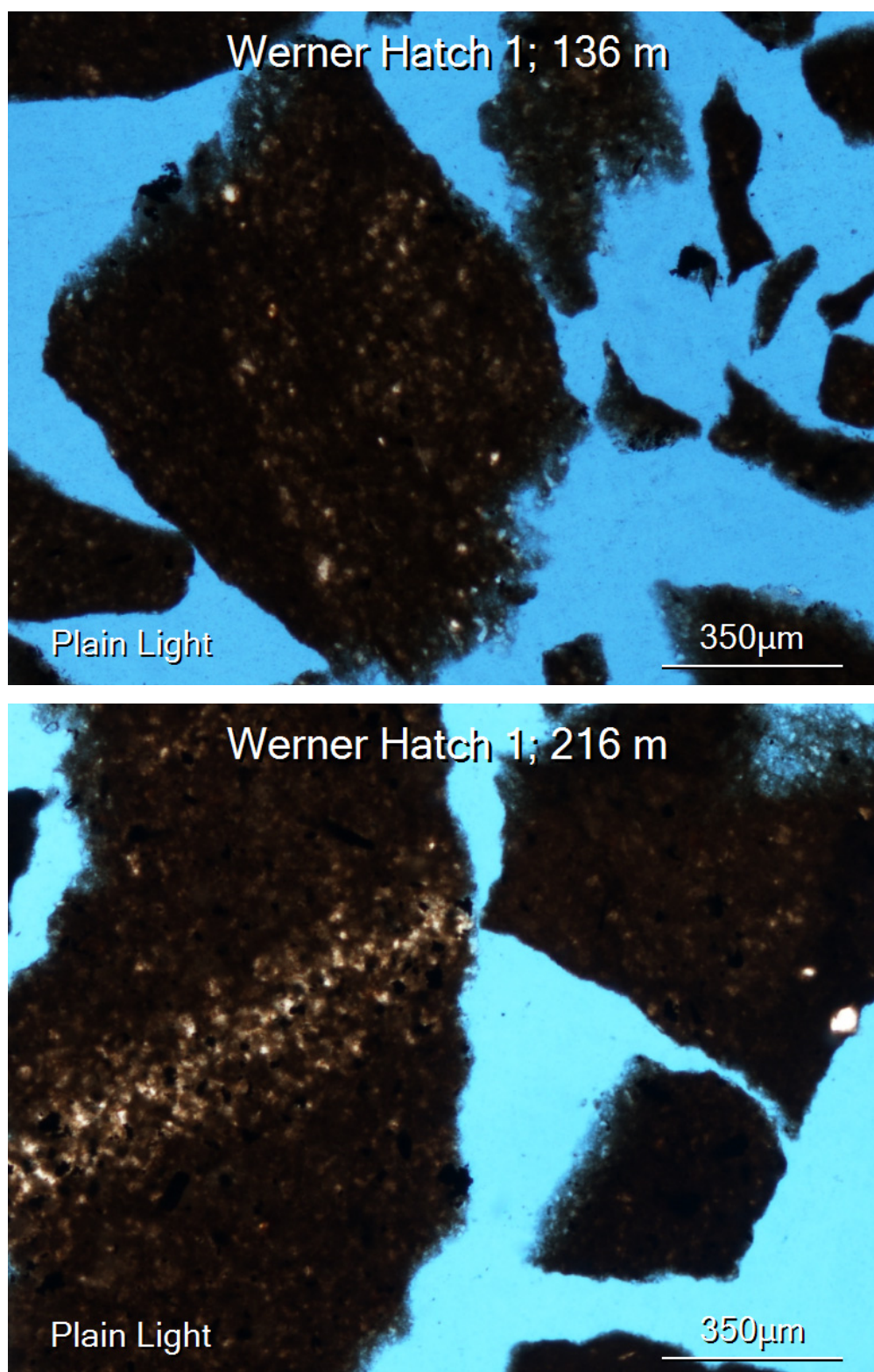


Figure 14: Photomicroscopy from Werner Hatch 1

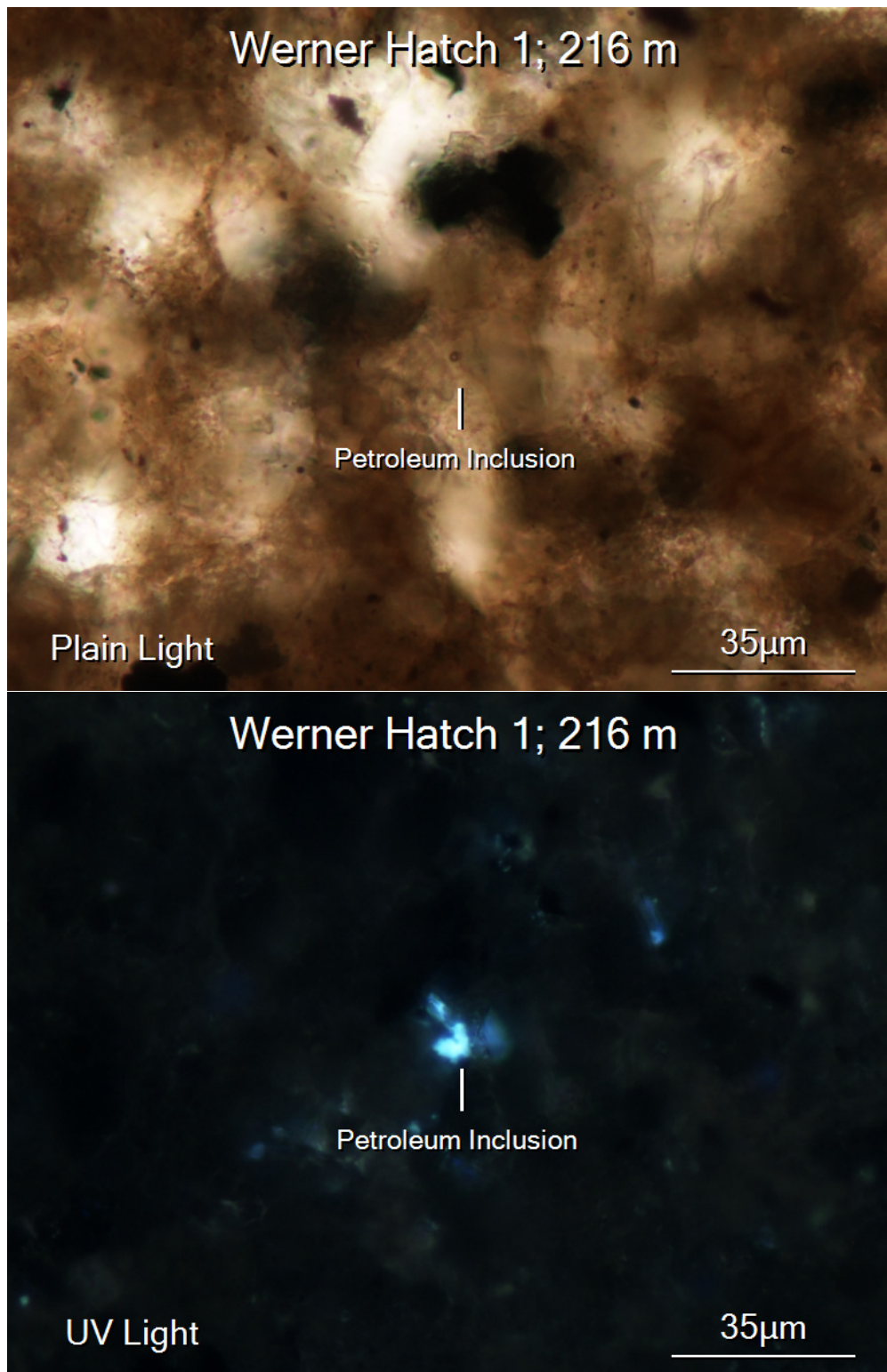


Figure 15: Photomicroscopy from Werner Hatch 1

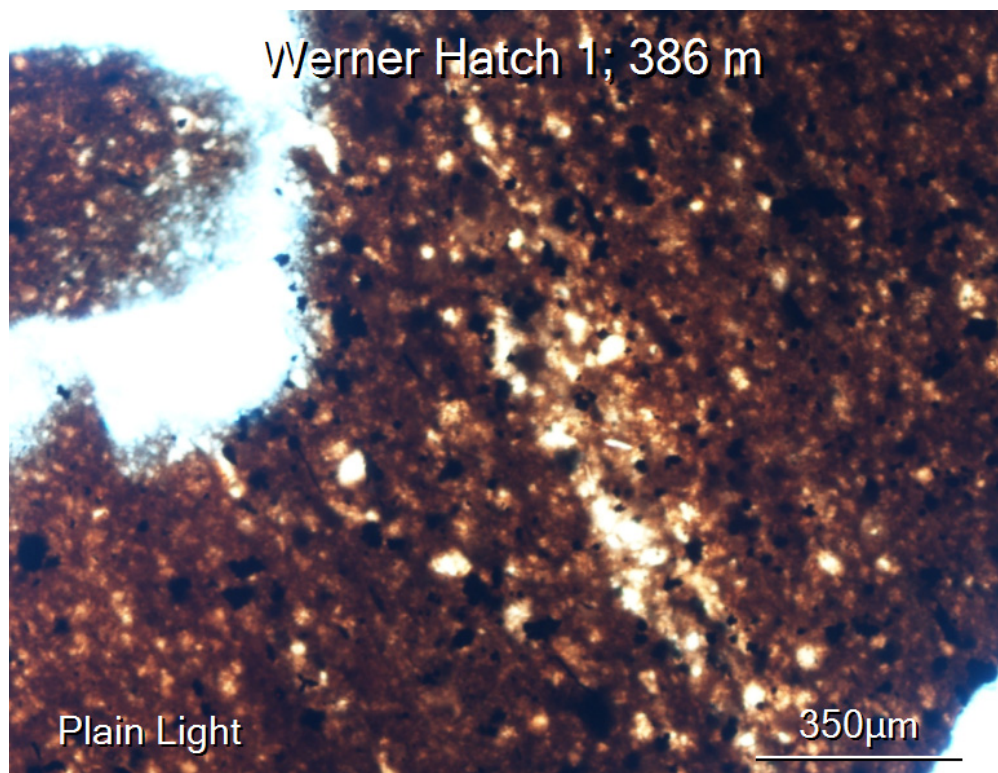


Figure 16: Photomicroscopy from Werner Hatch 1



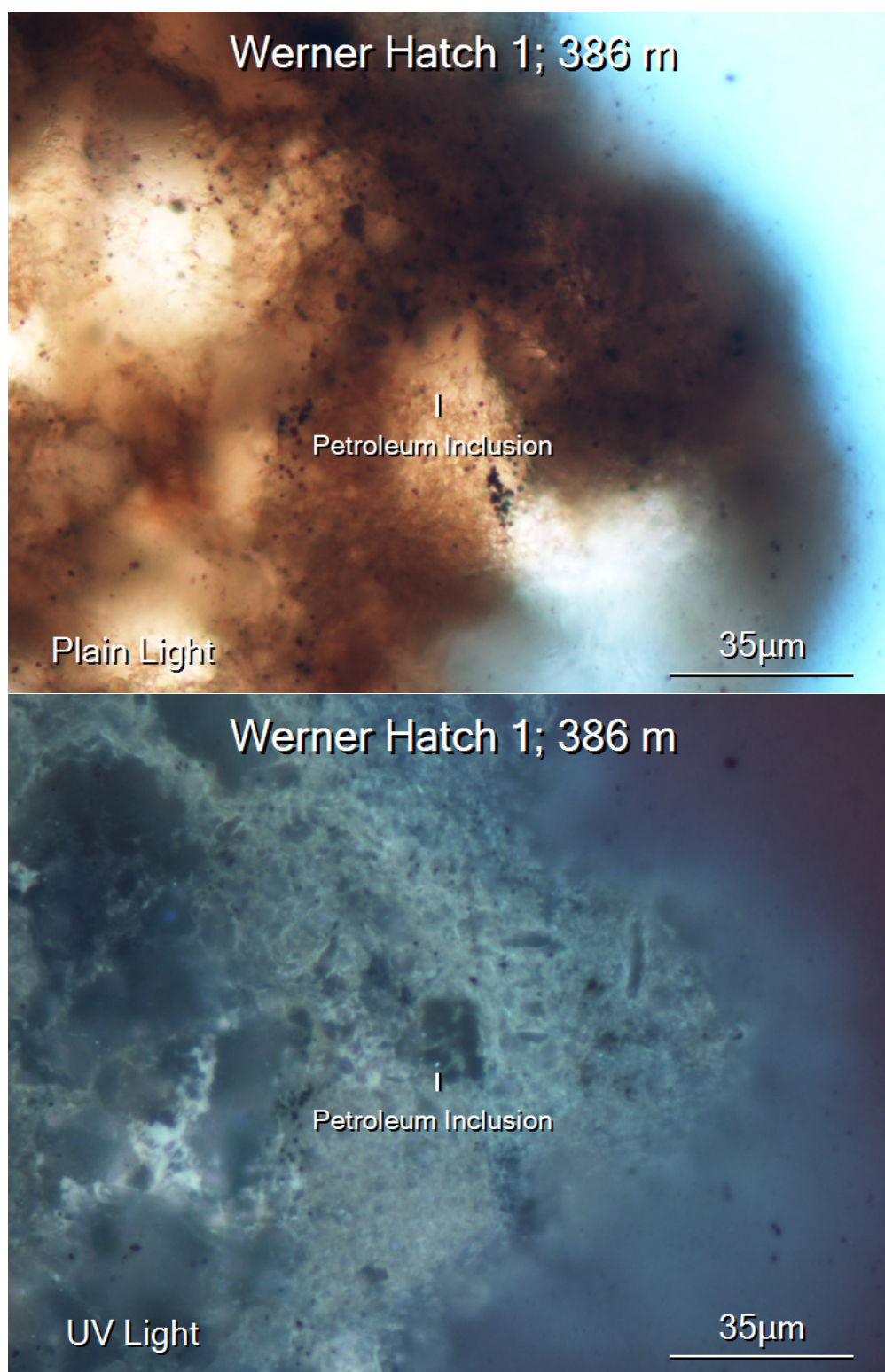


Figure 17: Photomicroscopy from Werner Hatch 1

## Appendices



## A Interpretation of Fluid Inclusion Stratigraphy (FIS) Data

### A.1 FIS Analysis

#### A.1.1 Introduction to FIS Analysis

Fluid Inclusion Stratigraphy involves the rapid, complete analysis of volatiles trapped as fluid inclusions in rock samples using quadrupole mass analyzers attached to an automated, high-vacuum sample introduction system. The technique documents the presence and relative bulk abundance of ionized volatile fragments with mass/charge ratio of  $1 \leq m/z \leq 180$  that have been released from fluid inclusions by crushing of natural samples. This includes most geologically important inorganic species as well as organic species with less than or equal to 13 carbon atoms. The resulting analysis of the petroleum fraction is comparable to the low molecular weight fraction of a whole-oil gas chromatographic - mass spectrometric (GCMS) analysis (without devolatilization of the gas fraction); hence, the major classes of hydrocarbons (e.g., aromatics, naphthenes and paraffins) are represented. Unlike GCMS, where the quadrupole is front-ended with a GC, boiling point separation is not achieved and all species are analyzed simultaneously. Hence, significant interference can occur among species with the same mass to charge ratio. However, what FIS lacks in compound specificity, it makes up for in sensitivity and speed, allowing detection of petroleum in samples that are well beyond the reach of standard GCMS methodologies.

Prior to analysis, samples of rock material are freed of significant interfering contamination by washing, picking and magnetic separation as necessary to remove drilling fluids, lost circulation materials, other solid mud additives such as gilsonite, and metallic particles from the drillstring. Cleaned samples are loaded with appropriate standards into specially designed autosamplers and are heated in a vacuum oven for a minimum of 24 hours. This is done to remove adsorbed organic and inorganic volatile material that could interfere with the analysis. The autosampling device is placed in the vacuum system and evacuated to appropriate high vacuum. Bulk fluid inclusion volatiles are afterwards instantaneously released from each sample in a sequential manner by automated mechanical crushing. Volatile organic and inorganic species are dynamically pumped through quadrupole mass analyzers where they are ionized, separated according to their mass/charge and recorded.

Fluid Inclusion Stratigraphy is unique in several ways: 1) the methodology and theoretical framework are the result of a long-standing research and development effort, 2) the cumulative experience and database of documented case histories are the most extensive in the world and 3) the technology represents the most rapid analytical capability of its kind available. The resulting dataset can provide a nearly continuous log of present and past pore fluid chemistry through the stratigraphic section penetrated by a well, and, given adequate sample coverage, the data can be mapped in two or three dimensions.

#### A.1.2 Introduction to FIS Data Interpretation

The following sections provide guidelines for interpreting Fluid Inclusion Stratigraphy (FIS) data that were developed during evaluation of a large number of wells from many geologic and structural environments over the years. This methodology was followed in preparing the annotated depth plots found at the front of this report and is adequate for most circumstances. There are two levels of interpretation to be considered:

1. Interpretation of FIS data by itself (basically describing what volatiles are present and in what relative proportion).
2. Interpretation of the significance of FIS data in a geologic context to answer a specific petroleum system question.

These guidelines concentrate on addressing the first level of interpretation, both because potential geologic scenarios are too variable to be thoroughly considered here, and because the end user is in the best position to judge the ultimate significance of these data after integrating the FIS data set with other information. When interpreting FIS data, the following statements apply:

1. FIS interpretations are generally qualitative.
2. Chemical relationships displayed in FIS data are either obvious or they are unreliable as exploration tools.
3. FIS interpretations are usually simple, but may be equivocal without supporting information.

### A.1.3 FIS Data Consists of Two Parts

There are two parts to a conventional FIS data set, and each must be evaluated in detail.

1. Stratigraphic profiles of critical species and species ratios with depth (Sections 4.1 & 4.2).
2. Individual mass spectra for each sample (Appendix C).

A mass spectrum is a graphical display of the log of the ion current (measured on the mass spectrometers' detectors) as a function of the mass-to-charge ratio ( $m/z$ ) of the detected ions (this will become clearer after reading the sections below). The amplitude of the ion current is proportional to the quantity of each type of ion, which, in turn, is proportional to the abundance of the species in the original gas mixture. Discrete peaks occur because the charged substances have discrete masses and discrete charges (usually single and positive).

There is a tendency for end users to concentrate on interpreting the first part of the data set (depth plots) and ignore the second (individual mass spectra). However, as will be shown, evaluation of individual FIS mass spectra is as important to the overall FIS interpretation as pattern-recognition of whole-oil chromatograms is to evaluating oil families. Imagine taking a single species present in a chromatogram and plotting it as a function of depth in the reservoir without ever considering its relationship to other species that are present. Certainly useful information results, but not nearly as much as could be offered by looking at the overall species distribution in the chromatogram in addition to the absolute abundance of a species or the ratio of two species as a function of depth. Similarly, both FIS depth plots and individual mass spectra are important to the final interpretation.

