Release of four fluid inclusion stratigraphy (FIS) reports in the Dan River basin, North Carolina, “A stratigraphic reconstruction of bulk volatile chemistry from fluid inclusions in core holes SO-C-01-81, SO-C-02-81, SO-C-01-15 and SO-C-01A-15, and RC-C-01-81,” by Fluid Inclusion Technologies, Inc. dated August 4, 2016 for the North Carolina Geological Survey

By

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Release of four fluid inclusion stratigraphy (FIS) reports in the Triassic Dan River basin, Stokes and Rockingham counties, North Carolina, "A stratigraphic reconstruction of bulk volatile chemistry from fluid inclusions in core holes SO-C-01-81, SO-C-02-81, SO-C-01-15 and SO-C-01A-15, and RC-C-01-81," by Fluid Inclusion Technologies, Inc. dated August 4, 2016 for the North Carolina Geological Survey

By Jeffrey C. Reid

Abstract

This report releases the original fluid inclusion stratigraphy (FIS) data reports used for the recent evaluation for hydrocarbons and helium of the Dan River basin, Stokes and Rockingham counties, North Carolina.

The FIS data was obtained from existing core samples in three drill holes drilled in 1981: SO-C-01-81, SO-C-02-81 (both in Stokes County), and core hole RC-C-01-81 (Rockingham County). In addition, core samples were obtained from core hole SO-C-01-15 and the side track hole (SO-C-01A-15) drilled to capture a coaly section lost in drilling. Both cores were drilled in 2015 in Stokes County by the North Carolina Geological Survey. Drill core from the side track hole degassed as it was removed from the core barrel. Core holes SO-C-01-15 and SO-C-01A-15 were analyzed in the same FIS package. All samples were from cores. A summary of fluid inclusions and the FIS method is included to provide context for the data.

The data were included in **Reid *et al.* (2018)**, and **Reid *et al.* (2015)**.

Objectives

This report releases the title reports on fluid inclusion stratigraphy (FIS) for five core holes along strike in the Walnut Cove Formation, Dan River basin of Triassic age in Stokes and Rockingham counties, North Carolina. The primary goal of the analysis was to determine the gas chemistry as well as the hydrocarbon and helium potential within the tested sections. Most samples were from the Walnut Cove Formation, but a few were from the overlying Dry Fork Formation.

The FIS reports were commissioned by the North Carolina Geological Survey using state appropriated funds to further the understanding of hydrocarbon and helium (and other noble gases) potential in North Carolina. The study was done by Fluid Inclusion Technologies (FIT), Inc. formerly of Broken Arrow, Oklahoma. FIT is a Schlumberger company now based in Houston.

The FIS data was obtained from existing core samples in three drill holes drilled in 1981: SO-C-01-81, SO-C-02-81 (both in Stokes County), and core hole RC-C-01-81 (Rockingham County). The cores are curated in the North Carolina Geological Survey's repository located in Raleigh, North Carolina. In addition, core samples were obtained from core hole SO-C-01-15 and the side track hole (SO-C-01A-15), both drilled in 2015 in Stokes County by the North Carolina Geological Survey. The side track hole (SO-C-01A-15) drilled to capture a coaly section lost in drilling. Drill core from the side track hole degassed as it was removed from the core barrel. Core holes SO-C-01-15 and SO-C-01A-15 were analyzed in the same FIS package. All samples were from cores. Each other drill hole has a separate FIS report (see Appendices 1-4). The table (below) indicates the total number of core samples and depth intervals sampled from each core.

Core hole	*Number of samples*	*Depth interval sampled (ft)*
SO-C-01-81	61	46-626 ft
SO-C-02-81	78	53-806 ft
RC-C-01-81	40	88-479 ft
SO-C-01-15	6	197.3-204.5 ft
SO-C-01A-15	40	10-276 ft

These FIS data were incorporated into **Reid *et al.* (2018)**. **Reid *et al.* (2015a)**, provide a description of the 2015 core hole and side track hole. Because helium and other noble gases had already been confirmed from two shut-in wells in the Sanford sub-basin, Deep River basin (**Reid *et al.*, 2015b,c**), the FIS method was specifically tuned to detect helium for this study. The other noble gases are in lower concentrations not detectable by FIS, may remain undetected.

Fluid inclusion stratigraphy

Fluid inclusion stratigraphy (FIS) is the chemical analysis of fluid inclusions. These inclusions are microscopic traces of past or now-existing subsurface fluids that became entrapped in rocks during burial. Because they are completely encapsulated within their host minerals, they are distinctive from adsorbed or residual fluids in open porosity. Therefore, they are not subject to evaporation during sample storage, loss of light ends during sampling from depth, or contamination from the mud system. Fluid inclusions endure in the geologic record although parent fluids have moved on. This, the inclusions preserve the fluid history of the area. Samples are volatilized in a vacuum resulting in basic fluid analysis.

Conclusions

Fluid inclusion stratigraphy (FIS) is an important analytical tool in these core holes to improve the understanding of the hydrocarbon and helium (and potentially other noble gases) potential in the Dan River basin, Stokes and Rockingham counties, North Carolina. Details of the conclusions derived from these data are in **Reid *et al.* (2018)**, and **Reid *et al.* (2015a)**.

References

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Appendices

Appendix 1

“A stratigraphic reconstruction of bulk volatile chemistry from fluid inclusions in: SO-C-01-81,” Fluid Inclusion Technologies, Inc. report FIS# FI160559a prepared August 4, 2016 for the North Carolina Geological Survey, 80p.

Appendix 2

“A stratigraphic reconstruction of bulk volatile chemistry from fluid inclusions in: SO-C-02-81,” Fluid Inclusion Technologies, Inc. report FIS# FI160559c prepared August 4, 2016 for the North Carolina Geological Survey, 88p.

Appendix 3

“A stratigraphic reconstruction of bulk volatile chemistry from fluid inclusions in: SO-C-01-15 and 1A,” Fluid Inclusion Technologies, Inc. report FIS# FI160559g prepared August 4, 2016 for the North Carolina Geological Survey, 79p.

Appendix 4

“A stratigraphic reconstruction of bulk volatile chemistry from fluid inclusions in: RC-C-01-81,” Fluid Inclusion Technologies, Inc. report FIS# FI160559e prepared August 4, 2016 for the North Carolina Geological Survey, 74p.

Appendices

Appendix 1

“A stratigraphic reconstruction of bulk volatile chemistry from fluid inclusions in: SO-C-01-81,” Fluid Inclusion Technologies, Inc. report FIS# FI160559a prepared August 4, 2016 for the North Carolina Geological Survey, 80p.

UWI# 999999999999
FIS# FI160559a

A Schlumberger Company

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

SO-C-1-81

Prepared August 4, 2016 for

NC Geological Survey

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

SO-C-1-81

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by
FIT
A Schlumberger Company

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Executive Summary for well: SO-C-1-81

1 FIS Summary for SO-C-1-81

SO-C-1-81 is a shallow legacy core hole drilled in 1981 within the Dan River Basin. FIS analysis was performed on a total of 61 core samples from 48-626 ft. This study was completed in conjunction with three other wells (SO-C-2-81 in report FI160559c; RC-C-1-81 in report FI160559e; SO-C-1-15 and 1A-15 in report FI160559g). The primary goal of the analysis was to determine the gas chemistry and hydrocarbon potential within the tested section. The areas of particular interest are the Triassic-Age Walnut Cove Formation and the overlying Dry Fork Formation.

FIS data from the interval above 278 ft (Walnut Cove Formation) display dry gas responses with wet gas spectra at 97 ft and 143 ft. Liquid hydrocarbon signals are slightly elevated at 59-61 ft, 97 ft, and 143 ft (and more broadly above 153 ft). Decoupling of gas and liquids responses suggest possible contributions from intercalated kerogen to heavier hydrocarbons, and a separate phase of migrated drier gas. CS2 and minor SO2 of probable thermal origin is noted at 143 ft. No visible liquid petroleum inclusions were identified in a thin section from 97 ft (carbonate cemented sandstone with no visible porosity).

The basal section at 286-626 ft (Walnut Cove to Pine Hall Formations?) illustrates dry gas FIS responses with a single wet gas response at 406 ft. Stronger methane concentrations are recorded at 347 ft, 383-412 ft, and 492 ft, with the middle interval being most significant. Liquid hydrocarbon signals also increase at 406 ft and 541 ft and are partially coupled with methane, suggesting a common source, at least in part. Sulfur species, including CS2, SO2 and minor H2S of probable thermal origin (i.e., via thermochemical sulfate reduction) are identified at 286 ft, 347 ft, 383-412 ft, and 492 ft. Helium tends to covary with methane and shows highest responses at 143 ft and 391-412 ft. Maximum concentrations with respect to methane are on the order of 250 ppm, although mostly values are below 100 ppm. Helium can indicate an ancient fraction of arkosic detritus, a deep sourced component of hydrocarbon gas, or diagenetic involvement of deep basin brines (or emplacement of gas that sparged helium from these brines). CO2 signals increase noticeably at 391-412 ft, and may be produced by thermochemical sulfate reduction along with the abovementioned sulfur species.

Three thin sections were evaluated from the section described in the previous paragraph. A thin section from 412 ft contains rare, white-fluorescent, upper-moderate gravity liquid petroleum inclusions in sandstone (probable gas-rich gas condensate), indicating a possible liquid hydrocarbon migration event. This sample also contains pale white-fluorescent and non-fluorescent wet to dry gas inclusions in fractured detrital quartz grains. High abundance suggests significant saturation of gas, although porosity is low and gas-generation/emplacement appears to have occurred after much of the reservoir quality had been degraded by compaction and cementation. No visible oil or gas inclusions were identified in the other two thin sections at 406 ft and 492 ft, however, gas inclusions can be difficult to identify in some cases. Rocks are predominantly sands and sandy carbonates with lesser shale. Shale contains minor to appreciable gas-prone kerogen (most prominent at 412 ft). It is most likely that gas inclusions were proximally generated from this organic material. Appreciable dead petroleum stain (probable pyrobitumen) is also noted at this depth, with lesser occurrences at 492 ft.

2 FIS Chemical Zonation

48 ft to 278 ft :

Dry gas: 92%

Wet gas: 8%

Hydrocarbon species to C7 are observed in this zone. No proximity to pay signal is recorded. Sulfur species are rarely present.

Slide @ 97 ft: No liquid petroleum inclusions, significant stain or kerogen are observed.

286 ft to 626 ft :

Dry gas: 94%

Wet gas: 3%

Low hydrocarbon responses: 3%

Hydrocarbon species to C6 are present in this interval. Proximity to gas indications are rare. There are no proximity to liquid petroleum indications recorded in this zone. Sulfur species are intermittently found.

Slide @ 406 ft: Several occurrences of gas prone kerogen are present.

Slide @ 412 ft: Population 1: Rare, upper moderate gravity petroleum inclusions are indicated. Population 2: Several, high gravity petroleum inclusions are preserved. Population 3: Common, indeterminate gravity petroleum inclusions are documented. Common occurrences of gas prone kerogen are preserved. Common occurrences of dead stain are preserved.

Slide @ 492 ft: Several occurrences of gas prone kerogen are documented. Rare occurrences of dead stain are documented.

Summary of Results for well: SO-C-1-81

This report contains Fluid Inclusion Stratigraphy and Fluid Inclusion Petrography results for SO-C-1-81 and was prepared for NC Geological Survey by *Fluid Inclusion Technologies, 2217 N. Yellowood Ave., Broken Arrow, OK 74133; ph: (918) 461-8984; fax: (918) 461-2085; www.fittulsa.com.*

Table I: Logistical Information

Client:	**NC Geological Survey**	Analyzed Depth:	**48 - 626 Feet**
Well:	**SO-C-1-81**	Sample Spacing:	**See Individual Spectra**
		Sample Total:	**61**

Table II: Fluid Inclusion Petrography from SO-C-1-81

Well Name: SO-C-1-81																					
Sample Depth	**Rock Type**		**Petroleum Fluid Inclusion Populations**												**Kerogen (possible source rk)**					**Bitu-men**	
			Population 1				**Population 2**				**Population 3**										
***Units:* (Feet)**	*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*
97	ccss																				
406	sdcb,sh														sh	gp		sv			
412	ss,sh,cb		wt	um	dq	r	wt	h	dq	sv	no		dq	c	sh	gp		c		ds	c
492	sdcb,sh														sh	gp		sv		ds	r

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: ccss =
an: anhydrite	wt: white	qc: quartz cement	go: oil and gas prone	carbonate-cemented
ch: chert	bl: blue	df: frac detrital feldspar	op: oil prone	sandstone, sdcb =
co: coal	l: low	cm: matrix carbonate	gp: gas prone	sandy carbonate
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	
NHC	non-hydrocarbon	**MP**	migration pathway	**OWC**	oil-water contact
DG	dry gas	**PC**	present day ptrlm column	**GWC**	gas-water contact
WG	wet gas	**PPC**	paleo-ptrlm column	**GOC**	gas-oil contact
GC	gas condensate	**RI**	recycled ptrlm inclusions	**POWC**	paleo-oil-water contact
VO	volatile oil	**SR**	source rock	**PGWC**	paleo-gas-water contact
O	oil	**GP**	gas prone kerogen	**PGOC**	paleo-gas-oil contact
BD	biodegraded	**OP**	oil prone kerogen		
TA	thermally altered	**OGP**	oil and gas prone kerogen		
		CNT	contamination		

Water-Soluble Anomalies		Miscellaneous	
WS	undifferentiated water-soluble anomaly	**SL**	seal
WSSR	source rock related water-soluble anomaly	**MS**	microseep
WSTA	water-soluble anomaly sourced from thermal alteration		
PTPL	proximity to oil or gas-condensate		
PTPG	proximity to gas		

Petrographic Observations					
A	abundant	**IG**	igneous rock	**SA**	salt
AN	anhydite	**L**	low	**SH**	shale
BL	blue	**LG**	large	**SI**	siltstone
BR	brown	**M**	moderate	**SM**	small
C	common	**MD**	medium	**SS**	sandstone
CB	carbonate	**MT**	metamorphic rock	**ST**	petroleum stain
CC	carbonate cement	**NO**	none	**SV**	several
CH	chert	**OR**	orange	**UL**	upper-low
CM	matrix carbonate	**PB**	pyrobitumen	**UM**	upper-moderate
CO	coal	**PF**	pore filling bitumen	**V**	variable
DF	detrital feldspar	**PR**	pore rimming bitumen	**W**	weak
DQ	detrital quartz	**QC**	quartz cement	**WT**	white
DR	quartz dust rim	**R**	rare	**XA**	extremely abundant
H	high	**S**	strong	**YL**	yellow

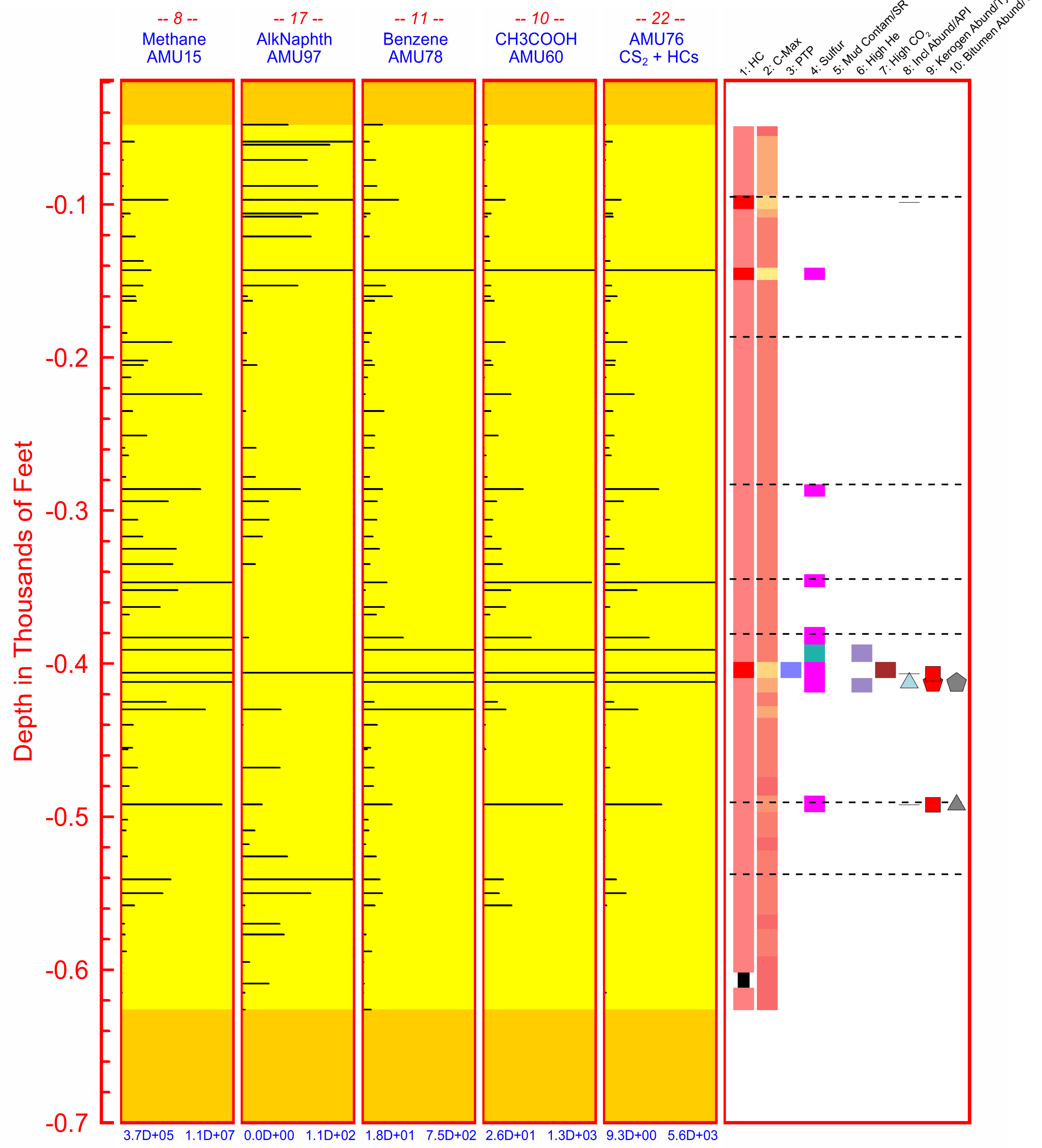


Figure 1: FIS Summary Tracks (see Sect. A for further explanation)

1: HC	2: C-Max	3: PTP	4: Sulfur	5: MC/SR	6 & 7: He/CO$_2$
■ NH ■ WG ■ GC-Oil ■ DG ■ WG-GC	■ C_1 ■ C_3 ■ C_5 ■ C_7 ■ C_9 ■ C_{11} ■ C_{13} ■ C_2 ■ C_4 ■ C_6 ■ C_8 ■ C_{10} ■ C_{12}	■ Gas ■ Liquid	■ Sulfur ■ S2-SO2	■ Mud Contam ■ Source Rock	■ 6: High He ■ 7: High CO$_2$

Legend (cont)

8: Colors for Inclusion Abundance/API describe the API gravity of the liquid hydrocarbon inclusions:

- ▲ **Triangle:** Rare abundance **Brown:** Low Gravity
- ■ **Square:** Several abundance **Orange:** Upper Low gravity
- ⬟ **Pentagon:** Common abundance **Yellow:** Moderate gravity
- ⬢ **Hexagon:** Abundant **Light blue:** Upper Moderate gravity
- ● **Circle:** Extra Abundant **Blue:** High gravity

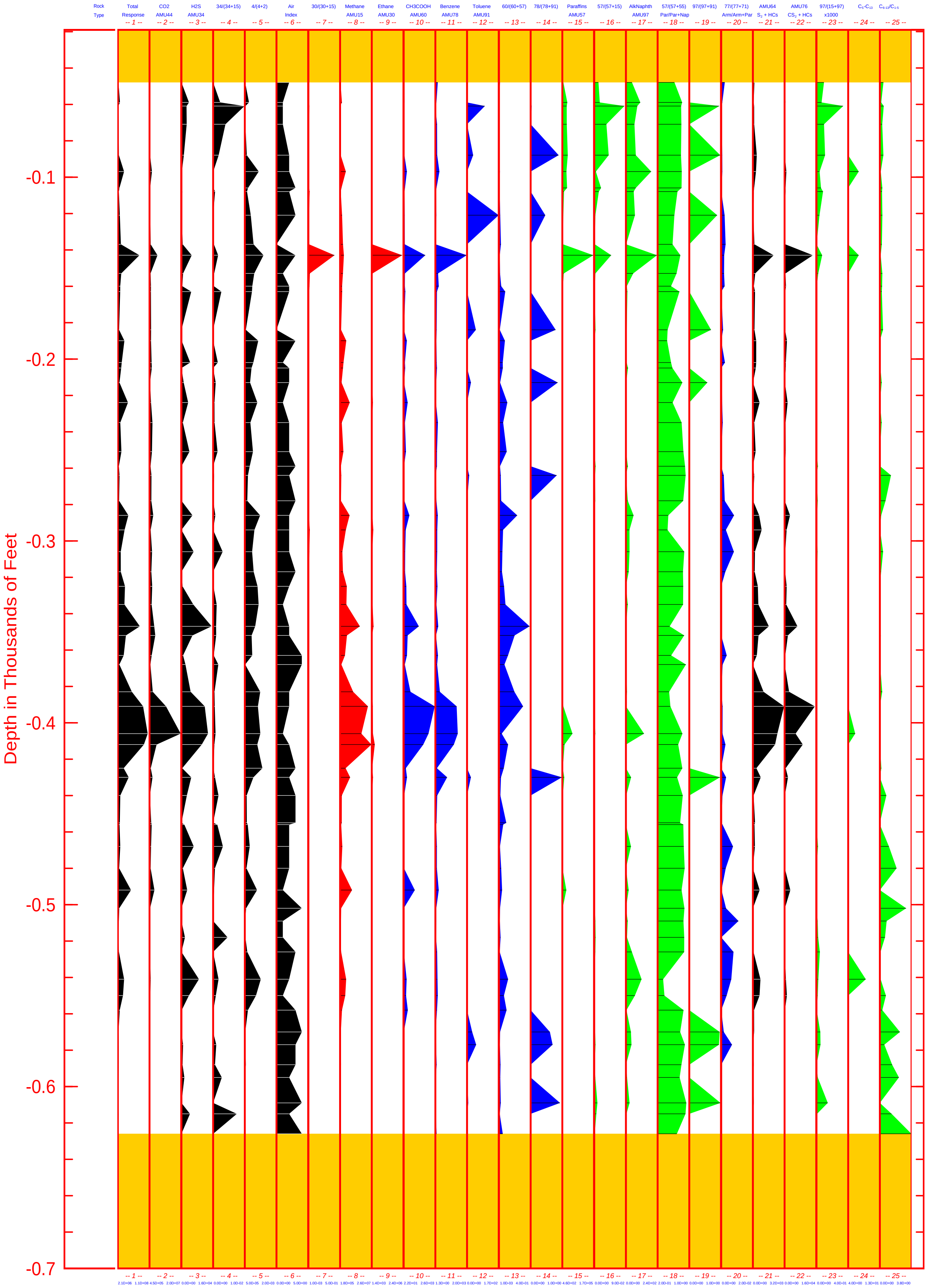
9: Colors for Kerogen indicate if the kerogen are oil prone, gas prone, or both

- ▲ **Triangle:** Rare kerogen abundance **Red:** Gas prone
- ■ **Square:** Several abundance **Orange:** Both oil and gas
- ⬟ **Pentagon:** Common kerogen abundance **Green:** Oil prone
- ⬢ **Hexagon:** Abundant **Red:** Gas prone
- ● **Circle:** Extra Abundant kerogen **Orange:** Both oil and gas

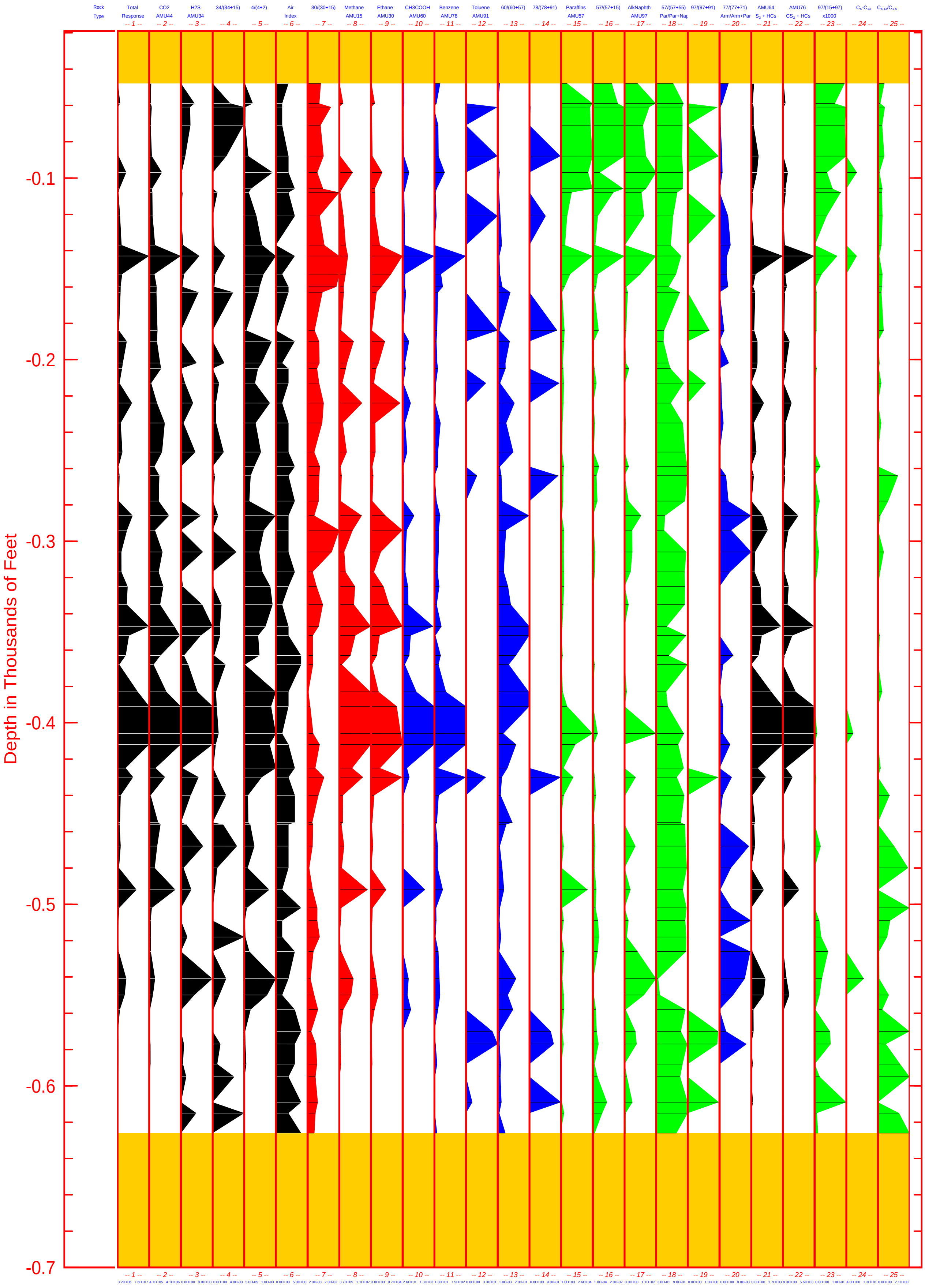
10: Colors for Bitumen indicate the bitumen type:

- ▲ **Triangle:** Rare bitumen abundance **Green:** Live stain
- ■ **Square:** Several bitumen **Gray:** Dead stain
- ⬟ **Pentagon:** Common kerogen abundance **Green:** Live stain
- ⬢ **Hexagon:** Abundant bitumen **Black:** Pore occluding
- ● **Circle:** Extra Abundant bitumen **Magenta:** Pyrobitumen

SO-C-1-81 : All FIS Data



SO-C-1-81: 90% of all FIS Data



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3 Overview of FIT, Inc. and Fluid Inclusion Stratigraphy

FIT, a Schlumberger Company, is a laboratory-based petroleum service organization established in 1997 and acquired by Schlumberger in November, 2015, 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 FIT 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 Compartmentallization** 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”.

3.1 General Logistics of Initiating an FIS Analysis

To Initiate an FIS Analysis: contact FIT[1] 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 FIT for sample preparation including any necessary crushing/sieving, subsampling and washing.

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), 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

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[1] FIT Inc., a Schlumberger Company affiliate, 2217 N. Yellowood Ave., Broken Arrow, 74012, USA., phone (918) 461-8984

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 SO-C-1-81 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. FI160559a-1.las – LAS-format, 26-column file containing recorded depth and Tracks 1-25 from the *FIT Analysis* of SO-C-1-81
2. FI160559a-2.las – LAS-format, 181-column file containing recorded depth and background corrected, normalized, standardized individual mass spectra (m/z 2-180) from the *FIT Analysis* of SO-C-1-81
3. FI160559a-s.pdf – PDF format, electronic file of the summary tracks from the *FIT Analysis* of SO-C-1-81
4. FI160559a-t.pdf – PDF format, electronic file of the petrography table from the *FIT Analysis* of SO-C-1-81
5. FI160559a-1.pdf – PDF format, electronic file of the final report (entire document) of the *FIT Analysis* of SO-C-1-81

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 (H_2^+)
4	helium ($^4He^+$)
15	C_1 fragment (CH_3^+); largely methane
30	C_2 fragment ($C_2H_6^+$); largely ethane
34	hydrogen sulfide (H_2S^+)
44	dominantly carbon dioxide (CO_2^+); possible C_3 fragment overlap
55	contribution from C_4 and greater naphthenes
57	contribution from C_4 and greater paraffins
60	dominantly acetic acid (CH_3COOH^+); possible dominance by carbonyl sulfide (COS^+) in some cases
64	S_2 or SO_2 plus hydrocarbons
71	contribution from C_5 and greater paraffins
76	CS_2 plus hydrocarbons
77	contribution from aromatic species
78	benzene ($C_6H_6^+$) with possible contribution by carbon disulfide (CS_2^+)
91	toluene ($C_7H_7^+$)
97	C_7 alkylated naphthene fragment

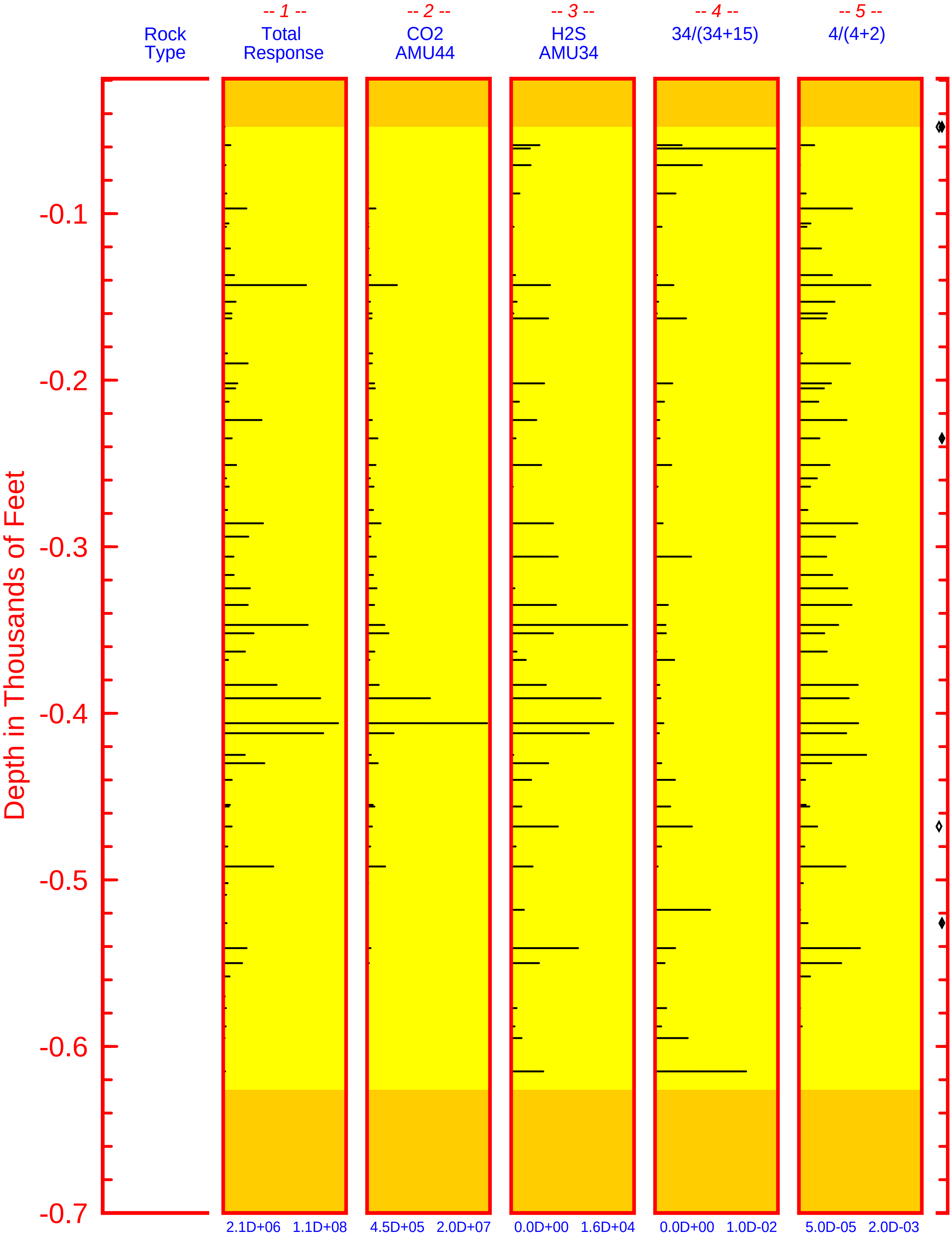


Figure 2: All FIS Data: Tracks 1 – 5 (see Sect. A.3 for explanation)

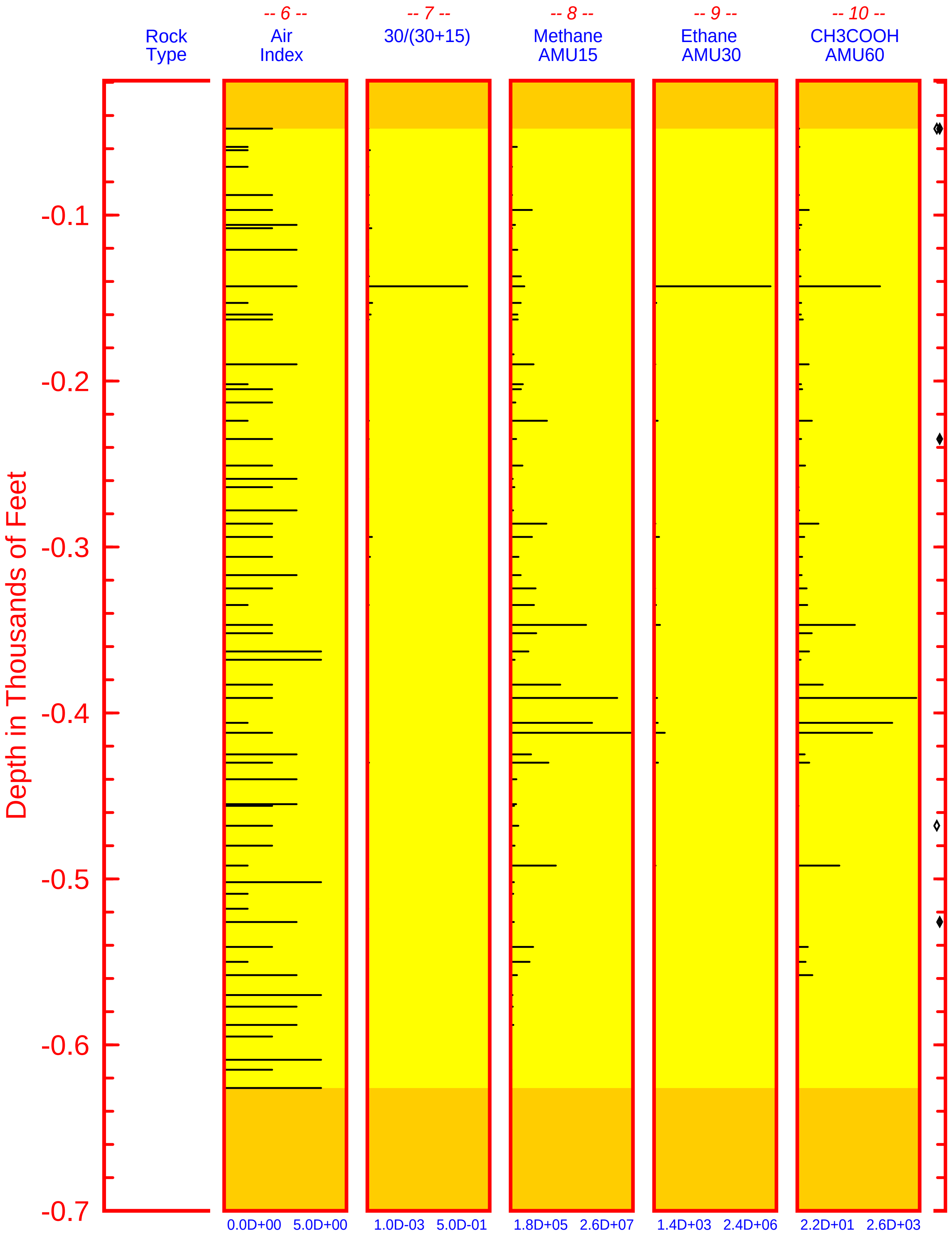


Figure 3: All FIS Data: Tracks 6 – 10 (see Sect. A.3 for explanation)