## A.2 FIS Mass Spectra

### A.2.1 Understanding FIS Mass Spectra

FIS data are collected on quadrupole mass spectrometers. These instruments distinguish among positively charged species using an electrodynamic field produced by application of combined RF and DC voltages to two pairs of metal rods in the filter section. A species



with a specific ratio of mass to charge ( $m/z$ ) will have a dynamically stable trajectory within the field formed by the voltages on the rods, while all other species are filtered out. By continuously varying the applied voltages, a range of charged substances can be sequentially stabilized and allowed to traverse the length of the filter assembly to the detector. FIS data currently provided consists of measured responses on  $m/z$  1-180. This mass range allows detection of all volatile inorganic species as well as organic compounds with up to 13 carbon atoms ( $C_{13}$ ). Detection is accomplished either with a Faraday cup, which reads ion currents directly from the filter without amplification, or by an electron multiplier, which amplifies the single charge of a given ion into a current.

In order for species to be detected they must be charged (ionized). This is accomplished by bombarding volatiles released from fluid inclusions with electrons that are thermionically emitted from a hot filament. Energy transference from electrons to neutral particles generally results in positively charged parent ions, while excess energy obtained by a molecule in the initial ionizing collision results in fragmentation of the parent molecule into several species. For a single parent molecule, the resulting mass spectrum is known as a fragmentation pattern. The distribution of ions from a given species can generally be predicted by considering all combinations of molecules and isotopic variants. The following example illustrates this concept.

Molecular carbon dioxide has a formula  $CO_2$  and most common molecular mass of 44. In detail, the mass of a given molecule of  $CO_2$  can be 44, 45, 46, 47, 48 or 49 because both carbon and oxygen have two significant, naturally occurring isotopes ( $^{12}C$ ,  $^{13}C$ ,  $^{16}O$ , and  $^{18}O$ ). Hence, the fragmentation pattern of  $CO_2$  would be expected to contain the singly charged species  $CO_2^+$ ,  $CO^+$ ,  $C^+$  and  $O^+$  with all possible isotopic permutations (14 possible masses). Additionally, doubly charged species can be produced. These species, although much rarer, have  $m/z$  of exactly half of their singly charged counterparts (e.g.,  $^{12}C^{16}O^{16}O^{++}$  has  $m/z$  of  $44/2 = 22$ ). Some peaks associated with doubly charged ions appear midway between two integer  $m/z$  locations (e.g.,  $^{13}C^{16}O^{16}O^{++}$  has  $m/z$  of  $45/2 = 22.5$ ). In general, instrument parameters favor the production of singly charged species. The relative frequency at which a given species will be produced and detected reflects natural isotopic abundance, ion production statistics and instrument parameters. In the above example of  $CO_2$ , the representative fragmentation pattern shown in Table V has been reported.

Table V: Partial Fragmentation Pattern for Carbon Dioxide

Mass	Species	Abundance	Mass	Species	Abundance
6	$^{12}C^{++}$	0.0005	28	$^{12}C^{16}O^+$	15
8	$^{16}O^{++}$	0.00046	29	$^{13}C^{16}O^+$	0.15
12	$^{12}C^+$	6.3	30	$^{12}C^{18}O^+$	0.029
13	$^{13}C^+$	0.063	31	$^{13}C^{18}O^+$	0.0029
16	$^{16}O^+$	13	44	$^{12}C^{16}O^{16}O^+$	100
18	$^{18}O^+$	0.0088	45	$^{13}C^{16}O^{16}O^+$	1.2
22	$^{12}C^{16}O^{16}O^{++}$	0.52	46	$^{12}C^{18}O^{16}O^+$	0.38
22.5	$^{13}C^{16}O^{16}O^{++}$	0.0047	47	$^{13}C^{18}O^{16}O^+$	0.0034
23	$^{12}C^{18}O^{16}O^{++}$	0.0012	48	$^{12}C^{18}O^{18}O^+$	0.00054
			49	$^{13}C^{18}O^{18}O^+$	0.000043

In spite of the usage in the previous paragraph, the term “parent peak” is generally given to the most intense peak of the mass spectrum of a single compound, while the term “molecular peak” is given to the singly charged ion with the same atomic mass as that of the pure compound. In the example above, both the parent and molecular peaks of  $\text{CO}_2$  occur at  $m/z = 44$ . It is frequently the case, however, that the most intense peak is not the molecular peak. For instance, many normal paraffins with three or more carbon atoms (n-propane and greater) have parent peaks at  $m/z = 43, 57$  or  $71$ .

Complex volatile mixtures have mass spectra characterized by multiple, interfering ions on a given  $m/z$ , making it difficult or impossible to find a “clean” peak indicative of a specific species. Generally, higher  $m/z$  positions display more interference, but even low  $m/z$  have these overlaps (e.g.  $\text{HD}^+$  and  $^3\text{He}^+$  both appear at  $m/z = 3$ ). This brings us back to one of the original points mentioned in the Introduction: mass spectra of multicomponent gas mixtures are qualitative in the sense that the absolute abundance of most species cannot be calculated. Nevertheless, similar compounds give similar fragmentation patterns that tend to be distinct from other classes of compounds. Because of this, the major classes of organic species (paraffins, naphthenes and aromatics) can be distinguished and their relative abundance estimated. Similarly, it is useful to consider the assemblage of anomalous peaks in a given mass spectrum, as these will often indicate the presence of compounds that are concentrated by similar subsurface processes (e.g., the water-soluble species benzene, toluene and acetic acid as the primary indicators of “proximal pay”). It is these assemblages that are most useful for distinguishing among major types of FIS mass spectra, as well as inferring the presence of a specific compound even where interfering ions are possible.

### A.2.2 Five Types of FIS Mass Spectra

FIS mass spectra can be classified into five end member types:

1. *Non-hydrocarbon FIS Mass Spectra*
2. *Gas-range Enriched FIS Mass Spectra*
3. *Liquid-range Enriched FIS Mass Spectra*
4. *Water-soluble Enriched FIS Mass Spectra*
5. *Sulfur-compound Enriched FIS Mass Spectra*

Mixtures and gradations among these ideal end members are common. In considering the fragmentation patterns of organic species, it is useful to keep in mind the general formulas for the three dominant hydrocarbon classes:

1. *Paraffins*:  $\text{C}_n\text{H}_{2n+2}$
2. *Naphthenes*:  $\text{C}_n\text{H}_{2n}$
3. *Aromatics*:  $\text{C}_n\text{H}_{2n-6}$

#### *Non-Hydrocarbon FIS Mass Spectra*

Non-hydrocarbon spectra generally show four major clusters or “humps” centered at approximately  $m/z$  15, 28, 42 and 55. The tallest three peaks in these spectra occur within the

first three clusters at  $m/z$  18, 28 and 44, and are attributable largely to water and carbon dioxide (with possible contributions from nitrogen on  $m/z$  28). Most of the other peaks in the  $m/z$  2-46 range of non-hydrocarbon spectra can be attributed to inorganic species or very minor organic contributions. Water and carbon dioxide are the two most abundant volatile species in subsurface pore fluids, hence their predominance here. FIS analysis is a bulk extraction technique, hence, many generations of fluid inclusions are potentially analyzed simultaneously. Because hydrocarbon inclusions are always present in much lower abundance than aqueous inclusions in a given rock volume, water and  $\text{CO}_2$  peaks will generally dominate all FIS mass spectra, even those displaying hydrocarbon enrichment.

The fourth cluster of peaks, centered on  $m/z$  55, represents minor amounts of hydrocarbons that are present in nearly all samples, as most hydrocarbons have a significant contribution in the  $m/z$  55-57 area. Note, however, that even the largest of these peaks is generally three orders of magnitude below the major non-hydrocarbon peaks. Also, note that  $m/z$  55 is commonly more abundant than  $m/z$  57. The  $m/z$  55 peak represents a major contribution from naphthenes, while the  $m/z$  57 peak is generally a primary paraffin peak. The relative enrichment of naphthenes over paraffins in aqueous-dominated (non-hydrocarbon) FIS spectra may reflect the relative solubility of these species in water, as the progression from least soluble to most soluble follows the general rule: paraffins < naphthenes < aromatics. It is probable that these minor species are dissolved within aqueous fluid inclusions. The solubility of even relatively insoluble  $\text{C}_4$  paraffin in water can be several hundred parts per million, well within the detection limit of the FIS system.

### *Gas-Range Enriched FIS Mass Spectra*

Gas-enriched spectra are characterized by strong responses on  $\text{C}_1$ - $\text{C}_5$  hydrocarbons with dwindling responses in the  $\text{C}_6$ - $\text{C}_8$  range, and essentially no response in the  $\text{C}_9$ + range. Drier gases may exhibit responses only in the  $\text{C}_1$ - $\text{C}_3$  range. Naturally occurring hydrocarbon gases tend to be dominated by short-chain paraffins; hence, these are the primary peaks to look for in identifying gas FIS spectra. Predominant peaks (parent and some significant subordinates with intensity of at least 10% of the parent) for low-molecular weight normal paraffins and naphthenes (cycloparaffins) are shown in Table VI.

Table VI: Partial Fragmentation Pattern for Gas-Range Hydrocarbons

Methane	Ethane	Propane	n-Butane	n-Pent	n-Hex	Cyclopent	Cyclohex
16(100%)	28	29	43	43	57	42	56
15	27	28	29	42	43	70(30%)	84(75%)
14	30(25%)	27	28	41	41	41	41
13	29	44(27%)	27	27	56	55	55
	26	43	41	28	29	39	42
		39	39	29	27	27	69
		41	42	57	42	40	27
			58(9%)	72(9%)	39	29	39
					86(15%)		

Here, molecular peaks are shown with their intensities relative to the parent peak. Note that the molecular peaks for C<sub>4</sub>-C<sub>6</sub> normal paraffins are not among the top five most intense peaks (a feature of fragmentation patterns that was mentioned previously). Considering the location of the above peaks, a gas-enriched mass spectrum should contain peak clusters at m/z 13-16, 26-30, 39-44 and 55-57. Note that this is precisely where the four peak clusters are located in the previously described non-hydrocarbon mass spectrum (where they were attributed largely to CO<sub>2</sub> and water, nitrogen and minor hydrocarbon contributions). The distinction lies in the relative proportion of these species. Gases can typically contain 90% C<sub>1</sub> and 95% C<sub>1</sub>-C<sub>3</sub>. Hence, FIS gas spectra typically have prominent C<sub>1</sub>-C<sub>3</sub> clusters. The water triad at m/z 16-18, which commonly shows a pattern of monotonic increase from 16 to 18 in non-hydrocarbon spectra can become disturbed at high gas concentrations so that masses 15 and 16 become dominant, even to the point of being more intense than mass 18. Similarly, the 26, 27, 39, 41 and 43 peaks generally display significantly higher intensities than in non-hydrocarbon spectra. The ratio of mass 57 to mass 55 (C<sub>4</sub>+ paraffins / C<sub>4</sub>+ naphthenes) may become quite high, reflecting the paraffinic nature of many gases.

#### *Liquid-Range Enriched FIS Mass Spectra*

FIS spectra that contain significant quantities of liquid-range petroleum species display repetitive peak clusters corresponding to fragments with successive carbon numbers in the C<sub>7</sub>-C<sub>13</sub> range as shown in Table VII.

Table VII: Partial Fragmentation Pattern for Liquid-Range Hydrocarbons

Carbon #	m/z Cluster	Parent (nC)	Molecular (nC)
C7	95-101	43, 57, 41	100(14%)
C8	109-115	43, 57, 41	114(7%)
C9	123-129	43, 57, 41	128(8%)
C10	137-143	43, 57, 41	142(7%)
C11	151-157	43, 57, 41	156(4%)
C12	165-171	57, 43, 71	170(8%)
C13	179-185	43, 57, 41	184(5%)

Note, again, that molecular peaks for high-molecular weight hydrocarbon species are generally only 5-15% of the parent peak. Also note that the three most intense peaks for the C<sub>7</sub>-C<sub>13</sub> paraffins are usually the same, and represent some of the most intense peaks previously identified for the C<sub>4</sub>-C<sub>6</sub> gas-range paraffins.

Only normal (straight-chain) paraffins have been considered in the above table. Typical C<sub>6</sub>-C<sub>10</sub> (gasoline) fractions contain 40% paraffins, 50% naphthenes and 10% aromatics by volume. Typical C<sub>11</sub>-C<sub>13</sub> (kerosene) fractions contain 30% paraffins, 50% naphthenes and 20% aromatics by volume. As the general formula for naphthenes suggests, molecular peaks are shifted downward by 2 m/z units (e.g., the C<sub>7</sub> naphthene molecular peak is at 98). Hence the major contribution at 43 for normal paraffins becomes 41 for naphthenes, 57 becomes 55, and so on. This is why the ratio of 57 to 55 is plotted in basic FIS data packages: to track the relative distribution of paraffinic and naphthenic compounds as well as the processes that fractionate them (e.g., dissolution in an aqueous phase; recall the solubility law for hydrocarbon species). Aromatic fragmentation patterns will be considered under the explanation of

water-soluble FIS mass spectra.

Natural liquid petroleum is a complex mixture containing hundreds of specific compounds within these classes. Thus, the qualitative nature of FIS mass spectra is reiterated. Major classes of organic compounds can be identified, distinguished and tracked semi-quantitatively, but specific compounds cannot be quantified except under special circumstances. From the foregoing discussion it becomes apparent that even though the FIS analytical procedure does not scan past the molecular peak of  $nC_{12}$ , contributions on low molecular weight species can include species well above  $C_{13}$ . The maximum carbon number contributing to the FIS mass spectrum is limited only by the volatility of the given compounds within the high vacuum system and their abundance. However, it is unlikely that  $C_{20}+$  compounds contribute significantly to FIS responses, given their volumetrically low abundance and vapor pressures.

#### *Water-Soluble Enriched FIS Mass Spectra*

FIS mass spectra containing anomalous concentrations of water-soluble volatile species are perhaps the most interesting of the main spectral types. Key indicator species are acetic acid, benzene and toluene (see Table VIII). Other common compounds include methane, ethane and carbon dioxide (fragmentation patterns previously outlined).

Table VIII: Partial Fragmentation Pattern for Water-Soluble Species

Formic A.	Acetic A.	Propionic A.	Butyric A.	Benzene	Toluene	Xylenes
29	43	28	60	78(100%)	91	91
46(61%)	45	29	73	77	92(75%)	106(65%)
45	60(60%)	74(79%)	27	52	39	105
28	15	45	41	51	65	39
17	42	73	42	50	51	51
44	29	57	43	39	63	77
			88(3%)			

Aromatics tend to have strong molecular peaks, unlike many paraffinic and naphthenic compounds. The species above are easily identified in mass spectra because major peaks occur within the valleys formed between the peak clusters of predominant paraffinic and naphthenic ions. These species (particularly aromatics) are present at some level in most FIS spectra that contain liquid-range hydrocarbons, because, as outlined above, aromatic species comprise 10-30% of most oils by volume. However, typically, aromatic peaks are 0.5-1 order of magnitude less intense than the adjacent paraffin/naphthene  $m/z$  cluster. Although there are no quantitative rules, aromatics are considered anomalous when visual aromatic peak heights becomes sub-equal to, or greater than, adjacent paraffin/naphthene peak clusters. Aromatic peak heights 1-2 orders of magnitude higher than the adjacent peak clusters are not uncommon in FIS spectra that indicate strong enrichment of water-soluble species.

Organic acids represent the most common organic species reported from formation water analyses, and of these, the mono-functional acids dominate. Acetic acid and propionic acid generally have the highest reported concentrations and abundance generally decreases with increased carbon number. As can be seen from the table above, some major peaks have potential interferences with  $CO_2$ . The most promising peaks for recognition of organic acids

are  $m/z$  60 and, perhaps, 73-74. Organic acids are considered to be present in anomalous concentration when a distinct peak occurs at  $m/z$  60. In the absence of organic acids this location generally lies in a “peak-height valley”, even on hydrocarbon-enriched FIS mass spectra. In extremely enriched samples the intensity of the 60 peak is greater than all masses in the 60-180  $m/z$  range.

Where anomalous, the assemblage of species outlined above are present in proportions much different (and greater) than their concentrations in typical petroleum. The commonality that they hold is their relatively high solubility in water compared to paraffinic and naphthenic compounds of similar molecular weight. For instance, benzene is about 100-300 times more soluble in water than n-hexane, and about 3 times more soluble than toluene. Acetic acid is completely miscible in water. Benzene concentrations of several 10's of ppm are typical of oilfield brines, while organic acid concentrations of several thousand ppm have been recognized. Hence, these species in FIS spectra are generally interpreted to be held in solution within aqueous inclusions, rather than present within a free hydrocarbon phase. The origins of these compounds are outlined in a later section, but the most interesting from an exploration standpoint involves stripping from present-day petroleum accumulations and transport via diffusion into the surrounding water-dominated pore network. Considering relative solubility rules, one would predict that the ratio of paraffins to naphthenes (e.g., inferred by a  $m/z$  ratio such as 57/55) would be low. In fact, this is generally the case; further evidence that it is relative solubility in water that is driving the distribution of these species in water-soluble enriched FIS mass spectra.

#### *Sulfur-Compound Enriched FIS Mass Spectra*

The final type of end-member FIS mass spectrum contains anomalous concentrations of sulfur compounds. The species  $H_2S$ ,  $COS$ ,  $CS_2$  and  $SO_2$  and/or native sulfur gas are key indicators, although not all may be present in a given sample (see Table IX).

Table IX: Partial Fragmentation Pattern for Sulfur Compounds

$H_2S$	$COS$	$S_2(?)$	$SO_2$	$CS_2$	$S_8$
34(100%)	60(100%)	64	64(100%)	76(100%)	64
32	32	32	48	32	256(60%)
33	28		32	44	160
				78	128
					192
					258
					96
					32

As can be seen, sulfur compounds tend to have strong molecular peaks, and enrichment is indicated if some combination of the  $m/z$  peaks 34, 60, 64 and 76 display anomalous intensities. Because these  $m/z$  positions generally occur in abundance valleys, the same qualitative rules apply as for acetic acid; namely, if a discrete peak is observed at one of these primary ion locations, the species is considered anomalous. The peak intensity need not rise to the level of the adjacent paraffin peak, although in extreme cases, it may. The 60 peak has a major interference with organic acids as outlined in the previous section. Hence the presence of  $COS$

is inferred (but not demonstrated) only in the presence of other sulfur species. The  $m/z$  32 would appear to be a good one for indicating sulfur presence; however, this ion location suffers major potential interference from atmospheric oxygen ( $O_2^+$ ).