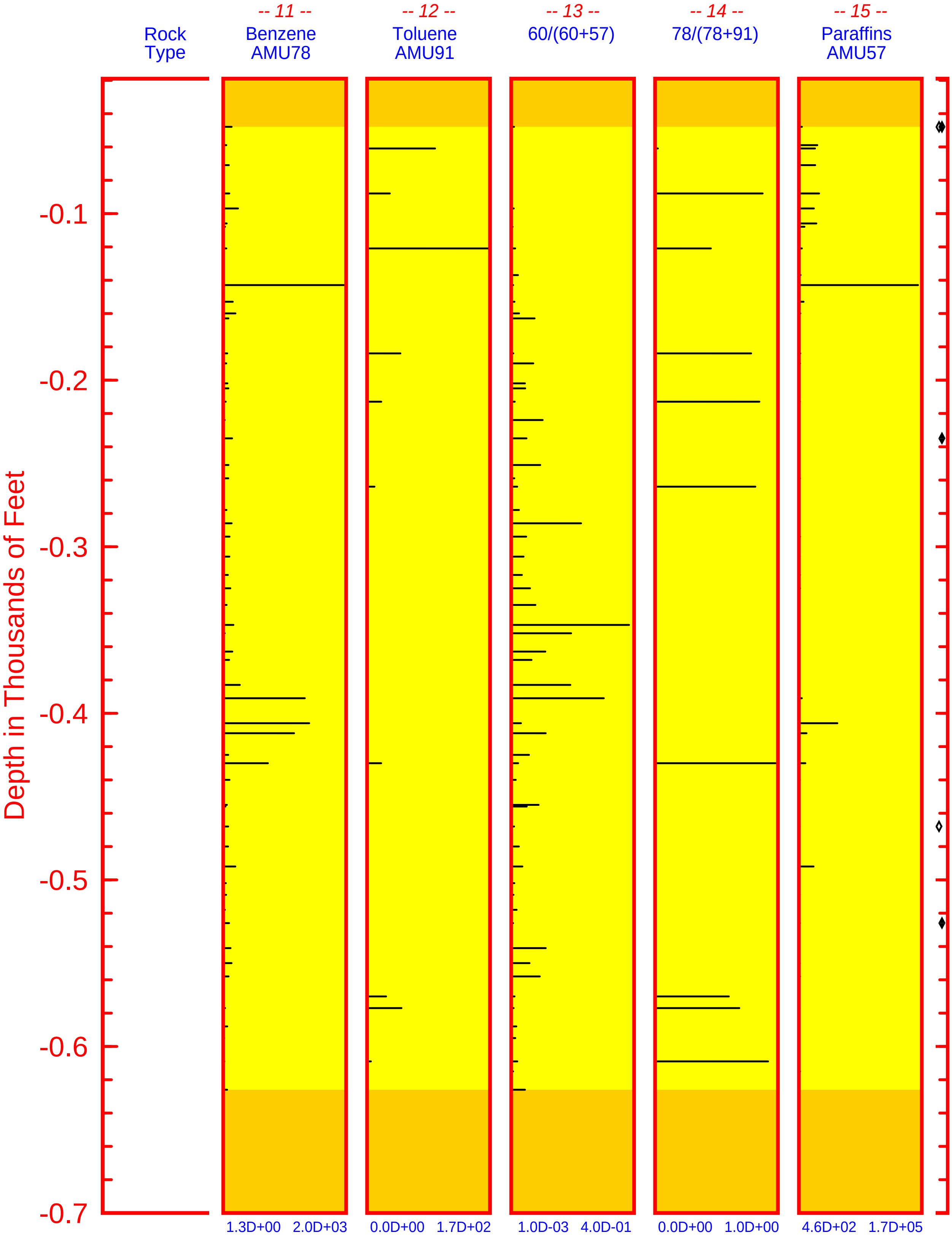


Figure 4: All FIS Data: Tracks 11 – 15 (see Sect. A.3 for explanation)

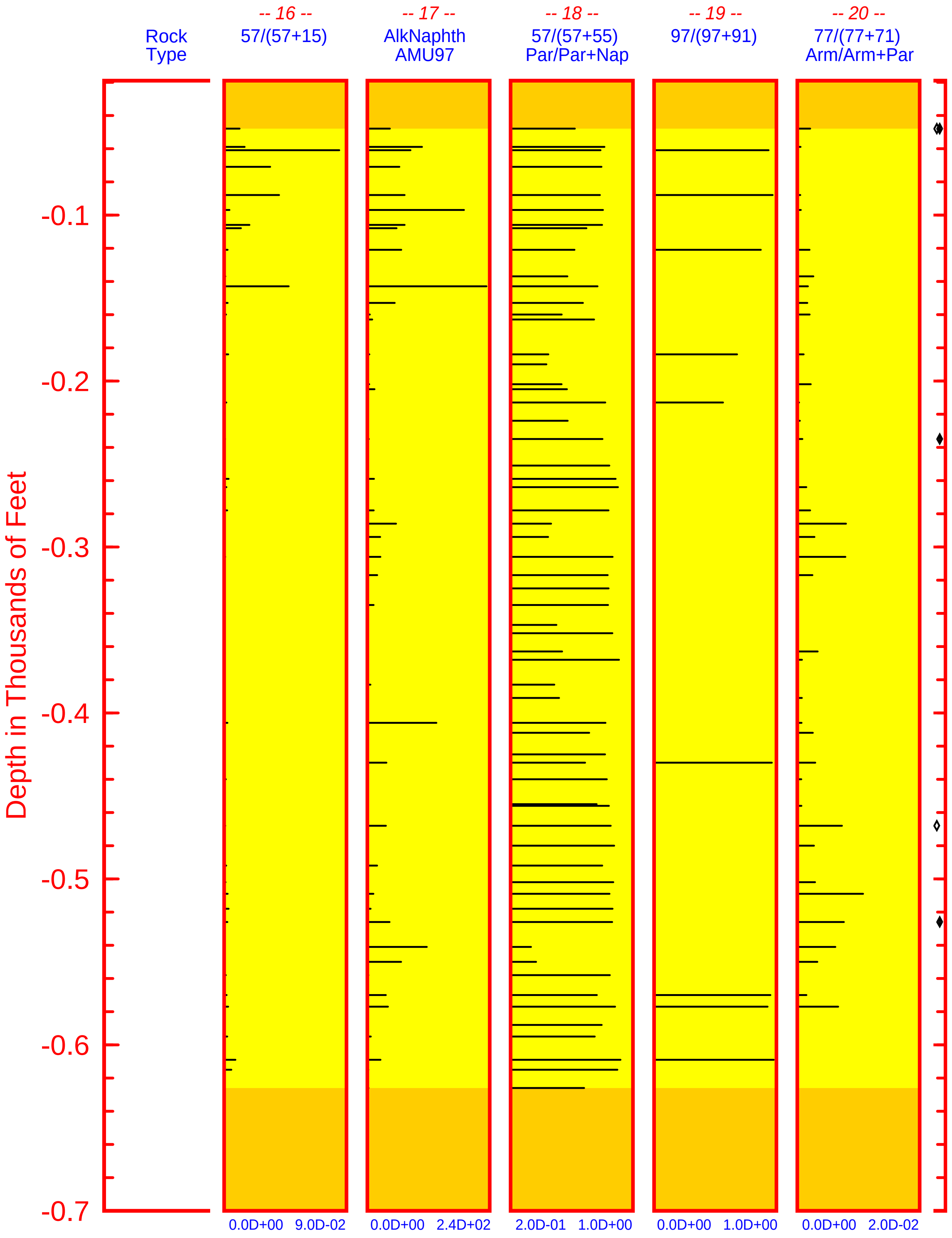


Figure 5: All FIS Data: Tracks 16 – 20 (see Sect. A.3 for explanation)

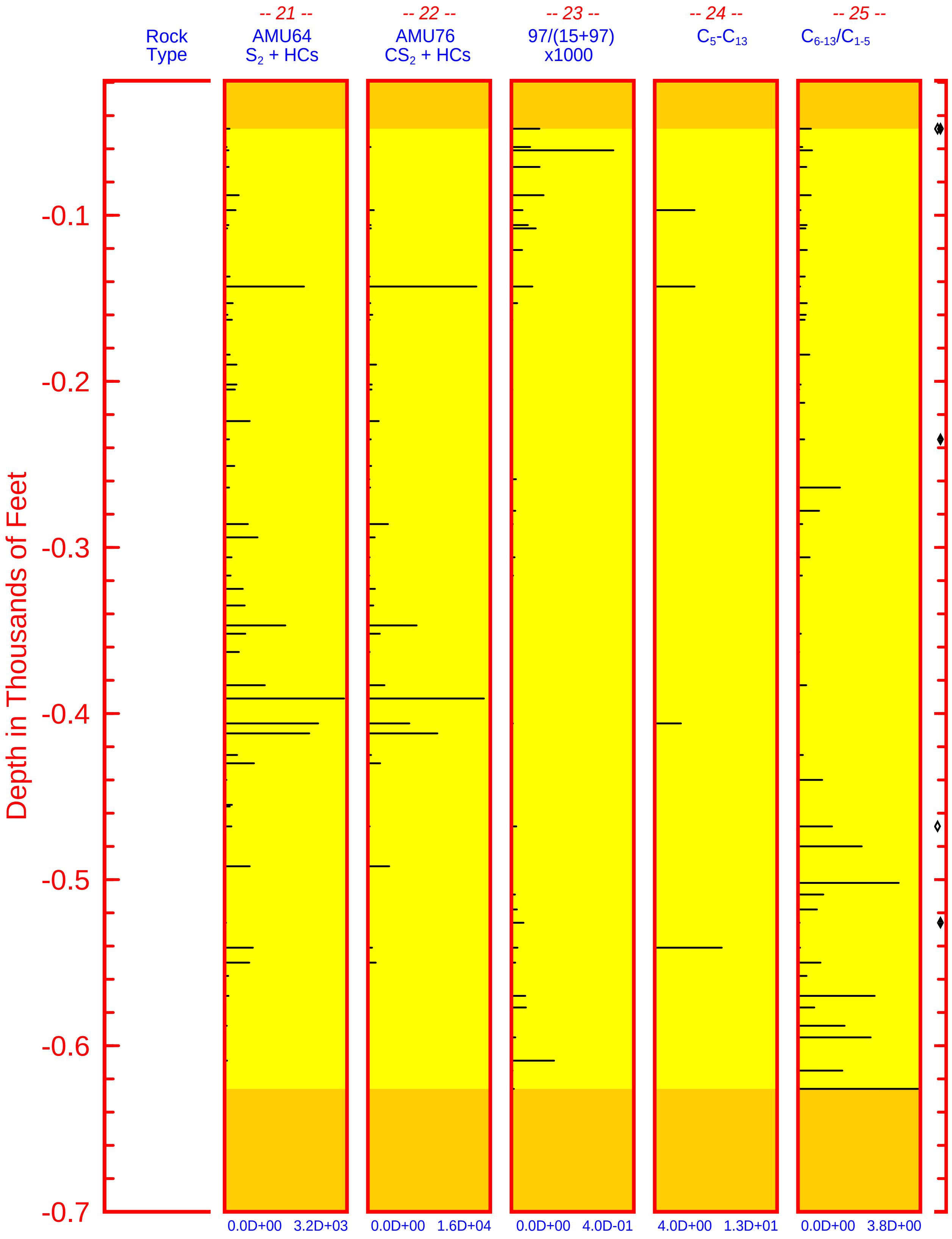


Figure 6: All FIS Data: Tracks 21 – 25 (see Sect. A.3 for explanation)

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.

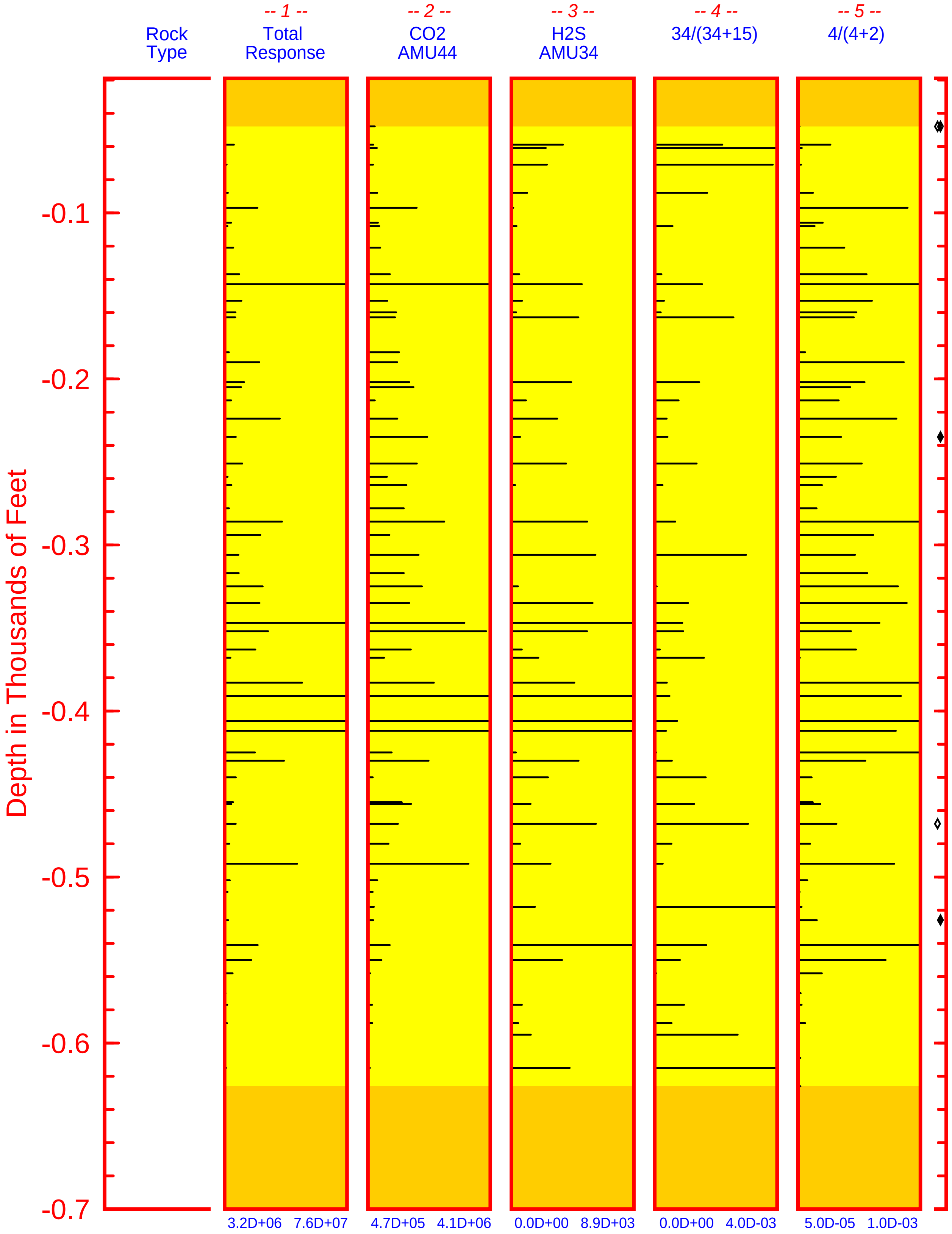


Figure 7: 90% of all FIS Data: Tracks 1 – 5 (see Sect. A.3 for explanation)

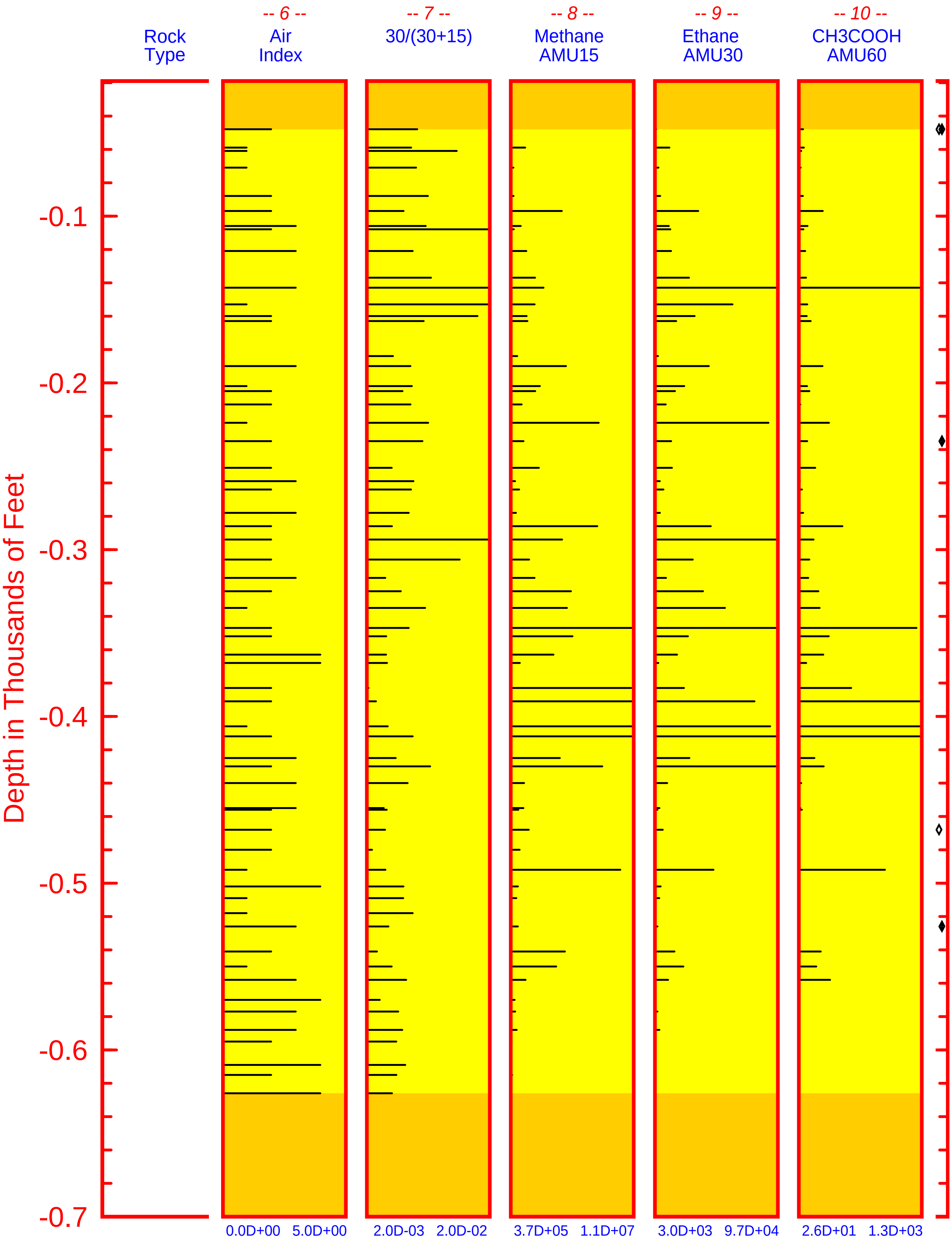


Figure 8: 90% of all FIS Data: Tracks 6 – 10 (see Sect. A.3 for explanation)

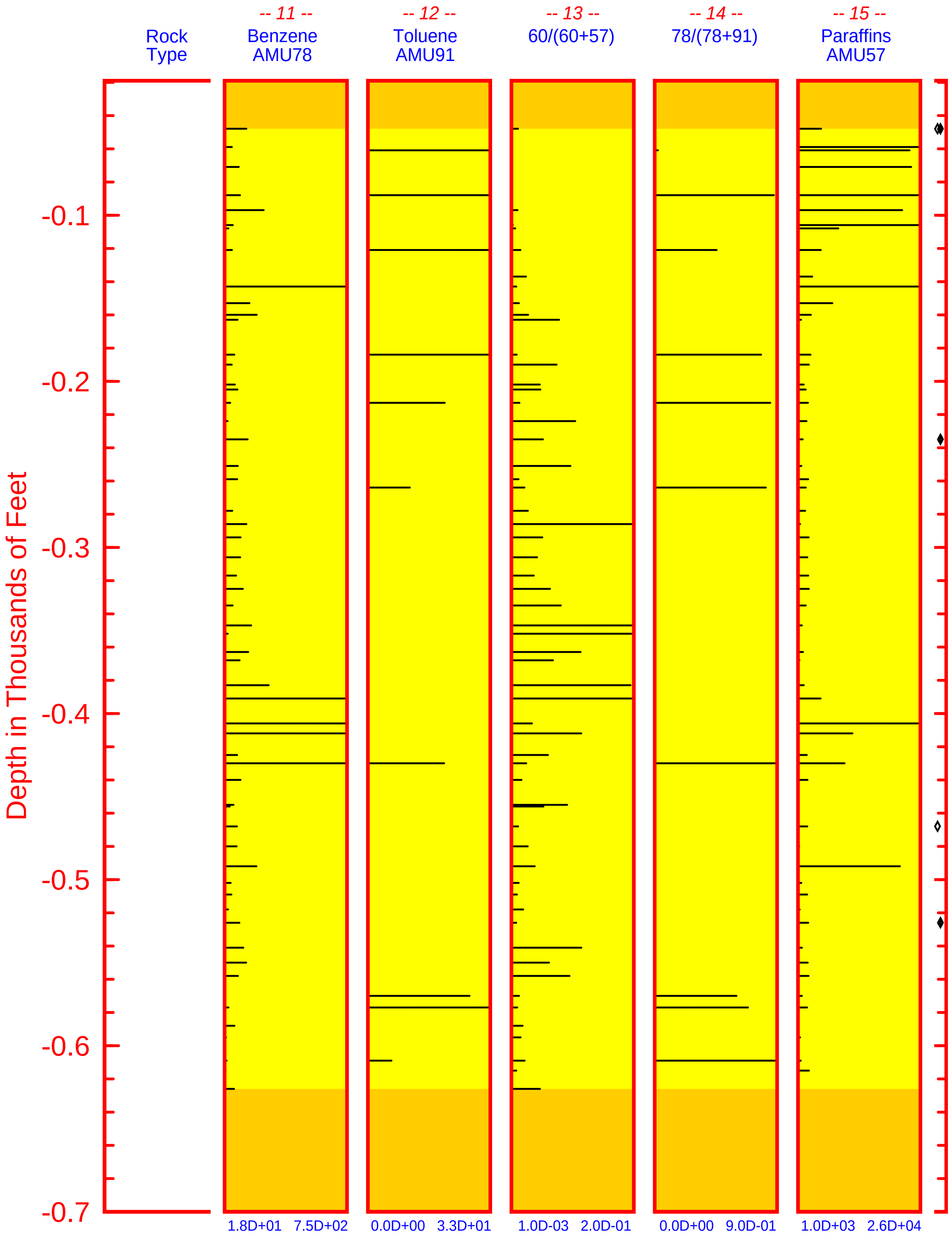


Figure 9: 90% of all FIS Data: Tracks 11 – 15 (see Sect. A.3 for explanation)

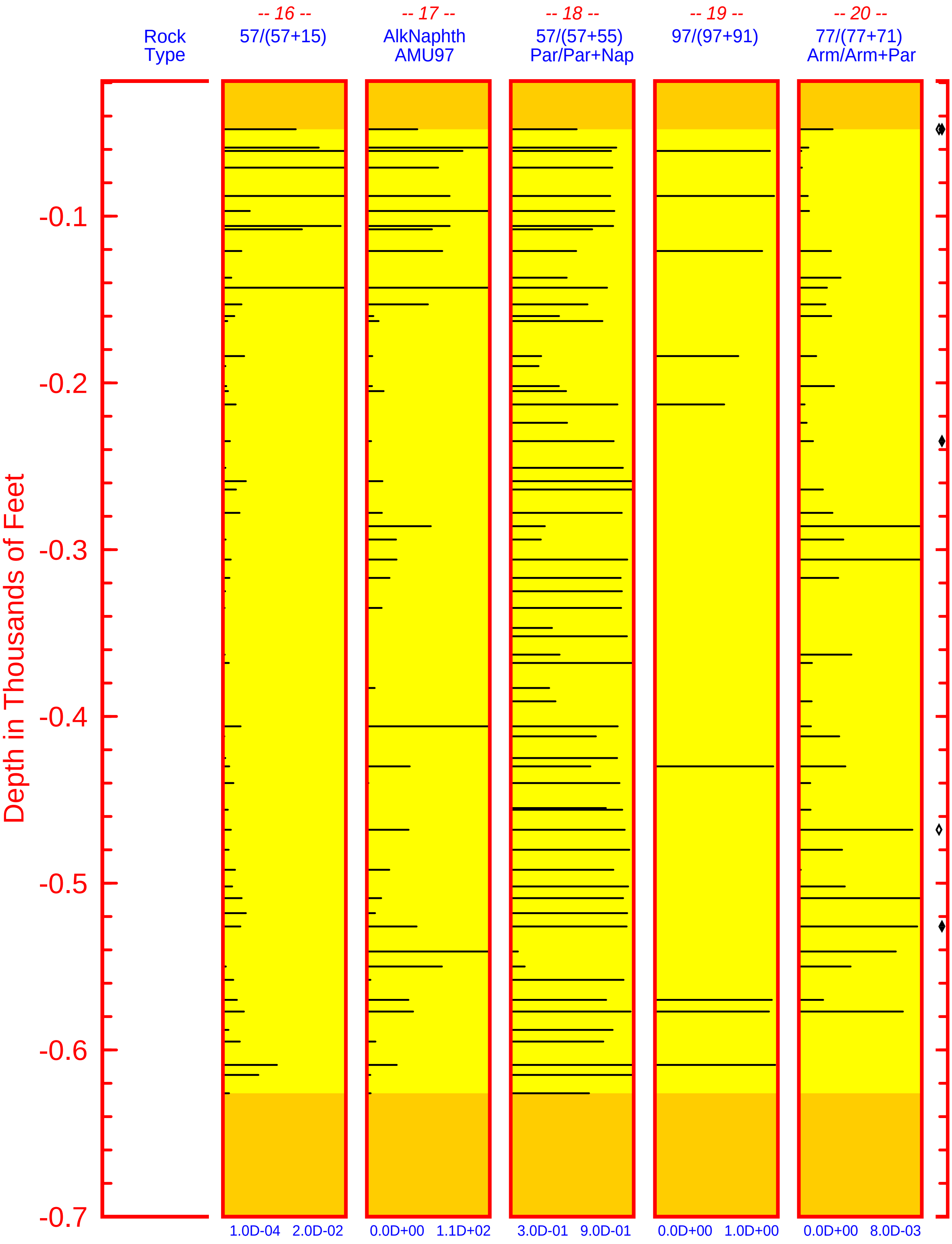


Figure 10: 90% of all FIS Data: Tracks 16 – 20 (see Sect. A.3 for explanation)

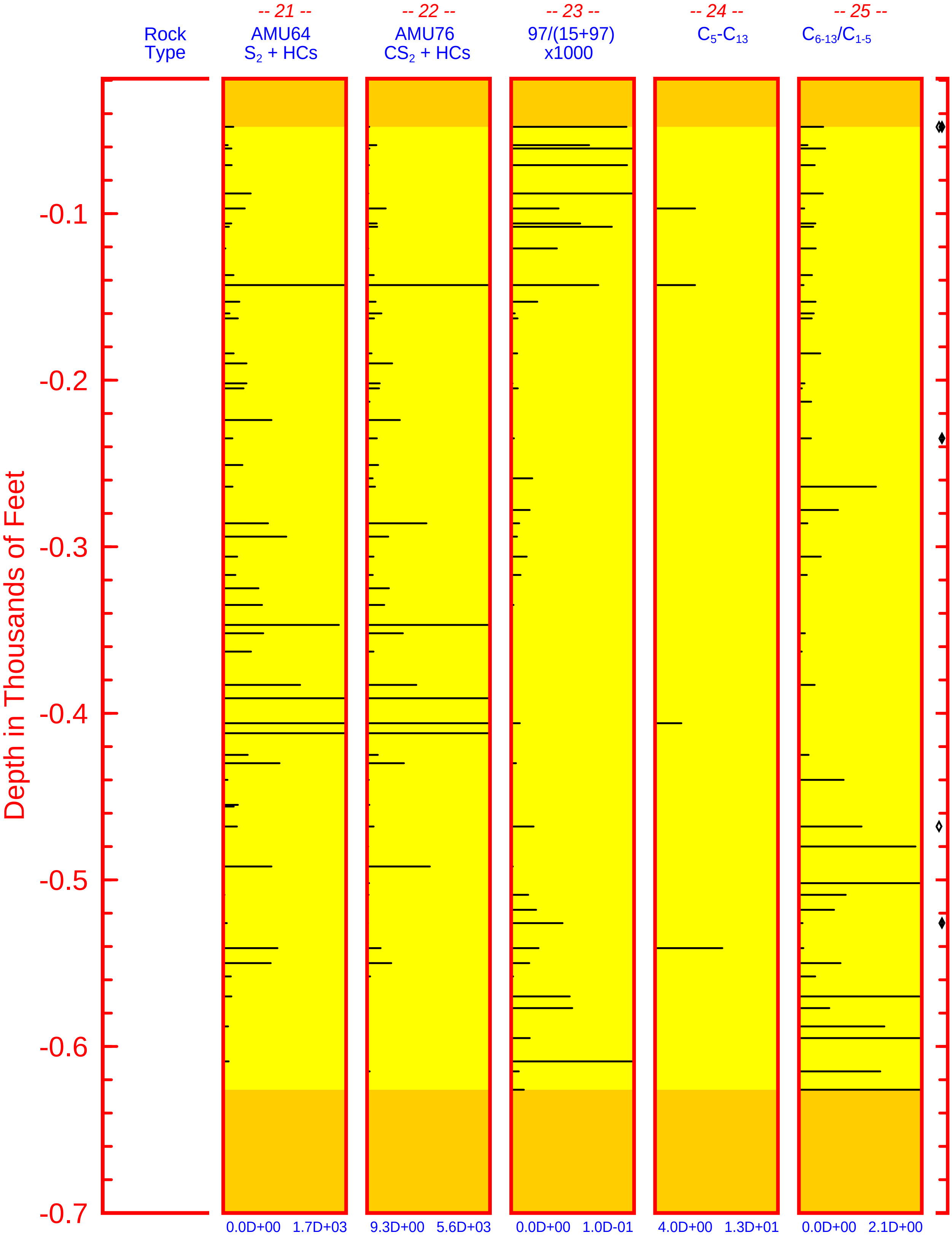


Figure 11: 90% of all FIS Data: Tracks 21 – 25 (see Sect. A.3 for explanation)

5 Photomicroscopy

Thin sections were prepared from SO-C-1-81 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 SO-C-1-81 at the depths indicated.