Care must be taken when interpreting sulfur-enriched FIS spectra, because at first glance they resemble the water-soluble enriched spectra. Ideally, the distinction lies in the location of  $CS_2$  at  $m/z$  76 (as opposed to benzene at 78),  $H_2S$  at  $m/z$  34 and  $S_2^+$  and/or  $SO_2$  at  $m/z$  64.  $SO_2$  presence can be verified by the presence of a paired anomaly at 64 and 48. In practice, it is sometimes difficult to distinguish between sulfur-enrichment and water-soluble species enrichment when these species are not strongly anomalous, and combinations of the two spectra occur as well.

### A.2.3 Summary of the Five Spectral Types

The above is a relatively detailed account of the characteristics of the five major classes of FIS mass spectra. In the end, however, the best way to recognize and distinguish among spectral types is to compare them to the end-member examples presented herein and categorize them by eye. After examining a few examples of each, pattern recognition will become easy. Understanding the complexities outlined in the previous sections is important, but usually unnecessary for first-order interpretation of FIS mass spectra. To summarize:

*Non-hydrocarbon Spectra:* Characterized by four peak clusters centered on  $m/z$  15, 28, 42 and 55; the first three being dominant. Most peaks are attributable to water and carbon dioxide.

*Gas-range enriched:* Characterized by strong responses on  $C_1$ - $C_5$  ( $m/z$  12-72) and lesser intensities on higher molecular weight ion locations. Peak clusters may be more broad at  $m/z$  12-30 and 37-46. Predominance of masses 15 and 16, and high 57/55 ratios is possible.

*Liquid-range enriched:* Characterized by the presence of  $C_7$ - $C_{13}+$  species as regularly-spaced peak clusters in the  $m/z$  95-180 range, which are dominated by ions from paraffinic and naphthenic compounds. Aromatic species contribute subordinate peak clusters between the paraffin-naphthene peaks (although, typically only benzene, toluene and xylenes are resolved).

*Water-soluble enriched:* Characterized by methane, ethane, organic acids, benzene and toluene. Acetic Acid ( $m/z$  60) and aromatic peak clusters ( $m/z$  78, 91, 105) attain intensities near or greater than those of adjacent paraffin-naphthene peak clusters.

*Sulfur-compound enriched:* Characterized by the presence of  $H_2S$ ,  $COS$ ,  $CS_2$  and  $SO_2$  and/or native sulfur gas as indicated by anomalies on some combination of the  $m/z$  peaks 34, 48, 60, 64 and 76.

### A.2.4 Combinations of Spectral Types

Combined FIS spectra are common, and appear as superimposed end member types. Although combinations of all end member spectra have been noted, the most common are gas + liquids and liquids + water-solubles. Recall that FIS is a bulk technique and samples the entire fluid history of the pore system. Hence, mixed FIS spectra might be expected if the sample has experienced temporally distinct charges of petroleum (or brine) types or contained a heterogeneous (immiscible) fluid in the pore system at some time.

### A.3 Interpreting FIS Track Plots and Petrographic Data in a Geologic Context

Fluid inclusions are the only direct records of paleofluids existing in the subsurface, and as such, have the potential to record conditions accompanying geologic processes, including petroleum migration. By studying the subsurface distribution of paleofluid chemistries with FIS, one can obtain valuable and unique information on three major exploration topics:

1. Petroleum migration or paleocharge
2. Seals
3. Proximity to undrilled pay

and two major production topics:

1. Pay zone and bypassed pay delimitation
2. Reservoir compartmentalization.

The previous discussions have concentrated on identifying spectral types in FIS data. This is a necessary first interpretive step. The next task is to evaluate the significance of FIS depth trends in their own right (now knowing their spectral origins), and eventually, in light of other available information to answer specific questions, such as were enumerated above. Petrographic data from anomalous fluid inclusion zones are often critical elements of these higher order interpretations, as will be seen, which why petrographic follow-up work is conducted as a routine part of every FIS analysis (see Table of Petrographic Observations).

#### A.3.1 Significance of FIS petroleum indications

The most basic question that FIS can address is “Is there any evidence for present or past petroleum in this borehole?” Documentation of an FIS hydrocarbon anomaly generally provides a positive answer to this question, but could indicate other processes as well. Possible explanations for an FIS hydrocarbon anomaly are discussed in the following paragraphs.

##### *Migration without trapping*

A migration pathway may be indicated when FIS responses are low or moderate, when contamination and recycled inclusions can be discounted, when quoted visual petroleum inclusion abundances are “rare” or “several” (see Table of Petrographic Observations), and when no other petrographic or log evidence of current petroleum charge is identified in the zone. There are a number of factors that influence inclusion abundance and, consequently, raw FIS response strength, including geologic setting, extent of diagenesis, rock type and permeability. However, it has been demonstrated that both visual petroleum inclusion abundance and FIS strength within many porous reservoir rocks is proportional to hydrocarbon saturation or paleosaturation in a relative sense. Because migration occurs at average bulk-volume petroleum saturations below those encountered in charged reservoirs, FIS signal strength and visual inclusion abundance are generally lower along migration pathways than in charged reservoirs from the same area.



### *Current Charge*

A zone that displays strong FIS hydrocarbon indications and high visual petroleum inclusion abundance (i.e., common, abundant or extremely abundant) may reflect penetrated pay, but could also indicate paleo-charge or, in some cases, a migration pathway (e.g., where inclusion abundance is enhanced by extensive microfracturing). A provisional interpretation of current charge is strengthened if residual petroleum (especially live oil stain) is identified in thin section, and particularly if water-soluble petroleum species (so-called “proximal pay indicators”; see below) are recorded in FIS data (e.g., in the seal overlying the anomaly, in the water leg underlying the anomaly, or in low permeability zones within the reservoir section itself). Any independent indications (e.g., from electric logs or mudlog gas shows) provide further encouragement.

### *Paleo-charge*

Intervals of strong FIS response, high visual inclusion abundance (i.e., common, abundant or extremely abundant) and significant bitumen (e.g., dead oil stain or asphaltic residue) without accompanying water-soluble anomalies or independent evidence of current charge, may represent a paleo-column, but could also represent current charge or in rare cases a migration pathway. The interpretation of paleo-charge is favored if a valid DST has shown the interval to be currently wet.

### *Recycled inclusions*

Very rarely, detritus that is generated from previous sedimentary rock may contain inherited petroleum inclusions. These inclusions must be recognized, as they clearly do not provide any useful information about the current petroleum system(s). Petrographic or microthermometric criteria can often be used to argue the origin of these inclusions, for instance, the presence of petroleum inclusions along recycled quartz overgrowths, or measured homogenization temperatures that are too high to have been produced during the current burial history. Associated FIS depth trends are usually erratic and poorly compartmentalized, and inclusion abundance is typically low. Inherited inclusions may be restricted to specific geologic units that derived detritus from a particular provenance, and are not found in intercalated chemical precipitates (e.g. bedded carbonates or diagenetic cements).

### *Heavy bitumen stain*

In some instances, pore-occluding bitumen may contribute to FIS signals. Here, solid petroleum behaves as any other cement, and is capable of trapping residual hydrocarbons as bitumen-hosted fluid inclusions. These may be invisible due to the opacity of the solid petroleum host. Petroleum species may also desorb from pore-occluding bitumen during crushing, much as they do from mature kerogen (see below). Bitumen-sourced FIS responses may be inferred when strongly anomalous zones contain low visible petroleum inclusion abundance but have significant amounts of bitumen (e.g., common, abundant or extremely abundant). Abundant pore-filling bitumen in porous rock implies significant petroleum saturation at some time, so low visual petroleum inclusion abundance is unexpected (and not commonly encountered). In such cases it is possible either that the size of the inclusions are below the resolution of the light microscope ( $< 1$  micron), that grain surface conditions (e.g., wettability) did not favor trapping of inclusions, or that the section was diagenetically quiescent during and after charging (i.e., little or no cementation or microfracturing).

### *Mature Source Rock*

Mature source rock can contribute to FIS responses. Here, the signal is the combined effect of species desorbed from freshly crushed kerogen surfaces and conventional fluid inclusions that represent trapped in-situ generated petroleum. The chemistry and strength of FIS responses in source rocks tend to reflect kerogen type and maturity, at least in a general sense. Hence, mature gas-prone kerogen with limited liquids potential typically gives dry gas responses, while mature source rocks with liquid-prone or mixed kerogen types (including some coals) tend to have significant responses on both gas and liquid-range petroleum species. Furthermore, as maturation proceeds, FIS hydrocarbon responses progress from low (immature) to high (mature) to low again or dry gas (overmature). These trends are very qualitative, and FIS response in source intervals should not be used as a substitute for classical source rock analysis techniques. An in situ origin (local generation) is suggested for FIS responses if petrographic data from the anomalous zone reveals low permeability rock containing significant quantities of mature kerogen (common, abundant or extremely abundant). Liquid-prone kerogen is likely to be mature if it exhibits moderate to strong orange fluorescence. Coal-related FIS responses are often quite waxy, may be enriched in aromatics, and typically have large relative contributions from higher molecular weight species (i.e., flat spectral profiles).

### *Contamination*

Except in rare cases, contamination is not a significant issue in FIS data. Pre-analytical washing and vacuum heating procedures are sufficient to remove most surface-adsorbed organic compounds that are volatile under FIS analytical conditions, including natural fluids such as residual oils, as well as elements of the mud system, including oil based mud. Insoluble organic additives (particularly natural materials like gilsonite) pose a greater threat, as they may not be removed by standard treatment, and can give responses similar to indigenous kerogen or bitumen. Infrequently, an organic-based mud system will contribute to FIS response, and in rare instances may be dominant. This tends to occur in recently drilled, unconsolidated mud-rich sections, which are difficult to wash without complete loss of sample. Contamination has also been suspected in some diapiric or bedded salt sections, where drilling encapsulation of these species is facilitated by the easily dissolved and precipitated halite. Processed contaminants often have a distinctive (and unnatural looking) chemistry, which might include extreme light end depletion, very low aromatics (particularly benzene, which may be removed for environmental reasons) or extremely high toluene (possibly residue from soxhlet extraction). Petrographic criteria can generally be used to assess the likelihood of contamination in a given anomalous FIS zone.

### **A.3.2 Petroleum Type and Quality**

Interpreted petroleum type and quality is based predominantly on the characteristics of individual mass spectra from each depth as already discussed (sample spectra are located in Appendix C). Three factors are considered: the maximum carbon number detected, the qualitative abundance of low molecular weight alkanes relative to high molecular weight alkanes (including the general slope of the imaginary line connecting the C<sub>1</sub>-C<sub>13</sub> alkanes), and the presence or absence of species or ratios indicative of bacterial or thermal alteration (including souring processes). It is important to note that the interpreted petroleum type assumes a single, uniform petroleum inclusion population. The actual migration or charging history, on the other hand, may have involved multiple pulses with different composition (e.g., oil and

gas) and the relative abundance of these inclusions will influence the bulk spectra. Additionally, total inclusion abundance will affect the spectra insofar as higher molecular weight species represent a smaller volumetric proportion of petroleum and are also less volatile, hence decrease below instrumentation detection limits before low molecular weight species. Consequently, some samples with low oil inclusion abundance generate wet gas mass spectra, for instance. Optical inclusion abundance and characteristics should be consulted, where provided, to verify the interpreted petroleum type (see Table of Petrographic Observations). With the above limitations in mind, the following petroleum types are identified on the basis of spectral characteristics:

*Dry gas:* mostly  $C_1$  with lesser  $C_2$ - $C_3$  and no higher hydrocarbons.

*Wet gas:*  $C_1$ - $C_9$  may be present, but  $C_6+$  species are in minimal abundance. The alkane slope is extreme.

*Gas-condensate:*  $C_1$ - $C_{11}$  may be present. The alkane slope is quite steep, reflecting a very gas-enriched phase.

*Volatile oil:*  $C_1$ - $C_{13}$  present. Slight gas-range enrichment is observed and the alkane slope is moderate to steep.