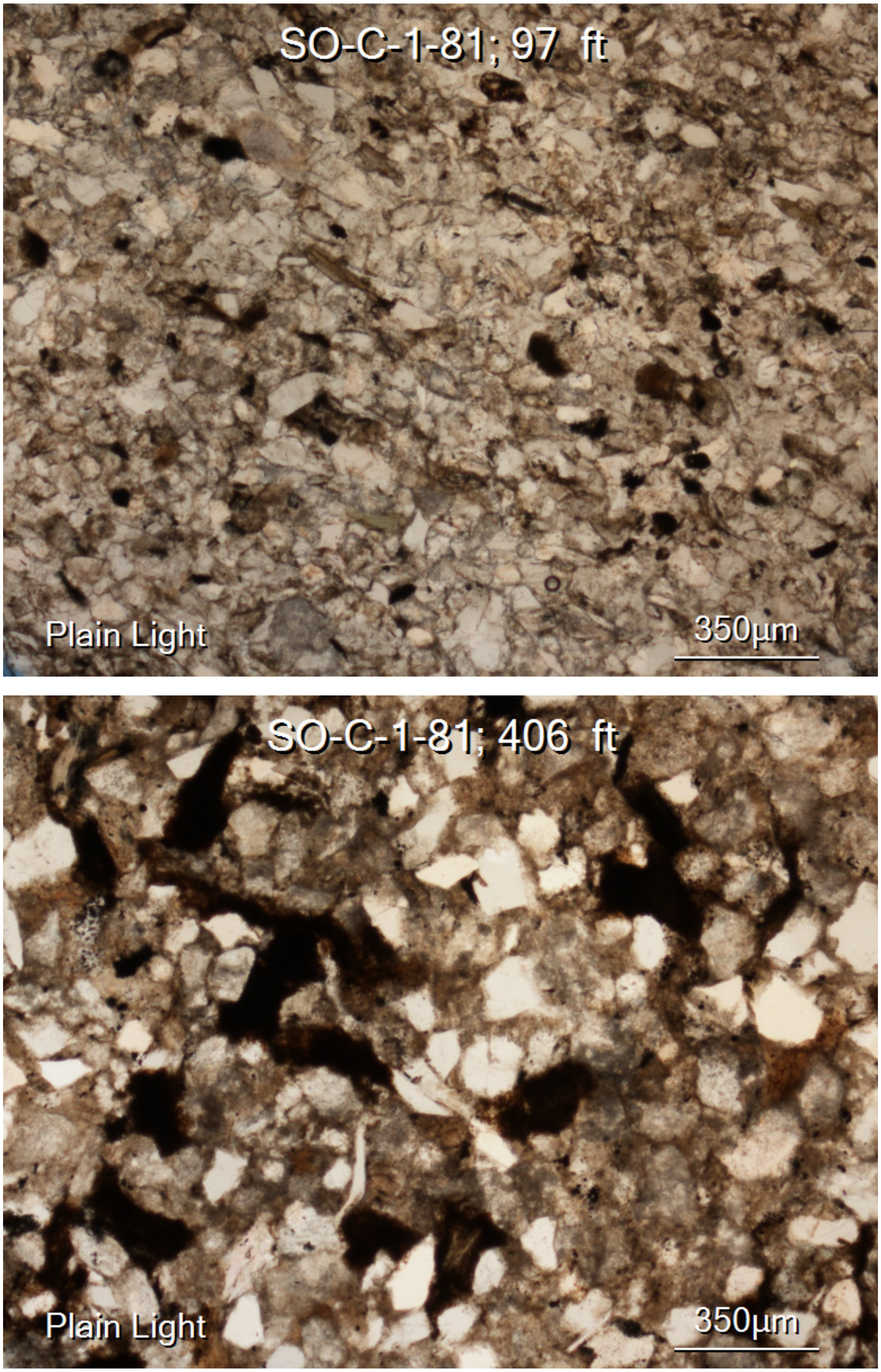


Figure 12: Photomicroscopy from SO-C-1-81

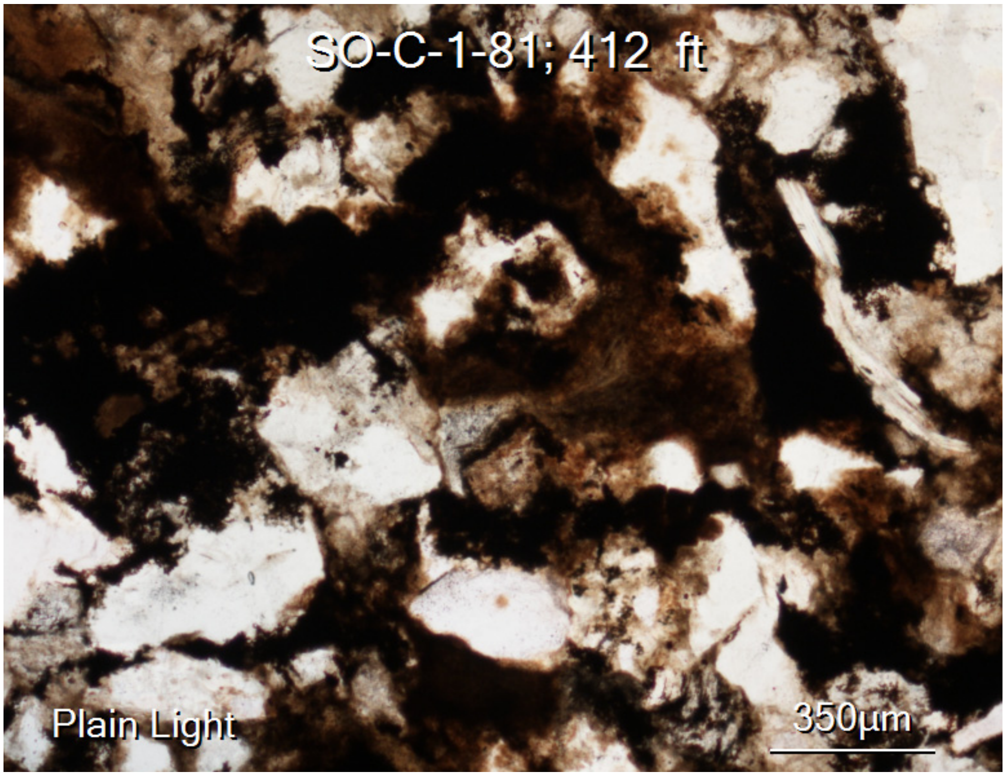


Figure 13: Photomicroscopy from SO-C-1-81

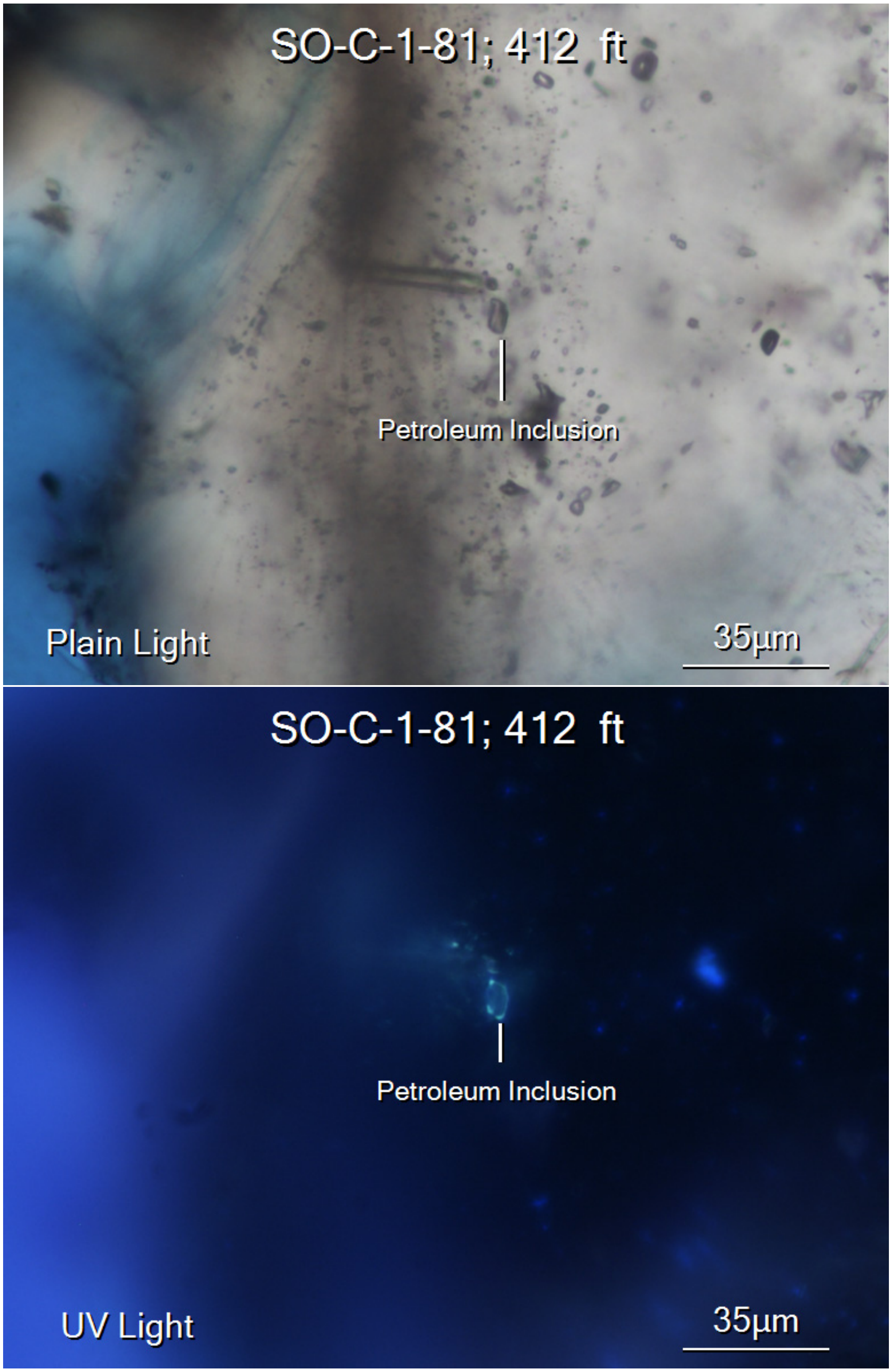


Figure 14: Photomicroscopy from SO-C-1-81

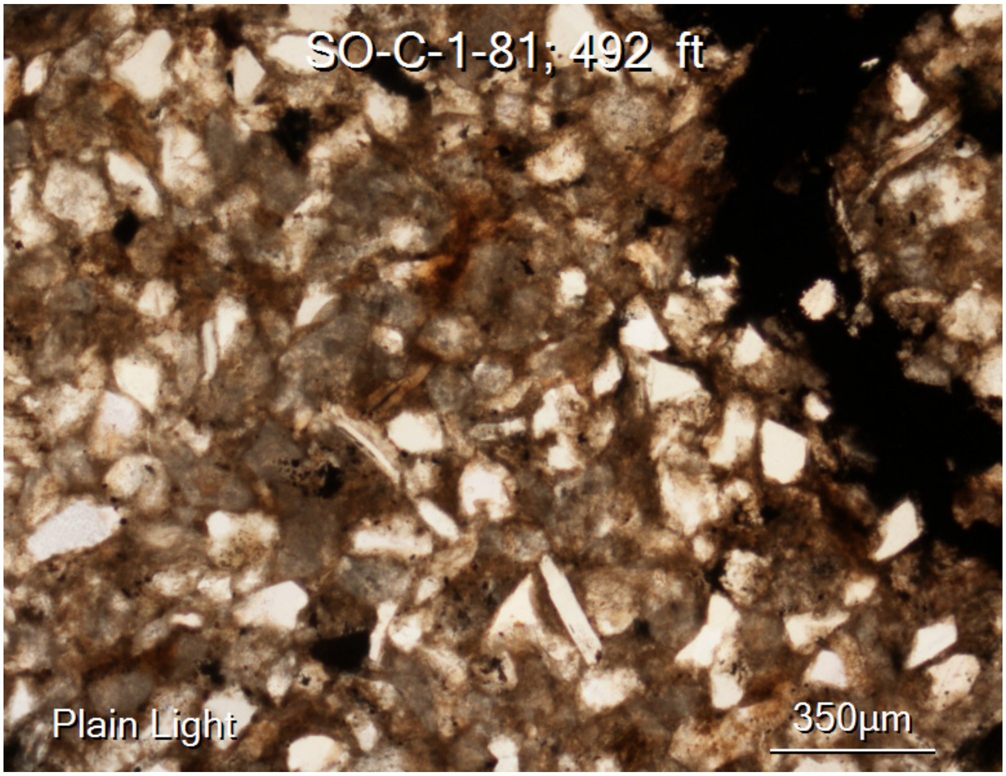


Figure 15: Photomicroscopy from SO-C-1-81

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 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. HD^+ and $^3He^+$ 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:* C_nH_{2n+2}
2. *Naphthenes:* C_nH_{2n}
3. *Aromatics:* C_nH_{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 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 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 C_1-C_5 hydrocarbons with dwindling responses in the C_6-C_8 range, and essentially no response in the C_9+ range. Drier gases may exhibit responses only in the C_1-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_4-C_6 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_2 and water, nitrogen and minor hydrocarbon contributions). The distinction lies in the relative proportion of these species. Gases can typically contain 90% C_1 and 95% C_1-C_3. Hence, FIS gas spectra typically have prominent C_1-C_3 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_4+ paraffins / C_4+ 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_7-C_{13} 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, 71	156(4%)
C12	165-171	57, 43, 71	170(8%)
C13	179-185	43, 57, 71	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_7-C_{13} paraffins are usually the same, and represent some of the most intense peaks previously identified for the C_4-C_6 gas-range paraffins.

Only normal (straight-chain) paraffins have been considered in the above table. Typical C_6-C_{10} (gasoline) fractions contain 40% paraffins, 50% naphthenes and 10% aromatics by volume. Typical C_{11}-C_{13} (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_7 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_1-C_{13} 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_2, 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 though 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 indictor species include light hydrocarbons, CO_2, possibly organic acids and aromatic compounds, and sulfurous volatiles, including H_2S, COS, CS_2, S_2 (+/- SO_2) and in some cases thiols. H_2S 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 downdip.

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 (CO_2^+), with possible minor contribution from C_3^+ hydrocarbon fragments and acetic acid. Anomalous values have been noted associated with pan-evaporative dolomitization of limestones in China and Oman. CO_2 response is often

high in proximity samples which show elevated levels of acetic acid. CO_2 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_2S^+). Anomalous values associated with petroleum may indicate sour oil or gas. H_2S is also noted at times in association with shallow dry gas of probable biogenic origin (including FIS microseeps) and with some proximity zones. H_2S is probably not quantitatively analyzed due to rapid scavenging by metallic surfaces of the analytical system.

Track 4: 34/(34+15) - $H_2S/(H_2S+\text{methane})$. Not frequently used, but ratio tends to be elevated in sour gas zones.

Track 5: 4/(4+2) - Helium fraction ${}^4He^+/({}^4He^+ + H_2^+)$; 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_3^+; mostly derived from methane, with minor contributions from all other paraffins and NH_2^+, 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 ($C_2H_6^+$). Use similar to that of methane ($m/z = 15$).

Track 10: $m/z = 60$ - Acetic aid (CH_3COOH), 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 ($C_6H_6^+$). 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 ($C_7H_7^+$). 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: $m/z = 76$ - CS_2 and C_6^+ hydrocarbons. 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: $C_5 - C_{13}$ 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 C_5 group is the highest molecular weight range hydrocarbon group present in a given sample, a ranking of 5 is assigned; if 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 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: C_{6-13}/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 (H_2^+); largely from H_2O, which makes up most of the evolved fluid in almost all samples.
- $m/z = 3$ - Deuterated hydrogen and helium-3 (HD and $^3He^+$).
- $m/z = 12$ - Carbon (C^+).
- $m/z = 14$ - Nitrogen (N^+) and 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. CH_2^+ will generally be accompanied by relatively larger responses on $m/z = 15$ (CH_3^+), and $m/z = 16$ (CH_4^+) (due to it's fragmentation origin from 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 (CH_4^+), but major interference by O^+ fragment of water.

- $m/z = 17$ - Dominated by OH^+ fragment from water
- $m/z = 18$ - Dominated by water parent peak (H_2O^+)
- $m/z = 22$ - Doubly charged carbon dioxide ($CO2^{2+}$); minor contribution from neon ($^{22}Ne^+$)
- $m/z = 28$ - Dominated by diatomic nitrogen (N_2^+) and CO^+ fragment from carbon dioxide. Minor C_2^+ hydrocarbon contribution
- $m/z = 32$ - Oxygen (O^+) and sulfur (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 $m/z = 34$ (H_2S), $m/z = 48$ (SO^+) and $m/z = 64$ (S_2^+, 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 (Ar^+) with possible significant interference by 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 (SO^+); also, C_4^+
- $m/z = 55$ - Naphthene fragment ($C_4H_7^+$). 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 ($C_5H_{11}^+$). Same use as $m/z = 57$.
- $m/z = 77$ - Aromatic fragment ($C_6H_5^+$). Same general use as for benzene and toluene.
- $m/z = 85$ - Paraffin fragment ($C_6H_{13}^+$). Same use as $m/z = 57$.
- $95 \leq m/z \leq 103$ - peaks centered within this range are mostly $C_7 - C_8$ fragments
- $110 \leq m/z \leq 115$ - peaks centered within this range are mostly $C_8 - C_9$ fragments
- $122 \leq m/z \leq 126$ - peaks centered within this range are mostly $C_9 - C_{10}$ fragments
- $134 \leq m/z \leq 138$ - peaks centered within this range are mostly $C_{10} - C_{11}$ fragments
- $148 \leq m/z \leq 152$ - peaks centered within this range are mostly $C_{11} - C_{12}$ fragments
- $160 \leq m/z \leq 164$ - peaks centered within this range are mostly $C_{12} - C_{13}$ fragments
- $175 \leq m/z \leq 180$ - peaks centered within this range are mostly $C_{13} - C_{14}$ 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 16. 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 inhomogenieties 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 17 and 18. 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 19. 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.

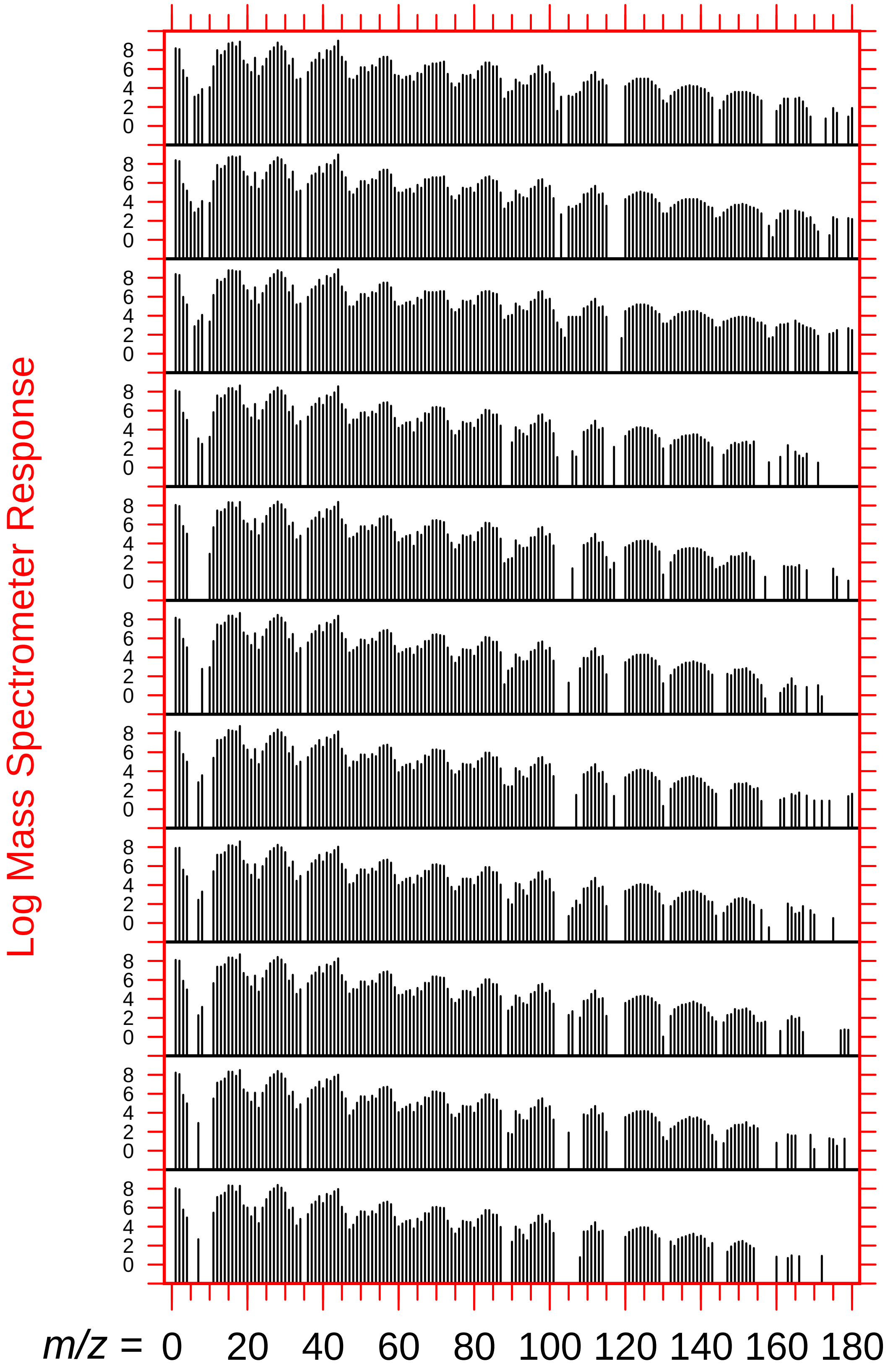


Figure 16: Oil Spectra

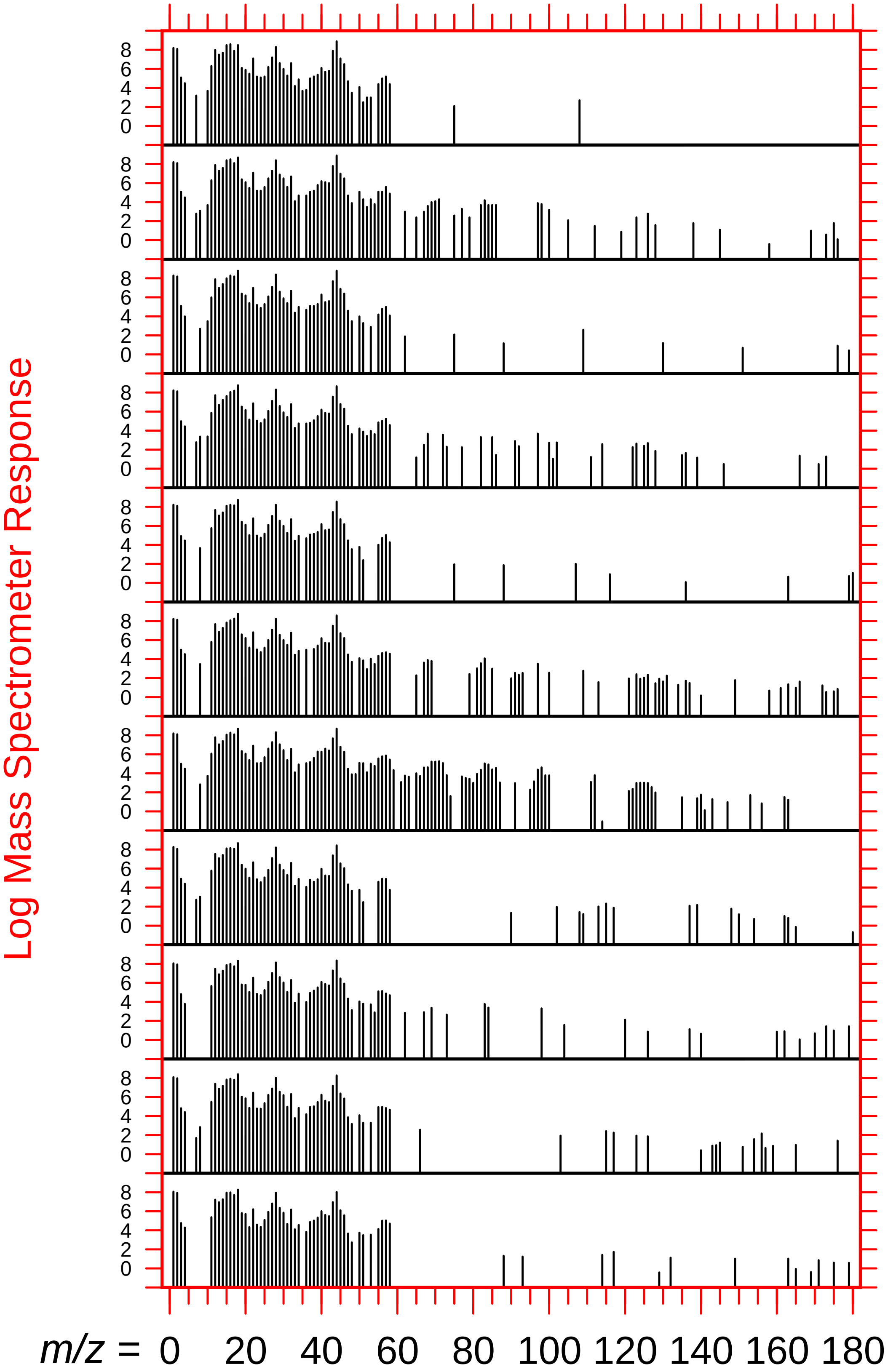


Figure 17: Frac Sand Spectra

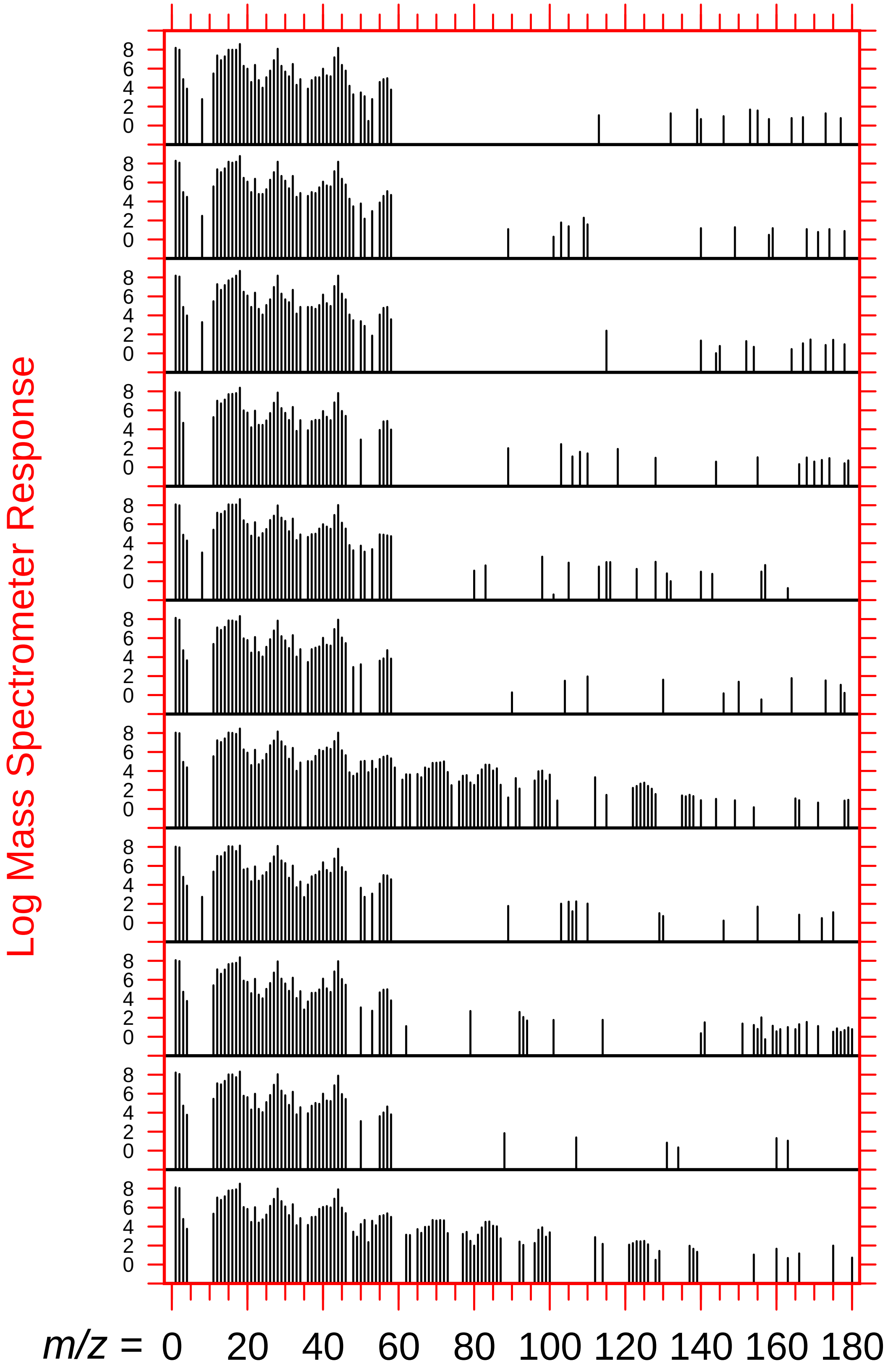


Figure 18: Frac Sand Spectra

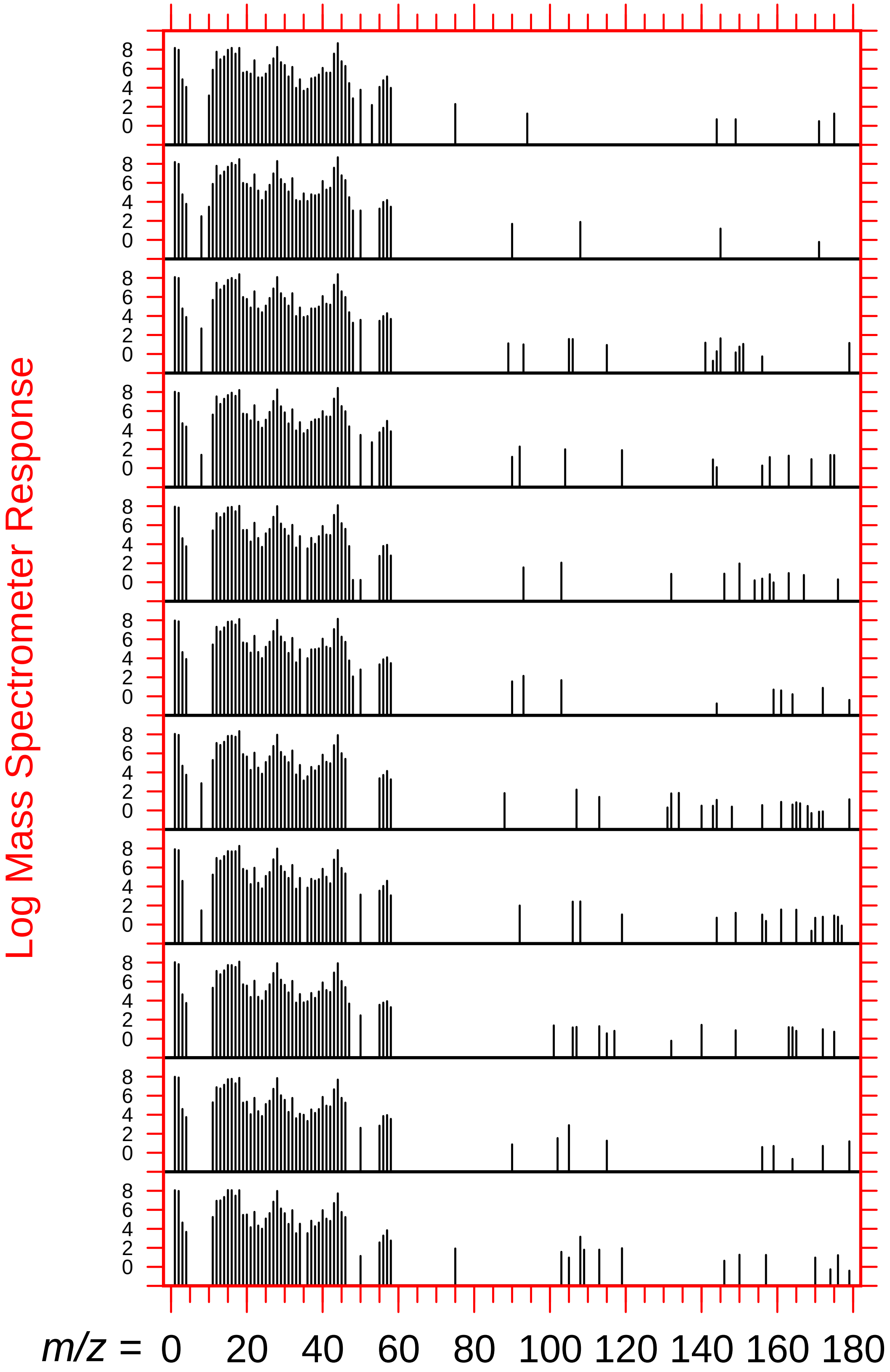


Figure 19: Cooked Frac Sand Spectra

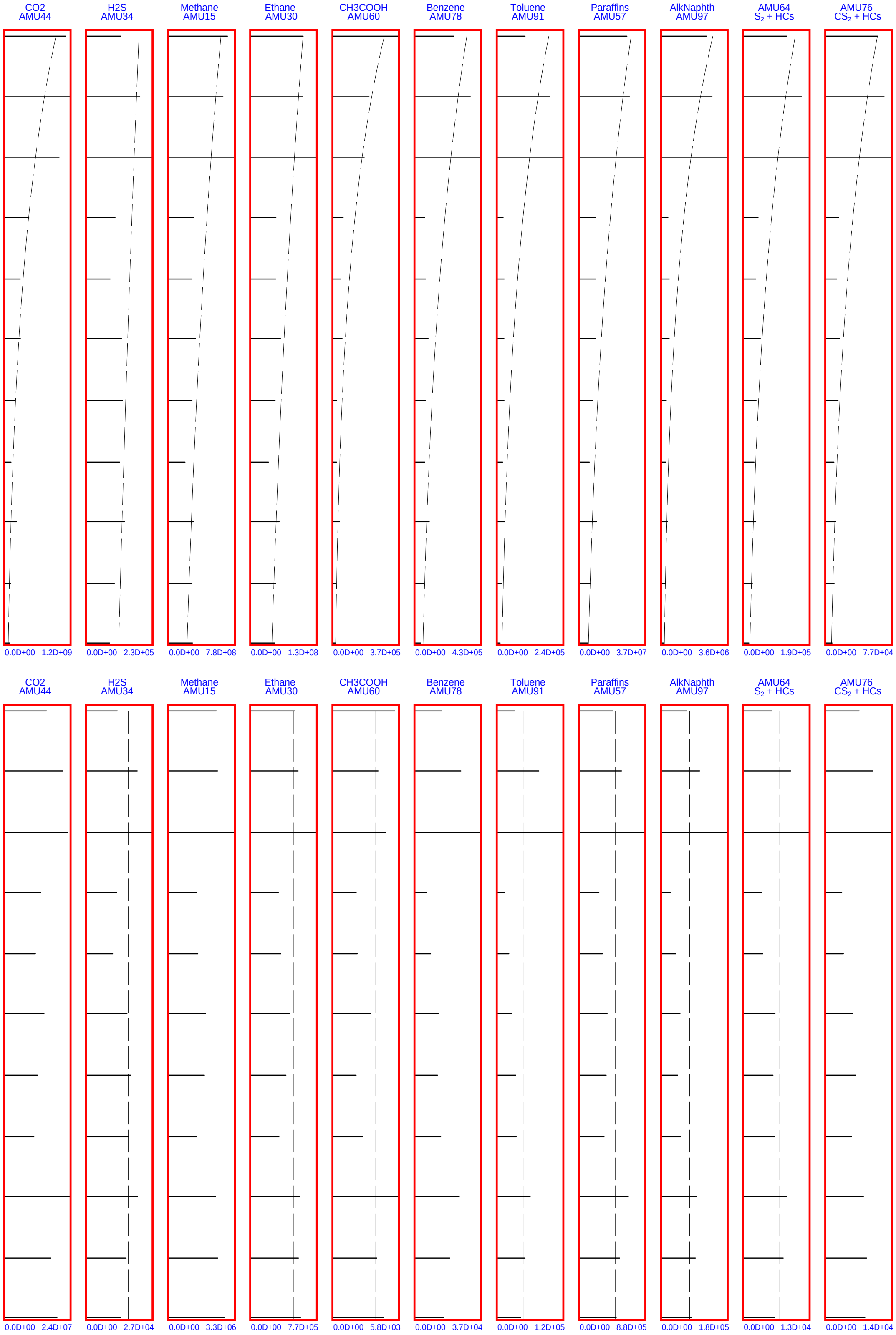
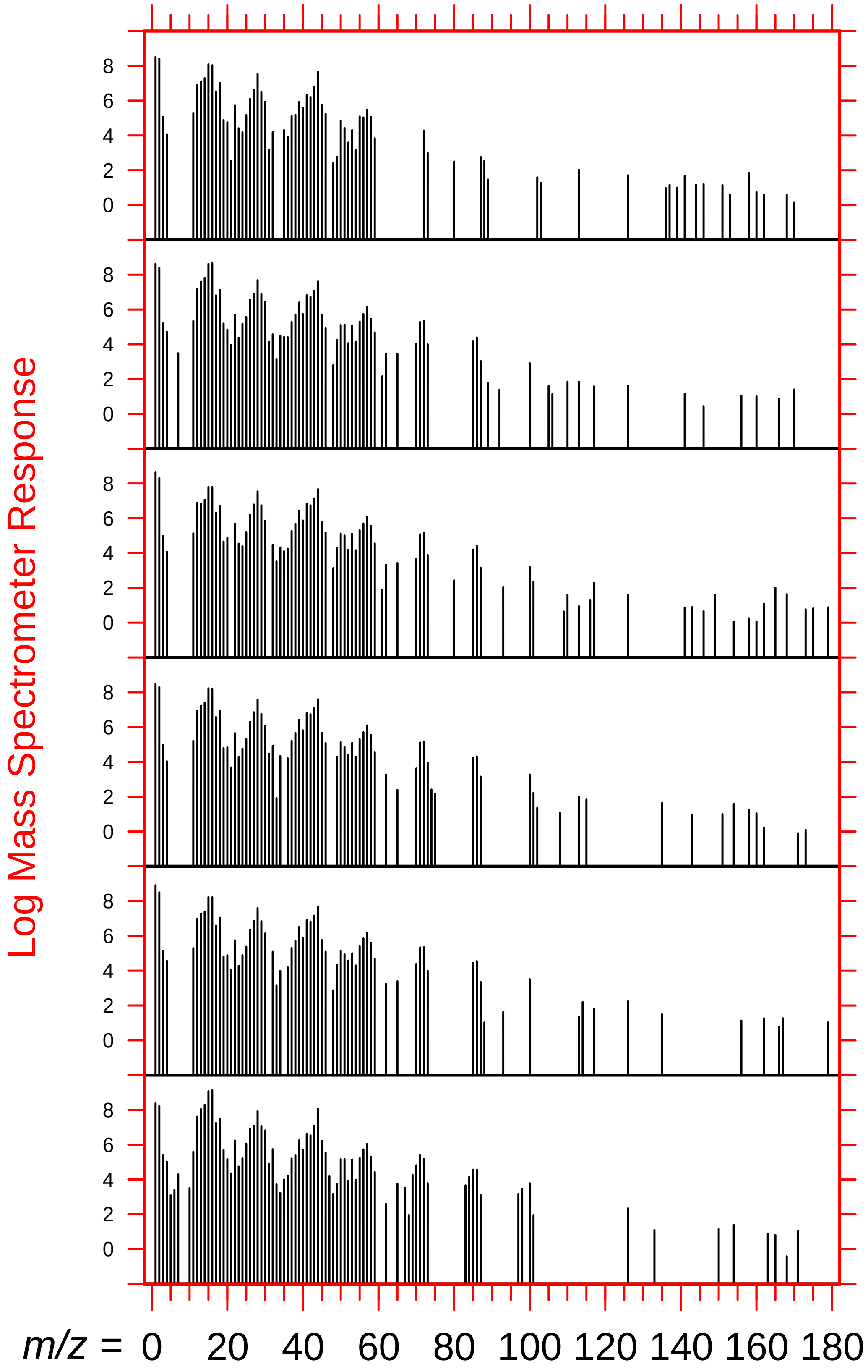
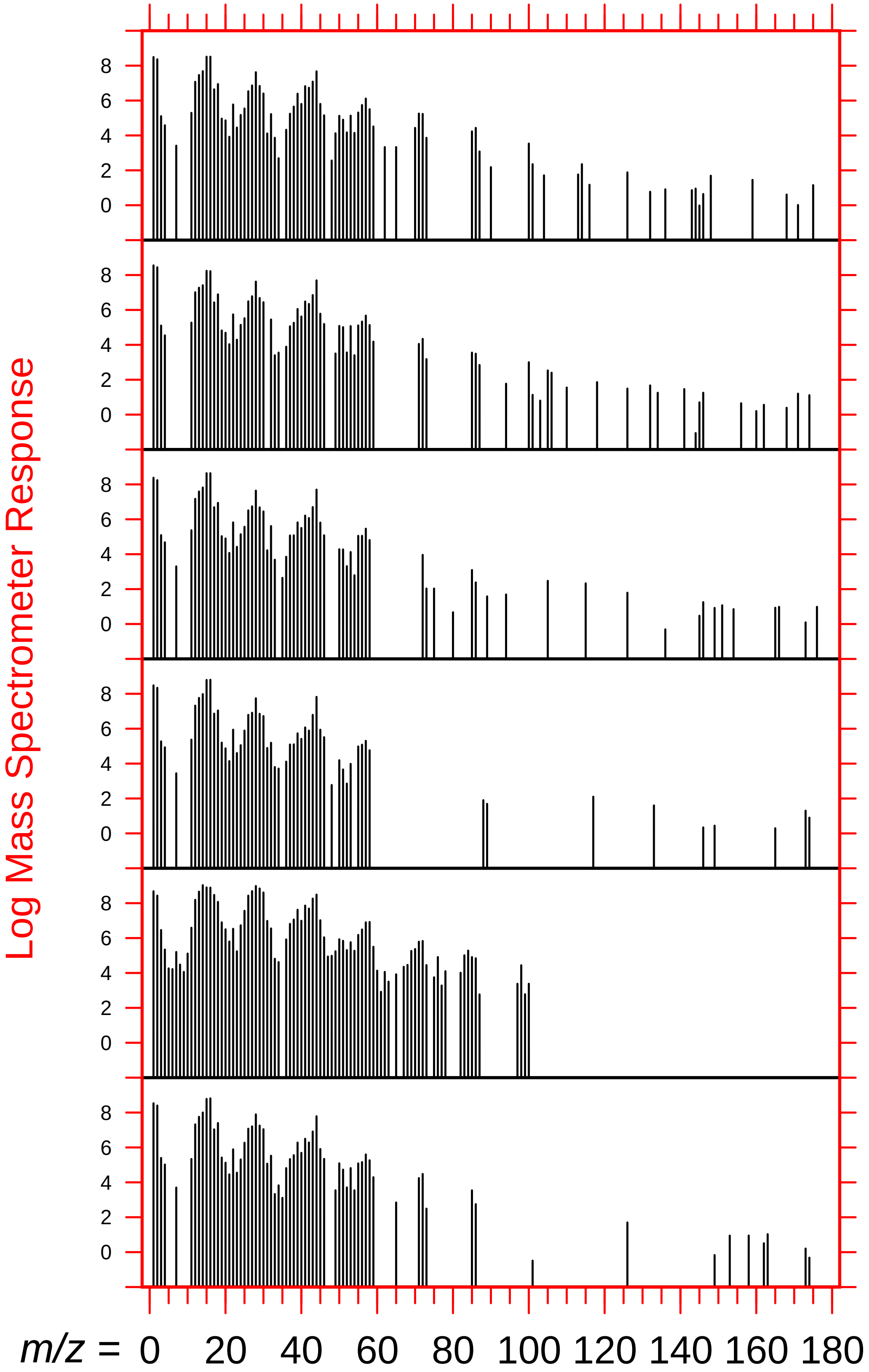


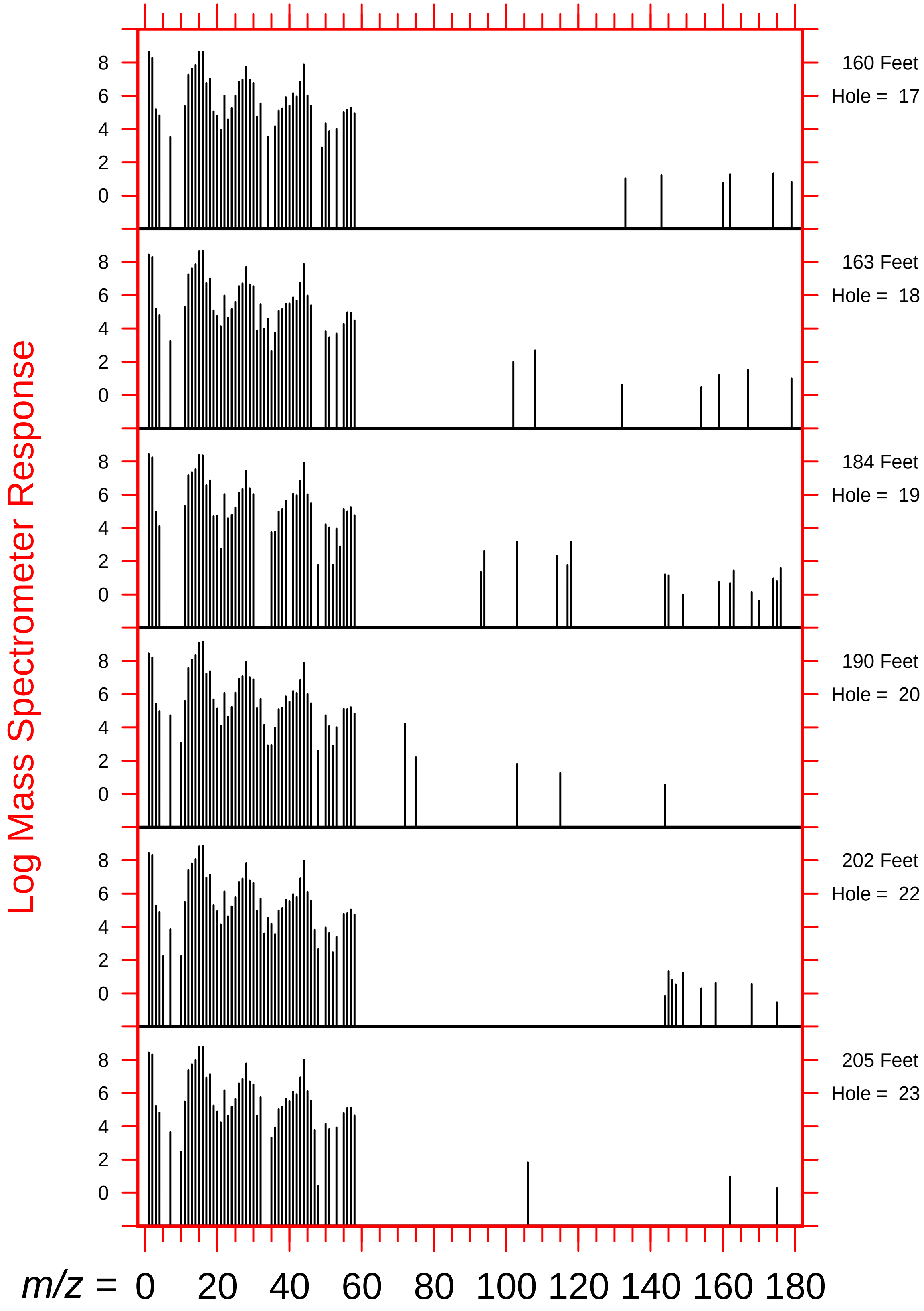
Figure 20: Kindblade Oil Standards Before (top) and After (bottom) Correction

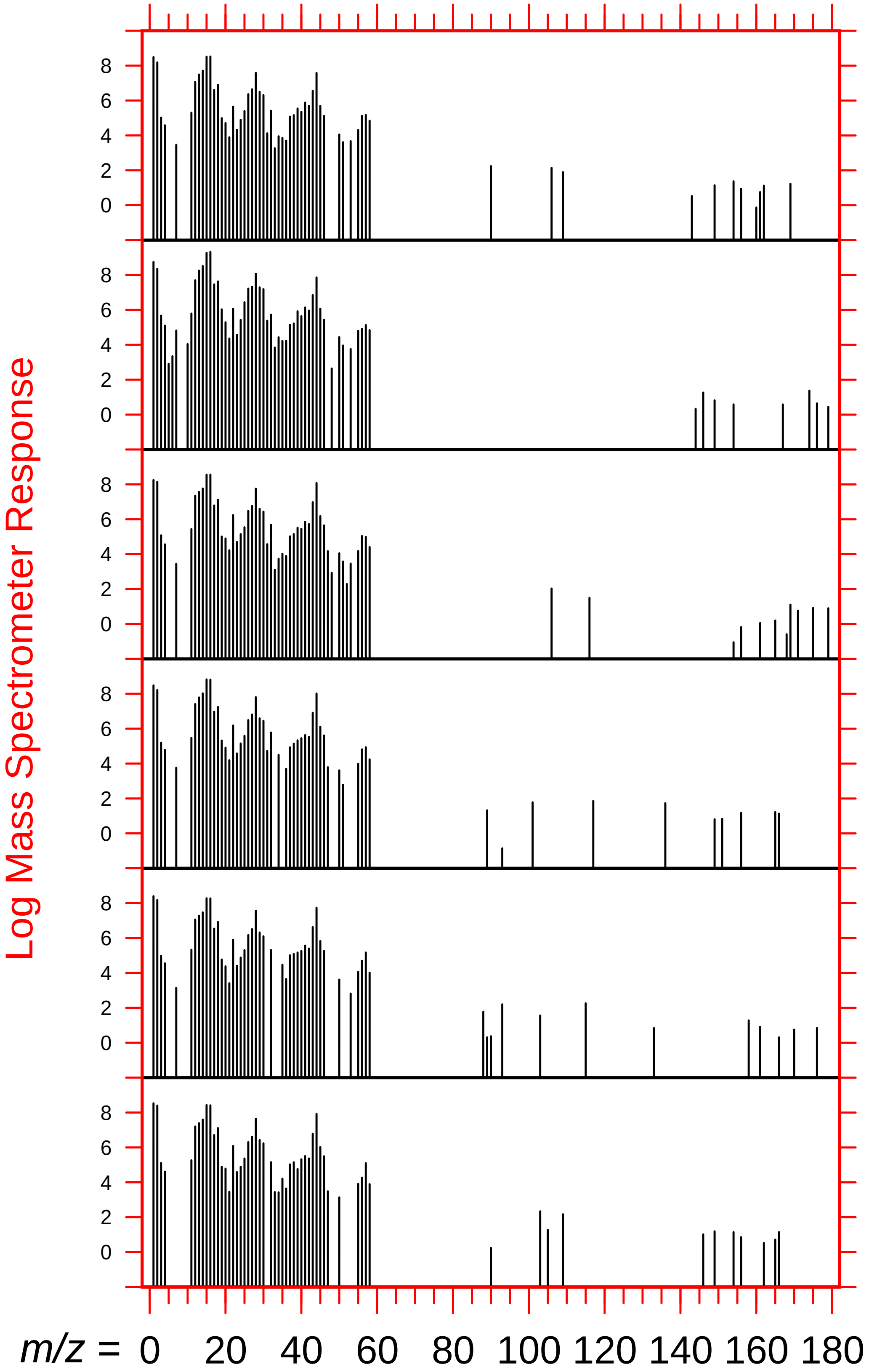
C Individual Spectra

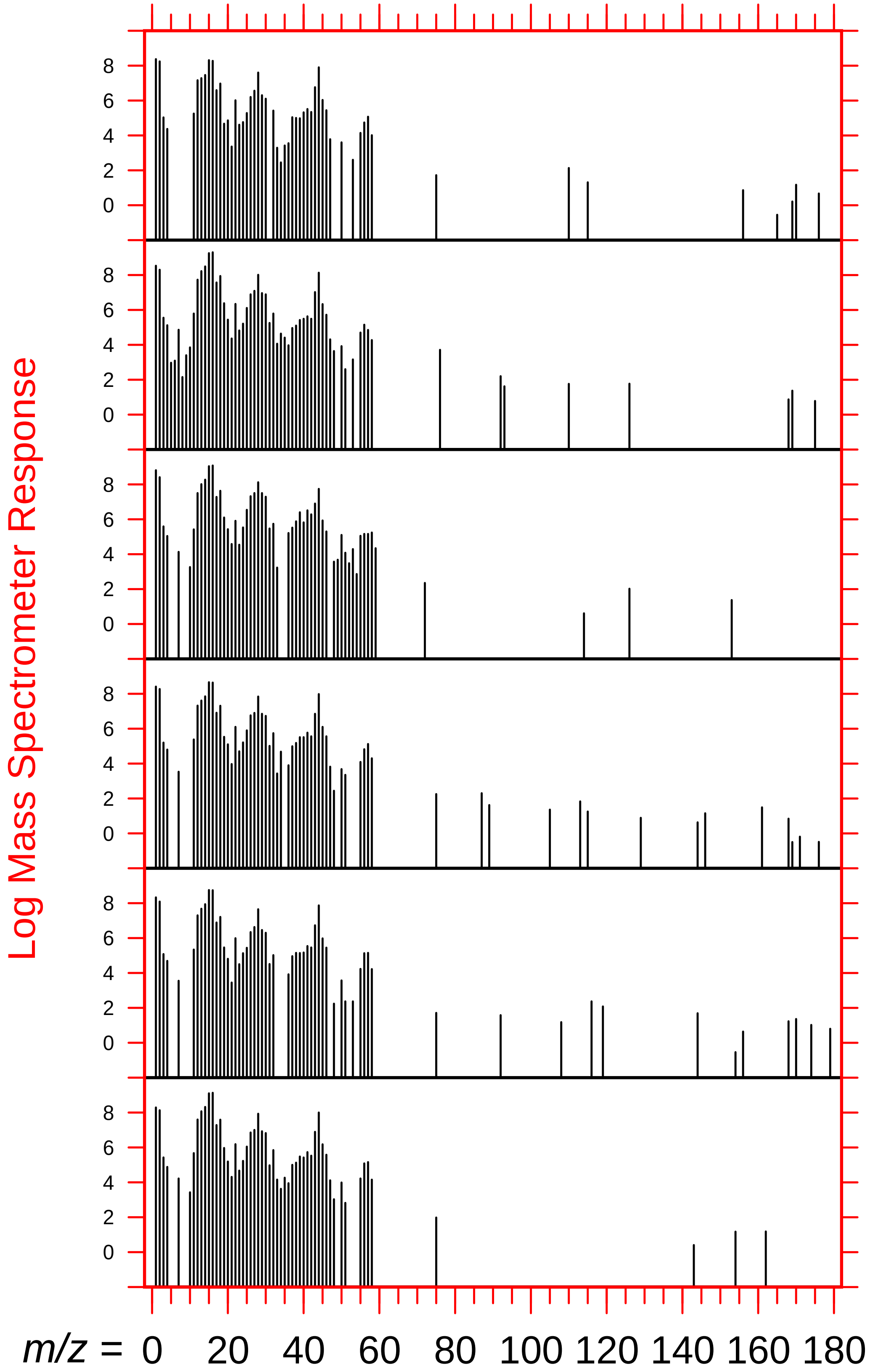
Individual spectra for each sample from SO-C-1-81 are shown on the following pages. Each spectrum is indexed according to depth and indicates the log of the millivolt response for atomic mass units (AMU, m/z) from $2 \leq m/z \leq 180$.

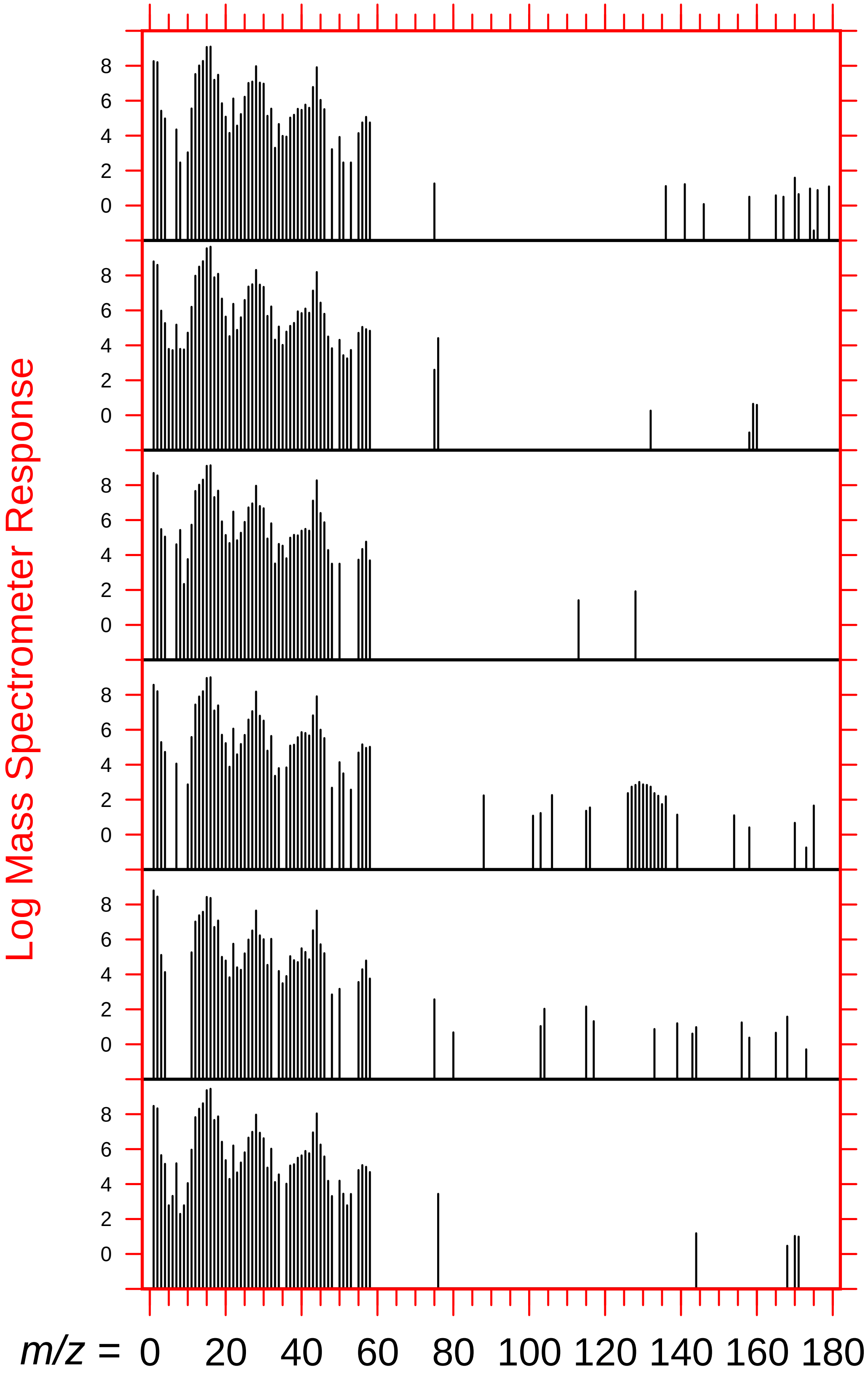

Log Mass Spectrometer Response
8
6
4
2
0
48 Feet
Hole = 2
59 Feet
Hole = 3
61 Feet
Hole = 4
71 Feet
Hole = 5
88 Feet
Hole = 7
97 Feet
Hole = 8
m/z = 0 20 40 60 80 100 120 140 160 180

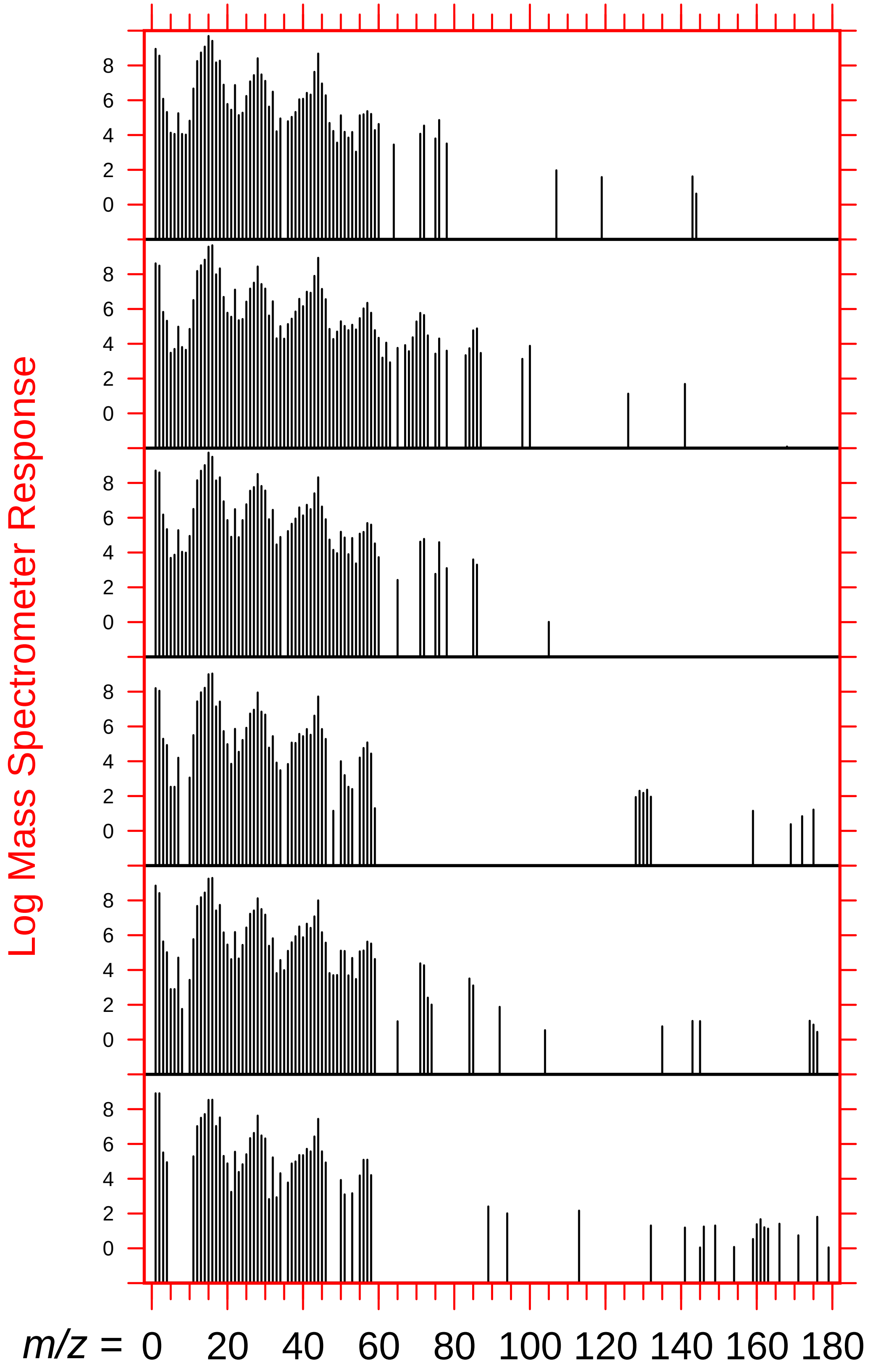

Log Mass Spectrometer Response
8
6
4
2
0
106 Feet
Hole = 9
108 Feet
Hole = 10
121 Feet
Hole = 12
137 Feet
Hole = 13
143 Feet
Hole = 14
153 Feet
Hole = 15
m/z = 0 20 40 60 80 100 120 140 160 180

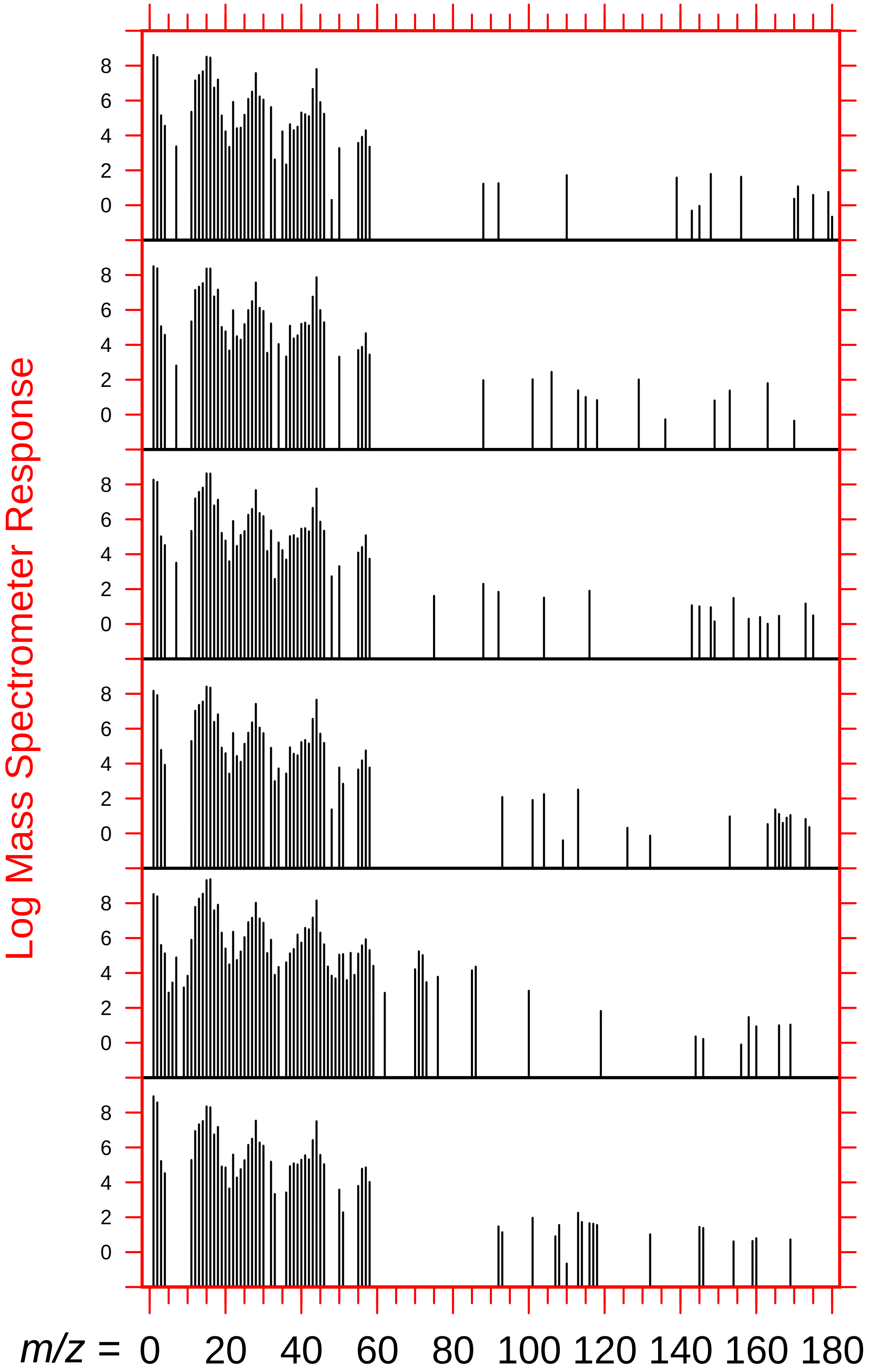

Log Mass Spectrometer Response
8
6
4
2
0
160 Feet
Hole = 17
163 Feet
Hole = 18
184 Feet
Hole = 19
190 Feet
Hole = 20
202 Feet
Hole = 22
205 Feet
Hole = 23
m/z = 0 20 40 60 80 100 120 140 160 180

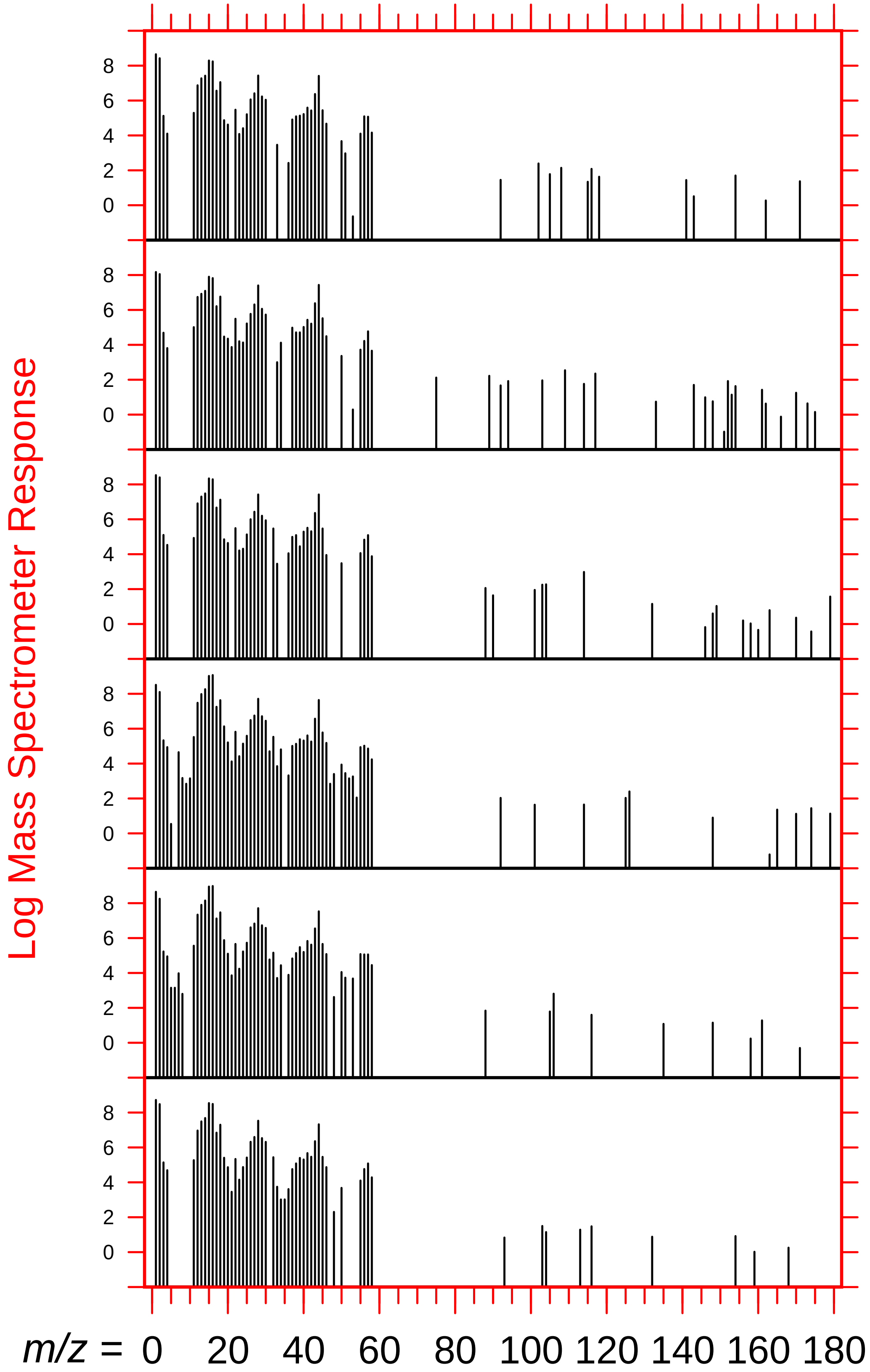

Log Mass Spectrometer Response
8
6
4
2
0
213 Feet
Hole = 24
224 Feet
Hole = 25
235 Feet
Hole = 27
251 Feet
Hole = 28
259 Feet
Hole = 29
264 Feet
Hole = 30
m/z = 0 20 40 60 80 100 120 140 160 180

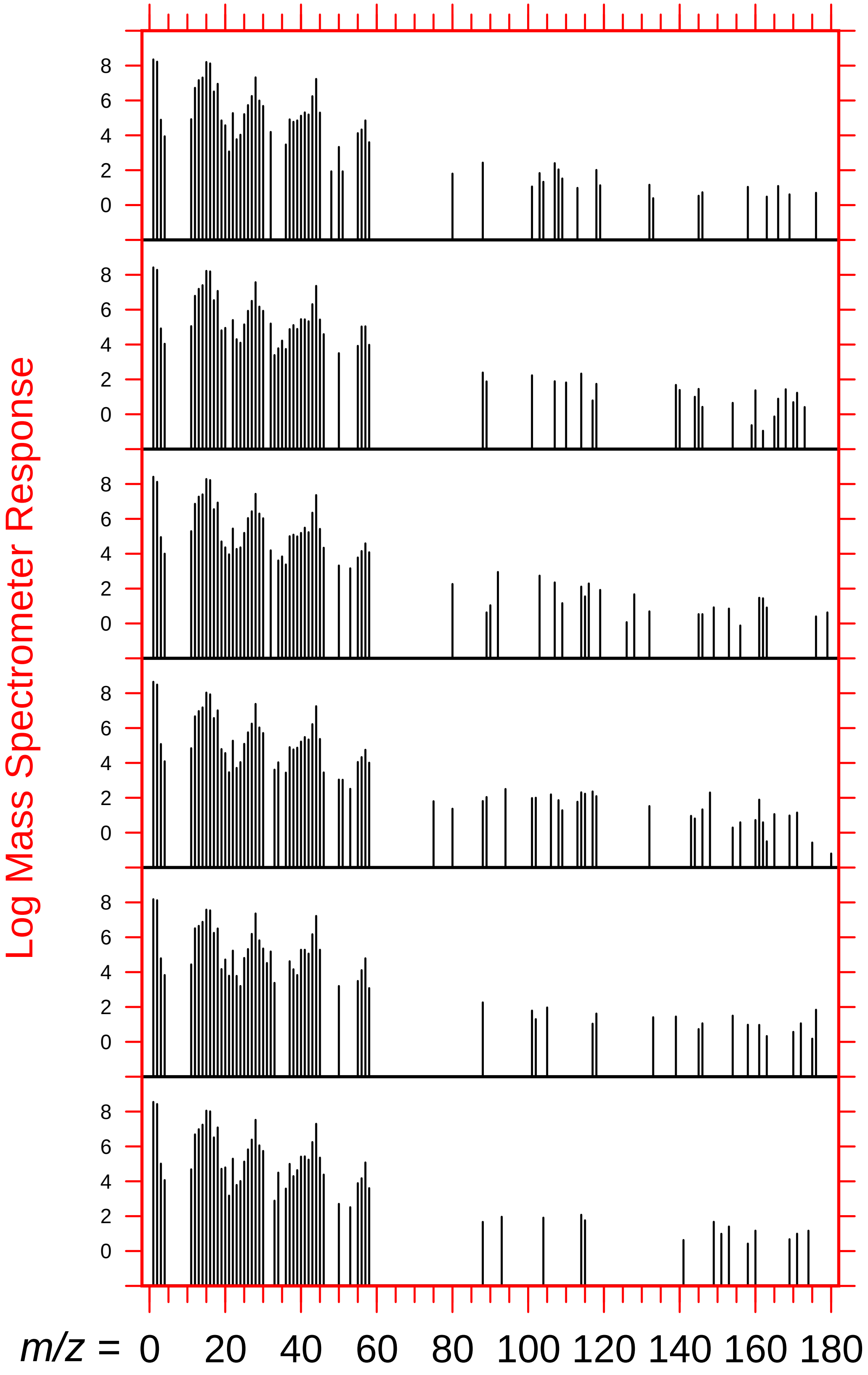

Log Mass Spectrometer Response
8
6
4
2
0
278 Feet
Hole = 31
286 Feet
Hole = 32
294 Feet
Hole = 34
306 Feet
Hole = 35
317 Feet
Hole = 36
325 Feet
Hole = 37
m/z = 0 20 40 60 80 100 120 140 160 180