*Oil:*  $C_1$ - $C_{13}$  is present. The alkane slope may be flat to moderate.

Biodegradation is suggested if sulfur compounds such as  $H_2S$ , COS,  $CS_2$ ,  $S_2$  (+/-  $SO_2$ ) and/or thiols are present in addition to petroleum species. Ratios of paraffins to naphthenes may be low as well, as bacteria typically prefer to metabolize alkanes compared to other classes of petroleum compounds. Petrographic data may provide further evidence for biodegradation in the form of low-gravity petroleum inclusions. Bacterial activity is generally restricted to maximum burial temperatures below 65-70°C; hence FIS evidence of biodegradation is most commonly observed in rocks that are currently below this temperature.

Thermal alteration of liquid petroleum species can produce spectra very similar to those generated from biodegraded hydrocarbons, because the products of two common processes, bacterial sulfate reduction (BSR) and thermochemical sulfate reduction (TSR), are essentially identical. The best distinction is made from current bottom-hole temperature data, which, if above 140°C or so may be indicative of TSR, and if below 70°C or so is more consistent with BSR. Potential interpretive problems arise in the intervening temperature range, when deeply buried sediments are unroofed or when petroleum altered at shallow depths becomes buried to greater depth. Petrographic data may help, as pyrobitumen frequently accompanies TSR, while low-gravity liquid petroleum inclusions often occur in association with bacterially altered oils. Additional temperature or thermal maturity data (including fluid inclusion homogenization temperatures) may also be useful.

The presence of significant amounts of sulfur species can indicate a sour petroleum phase, where the souring process may in some cases be a reflection of the source rock, but could also reflect BSR or TSR. A study of TSR sour gas pools in Canada suggests that evaluating the relative proportion of products and reactants can provide a measure of sour gas potential. As TSR progresses, long-chain alkanes decrease while low molecular weight petroleum species increase along with  $CO_2$ , aromatics organic acids and the various sulfur compounds enumerated above. Ironically,  $H_2S$  alone may not be as accurate an indicator of  $H_2S$  content, as it is scavenged naturally (e.g., to form pyrite in iron-rich rocks) and by the metallic internal surfaces of the analytical system.

### A.3.3 Water-soluble Anomalies and Proximal Pay Indications

Water-soluble species, particularly benzene and toluene, have been used for decades to search for geochemical halos surrounding petroleum accumulations. The limitation of conventional techniques is that fluid samples are rarely intentionally collected from wet reservoirs. However, similar water-soluble species anomalies have been found in FIS data. Compounds generally include some subset of the following: methane, ethane, CO<sub>2</sub>, acetic acid, benzene, toluene and xylenes, as well as low paraffin-to-naphthene and high aromatic-to-paraffin ratios. There are three dominant sources of this FIS volatile suite: maturation of kerogen-rich rock, thermal alteration of liquid petroleum, and diffusive stripping from a present-day charged petroleum reservoir proximal to the borehole. The latter of these three possibilities is the most important from an exploration standpoint, and is the FIS analog of the classic technique of analyzing formation fluids for benzene.

Criteria to distinguish among the three potential sources of water-soluble anomalies are often found during petrographic examination. A kerogen source may be inferred if the interval contains a substantial amount of mature kerogen, and where FIS responses include appreciable contributions from other hydrocarbon species (e.g., where water-soluble species are superimposed on an otherwise normal hydrocarbon response). Thermal alteration may be expected if pyrobitumen is present, and, particularly, if sulfur compounds are also detected in FIS data (see discussion above). These species may have resulted from thermochemical sulfate reduction at temperatures above 140°C. Extreme examples of this process are found in deep Devonian sour gas pools of the Western Canada Sedimentary Basin.

True “proximity to pay” (a.k.a., PTP) anomalies tend to occur in cuttings from shale rich lithologies, that are geometrically connected to penetrated or lateral pay. Examples include top or lateral lithologic or structural seals to a charged reservoir, and transition zones or water legs underlying petroleum. The signal is always a present-day feature and is thought to result from drilling encapsulation of penetrated pore fluids within easily sheared or thermally reconstituted lithologies. A significant amount of unpublished analytical data as well as a large body of empirical observation support this interpretation, although details of the process are still debated. Petrographic criteria are generally sufficient to interpret PTP signals, and these include absence of evidence for the other two possible origins, as well as presence of distinctively sheared, shale-rich cuttings.

PTP signals can be found along with direct FIS hydrocarbon indications in flushed reservoirs. Here, the water-soluble anomalies may be sourced from irreducible petroleum saturation with the paleo-reservoir, or may indicate an updip charge (possibly the leaked or structurally disturbed petroleum column that once resided at the well location).

PTP anomalies can be classified into two chemical subtypes: acetic acid + benzene dominant, and benzene dominant. Acetic acid is thought to be sourced from high molecular weight compounds within the petroleum phase; hence, its presence suggests the nearby accumulation is oil or gas-condensate. Benzene without accompanying acetic acid suggests a drier petroleum phase, most likely wet gas. Dry gas generally does not give a PTP response because the key indicator species are not present in the petroleum phase, hence cannot be fractionated into nearby aqueous fluid.

When PTP anomalies are identified, a possible link to a nearby reservoir should be investigated. Many scenarios are possible, including an overlying penetrated charge, lateral production in a shallower section that is not under closure at the well location, or charge in remaining updip closure in a reservoir that tested wet at the well location.

#### A.3.4 Seals

FIS seals are inferred at boundaries marking abrupt changes in FIS species strength or chemistry. The underlying assumption is that detected fluids are more or less synchronous on either side of the boundary and that some process has prevented free mixing of species across this barrier. In detail the boundary may represent a change in lithology, poroperm or a structural element. In the case of in-situ generated petroleum the boundary might represent a transition from poor to better source rock, or immature to mature source intervals. In the case of migrated petroleum the boundary might represent the extent of petroleum migration through porous rock, or the top seal to a present or past petroleum column. Basal compartment limits may represent seals or, in some cases, fluid contacts or paleocontacts (see below). In general, only the tops of FIS compartments are identified on interpreted FIS depth plots. If fluids were not synchronous on either side of the compartment boundary (e.g. a post-migration unconformity) then the seal interpretation would be in error. Seals may be selective or chromatographic, in which case low molecular weight species may migrate across the boundary, while higher molecular weight species do not.

#### A.3.5 Microseepage

FIS microseeps are analogous to gas chimneys seen in seismic data, and surface manifestations of deeper charge identified in surface geochemical surveys. They are interpreted to result from near-vertical migration of light hydrocarbons followed by bacterial alteration in the shallow subsurface at temperature-depth conditions permissible for bacterial activity. Most bacteria are restricted to temperatures below 65-70°C; hence, anomalies may be observed in the upper 1-3 km of rock column, depending on the prevailing geothermal gradient. Key indicator species include light hydrocarbons, CO<sub>2</sub>, possibly organic acids and aromatic compounds, and sulfurous volatiles, including H<sub>2</sub>S, COS, CS<sub>2</sub>, S<sub>2</sub> (+/- SO<sub>2</sub>) and in some cases thiols. H<sub>2</sub>S is often sequestered within pyrite in iron-rich siliciclastics, hence is less common in shale-bearing lithologies. Inclusion formation in such low temperature environments may be aided by precipitation of bacterial carbonate. FIS microseeps are geometrically distinct, often beginning at the surface and abruptly disappearing at the appropriate temperature-controlled depth.

The presence of an FIS microseep appears to be a good indicator of deeper charge in the immediate vicinity, although weak seeps may represent regional signals within shallow aquifers. Data suggest that these anomalies overlie 75-80% of productive reservoirs, while only 10% of non-productive areas display similar signals. Hence, the presence of a strong seep within a dry hole might indicate deeper or nearby lateral charge in the area.

#### A.3.6 Fluid Contacts

The basal boundary (abrupt or transitional) of any strong FIS compartment is a candidate for a present or past fluid contact, although the interpretation is often equivocal. The most compelling evidence for a present day contact occurs where hydrocarbon-dominant FIS signals (the petroleum leg) give way to water-soluble dominant signals (PTP in the water leg) and where visual petroleum inclusion abundance displays a parallel decrease. When inclusion abundance is high in the petroleum zone but PTP signals are not present in the water leg, it is possible that a paleo-charge is recorded. If the base of the anomaly corresponds to the base of the reservoir, or an abrupt decrease in reservoir quality, then the actual fluid contact (or

paleo-contact) may reside further down dip.

## A.4 Individual Track Plots

### A.4.1 Explanation and Significance of Individual Track Plots

The following is a synopsis of the significance of the different patterns of mass abundances and abundance ratios shown in Tracks 1-25. Note that not all species are quantified using their parent or molecular peaks (e.g., methane at  $m/z = 15$ ) in order to minimize interfering contributions from other species.

### A.4.2 Ratios vs. Absolute Abundance

Both ratios of key ionized compounds as well as absolute abundances of key compounds (relative to a natural oil inclusion standard) are used in interpretation. Absolute abundances of species can be influenced by the efficiency of inclusion formation, the size distribution of the inclusions, the saturation and residence time of the fluid within the pore system and the relative proportion of fluid of a given composition that moved through that stratigraphic compartment. Chemical ratios, on the other hand, are not as susceptible to lithologic/diagenetic controls on inclusion formation/distribution, hence, may be better suited for displaying chemical compartments in some cases. They are also useful for enhancing some of the subtle trends within the data, and for characterizing chemical variability among petroleum inclusion compartments, which could be related to source, timing, or migration process. Ratio plots are not completely independent of inclusion abundance, as the intensity of mass spectrometer responses is somewhat non-linear with respect to ion concentration. Both types of plots should be considered during interpretation.

**Track 1:** Total Response - This represents the sum of the positive responses on all measured masses from  $1 \leq m/z \leq 180$ . These data are potentially useful for some data normalization schemes, or for estimating the relative percentage of a given compound in the analyzed sample. Note that responses are generally dominated by water and carbon dioxide, and that absolute quantification is not possible because water cannot be quantitatively analyzed with this system. The polar nature of water causes it to adhere to metallic surfaces inside the instrument resulting in false readings by the detector. However, two characteristics of the total response are noteworthy. First, total responses are often orders of magnitude greater for samples yielding proximity spectra than for other samples originating outside the hydrocarbon zone, even though the lithologies are usually clay rich, hence low in natural inclusion abundance. This is one line of evidence that leads us to hypothesize that proximity samples are dominated by drilling induced inclusions which trap some of the present day formation fluid. Secondly, inferred petroleum migration compartments are often characterized by high total responses. This suggests that both organic and inorganic inclusions are anomalously represented within these compartments. The significance of this correlation is not fully understood, but may document a fracture forming process occurring during focused movement of basinal fluids, including petroleum. If so, it may eventually provide additional information about the nature and mechanisms of secondary petroleum migration.

**Track 2:**  $m/z = 44$  Dominant peak for carbon dioxide ( $\text{CO}_2^+$ ), with possible minor contribution from  $\text{C}_3^+$  hydrocarbon fragments and acetic acid. Anomalous values have been noted associated with pan-evaporative dolomitization of limestones in China and Oman.  $\text{CO}_2$  response is often

high in proximity samples which show elevated levels of acetic acid. CO<sub>2</sub> is generally present in anomalous concentrations in FIS microseeps, where it is a product of bacterial alteration of seeping light hydrocarbons.

**Track 3:**  $m/z = 34$  - Dominant peak for hydrogen sulfide (H<sub>2</sub>S<sup>+</sup>). Anomalous values associated with petroleum may indicate sour oil or gas. H<sub>2</sub>S is also noted at times in association with shallow dry gas of probable biogenic origin (including FIS microseeps) and with some proximity zones. H<sub>2</sub>S is probably not quantitatively analyzed due to rapid scavenging by metallic surfaces of the analytical system.

**Track 4:**  $34/(34+15)$  - H<sub>2</sub>S/(H<sub>2</sub>S+methane). Not frequently used, but ratio tends to be elevated in sour gas zones.

**Track 5:**  $4/(4+2)$  - Helium fraction  ${}^4\text{He}^+/({}^4\text{He}^+ + \text{H}_2^+)$ ; ratioed to mass  $m/z = 2$  to indicate the presence of anomalous He. Helium anomalies have been found in association with unconformities, thrust faults which sole in crystalline rocks, arkosic detritus sourced from such crystalline rocks (e.g., granite wash), gas sourced from old, radioactive shales and mafic hypabyssal volcanic rocks. An abrupt change in helium abundance has been documented within Precambrian rocks worldwide. It is possible that this reflects a fundamental evolutionary step in the Precambrian atmosphere.

**Track 6:** Air Confidence - This represents the results of an algorithm which performs five tests for the presence of the air components nitrogen, oxygen, and argon. The plot is scaled in integer values from zero to five, corresponding to zero to five positive tests. Values in the 4-5 range indicate a high confidence for air. Some anomalies may represent small leaks in the vacuum system. Natural air inclusions have been recognized in vadose cements below paleoexposure surfaces, as well as in some aeolian sands and evaporites.

**Track 7:**  $30/(30+15)$  - ethane/(ethane+methane). Except for very dry gas, petroleum migration zones generally show elevated ratios of ethane to methane, provided that the petroleum is transported as a separate phase. Petroleum transported as a dissolved solute species in aqueous solution (e.g., in the case of proximity) may have low ratios of ethane to methane, due to the relatively higher solubility of methane in solution.

**Track 8:**  $m/z = 15$  - CH<sub>3</sub><sup>+</sup>; mostly derived from methane, with minor contributions from all other paraffins and NH<sub>2</sub><sup>+</sup>, if present. Used as a relatively clean peak for methane; response is nearly as great as for the methane molecular peak. Anomalies are associated with oil and gas migration as well as water zones carrying significant dissolved gas. Distinction between dry gas and oil is accomplished by comparing responses on higher molecular weight fragments (e.g.,  $m/z = 97$ ). Transport in aqueous solution is suggested by co-occurrence of other water-soluble hydrocarbons as well as high ratios of water soluble to water insoluble species (e.g., 60/57, 55/57, 77/71). Methane dominated dry gas of possible biogenic origin is often documented in offshore wells at depths above 1200 m. These zones also often indicate anomalous sulfur species, which might document the activity of sulfate-reducing bacteria. In rapidly buried, relatively young sections, (e.g., offshore Trinidad and Gulf Coast) biogenic gas inclusions may be detected to much greater depths. These are FIS microseeps and are thought to sourced from leakage of light petroleum from depth.

**Track 9:**  $m/z = 30$  - Ethane molecular peak (C<sub>2</sub>H<sub>6</sub><sup>+</sup>). Use similar to that of methane ( $m/z = 15$ ).

**Track 10:**  $m/z = 60$  - Acetic acid ( $\text{CH}_3\text{COOH}$ ), with possible contribution from COS in some environments. Acetic acid anomalies may be sourced from source rock maturation, thermal alteration of liquid petroleum or diffusive stripping from oil or gas-condensate accumulations (the latter are known as proximity-to-pay indications or PTP). It is thought that PTP represent samples of present day formation fluids, which are entrapped during drilling, probably through thermal and mechanical processes acting on clay-bearing lithologies in the neighborhood of the drill bit. Our understanding of the sources and sinks of organic acids and water-soluble aromatics, particularly benzene, suggest that the signal must be actively fed; hence, it is unlikely that we would see these signals preserved for geologic time in paleo-reservoirs, or along migration paths, although this has not been fully demonstrated. The strength of the signal is dependent on so many variables, including drilling conditions, lithology, formation fluid and oil chemistry, temperature, hydrodynamics, etc., that it is doubtful that quantitative assessment of distance from accumulation is possible. As with most FIS interpretations, documenting proximity is deemed significant, while its absence is not necessarily so, unless a particular area is well calibrated. Thermal processes within the reservoir in which liquid-range petroleum is broken down to lower molecular weight petroleum with one byproduct being organic acid probably source acetic acid, in the context described above. As such, the presence of organic acid anomalies with benzene and or toluene anomalies suggests that the accumulation has some liquid-range component, although a few barrels of condensate per MMCF of gas appears to be enough to provide a signal, at least in relatively low salinity formation fluids which are very close to pay zones. As mentioned above, other sources of organic acids are possible, including maturation of source rocks (particularly coals), severe thermal degradation of oil (particularly during thermochemical sulfate reduction) and stripping from residual oil in high Sw zones or recently flushed reservoirs; hence, the nearby reservoired hydrocarbons may very well be subeconomic. COS and acetic acid can be expected in some of the same environments, so the distinction between the two is not always possible. However, COS tends to be less water soluble, and has a higher affinity for the petroleum phase than acetic acid.

**Track 11:**  $m/z = 78$  - Benzene ( $\text{C}_6\text{H}_6^+$ ). High values are associated with samples containing inclusions with liquid-range petroleum, as well as samples displaying “proximity” signals. A distinction can be made between these two by looking at individual spectra, or by comparing the response on the relatively insoluble paraffins (e.g.,  $m/z = 57$  or  $71$ ). Note however, that some samples may indicate both oil inclusions and proximity to pay; and it is here that individual mass spectra must be studied. Such mixed spectra are indicative of some pay zones (particularly those with significant Sw, as well as zones through which petroleum has migrated, and are now water wet, but are presently in communication with the previously migrated petroleum. Benzene rich proximity signals without associated acetic acid may indicate a nearby wet gas accumulation.

**Track 12:**  $m/z = 91$  - Toluene ( $\text{C}_7\text{H}_7^+$ ). This ion is interpreted in much the same way as benzene ( $m/z = 78$ ). However, toluene has lower water solubility, so tends to be less anomalous or even absent from some proximity zones.

**Track 13:**  $60/(60+57)$  - Acetic acid/(acetic acid + paraffins). This ratio tends to deflect to higher values in water bearing zones and shallow microseeps and to lower values in petroleum inclusion zones. Very high values are associated with proximity zones. Acetic acid has tremendous water solubility, while paraffins are relatively insoluble in water.



- Track 14:**  $78/(78+91)$  - benzene/(benzene+toluene). This ratio is of limited utility in many cases, as these species are often not abundant enough to provide a coherent depth plot. In some cases, oil inclusion zones tend to deflect toward lower values, while proximity zones tend to deflect toward higher values. This is because oils typically have benzene to toluene ratios of about 0.5, while benzene has about 3 times higher solubility than toluene in water. Water washed oils will have lower ratios as will oils that have lost lighter ends through a semi-permeable seal.
- Track 15:**  $m/z = 57$  - Paraffin fragment ( $C_4H_9^+$ ). Anomalous values are associated with zones of oil and wet gas inclusions. Paraffins have lower solubility than other hydrocarbon classes, hence ratioing to these can define migration and reservoir processes (see next entries).
- Track 16:**  $57/(57+15)$  - Paraffins/(paraffins+methane). This ratio plot displays the proportion of  $C_4$  and greater paraffins relative to methane. The ratio will generally deflect to higher values in oil inclusion zones and toward lower values in dry gas zones. The ratio will also generally decrease within proximity zones due to the high solubility of methane relative to  $C_4^+$  paraffins in aqueous solution.
- Track 17:**  $m/z = 97$  - Alkylated naphthenes fragment ( $C_7H_{13}^+$ ); basically naphthenes with methyl chains. This species tends to be anomalously high in petroleum inclusion zones which contain an appreciable liquid component (e.g., oils and condensates).
- Track 18:**  $57/(57+55)$  - Paraffins/(paraffins+naphthenes). This ratio can be used for several purposes. Very low values are indicative of biodegraded oil, because bacteria prefer the paraffinic fraction. Low values are also documented in some proximity zones, due to the limited solubility of paraffins relative to naphthenes in aqueous solutions. Very high values are typical of dry gas zones as gases tend to be enriched in paraffins, although this trend must be used with caution. It is better to observe the relative change in this ratio with depth: If it decreases from baseline through a petroleum inclusion zone, liquid petroleum is more likely; if it increases, a lighter fraction might be expected. Again, these are generalizations which must be used cautiously. It is always best to follow up FIS work with thin section petrography to further investigate the characteristics of the entrapped petroleum phase. This ratio may also be used to identify transition zones from low to high Sw, and low-contrast pay zones. In general, we find that residual oil within water-rich zones under pay intervals tends to have higher ratios, probably due to the washing of more soluble naphthenes from the petroleum prior to entrapment. However, the water leg itself may have low ratios due to preferential concentration of naphthenes in the water phase.
- Track 19:**  $97/(97+91)$  - Alkylated naphthenes/(alkylated naphthenes + toluene). This ratio tends to deflect toward higher values in zones containing liquid petroleum inclusions and toward lower values in proximity zones. Alkylated naphthenes are relatively water insoluble as compared to toluene.
- Track 20:**  $77/(77+71)$  -  $C_6^+$  aromatics/( $C_5^+$  paraffins+ $C_6^+$  aromatics). This ratio tends to deflect toward higher values in zones of proximity and toward lower values in zones containing liquid petroleum inclusions. Both trends reflect the relative solubility of aromatics (high) and paraffins (low).
- Track 21:**  $m/z = 64$  -  $C_5^+$ ,  $S_2$  and  $SO_2$ . Volatilized native sulfur has been noted in conjunction with sour gas pools in Canada, and, along with other chemical indicators may indicate sour gas risk. In some cases, mass 64 appears to be concentrated in water legs to these pools, or

wet reservoir sections that are plumbed to a deeper source of these species. It has also been found in conjunction with FIS microseeps.

**Track 22:**  $m/z = 76$  -  $\text{CS}_2$  and  $\text{C}_6^+$  hydrocarbons.  $\text{CS}_2$  has been found in conjunction with biodegraded hydrocarbons, in association with FIS microseeps and as a byproduct of thermochemical sulfate reduction.

**Track 23:**  $97/(15+97)*1000$  - Alkylated naphthene/(alkylated naphthene + methane) - This track can be used to illustrate the relative proportions of low and high molecular weight species. The track deflects to higher values in oily or light end depleted zones and to lower values in gassy zones.

**Track 24:**  $\text{C}_5 - \text{C}_{13}$  Presence - This algorithm records the highest molecular weight range hydrocarbon group present in each individual spectra, and provides a quick visual record of zones containing the corresponding petroleum compounds. For example, if the  $\text{C}_5$  group is the highest molecular weight range hydrocarbon group present in a given sample, a ranking of 5 is assigned; if  $\text{C}_6$  is the highest carbon number represented, then a ranking of 6 is assigned, and so on until a ranking of 13 is assigned if the presence of species in the  $\text{C}_{13}$  range is detected. Mathematically, the algorithm tests for the presence of a group (i.e., carbon number) by scanning the spectra for a coherent signal comprised of at least two out of three of the major peaks associated with the particular molecular weight range.

**Track 25:**  $\text{C}_{6-13}/\text{C}_{1-5}$  - A semi-quantitative parameter relating the abundance of liquid-range hydrocarbons to gas-range hydrocarbons. The ratio can be used in a qualitative sense to construct “psuedo GOR’s”.

#### A.4.3 Mass Assignments

In addition to the Tracks 1-25 described above, mass spectra over the range  $1 \leq m/z \leq 180$  are presented for each individual sample in Appendix C. The following descriptions contain additional information about species assignments for individual masses:

- $m/z = 2$  - Hydrogen ( $\text{H}_2^+$ ); largely from  $\text{H}_2\text{O}$ , which makes up most of the evolved fluid in almost all samples.
- $m/z = 3$  - Deuterated hydrogen and helium-3 ( $\text{HD}$  and  $^3\text{He}^+$ ).
- $m/z = 12$  - Carbon ( $\text{C}^+$ ).
- $m/z = 14$  - Nitrogen ( $\text{N}^+$ ) and  $\text{CH}_2^+$ ; Nitrogen in conjunction with argon and oxygen anomalies suggests air. If not an analytical artifact (episodic burps of atmosphere leak into the analytical chamber), the presence of air may indicate a vadose zone below a subaerial exposure, or the presence of aeolean sand. If response on mass  $m/z = 14$  exceeds that on masses  $m/z = 13$  and  $m/z = 15$  then nitrogen is likely present.  $\text{CH}_2^+$  will generally be accompanied by relatively larger responses on  $m/z = 15$  ( $\text{CH}_3^+$ ), and  $m/z = 16$  ( $\text{CH}_4^+$ ) (due to it’s fragmentation origin from  $\text{CH}_4$ , for instance). The most convincing distinction between analytical artifact and paleo-air occurs when several closely spaced samples have air anomalies, or when several replicate analyses of the same sample give the same result.
- $m/z = 16$  - Molecular peak for methane ( $\text{CH}_4^+$ ), but major interference by  $\text{O}^+$  fragment of water.