Log Mass Spectrometer Response
8
6
4
2
0
335 Feet
Hole = 38
347 Feet
Hole = 39
352 Feet
Hole = 41
363 Feet
Hole = 42
368 Feet
Hole = 43
383 Feet
Hole = 44
m/z = 0 20 40 60 80 100 120 140 160 180

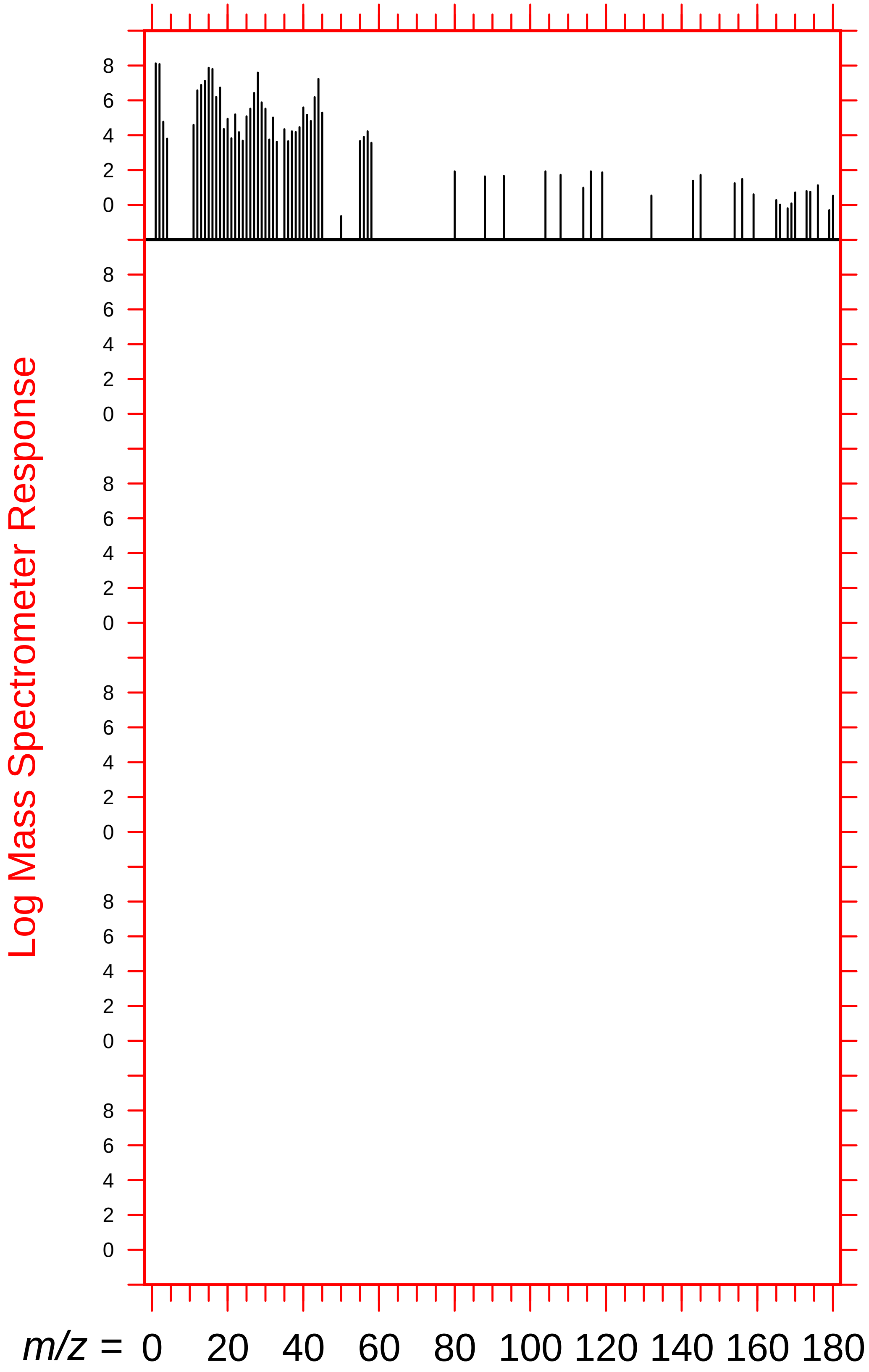

Log Mass Spectrometer Response
8
6
4
2
0
391 Feet
Hole = 45
406 Feet
Hole = 46
412 Feet
Hole = 48
425 Feet
Hole = 49
430 Feet
Hole = 50
440 Feet
Hole = 51
m/z = 0 20 40 60 80 100 120 140 160 180


Log Mass Spectrometer Response
8
6
4
2
0
455 Feet
Hole = 52
456 Feet
Hole = 53
468 Feet
Hole = 55
480 Feet
Hole = 56
492 Feet
Hole = 57
502 Feet
Hole = 58
m/z = 0 20 40 60 80 100 120 140 160 180


Log Mass Spectrometer Response
8
6
4
2
0
509 Feet
Hole = 59
518 Feet
Hole = 60
526 Feet
Hole = 62
541 Feet
Hole = 63
550 Feet
Hole = 64
558 Feet
Hole = 65
m/z = 0 20 40 60 80 100 120 140 160 180



Log Mass Spectrometer Response
8
6
4
2
0
570 Feet
Hole = 66
577 Feet
Hole = 67
588 Feet
Hole = 68
595 Feet
Hole = 70
609 Feet
Hole = 71
615 Feet
Hole = 72
m/z = 0 20 40 60 80 100 120 140 160 180


626 Feet
Hole = 73
Log Mass Spectrometer Response
8
6
4
2
0
m/z = 0 20 40 60 80 100 120 140 160 180

Appendix 2

“A stratigraphic reconstruction of bulk volatile chemistry from fluid inclusions in: SO-C-02-81,” Fluid Inclusion Technologies, Inc. report FIS# FI160559c prepared August 4, 2016 for the North Carolina Geological Survey, 88p.

UWI# 999999999999
FIS# FI160559c

A Schlumberger Company

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

SO-C-2-81

Prepared August 4, 2016 for

NC Geological Survey

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Data Reduction: FITsolve-6 http://www.fittulsa.com

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

SO-C-2-81

Prepared August 4, 2016
by
FIT
A Schlumberger Company

FIT
A Schlumberger Company

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Executive Summary for well: SO-C-2-81

1 FIS Summary for SO-C-2-81

SO-C-2-81 is a shallow legacy core hole drilled in the Dan River Basin in 1981. Petroliferous odors were noted in core samples at 198 ft, 210 ft, 332-338 ft, and 344 ft. Possible coal was observed at 340-342 ft. Organic lenses were recorded at 550 ft and 669 ft. Cores from 563 ft and 565-568 ft are organic-rich. At 702-703 ft and 721 ft high angle fractures filled with dark minerals and another set filled with light-colored minerals were observed in the cores. FIS analysis was performed on a total of 78 core samples from 53-806 ft. This study was performed in conjunction with three other wells (SO-C-1-81 in report FI160559a; RC-C-1-81 in report FI160559e; SO-C-1-15 and 1A-15 in report FI160559g). The primary goals of the analysis were to use FIS to determine gas chemistry and hydrocarbon potential. The areas of particular interest are the Walnut Cove Formation and overlying Dry Fork Formation.

The section above 288 ft (Walnut Cove Formation) shows dry gas FIS responses with a single wet gas spectrum at 86 ft. Methane concentrations are elevated at 82-86 ft and 183 ft. CS2 of probable thermal (thermochemical sulfate reduction) origin is noted at 82-86 ft and 183 ft. SO2 +/- S2 is identified at 86 ft. H2S is slightly elevated above 121 ft. Helium concentrations increase slightly at 86 ft, along with CO2. Helium can indicate an ancient fraction of arkosic detritus, a deep sourced component of hydrocarbon gas, or diagenetic involvement of deep basin brines (or influx of gas that extracted helium from these brines). Maximum concentrations with respect to methane are fairly low, however, at about 100 ppm. No thin sections were prepared from this interval.

FIS data from the interval at 293-548 ft (Walnut Cove Formation) display dry gas responses with a few isolated wet gas signals at 404 ft, 499 ft, and 548 ft. Stronger methane or liquid hydrocarbon concentrations are documented at 293 ft, 404 ft, 499 ft, 534 ft, and 548 ft. CS2 of probable thermal origin is identified at 293 ft, 404 ft, 499 ft, and 534 ft, and sulfur species in general (including H2S and SO2) are intermittently anomalous at 404-630 ft (e.g., into the underlying basal section described below). Higher helium signals are detected broadly below 293 ft, but generally at less than 100 ppm with respect to methane.

Three thin sections were examined from the interval described above. Samples from 404 ft and 499 ft contain common occurrences of white or blue-fluorescent, high gravity, gas-rich gas-condensate to wet gas inclusions in sandstone. Common, non-fluorescent, dry gas inclusions are present as well. High inclusion abundance suggests the possibility that this zone contained elevated wet gas saturation at some time. Trace yellow fluorescing inclusions were also identified in sandstone or carbonate at 404 ft and 499 ft. The remaining thin section at 548 ft contains only rare, visible white-fluorescent high gravity wet gas inclusions in sandstone, potentially suggesting lower saturation or paleo-saturation. Shale contains trace gas-prone kerogen; hence, most hydrocarbons are interpreted to be migrated.

Most inclusions in the above section occur in what appear to be relatively late, compactional or tectonic-related microfractures. The presence of epidote (with chlorite) as a greenschist-grade metamorphic mineral in some samples (e.g., 499 ft and 548 ft) appears to indicate maximum burial temperatures of at least 250°C, potentially significantly higher (e.g., above 300°C). This would imply conditions that do not allow preservation of liquid hydrocarbons, even as trace condensate. It is possible that observed fluids in the fluid inclusion record were introduced during uplift from a less mature source rock (they appear to be clearly migrated in any case). Collection of entrapment temperature data from aqueous fluid inclusions that coexist with petroleum inclusions may provide constraints on conditions attending hydrocarbon migration to help address this issue (e.g., when compared to in situ maturities). Likewise, extraction and analysis of gas and liquid fractions of fluid inclusions via GC-CSIA and GC-MS-MS analysis, respectively, may help determine the maturity and source of the encapsulated fluids and allow quantification of diamondoids, which are not as susceptible to degradation during maturation.

The basal section at 563-806 ft (Pine Hall Formation) gives mostly dry gas FIS responses. Rare, isolated wet gas spectra were recorded at 618 ft and 692 ft. Decoupled, trace liquid-range species are noted at 600-618 ft and 692-710 ft, potentially indicating indications of a multi-stage charge history. A higher helium response is noted at 613 ft, and in this case is significant with respect to methane at about 0.16% (1600 ppm). No visible hydrocarbon inclusions were identified in a thin section prepared from 721 ft (organic lean shale).

2 FIS Chemical Zonation

53 ft to 288 ft :

Dry gas: 93%

Wet gas: 2%

Low hydrocarbon responses: 4%

Hydrocarbon species to C6 are preserved in this section. No proximity to pay signal is preserved. Sulfur species are intermittently found.

293 ft to 548 ft :

Dry gas: 88%

Wet gas: 12%

Hydrocarbon species to C7 are recorded in this interval. No proximity to pay signal is preserved. Sulfur species are intermittently documented.

Slide @ 404 ft: Population 1: Common, high gravity petroleum inclusions are observed. Population 2: Rare, high gravity petroleum inclusions are indicated. Population 3: Common, indeterminate gravity petroleum inclusions are found. High petroleum saturation or paleo saturation is indicated by inclusion abundance. Rare occurrences of gas prone kerogen are indicated.

Slide @ 499 ft: Population 1: Common, high gravity petroleum inclusions are indicated. Population 2: Rare, high gravity petroleum inclusions are found. Population 3: Common, indeterminate gravity petroleum inclusions are documented. High petroleum saturation or paleo saturation is indicated by inclusion abundance. Rare occurrences of gas prone kerogen are recorded.

Slide @ 548 ft: Population 1: Rare, high gravity petroleum inclusions are found. Rare occurrences of gas prone kerogen are preserved.

563 ft to 806 ft :

Dry gas: 71%

Wet gas: 7%

Low hydrocarbon responses: 21%

Hydrocarbon species to C5 are recorded in this interval. No proximity to pay signal is indicated. Sulfur species are not found.

Slide @ 721 ft: Rare occurrences of gas prone kerogen are observed.

Summary of Results for well: SO-C-2-81

This report contains Fluid Inclusion Stratigraphy and Fluid Inclusion Petrography results for SO-C-2-81 and was prepared for NC Geological Survey by *Fluid Inclusion Technologies, 2217 N. Yellowood Ave., Broken Arrow, OK 74133; ph: (918) 461-8984; fax: (918) 461-2085; www.fittulsa.com.*

Table I: Logistical Information

Client:	**NC Geological Survey**	Analyzed Depth:	**53 - 806 Feet**
Well:	**SO-C-2-81**	Sample Spacing:	**See Individual Spectra**
		Sample Total:	**78**

Table II: Fluid Inclusion Petrography from SO-C-2-81

Well Name: SO-C-2-81																					
Sample Depth	**Rock Type**		**Petroleum Fluid Inclusion Populations**												**Kerogen (possible source rk)**					**Bitumen**	
			Population 1				**Population 2**				**Population 3**										
***Units:* (Feet)**	***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***
404	ss,tr cc,sh		wt	h	dq	c	yl	h	cc	r	no		dq	c	sh	gp		r			
499	ss,tr cb,sh		bl	h	dq	c	yl	h	dq	r	no		dq	c	sh	gp		r			
548	ss,tr sh		wt	h	dq	r									sh	gp		r			
721	sh,tr ss														sh	gp		r			

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:
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	
NHC	non-hydrocarbon	**MP**	migration pathway	**OWC**	oil-water contact
DG	dry gas	**PC**	present day ptrlm column	**GWC**	gas-water contact
WG	wet gas	**PPC**	paleo-ptrlm column	**GOC**	gas-oil contact
GC	gas condensate	**RI**	recycled ptrlm inclusions	**POWC**	paleo-oil-water contact
VO	volatile oil	**SR**	source rock	**PGWC**	paleo-gas-water contact
O	oil	**GP**	gas prone kerogen	**PGOC**	paleo-gas-oil contact
BD	biodegraded	**OP**	oil prone kerogen		
TA	thermally altered	**OGP**	oil and gas prone kerogen		
		CNT	contamination		

Water-Soluble Anomalies		Miscellaneous	
WS	undifferentiated water-soluble anomaly	**SL**	seal
WSSR	source rock related water-soluble anomaly	**MS**	microseep
WSTA	water-soluble anomaly sourced from thermal alteration		
PTPL	proximity to oil or gas-condensate		
PTPG	proximity to gas		

Petrographic Observations					
A	abundant	**IG**	igneous rock	**SA**	salt
AN	anhydite	**L**	low	**SH**	shale
BL	blue	**LG**	large	**SI**	siltstone
BR	brown	**M**	moderate	**SM**	small
C	common	**MD**	medium	**SS**	sandstone
CB	carbonate	**MT**	metamorphic rock	**ST**	petroleum stain
CC	carbonate cement	**NO**	none	**SV**	several
CH	chert	**OR**	orange	**UL**	upper-low
CM	matrix carbonate	**PB**	pyrobitumen	**UM**	upper-moderate
CO	coal	**PF**	pore filling bitumen	**V**	variable
DF	detrital feldspar	**PR**	pore rimming bitumen	**W**	weak
DQ	detrital quartz	**QC**	quartz cement	**WT**	white
DR	quartz dust rim	**R**	rare	**XA**	extremely abundant
H	high	**S**	strong	**YL**	yellow

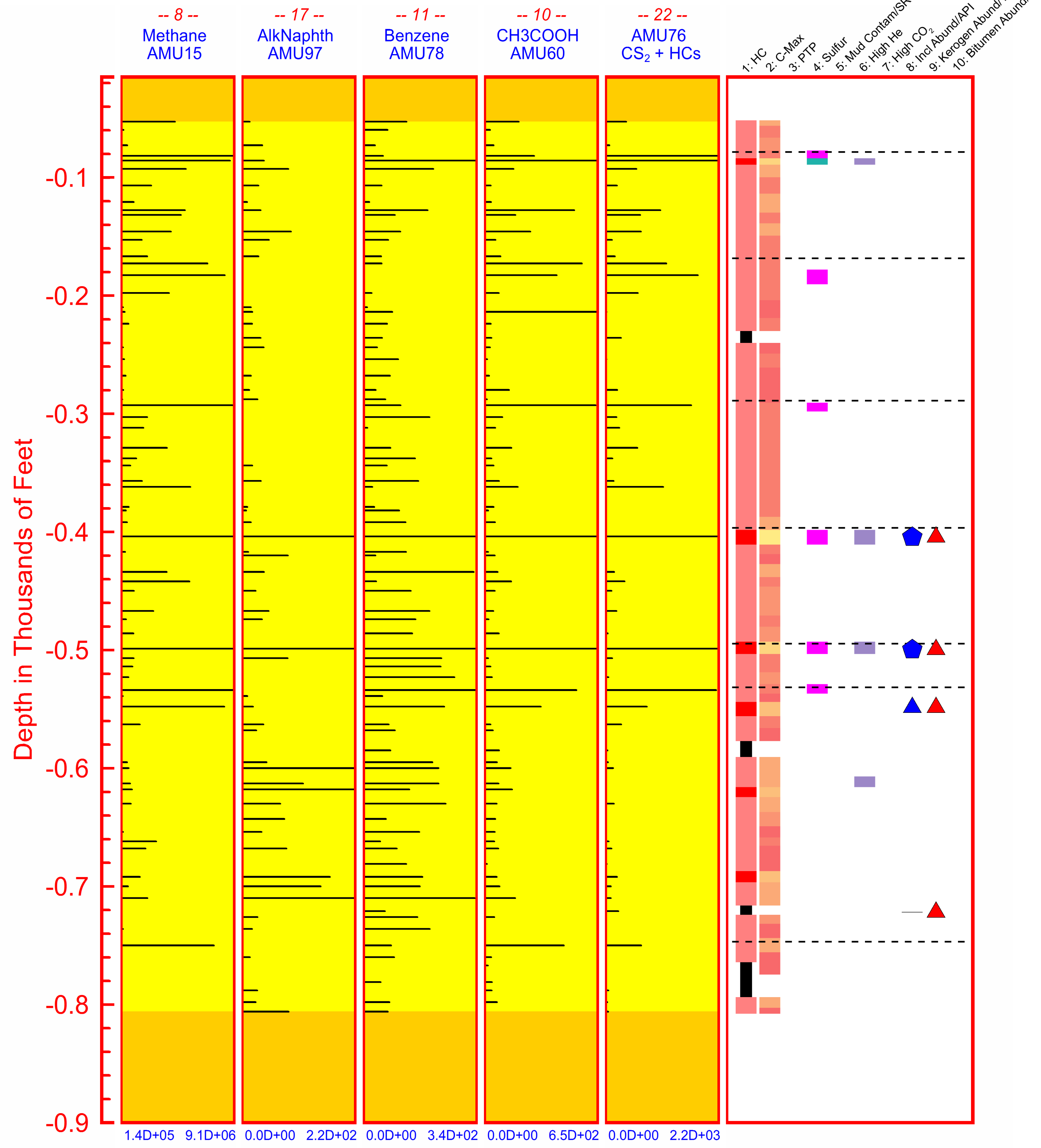


Figure 1: FIS Summary Tracks (see Sect. A for further explanation)

1: HC			2: C-Max							3: PTP	4: Sulfur	5: MC/SR	6 & 7: He/CO$_2$
■ NH	■ WG	■ GC-Oil	■ C_1	■ C_3	■ C_5	■ C_7	■ C_9	■ C_{11}	■ C_{13}	■ Gas	■ Sulfur	■ Mud Contam	■ 6: High He
■ DG	■ WG-GC		■ C_2	■ C_4	■ C_6	■ C_8	■ C_{10}	■ C_{12}		■ Liquid	■ S2-SO2	■ Source Rock	■ 7: High CO$_2$

Legend (cont)

8: Colors for Inclusion Abundance/API describe the API gravity of the liquid hydrocarbon inclusions:

- ▲ **Triangle:** Rare abundance **Brown:** Low Gravity
- ■ **Square:** Several abundance **Orange:** Upper Low gravity
- ⬟ **Pentagon:** Common abundance **Yellow:** Moderate gravity
- ⬢ **Hexagon:** Abundant **Light blue:** Upper Moderate gravity
- ● **Circle:** Extra Abundant **Blue:** High gravity

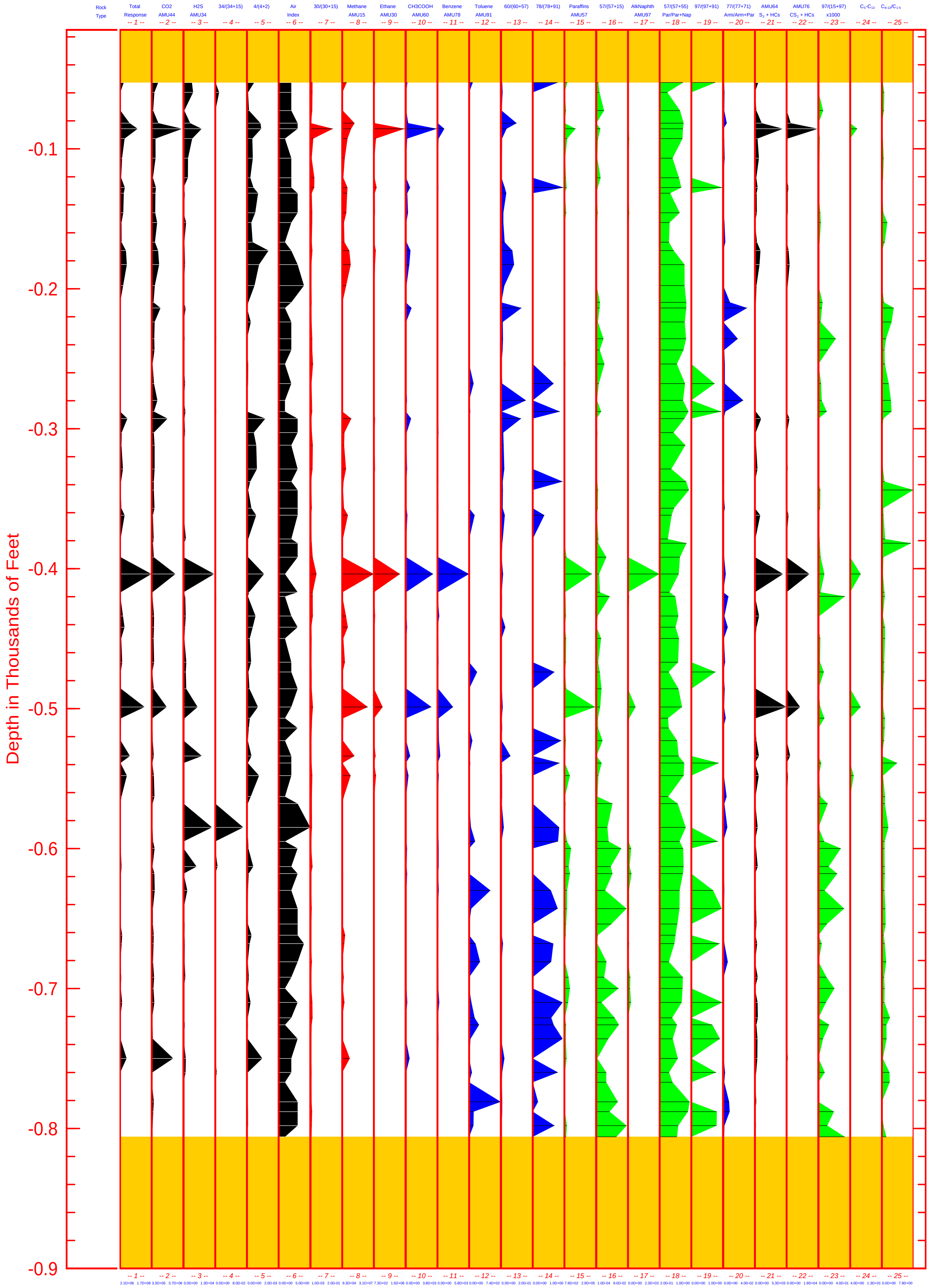
9: Colors for Kerogen indicate if the kerogen are oil prone, gas prone, or both

- ▲ **Triangle:** Rare kerogen abundance **Red:** Gas prone
- ■ **Square:** Several abundance **Orange:** Both oil and gas
- ⬟ **Pentagon:** Common kerogen abundance **Green:** Oil prone
- ⬢ **Hexagon:** Abundant **Red:** Gas prone
- ● **Circle:** Extra Abundant kerogen **Orange:** Both oil and gas

10: Colors for Bitumen indicate the bitumen type:

- ▲ **Triangle:** Rare bitumen abundance **Green:** Live stain
- ■ **Square:** Several bitumen **Gray:** Dead stain
- ⬟ **Pentagon:** Common kerogen abundance **Green:** Live stain
- ⬢ **Hexagon:** Abundant bitumen **Black:** Pore occluding
- ● **Circle:** Extra Abundant bitumen **Magenta:** Pyrobitumen

SO-C-2-81 : All FIS Data

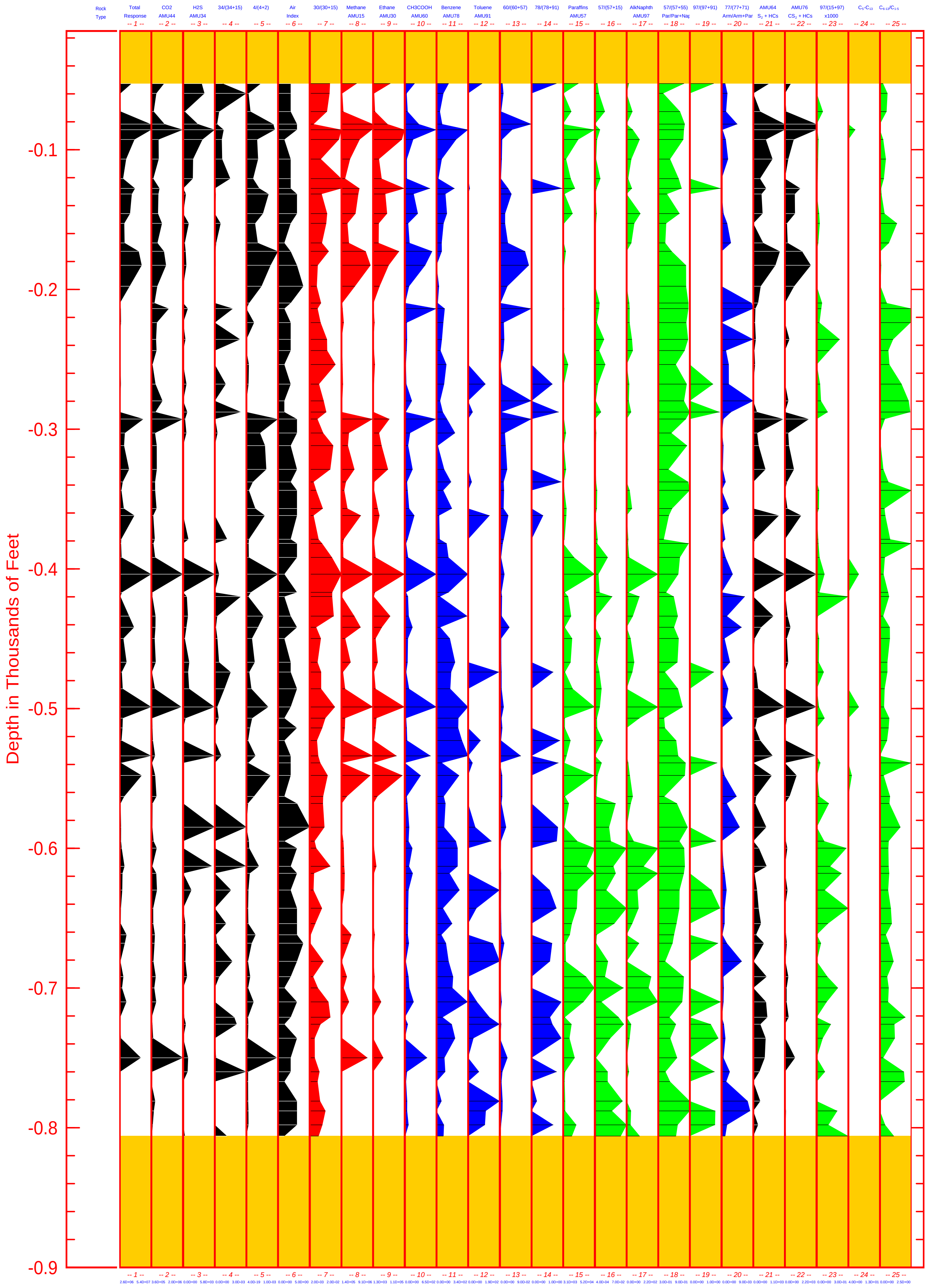


Fluid Inclusion Technologies, Inc.
http://www.fittulsa.com

A Schlumberger Company

UWI# 999999999999
FIS# *FI*160559*c*

SO-C-2-81 : 90% of all FIS Data



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3 Overview of FIT, Inc. and Fluid Inclusion Stratigraphy

FIT, a Schlumberger Company, is a laboratory-based petroleum service organization established in 1997 and acquired by Schlumberger in November, 2015, 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 FIT 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 Compartmentallization** 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".

3.1 General Logistics of Initiating an FIS Analysis

To Initiate an FIS Analysis: contact FIT[1] 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 FIT for sample preparation including any necessary crushing/sieving, subsampling and washing.

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), 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

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[1] FIT Inc., a Schlumberger Company affiliate, 2217 N. Yellowood Ave., Broken Arrow, 74012, USA., phone (918) 461-8984

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 SO-C-2-81 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. FI160559c-1.las – LAS-format, 26-column file containing recorded depth and Tracks 1-25 from the *FIT Analysis* of SO-C-2-81
2. FI160559c-2.las – LAS-format, 181-column file containing recorded depth and background corrected, normalized, standardized individual mass spectra (m/z 2-180) from the *FIT Analysis* of SO-C-2-81
3. FI160559c-s.pdf – PDF format, electronic file of the summary tracks from the *FIT Analysis* of SO-C-2-81
4. FI160559c-t.pdf – PDF format, electronic file of the petrography table from the *FIT Analysis* of SO-C-2-81
5. FI160559c-1.pdf – PDF format, electronic file of the final report (entire document) of the *FIT Analysis* of SO-C-2-81

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 (H_2^+)
4	helium ($^4He^+$)
15	C_1 fragment (CH_3^+); largely methane
30	C_2 fragment ($C_2H_6^+$); largely ethane
34	hydrogen sulfide (H_2S^+)
44	dominantly carbon dioxide (CO_2^+); possible C_3 fragment overlap
55	contribution from C_4 and greater naphthenes
57	contribution from C_4 and greater paraffins
60	dominantly acetic acid (CH_3COOH^+); possible dominance by carbonyl sulfide (COS^+) in some cases
64	S_2 or SO_2 plus hydrocarbons
71	contribution from C_5 and greater paraffins
76	CS_2 plus hydrocarbons
77	contribution from aromatic species
78	benzene ($C_6H_6^+$) with possible contribution by carbon disulfide (CS_2^+)
91	toluene ($C_7H_7^+$)
97	C_7 alkylated naphthene fragment

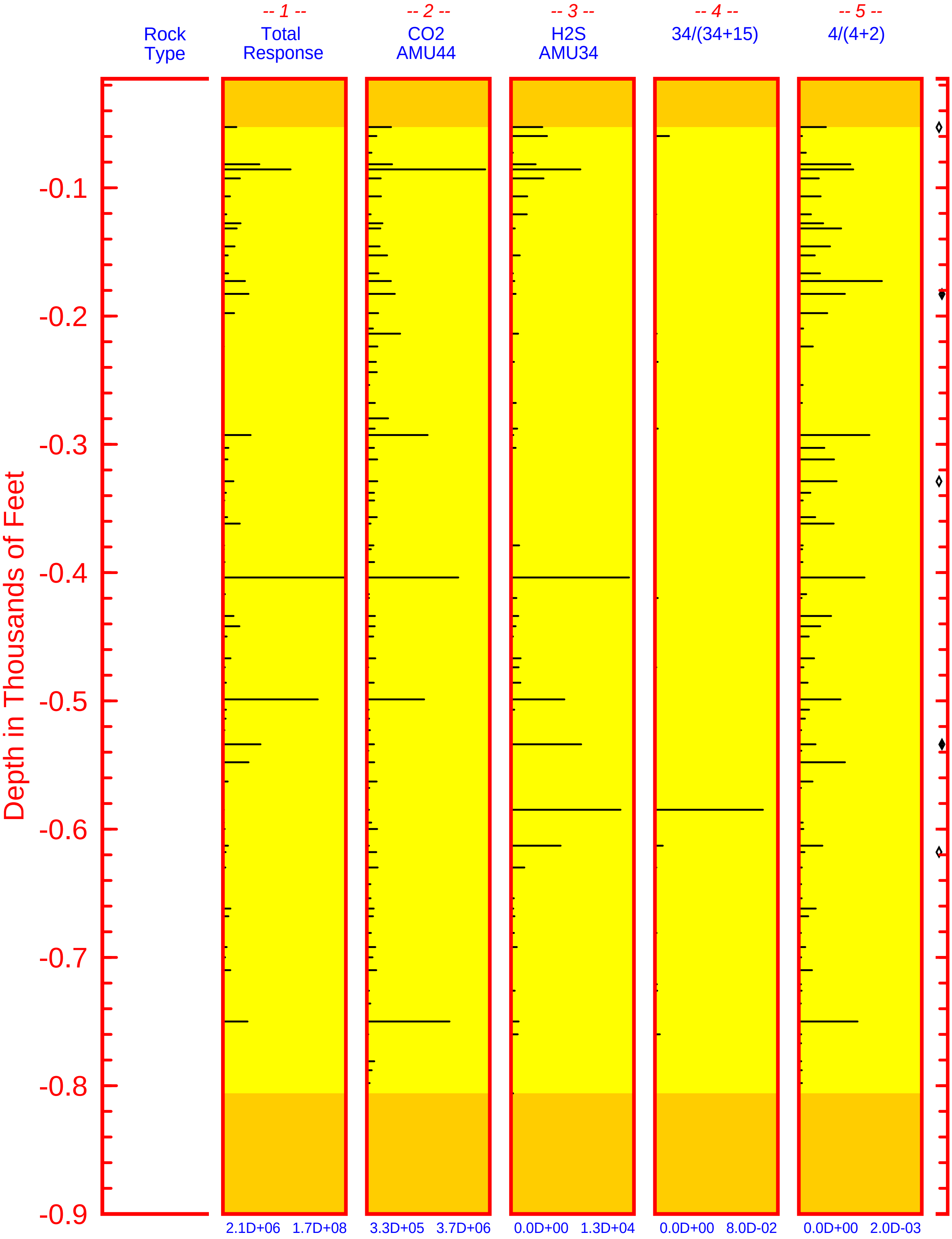


Figure 2: All FIS Data: Tracks 1 – 5 (see Sect. A.3 for explanation)