- $m/z = 17$  - Dominated by  $\text{OH}^+$  fragment from water
- $m/z = 18$  - Dominated by water parent peak ( $\text{H}_2\text{O}^+$ )
- $m/z = 22$  - Doubly charged carbon dioxide ( $\text{CO}_2^{2+}$ ); minor contribution from neon ( $^{22}\text{Ne}^+$ )
- $m/z = 28$  - Dominated by diatomic nitrogen ( $\text{N}_2^+$ ) and  $\text{CO}^+$  fragment from carbon dioxide. Minor  $\text{C}_2^+$  hydrocarbon contribution
- $m/z = 32$  - Oxygen ( $\text{O}^+$ ) and sulfur ( $\text{S}^+$ ). If  $m/z = 32$  is larger than  $m/z = 31$  and  $m/z = 33$ , oxygen is likely. If sulfur is present other likely peaks, such as  $m/z = 34$  ( $\text{H}_2\text{S}$ ),  $m/z = 48$  ( $\text{SO}^+$ ) and  $m/z = 64$  ( $\text{S}_2^+$ ,  $\text{SO}_2^+$ ) should be checked. Oxygen can be a possible paleoexposure indicator when used in conjunction with other peaks (see discussion on Air Confidence, and Nitrogen).
- $m/z = 40$  - Argon ( $\text{Ar}^+$ ) with possible significant interference by  $\text{C}_3^+$  hydrocarbon fragments. High value of  $m/z = 40$  relative to adjacent  $m/z = 39$  and  $m/z = 41$  peaks suggests argon.
- $m/z = 48$  - Sulfate fragment ( $\text{SO}^+$ ); also,  $\text{C}_4^+$
- $m/z = 55$  - Naphthene fragment ( $\text{C}_4\text{H}_7^+$ ). High values are found in petroleum inclusion bearing intervals. Naphthenes have intermediate solubility between aromatics and paraffins. This  $m/z$  is usually ratioed to  $m/z = 57$  (see below).
- $m/z = 71$  - Paraffin fragment ( $\text{C}_5\text{H}_{11}^+$ ). Same use as  $m/z = 57$ .
- $m/z = 77$  - Aromatic fragment ( $\text{C}_6\text{H}_5^+$ ). Same general use as for benzene and toluene.
- $m/z = 85$  - Paraffin fragment ( $\text{C}_6\text{H}_{13}^+$ ). Same use as  $m/z = 57$ .
- $95 \leq m/z \leq 103$  - peaks centered within this range are mostly  $\text{C}_7 - \text{C}_8$  fragments
- $110 \leq m/z \leq 115$  - peaks centered within this range are mostly  $\text{C}_8 - \text{C}_9$  fragments
- $122 \leq m/z \leq 126$  - peaks centered within this range are mostly  $\text{C}_9 - \text{C}_{10}$  fragments
- $134 \leq m/z \leq 138$  - peaks centered within this range are mostly  $\text{C}_{10} - \text{C}_{11}$  fragments
- $148 \leq m/z \leq 152$  - peaks centered within this range are mostly  $\text{C}_{11} - \text{C}_{12}$  fragments
- $160 \leq m/z \leq 164$  - peaks centered within this range are mostly  $\text{C}_{12} - \text{C}_{13}$  fragments
- $175 \leq m/z \leq 180$  - peaks centered within this range are mostly  $\text{C}_{13} - \text{C}_{14}$  fragments



## B Reference Spectra

In order to insure consistent and high-quality results during routine Fluid Inclusion Stratigraphic Analysis and the intercomparability of wells analyzed weeks, months or even years apart, a number of machine-dependent parameters are monitored on a daily basis through the analysis of internal analytical standards. Information recorded during these analyses are used to evaluate the performance of individual components of the stratigraphic analyzers. Additionally, this information permits characterization of any systematic fluxuations that may have affected species sensitivity during the course of an FIS Analysis and are, in fact, used quantify these effects during post-analytical data reduction. The natural materials used as internal standards are described briefly below.

### B.1 Oil Inclusion Reference Standards

Oil inclusion reference materials (petroleum inclusion-bearing siliceous carbonate rock fragments from the Kindblade Fm., Lawton, Oklahoma), are analyzed 11 times during each analytical run. The results are given in Figure 18. Ideally, spectra should show a whole-oil like signature with good representation of ionized fragments out to at least  $m/z \approx 150$ . Daily variation occurs due to inhomogenities in inclusion abundance and distribution within individual samples of this natural rock, as well as from minor instrumental fluctuations.

### B.2 Frac Sand Hydrocarbon Background Standards

Clean quartz sand, devoid of hydrocarbons, is analyzed 22 times during each analytical run. The results are given in Figures 19 and 20. Ideally, spectra should show no structured responses on  $m/z > 60$ .

### B.3 Cooked Frac Sand Hydrocarbon Background Standards

Clean quartz sand which has been heated to 1000°C to remove a large percentage of the fluid inclusion population is analyzed 11 times during each analytical run. The results are given in Figure 21. Ideally, these spectra should show approximately an order of magnitude less total response than those from the preceeding “Frac Sand Standard”, as well as an increase in air components (e.g., nitrogen at  $m/z = 28$ ; oxygen at  $m/z = 32$ ; argon at  $m/z = 40$ ) resulting from entrapment of air into evacuated cavities during the heating treatment. These spectra should also show little to no structured response for  $m/z > 60$ .

### B.4 Kindblade Trackplots

Selected peaks from oil inclusion inclusion reference standards used to monitor internal standardization and normalization procedures.