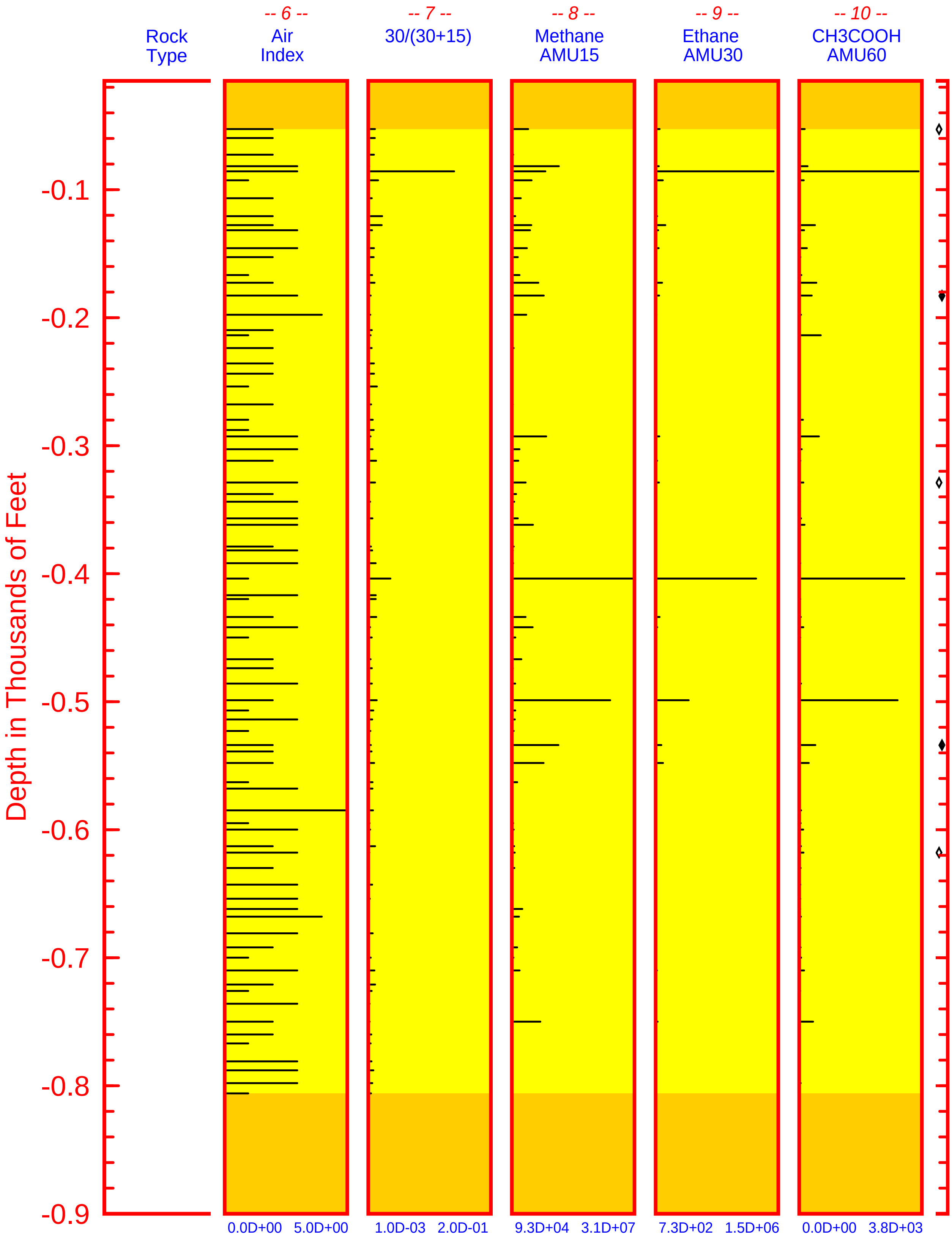


Figure 3: All FIS Data: Tracks 6 – 10 (see Sect. A.3 for explanation)

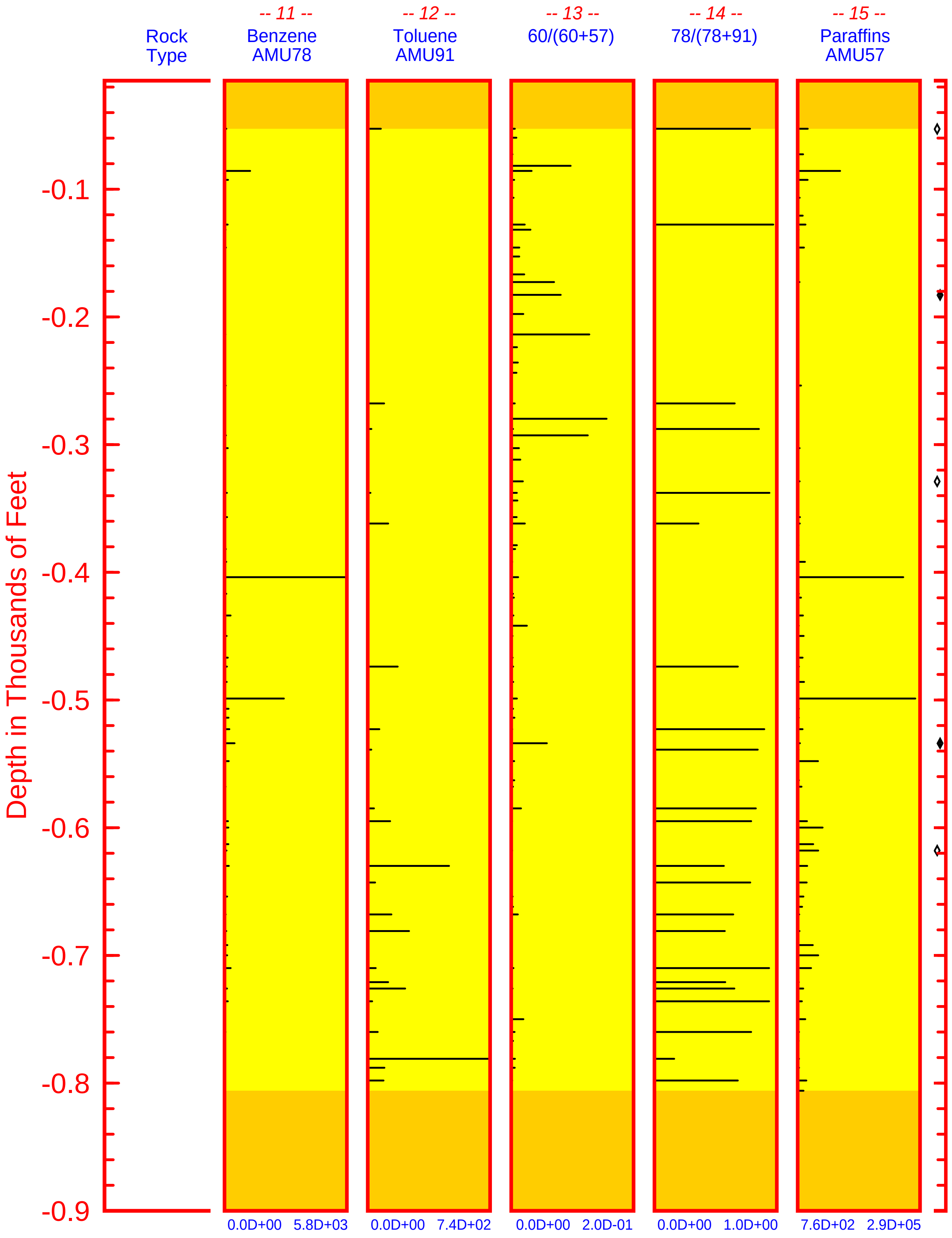


Figure 4: All FIS Data: Tracks 11 – 15 (see Sect. A.3 for explanation)

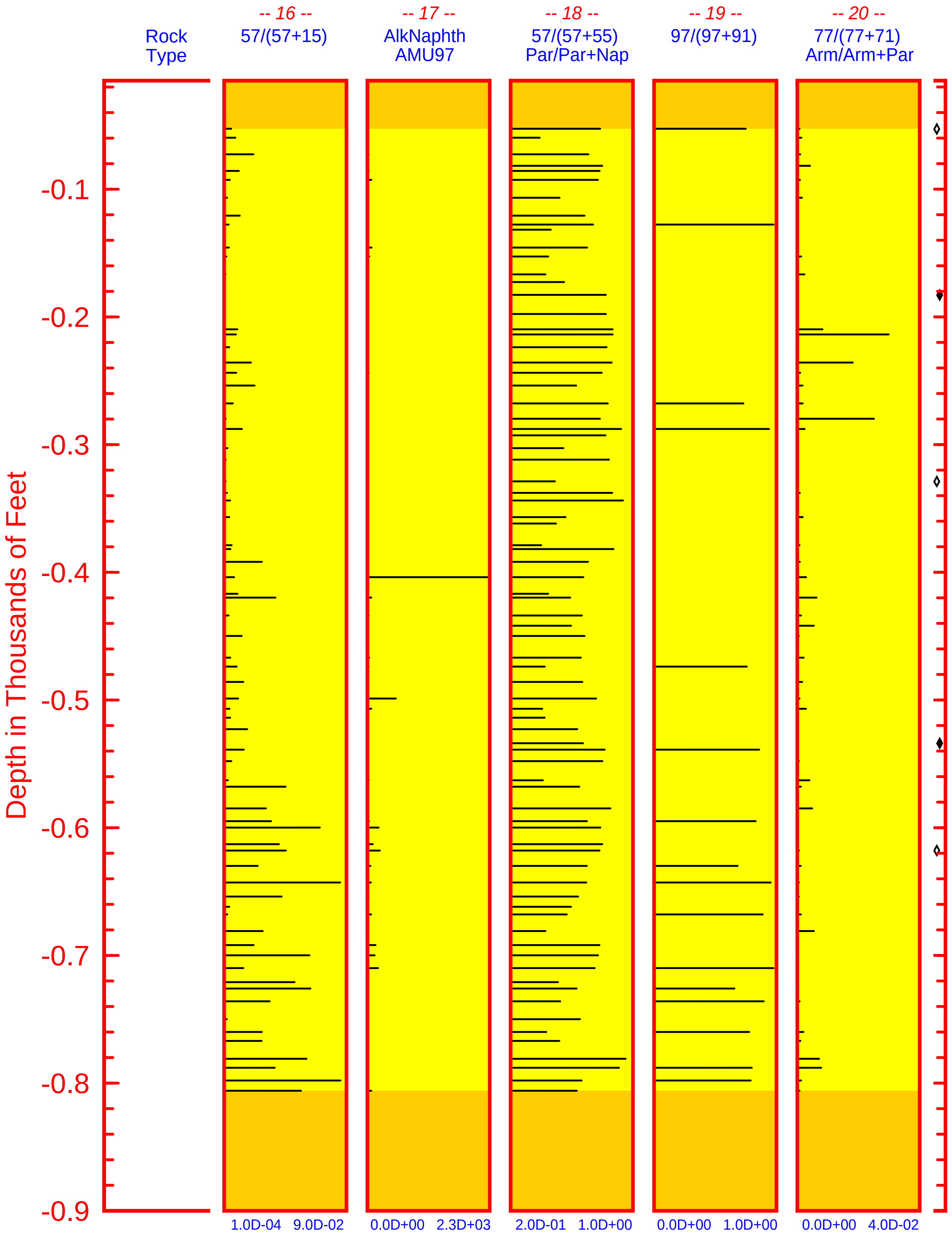


Figure 5: All FIS Data: Tracks 16 – 20 (see Sect. A.3 for explanation)

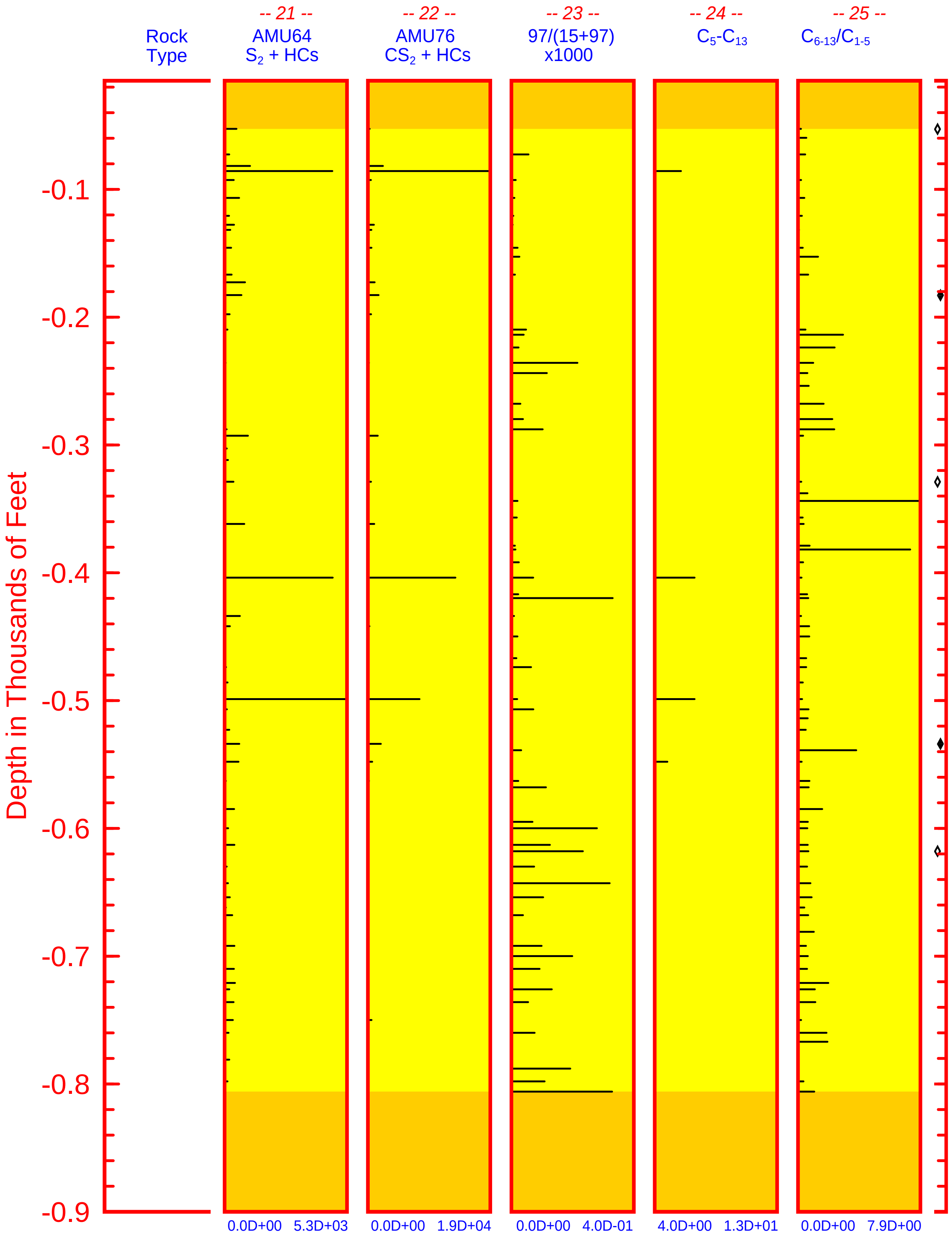


Figure 6: All FIS Data: Tracks 21 – 25 (see Sect. A.3 for explanation)

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.

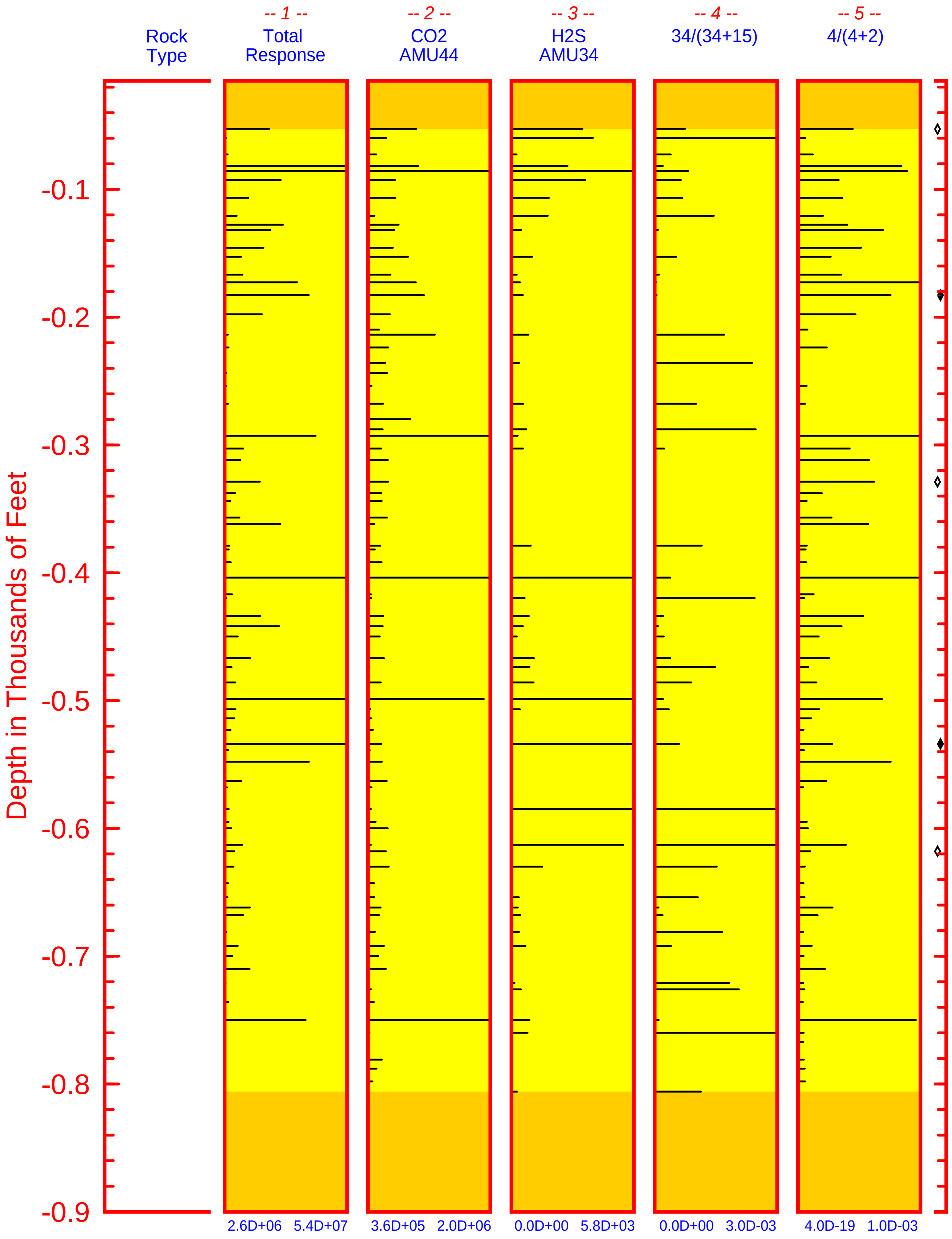


Figure 7: 90% of all FIS Data: Tracks 1 – 5 (see Sect. A.3 for explanation)

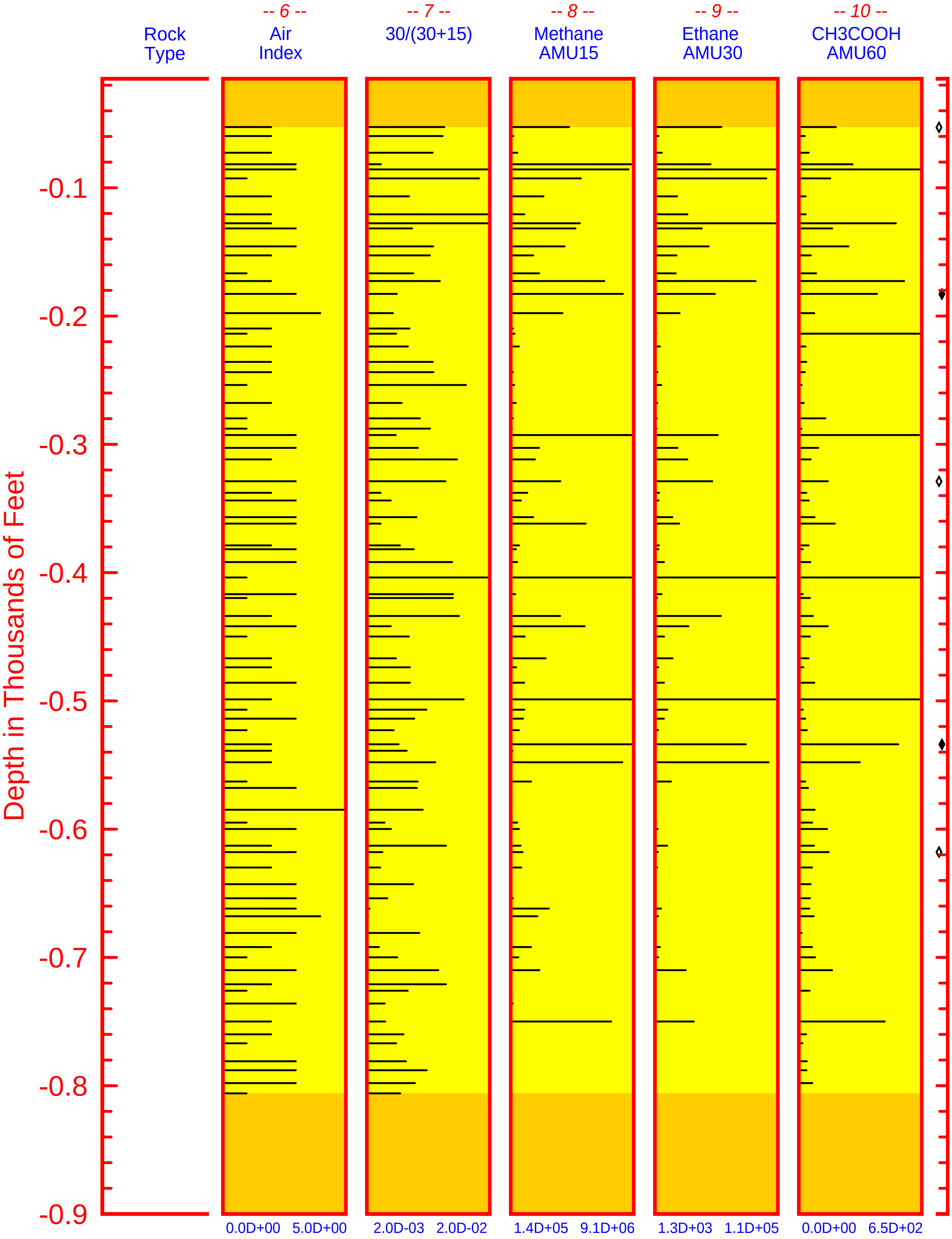


Figure 8: 90% of all FIS Data: Tracks 6 – 10 (see Sect. A.3 for explanation)

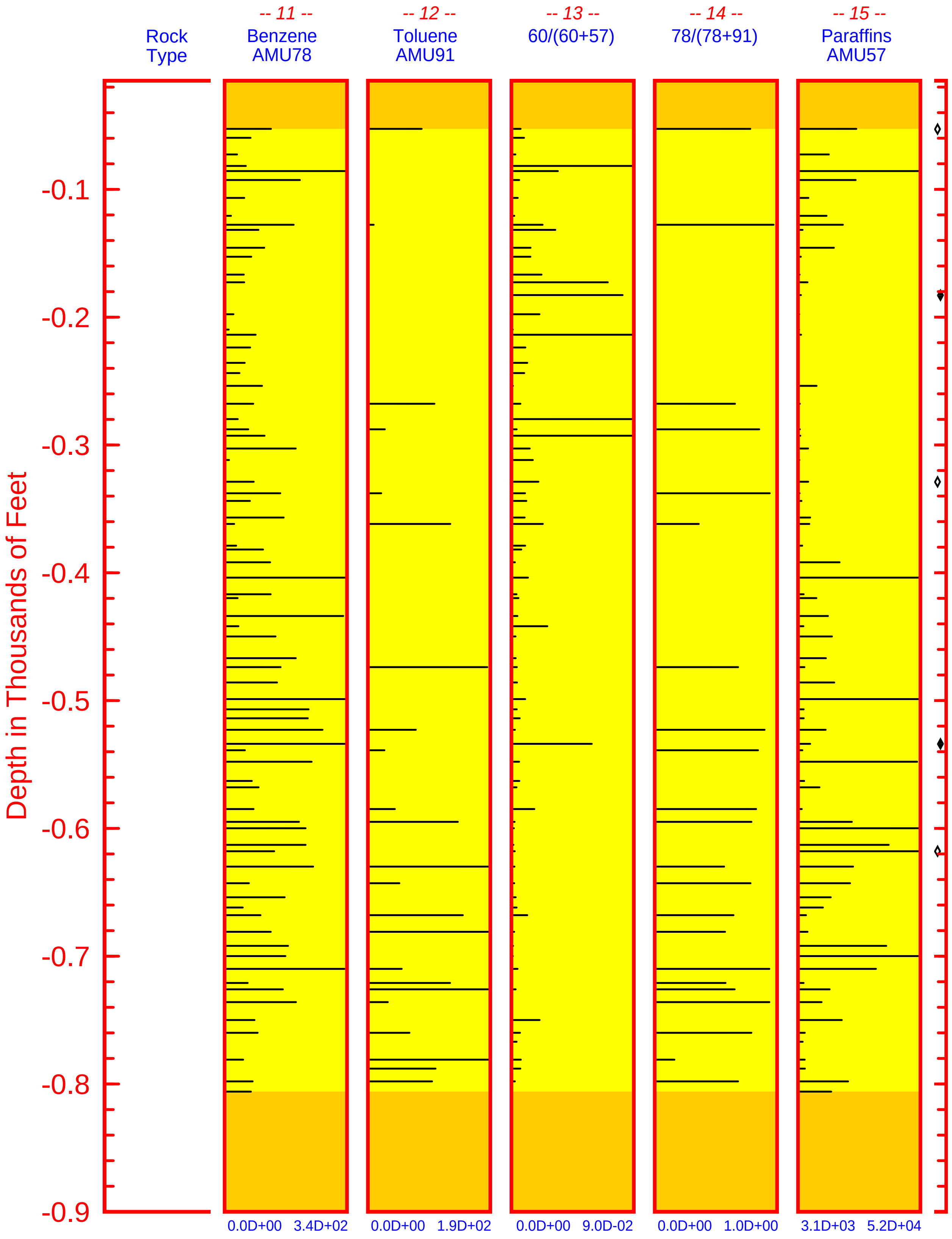


Figure 9: 90% of all FIS Data: Tracks 11 – 15 (see Sect. A.3 for explanation)

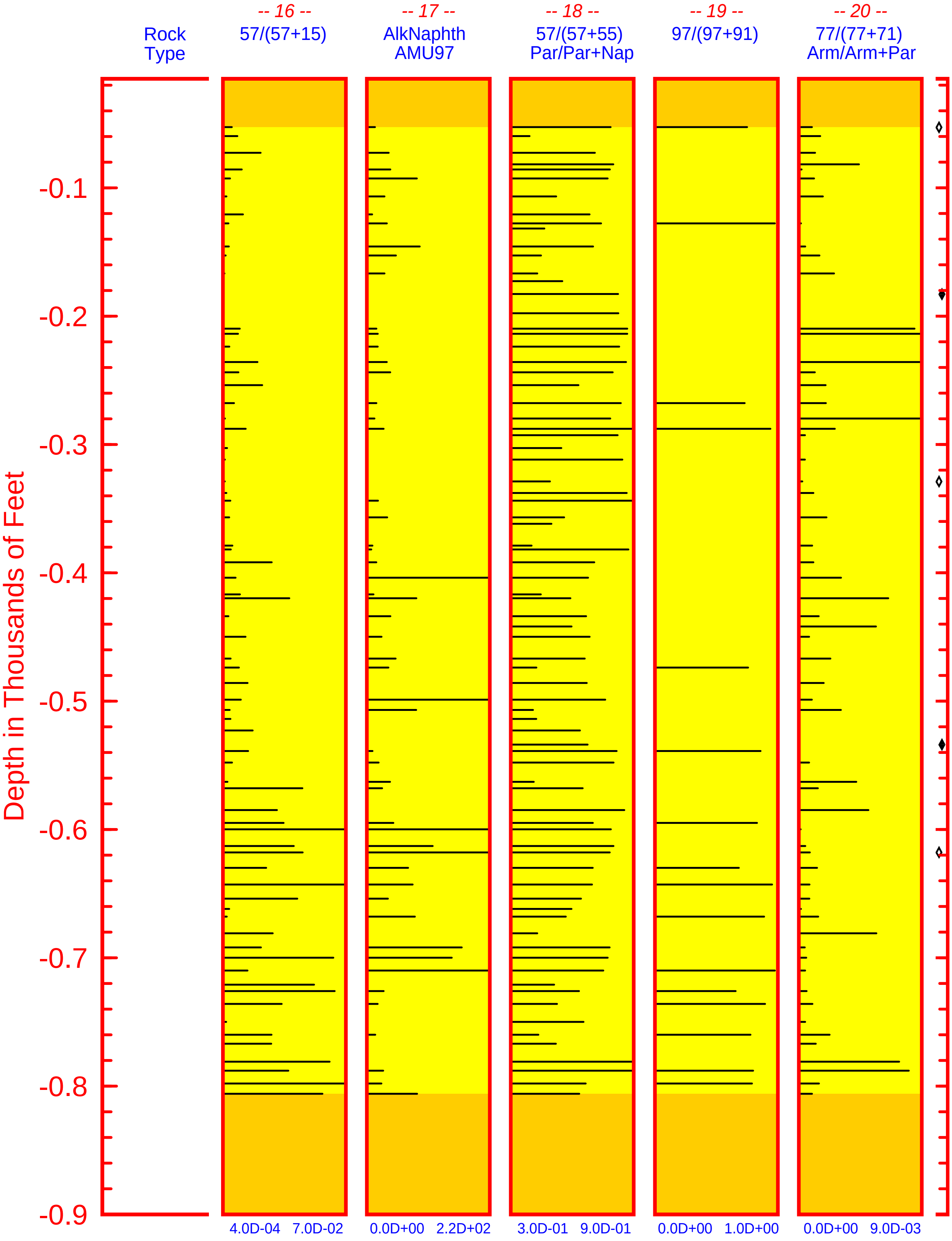


Figure 10: 90% of all FIS Data: Tracks 16 – 20 (see Sect. A.3 for explanation)

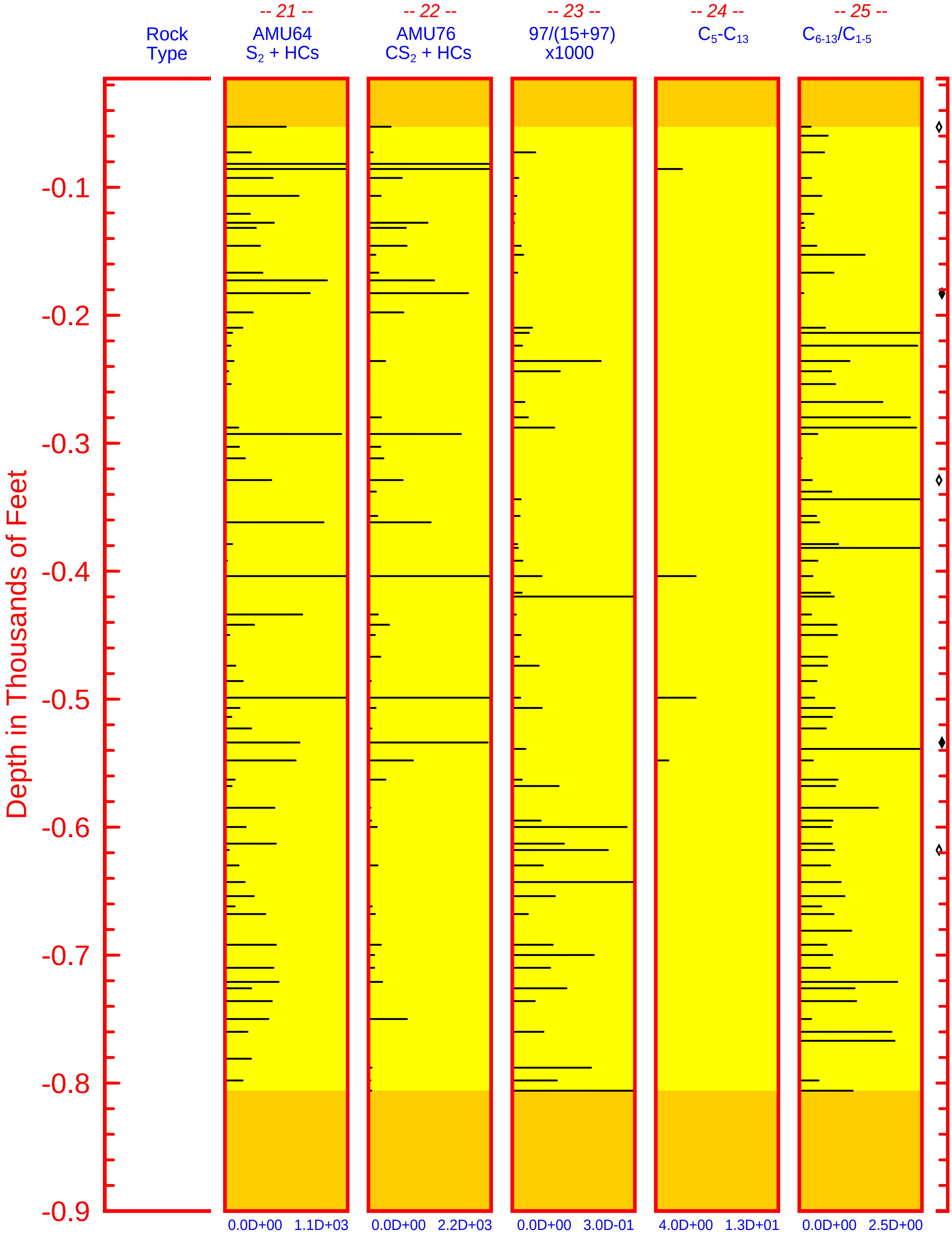


Figure 11: 90% of all FIS Data: Tracks 21 – 25 (see Sect. A.3 for explanation)

5 Photomicroscopy

Thin sections were prepared from SO-C-2-81 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 SO-C-2-81 at the depths indicated.