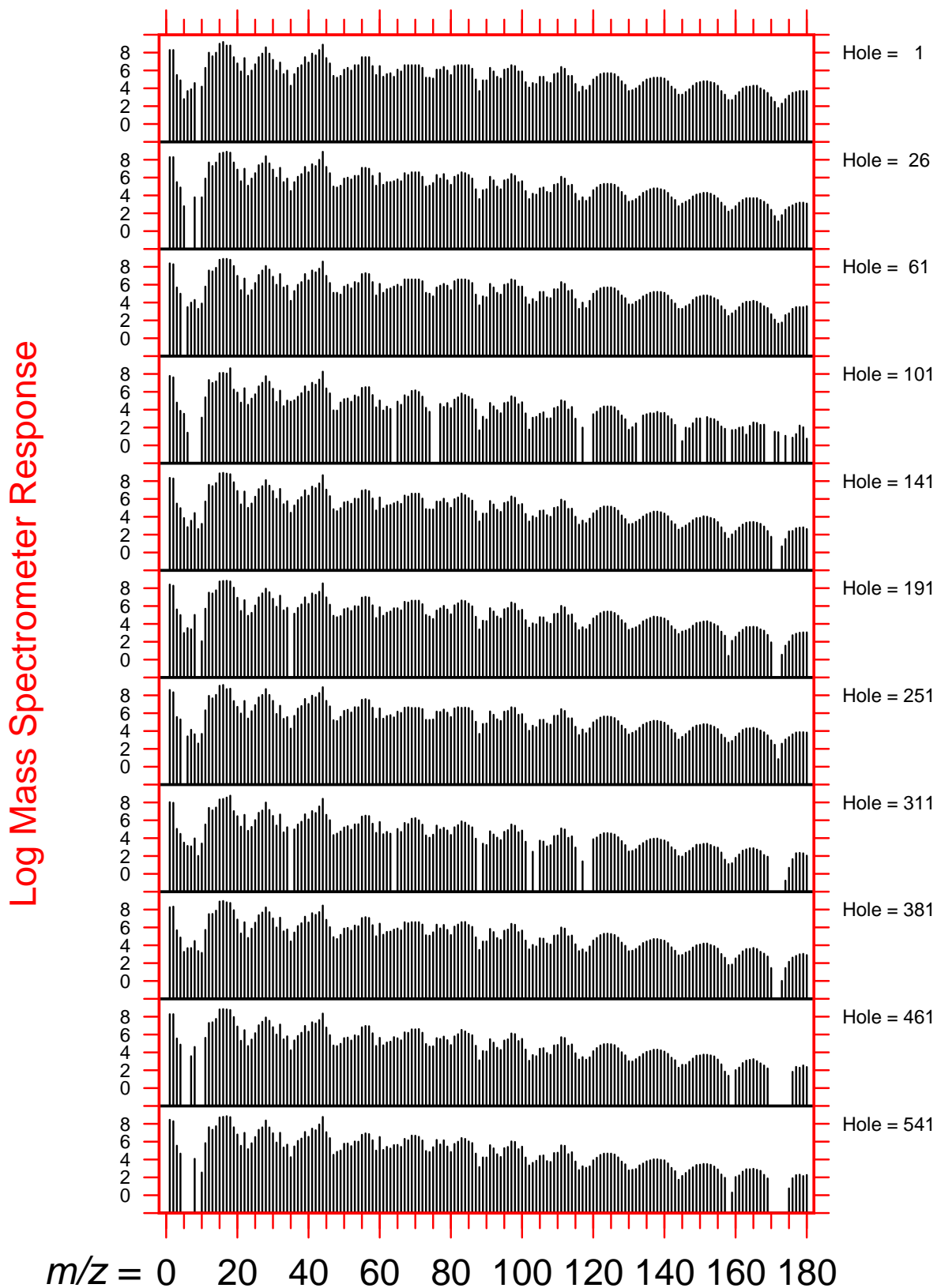


Figure 18: Oil Spectra

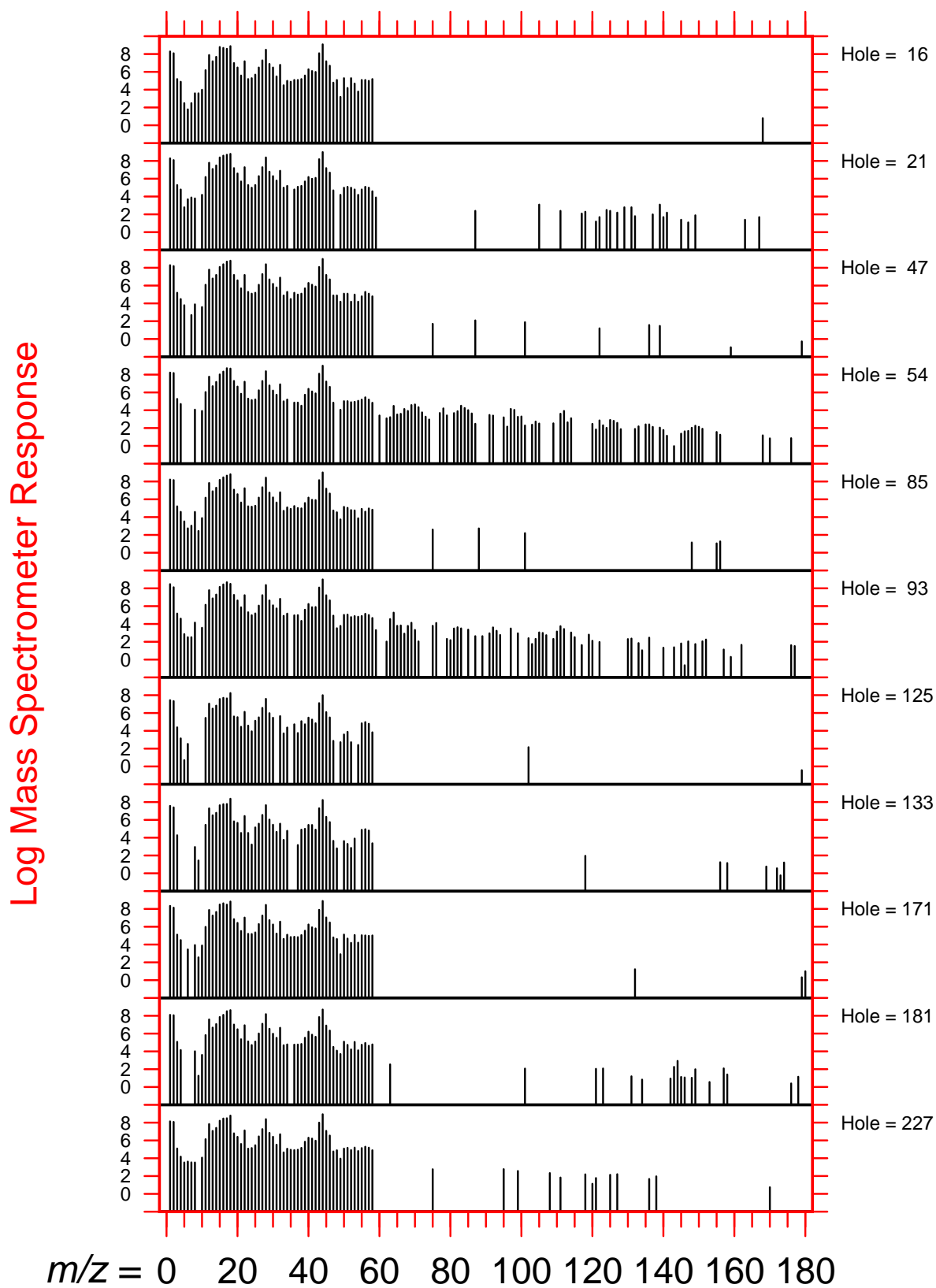


Figure 19: Frac Sand Spectra

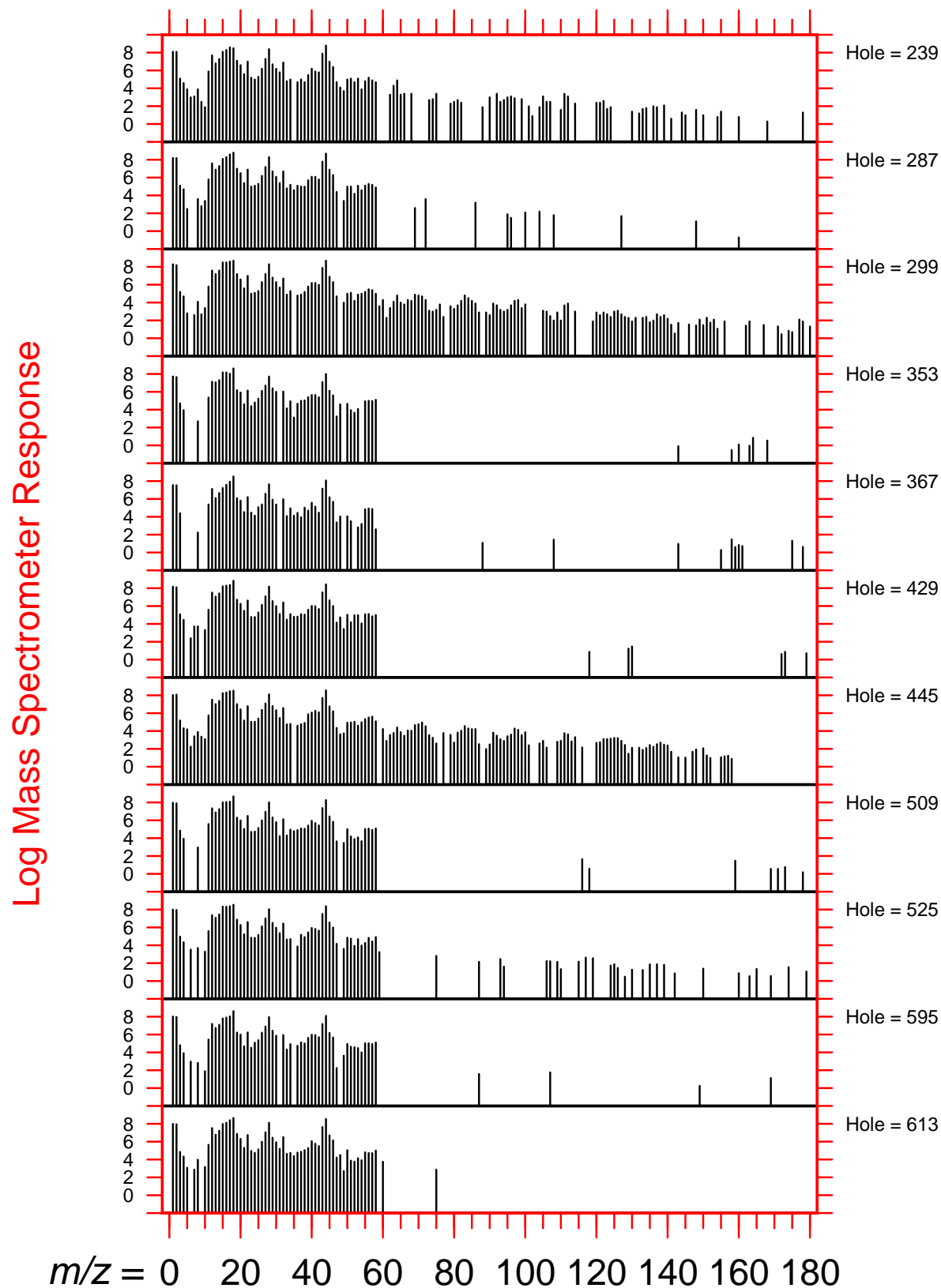


Figure 20: Frac Sand Spectra



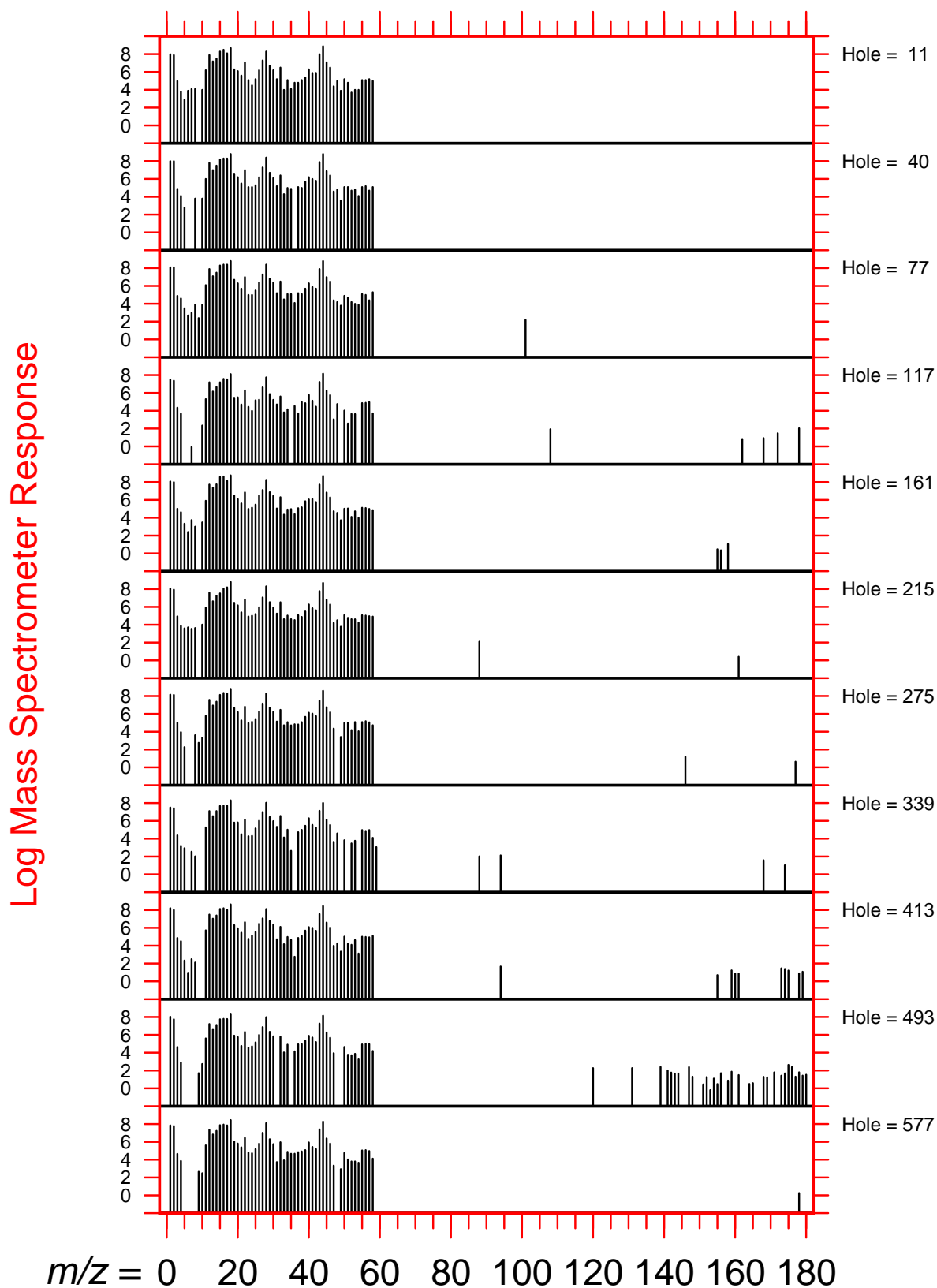


Figure 21: Cooked Frac Sand Spectra

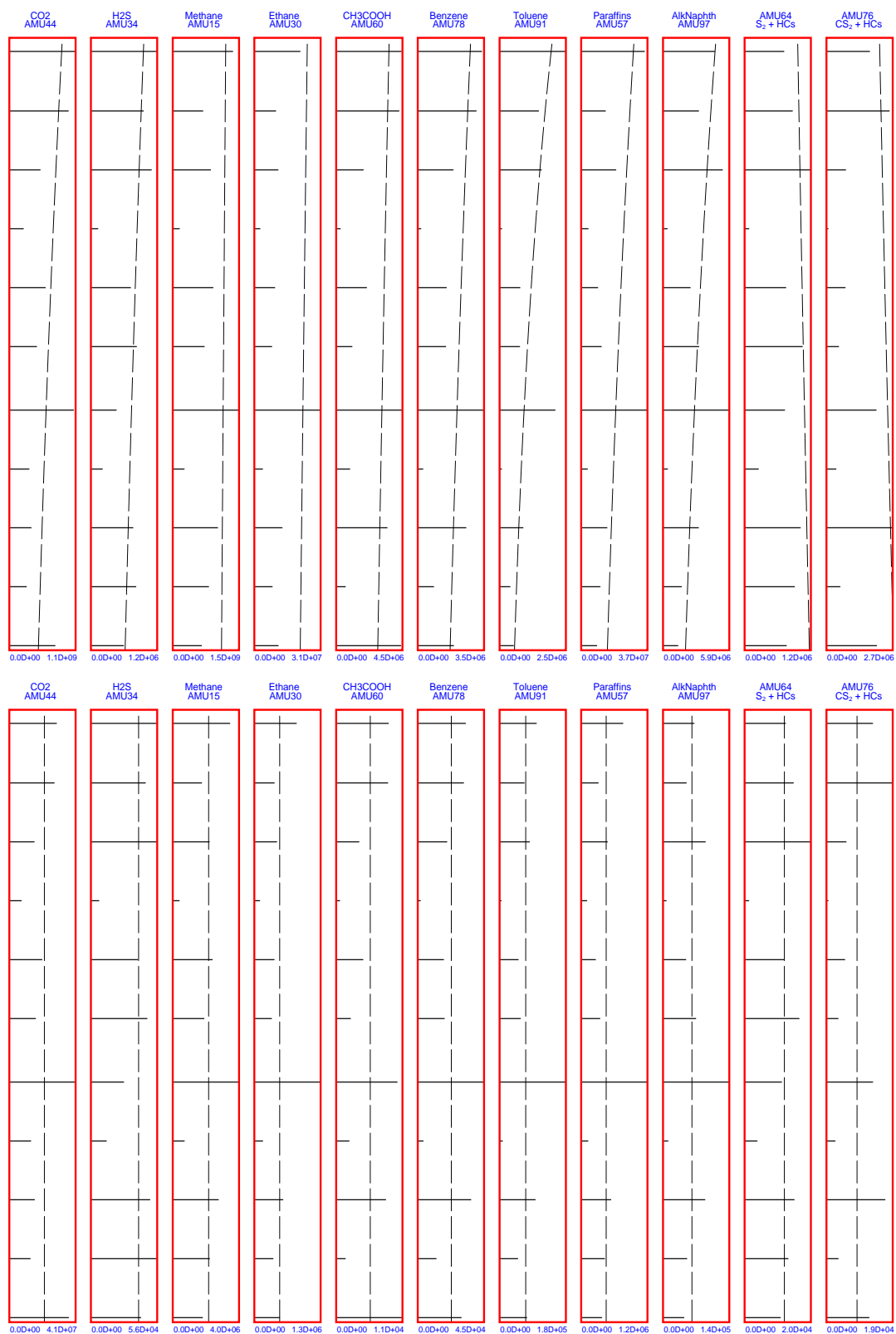


Figure 22: Kindblade Oil Standards Before (top) and After (bottom) Correction

## C Individual Spectra

Individual spectra for each sample from Werner Hatch 1 are shown on the following pages. Each spectrum is indexed according to depth and indicates the log of the millivolt response for atomic mass units (AMU,  $m/z$ ) from  $2 \leq m/z \leq 180$ .