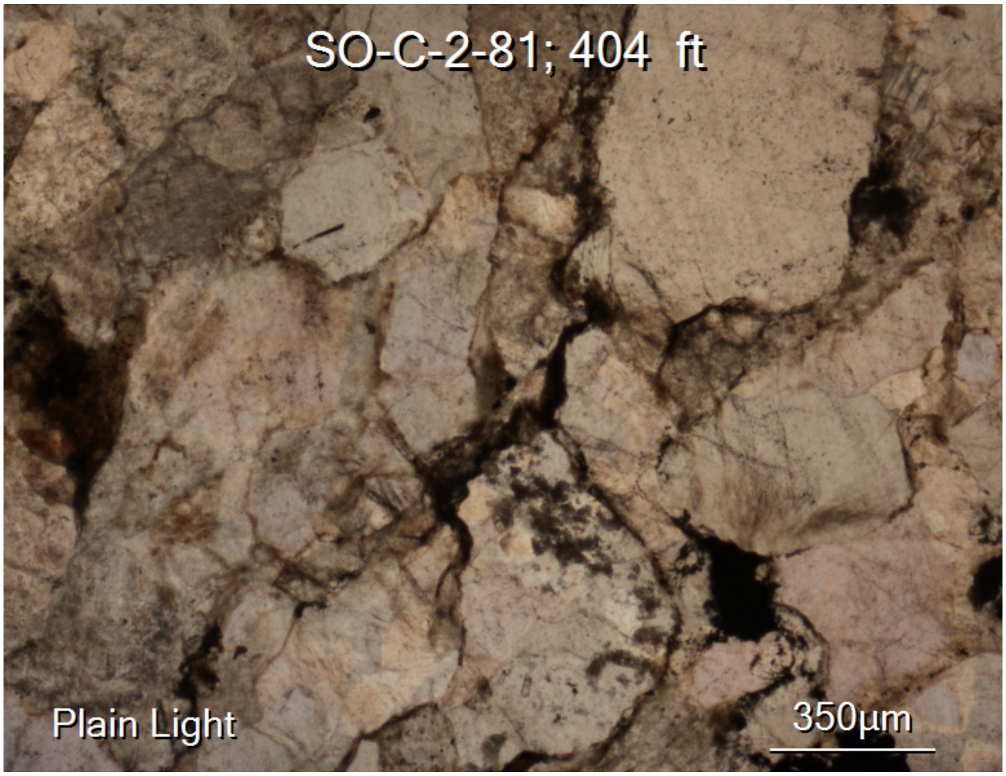


Figure 12: Photomicroscopy from SO-C-2-81

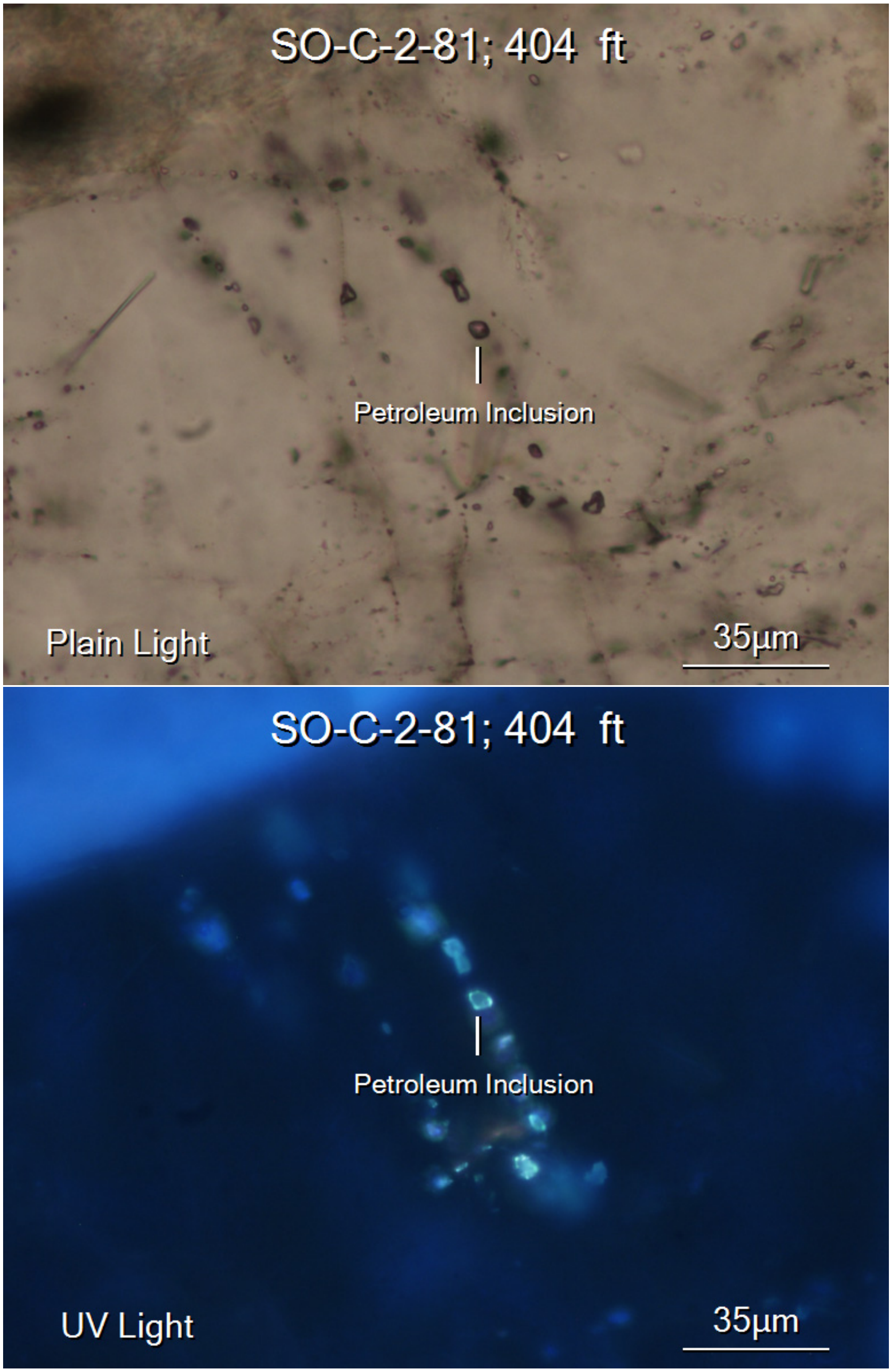


Figure 13: Photomicroscopy from SO-C-2-81

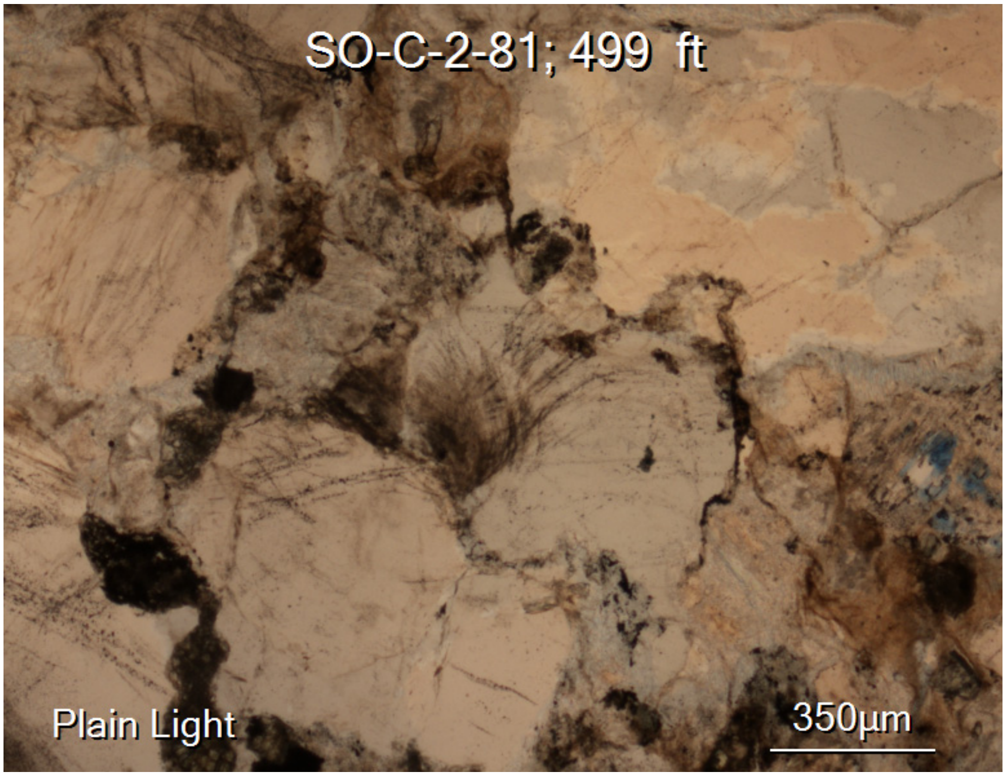


Figure 14: Photomicroscopy from SO-C-2-81

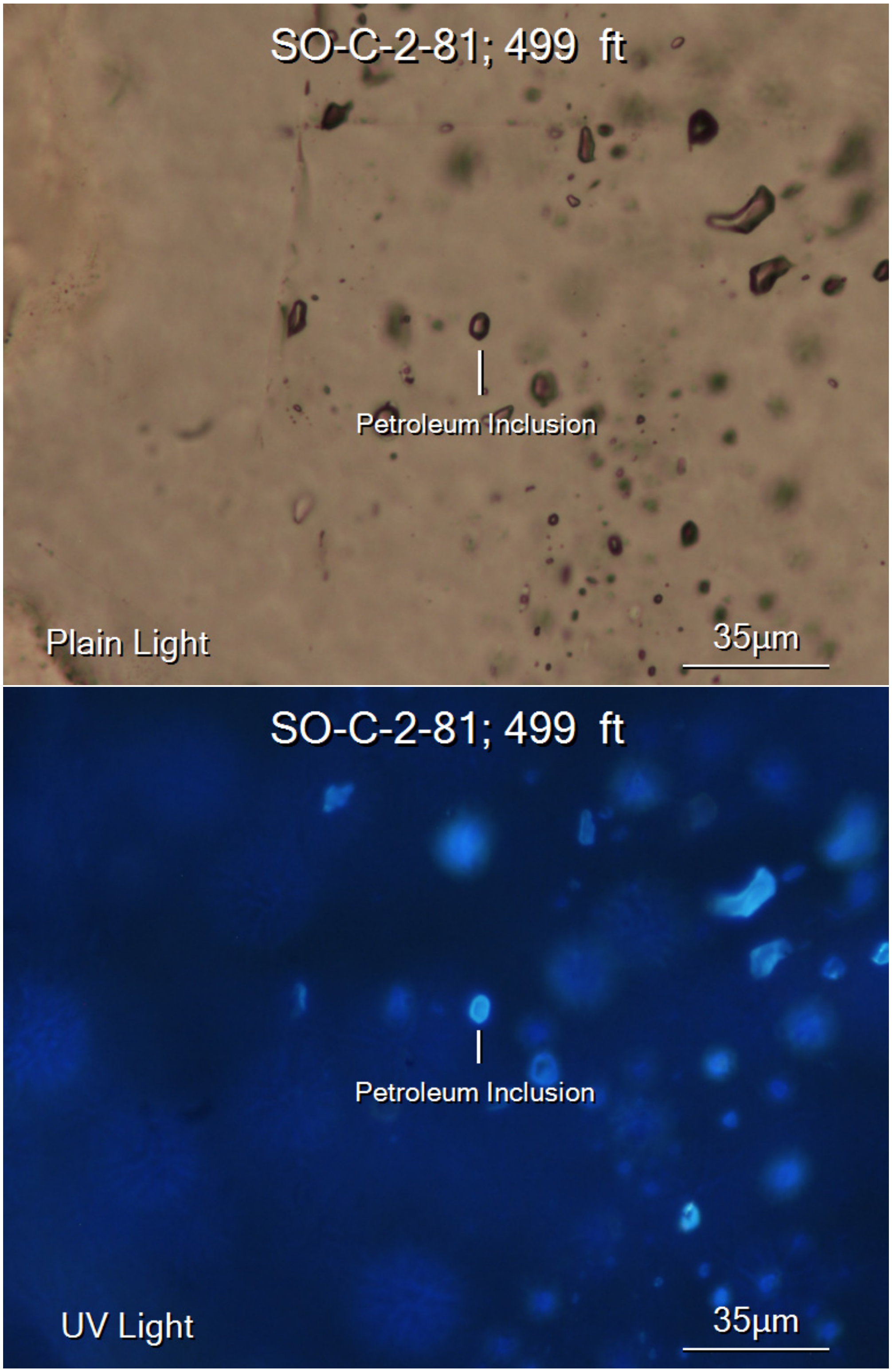


Figure 15: Photomicroscopy from SO-C-2-81

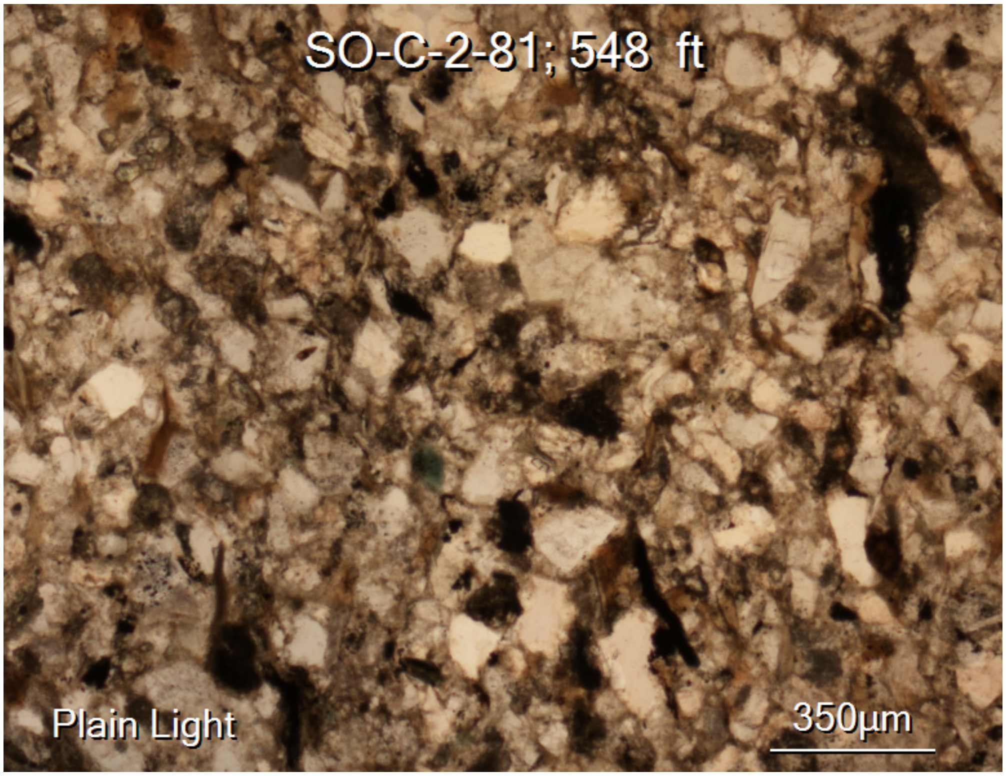


Figure 16: Photomicroscopy from SO-C-2-81

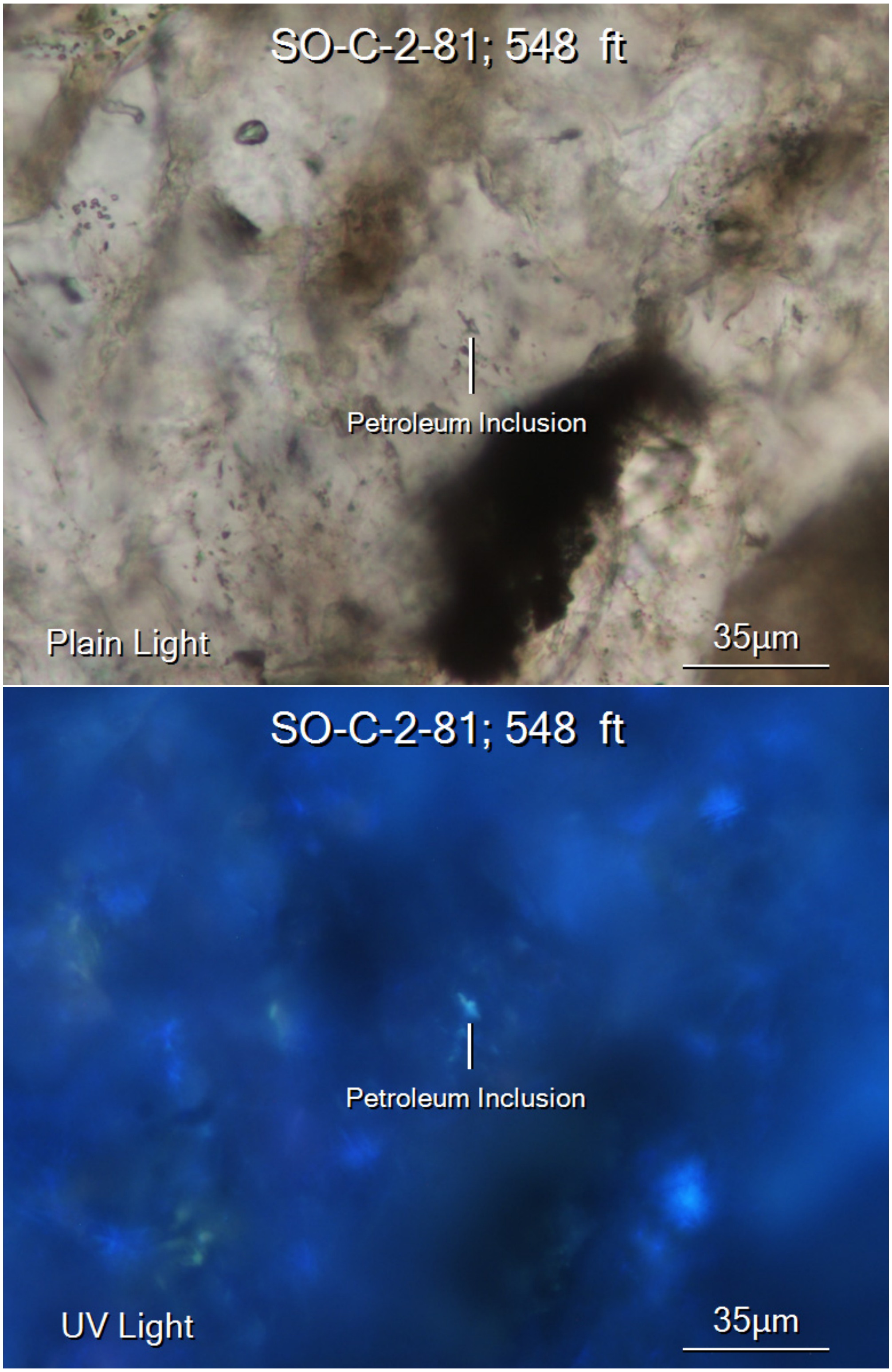


Figure 17: Photomicroscopy from SO-C-2-81

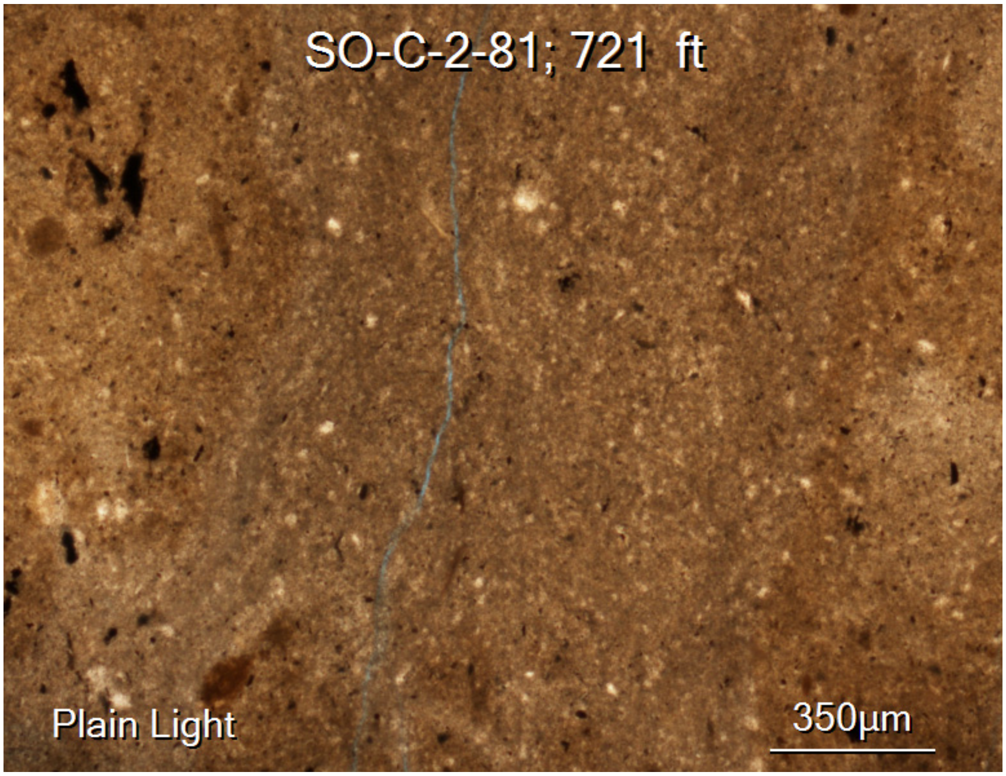


Figure 18: Photomicroscopy from SO-C-2-81

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 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. HD^+ and $^3He^+$ 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:* C_nH_{2n+2}
2. *Naphthenes:* C_nH_{2n}
3. *Aromatics:* C_nH_{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 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 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 C_1-C_5 hydrocarbons with dwindling responses in the C_6-C_8 range, and essentially no response in the C_9+ range. Drier gases may exhibit responses only in the C_1-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_4-C_6 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_2 and water, nitrogen and minor hydrocarbon contributions). The distinction lies in the relative proportion of these species. Gases can typically contain 90% C_1 and 95% C_1-C_3. Hence, FIS gas spectra typically have prominent C_1-C_3 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_4+ paraffins / C_4+ 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_7-C_{13} 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, 71	156(4%)
C12	165-171	57, 43, 71	170(8%)
C13	179-185	43, 57, 71	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_7-C_{13} paraffins are usually the same, and represent some of the most intense peaks previously identified for the C_4-C_6 gas-range paraffins.

Only normal (straight-chain) paraffins have been considered in the above table. Typical C_6-C_{10} (gasoline) fractions contain 40% paraffins, 50% naphthenes and 10% aromatics by volume. Typical C_{11}-C_{13} (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_7 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

$\mathbf{H_2S}$	**COS**	$\mathbf{S_2}$(?)	$\mathbf{SO_2}$	$\mathbf{CS_2}$	$\mathbf{S_8}$
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_1-C_{13} 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_2, 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 though 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 indictor species include light hydrocarbons, CO_2, possibly organic acids and aromatic compounds, and sulfurous volatiles, including H_2S, COS, CS_2, S_2 (+/- SO_2) and in some cases thiols. H_2S 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 downdip.

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 (CO_2^+), with possible minor contribution from C_3^+ hydrocarbon fragments and acetic acid. Anomalous values have been noted associated with pan-evaporative dolomitization of limestones in China and Oman. CO_2 response is often

high in proximity samples which show elevated levels of acetic acid. CO_2 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_2S^+). Anomalous values associated with petroleum may indicate sour oil or gas. H_2S is also noted at times in association with shallow dry gas of probable biogenic origin (including FIS microseeps) and with some proximity zones. H_2S is probably not quantitatively analyzed due to rapid scavenging by metallic surfaces of the analytical system.

Track 4: 34/(34+15) - $H_2S/(H_2S\text{+methane})$. Not frequently used, but ratio tends to be elevated in sour gas zones.

Track 5: 4/(4+2) - Helium fraction $^4He^+/(^4He^+ + H_2^+)$; 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_3^+; mostly derived from methane, with minor contributions from all other paraffins and NH_2^+, 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 ($C_2H_6^+$). Use similar to that of methane ($m/z = 15$).

Track 10: $m/z = 60$ - Acetic aid (CH_3COOH), 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 ($C_6H_6^+$). 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 ($C_7H_7^+$). 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: $m/z = 76$ - CS_2 and C_6^+ hydrocarbons. 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: $C_5 - C_{13}$ 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 C_5 group is the highest molecular weight range hydrocarbon group present in a given sample, a ranking of 5 is assigned; if 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 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: C_{6-13}/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 (H_2^+); largely from H_2O, which makes up most of the evolved fluid in almost all samples.
- $m/z = 3$ - Deuterated hydrogen and helium-3 (HD and $^3He^+$).
- $m/z = 12$ - Carbon (C^+).
- $m/z = 14$ - Nitrogen (N^+) and 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. CH_2^+ will generally be accompanied by relatively larger responses on $m/z = 15$ (CH_3^+), and $m/z = 16$ (CH_4^+) (due to it's fragmentation origin from 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 (CH_4^+), but major interference by O^+ fragment of water.

- $m/z = 17$ - Dominated by OH^+ fragment from water
- $m/z = 18$ - Dominated by water parent peak (H_2O^+)
- $m/z = 22$ - Doubly charged carbon dioxide ($CO2^{2+}$); minor contribution from neon ($^{22}Ne^+$)
- $m/z = 28$ - Dominated by diatomic nitrogen (N_2^+) and CO^+ fragment from carbon dioxide. Minor C_2^+ hydrocarbon contribution
- $m/z = 32$ - Oxygen (O^+) and sulfur (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 $m/z = 34$ (H_2S), $m/z = 48$ (SO^+) and $m/z = 64$ (S_2^+, 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 (Ar^+) with possible significant interference by 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 (SO^+); also, C_4^+
- $m/z = 55$ - Naphthene fragment ($C_4H_7^+$). 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 ($C_5H_{11}^+$). Same use as $m/z = 57$.
- $m/z = 77$ - Aromatic fragment ($C_6H_5^+$). Same general use as for benzene and toluene.
- $m/z = 85$ - Paraffin fragment ($C_6H_{13}^+$). Same use as $m/z = 57$.
- $95 \leq m/z \leq 103$ - peaks centered within this range are mostly $C_7 - C_8$ fragments
- $110 \leq m/z \leq 115$ - peaks centered within this range are mostly $C_8 - C_9$ fragments
- $122 \leq m/z \leq 126$ - peaks centered within this range are mostly $C_9 - C_{10}$ fragments
- $134 \leq m/z \leq 138$ - peaks centered within this range are mostly $C_{10} - C_{11}$ fragments
- $148 \leq m/z \leq 152$ - peaks centered within this range are mostly $C_{11} - C_{12}$ fragments
- $160 \leq m/z \leq 164$ - peaks centered within this range are mostly $C_{12} - C_{13}$ fragments
- $175 \leq m/z \leq 180$ - peaks centered within this range are mostly $C_{13} - C_{14}$ 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 19. 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 inhomogenieties 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 20 and 21. 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 22. 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.

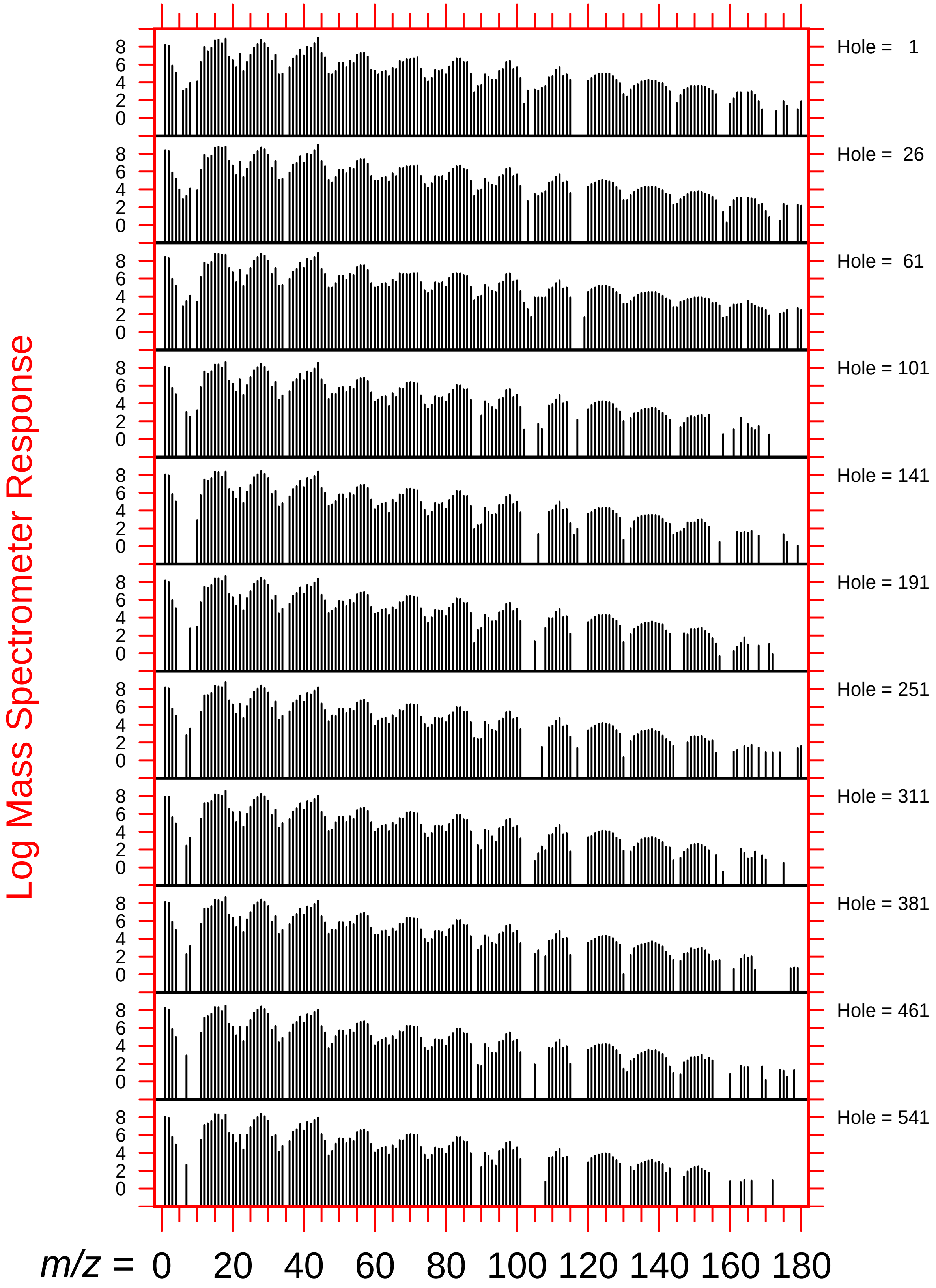


Figure 19: Oil Spectra

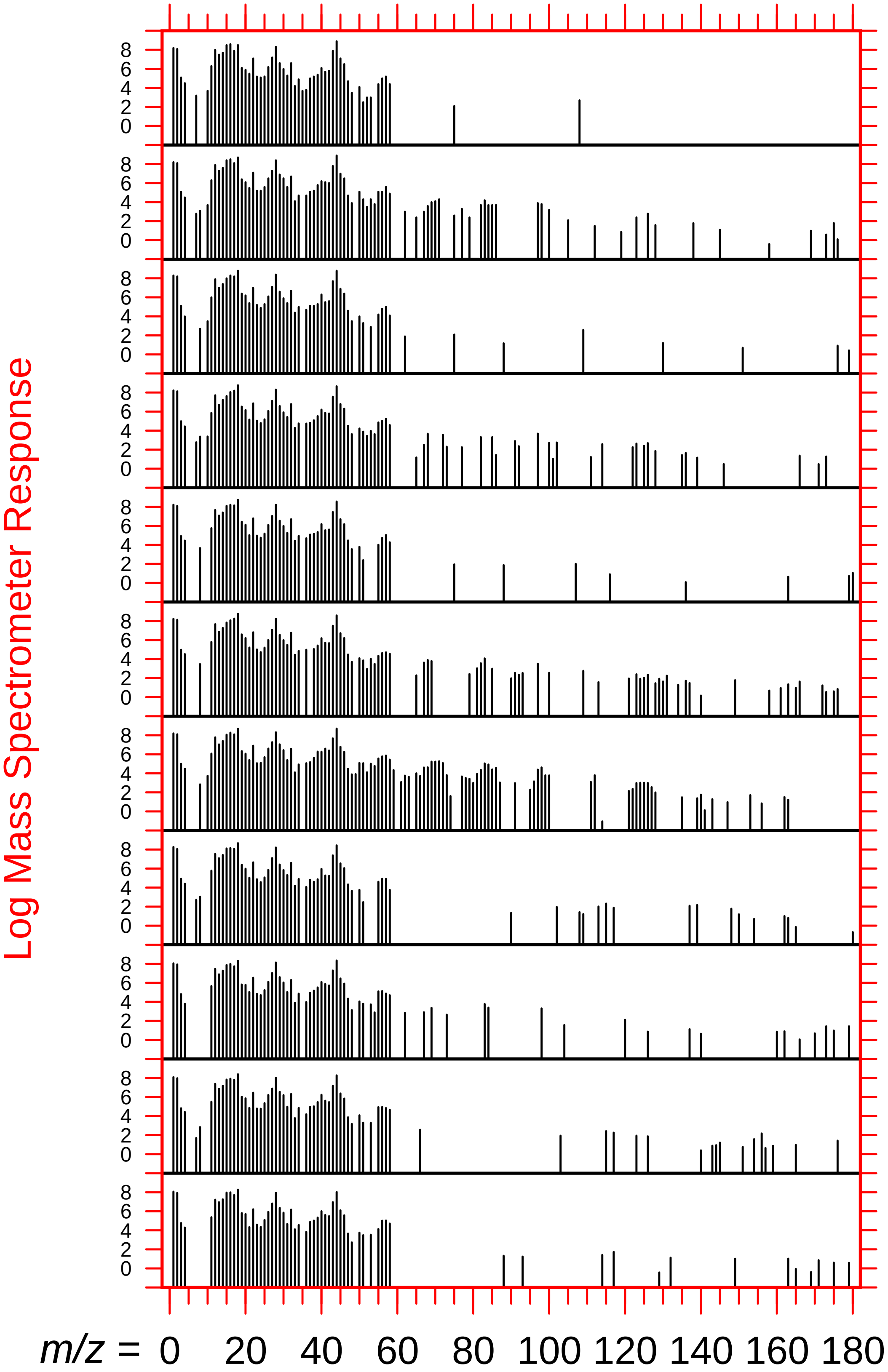


Figure 20: Frac Sand Spectra

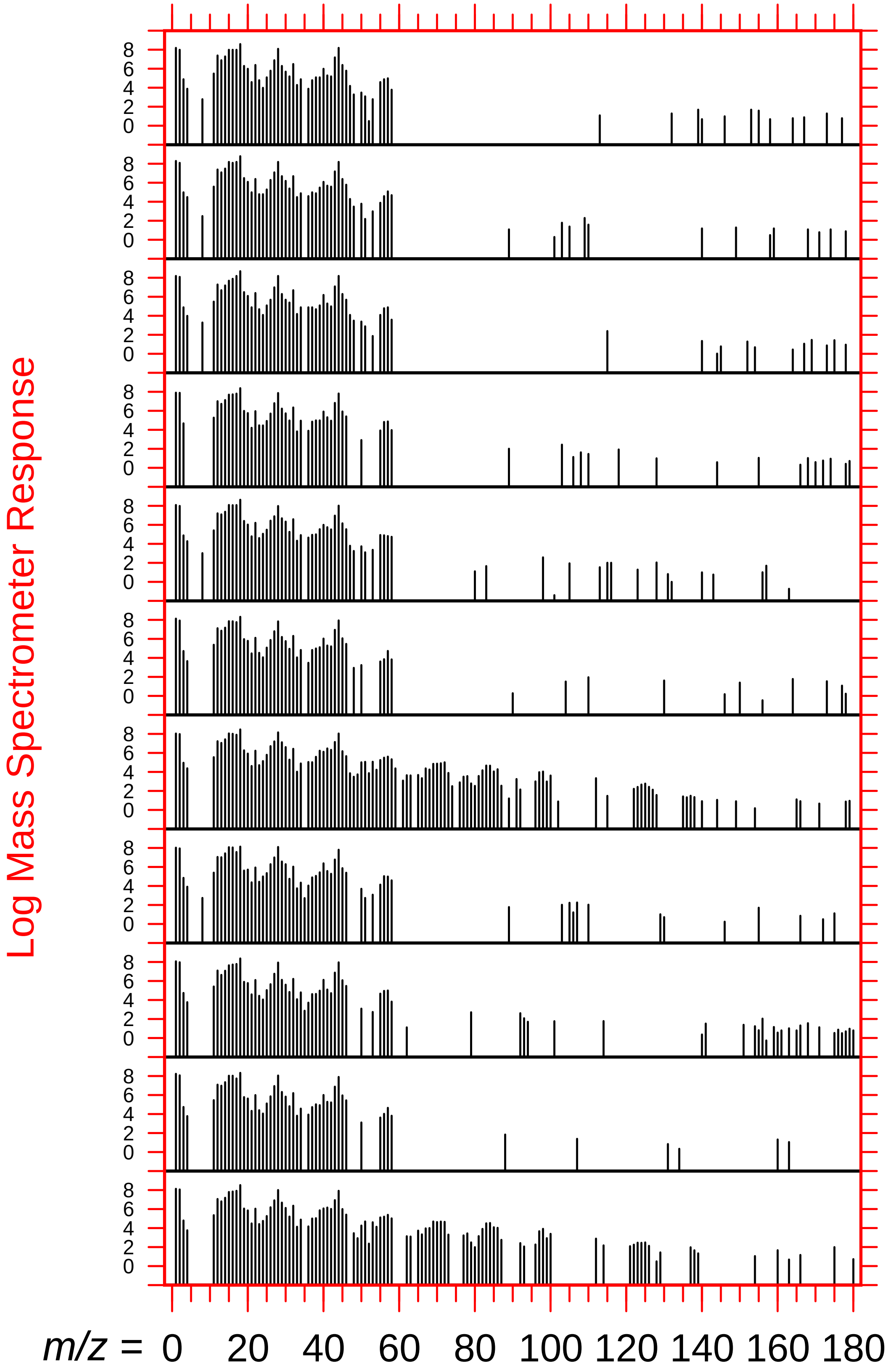


Figure 21: Frac Sand Spectra

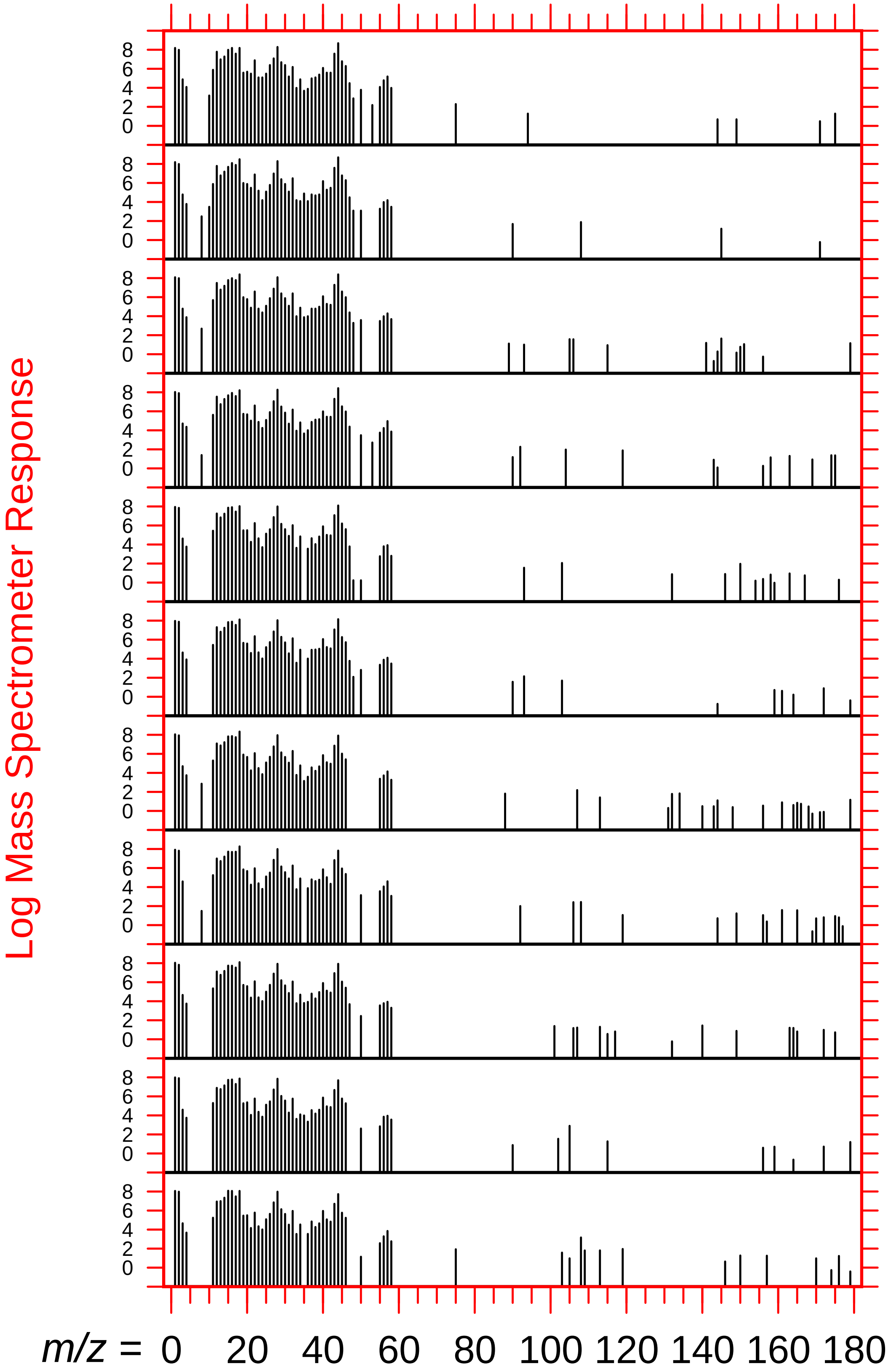


Figure 22: Cooked Frac Sand Spectra

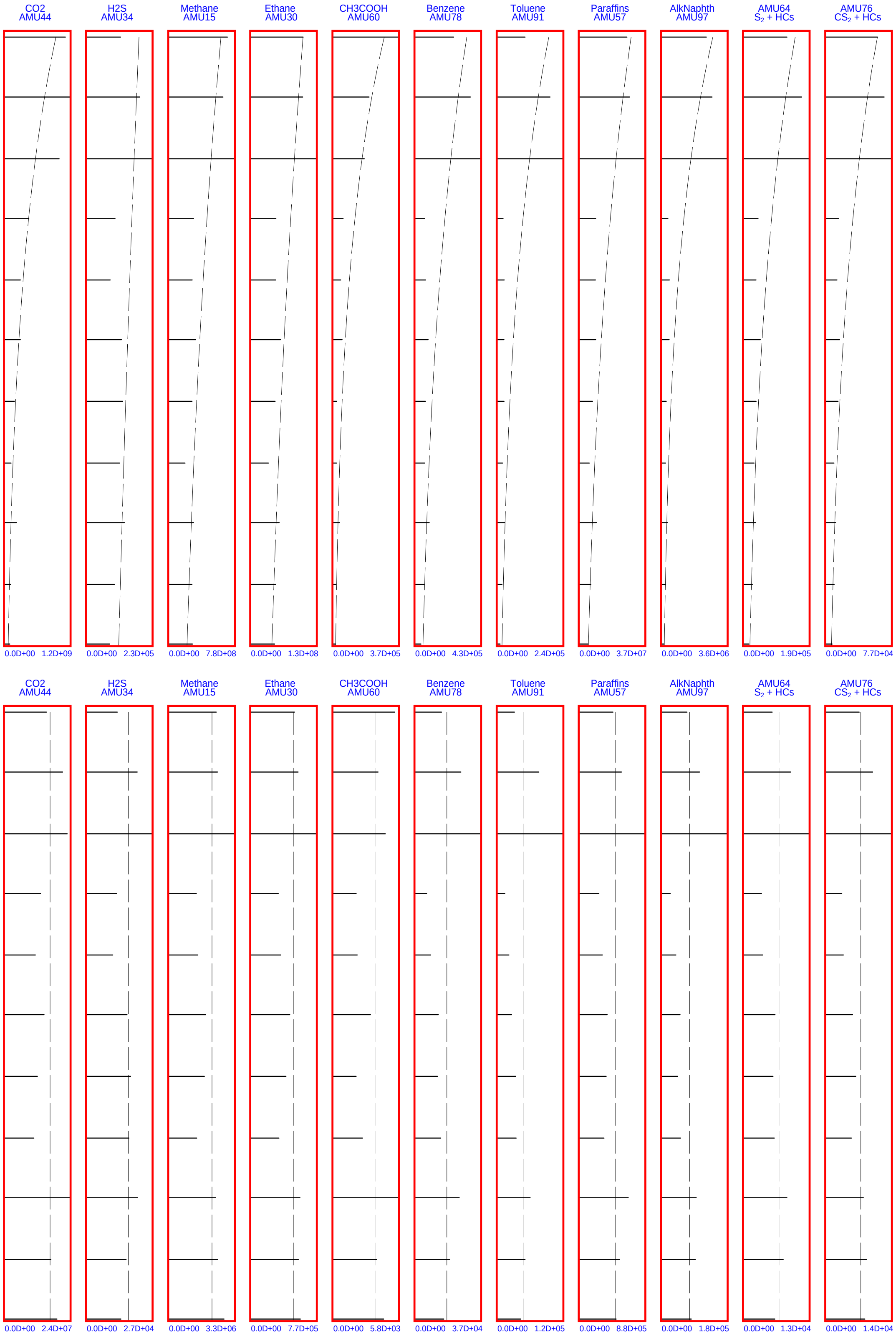
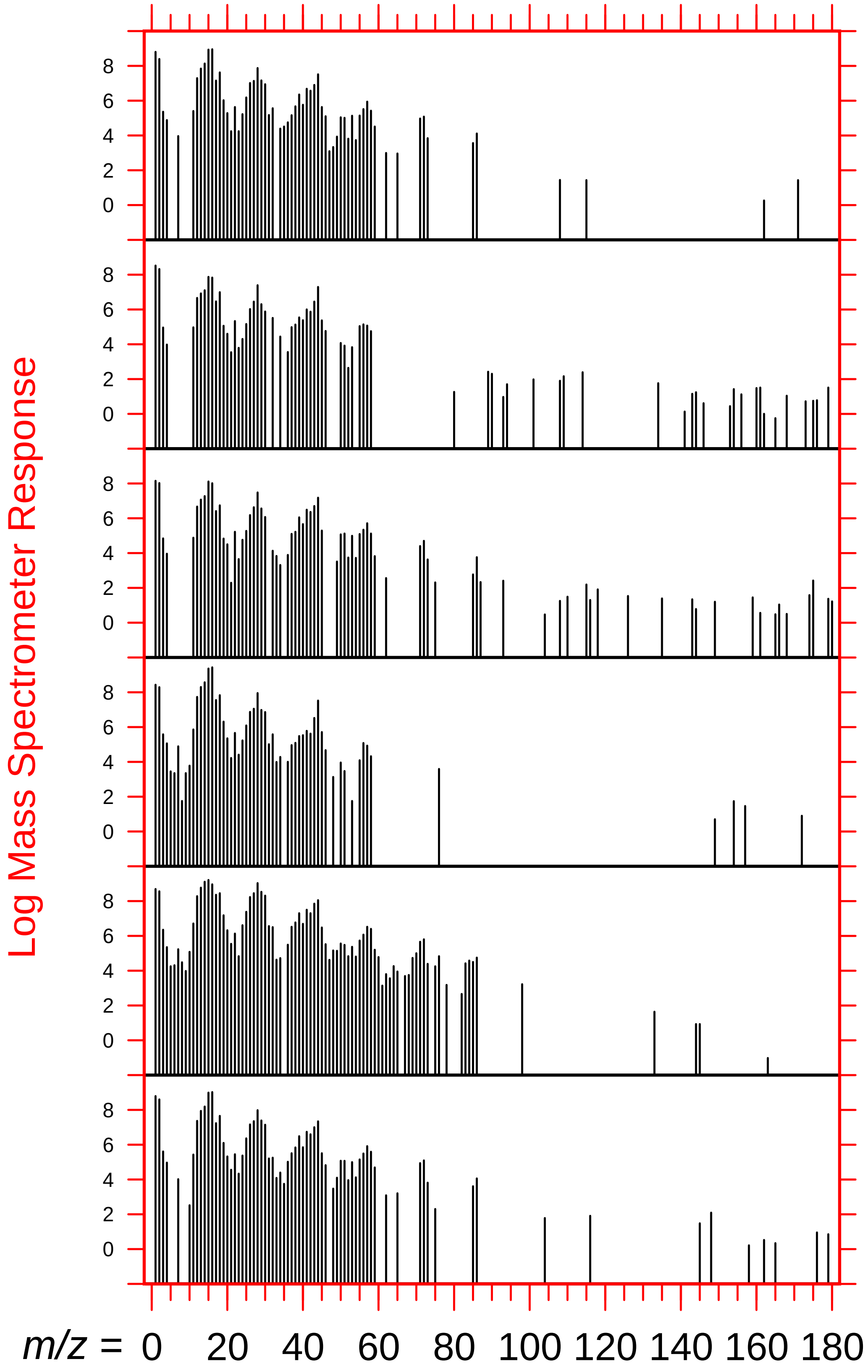
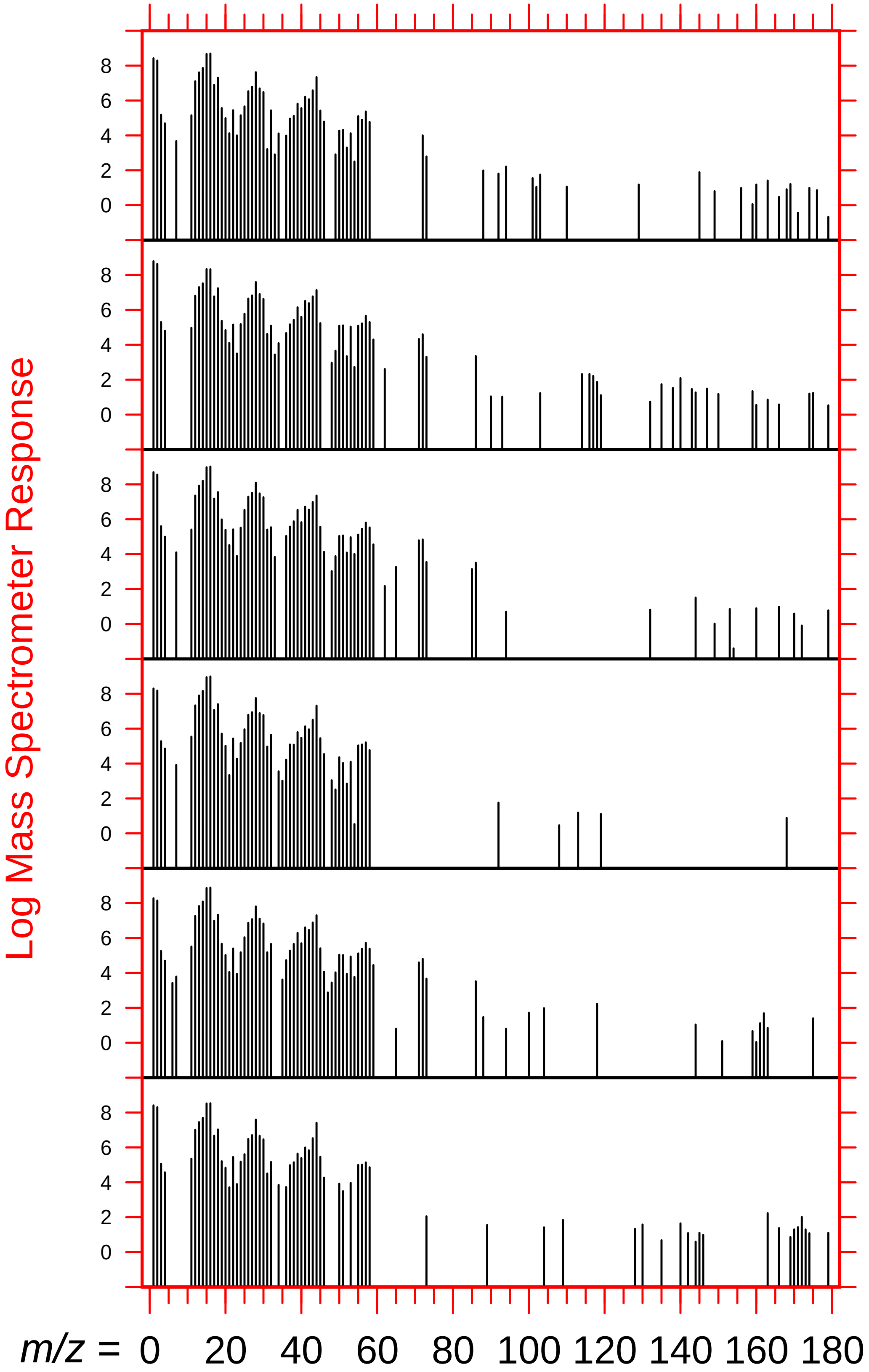


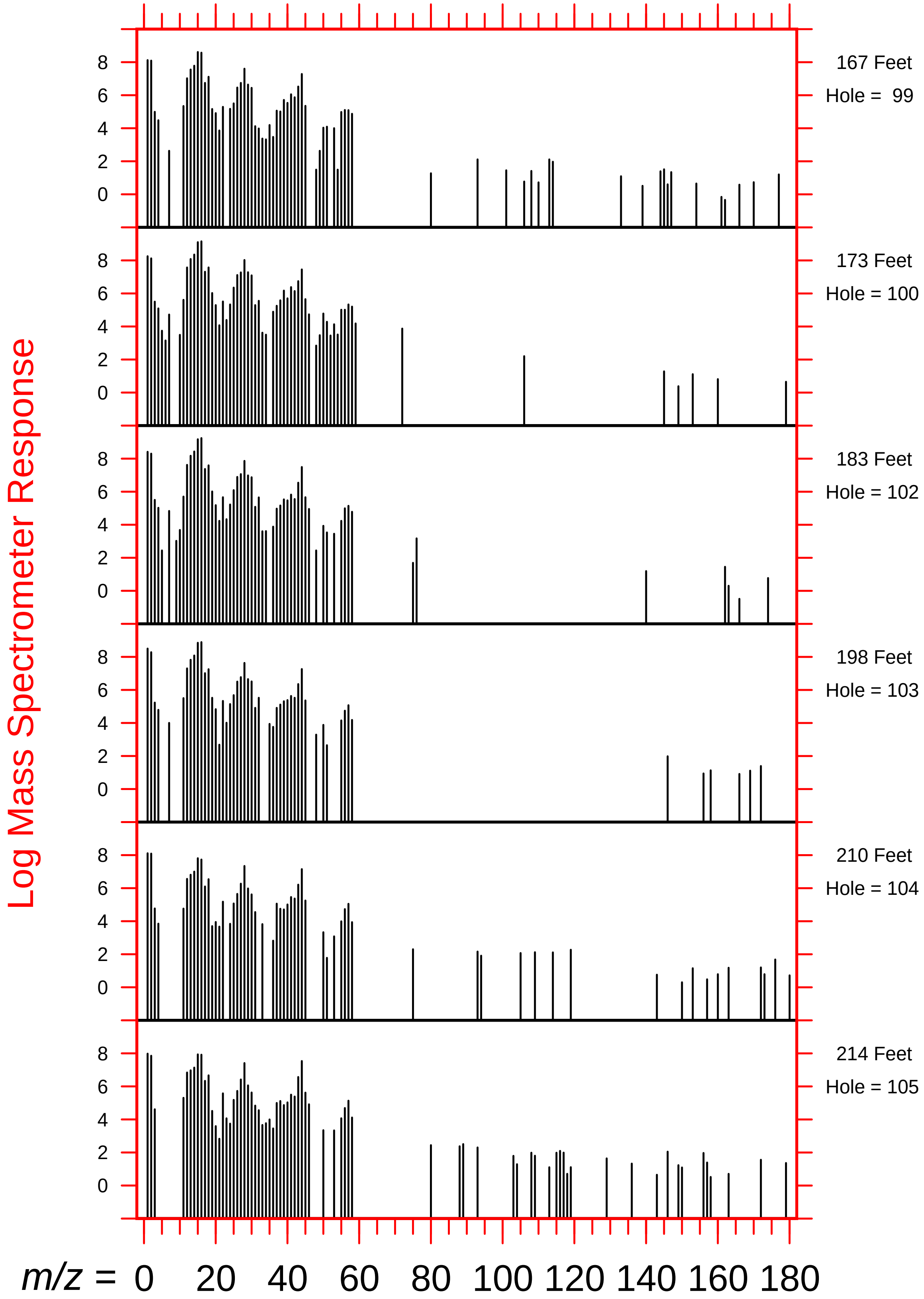
Figure 23: Kindblade Oil Standards Before (top) and After (bottom) Correction

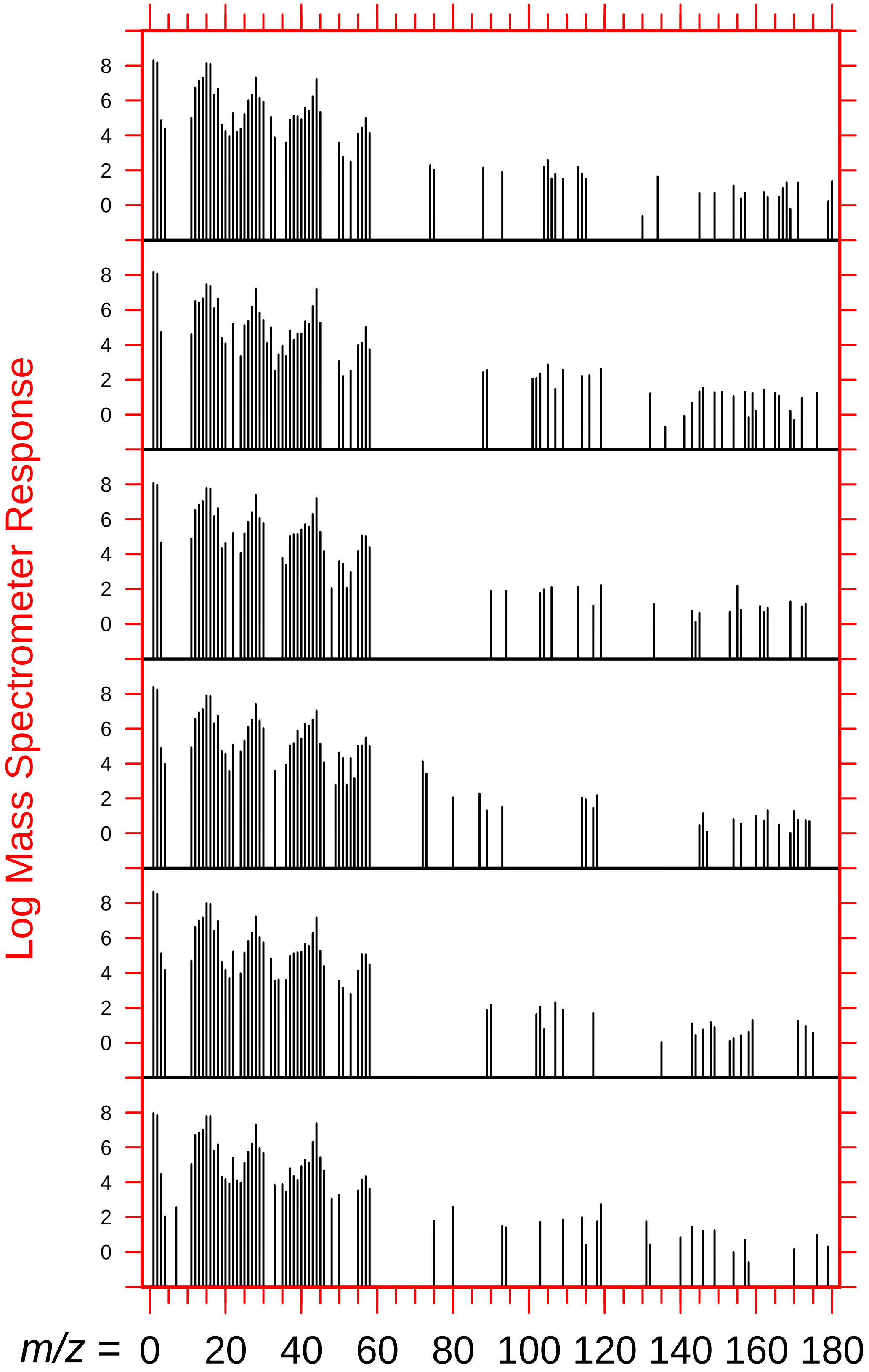
C Individual Spectra

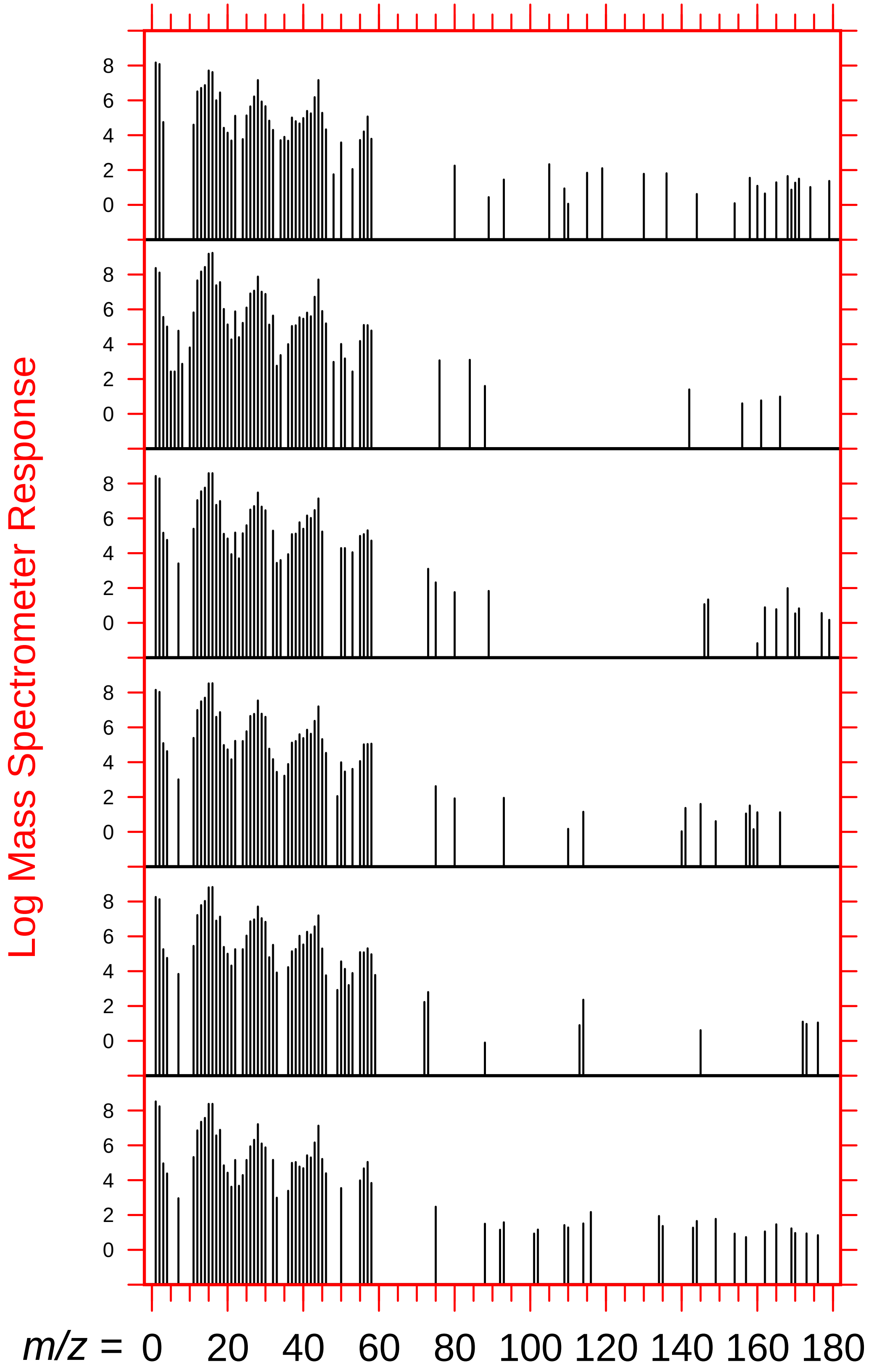
Individual spectra for each sample from SO-C-2-81 are shown on the following pages. Each spectrum is indexed according to depth and indicates the log of the millivolt response for atomic mass units (AMU, m/z) from $2 \leq m/z \leq 180$.

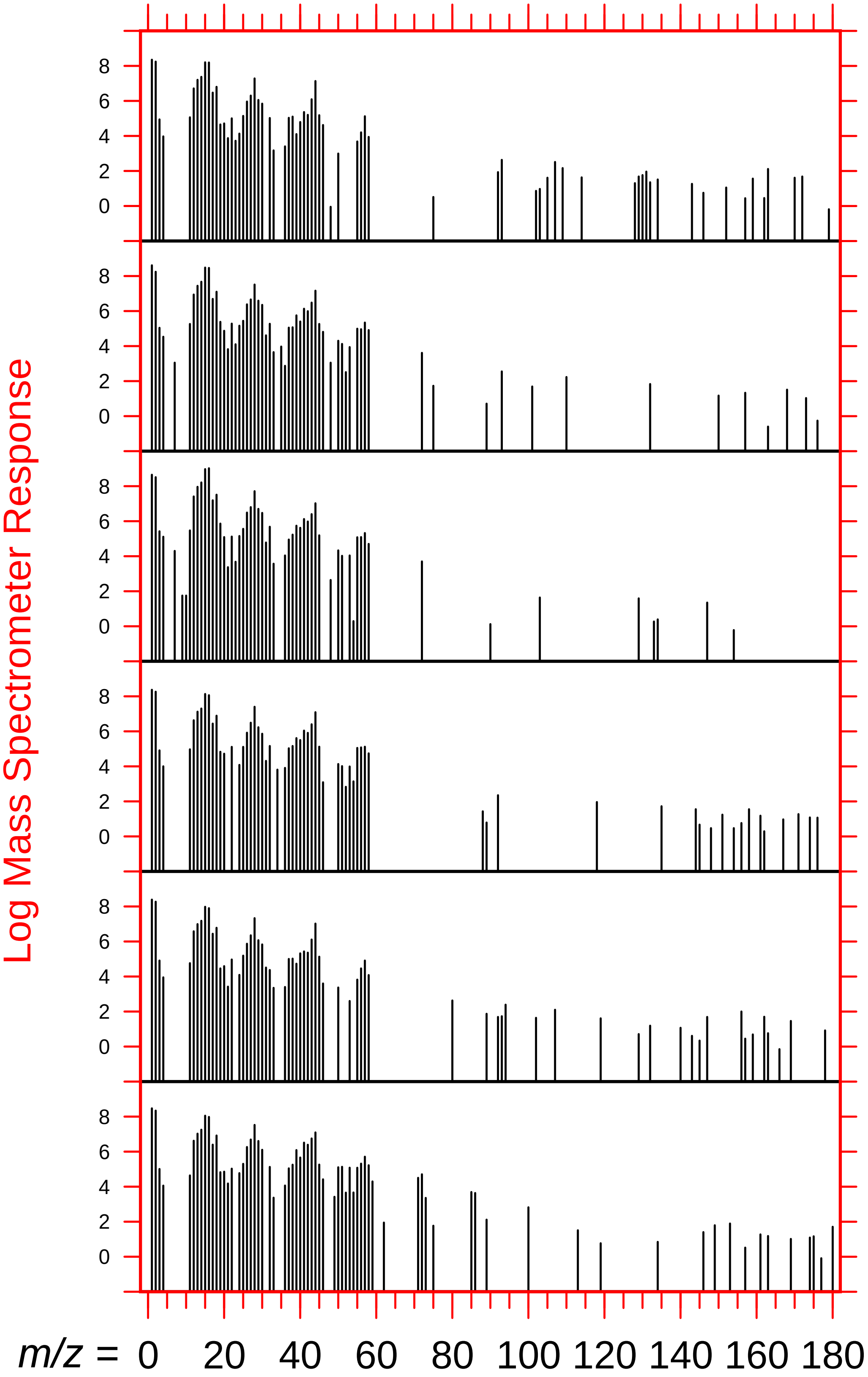

Log Mass Spectrometer Response
8
6
4
2
0
53 Feet
Hole = 86
60 Feet
Hole = 87
73 Feet
Hole = 88
82 Feet
Hole = 89
86 Feet
Hole = 90
93 Feet
Hole = 91
m/z = 0 20 40 60 80 100 120 140 160 180


Log Mass Spectrometer Response
8
6
4
2
0
107 Feet
Hole = 92
121 Feet
Hole = 94
128 Feet
Hole = 95
132 Feet
Hole = 96
146 Feet
Hole = 97
153 Feet
Hole = 98
m/z = 0
20
40
60
80
100
120
140
160
180


Log Mass Spectrometer Response
8
6
4
2
0
167 Feet
Hole = 99
173 Feet
Hole = 100
183 Feet
Hole = 102
198 Feet
Hole = 103
210 Feet
Hole = 104
214 Feet
Hole = 105
m/z = 0 20 40 60 80 100 120 140 160 180


Log Mass Spectrometer Response
8
6
4
2
0
224 Feet
Hole = 106
236 Feet
Hole = 107
244 Feet
Hole = 108
254 Feet
Hole = 110
268 Feet
Hole = 111
280 Feet
Hole = 112
m/z = 0 20 40 60 80 100 120 140 160 180


Log Mass Spectrometer Response
8
6
4
2
0
288 Feet
Hole = 113
293 Feet
Hole = 114
303 Feet
Hole = 115
312 Feet
Hole = 116
329 Feet
Hole = 118
338 Feet
Hole = 119
m/z = 0 20 40 60 80 100 120 140 160 180


Log Mass Spectrometer Response
8
6
4
2
0
344 Feet
Hole = 120
357 Feet
Hole = 121
362 Feet
Hole = 122
379 Feet
Hole = 123
382 Feet
Hole = 124
392 Feet
Hole = 126
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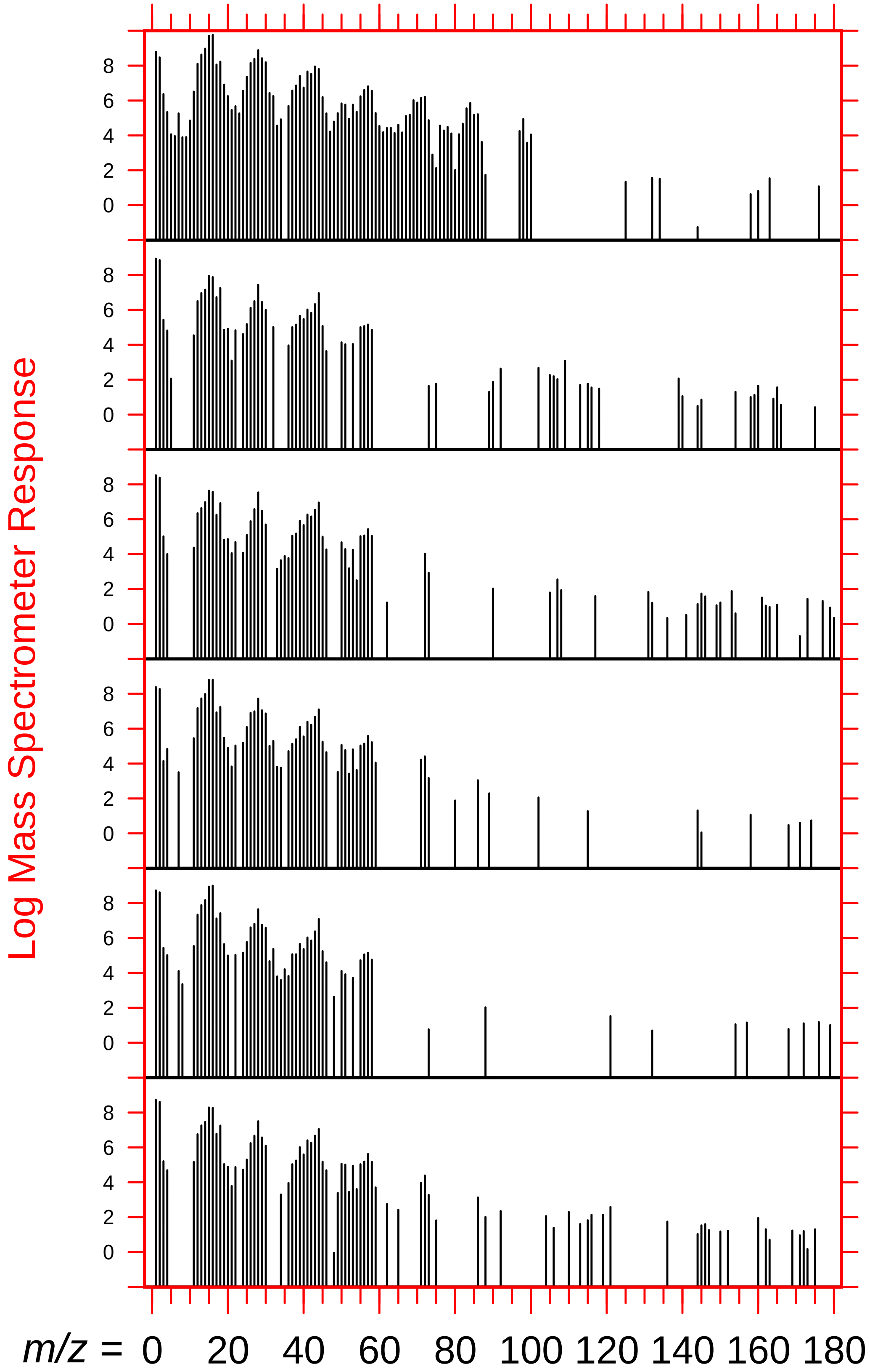
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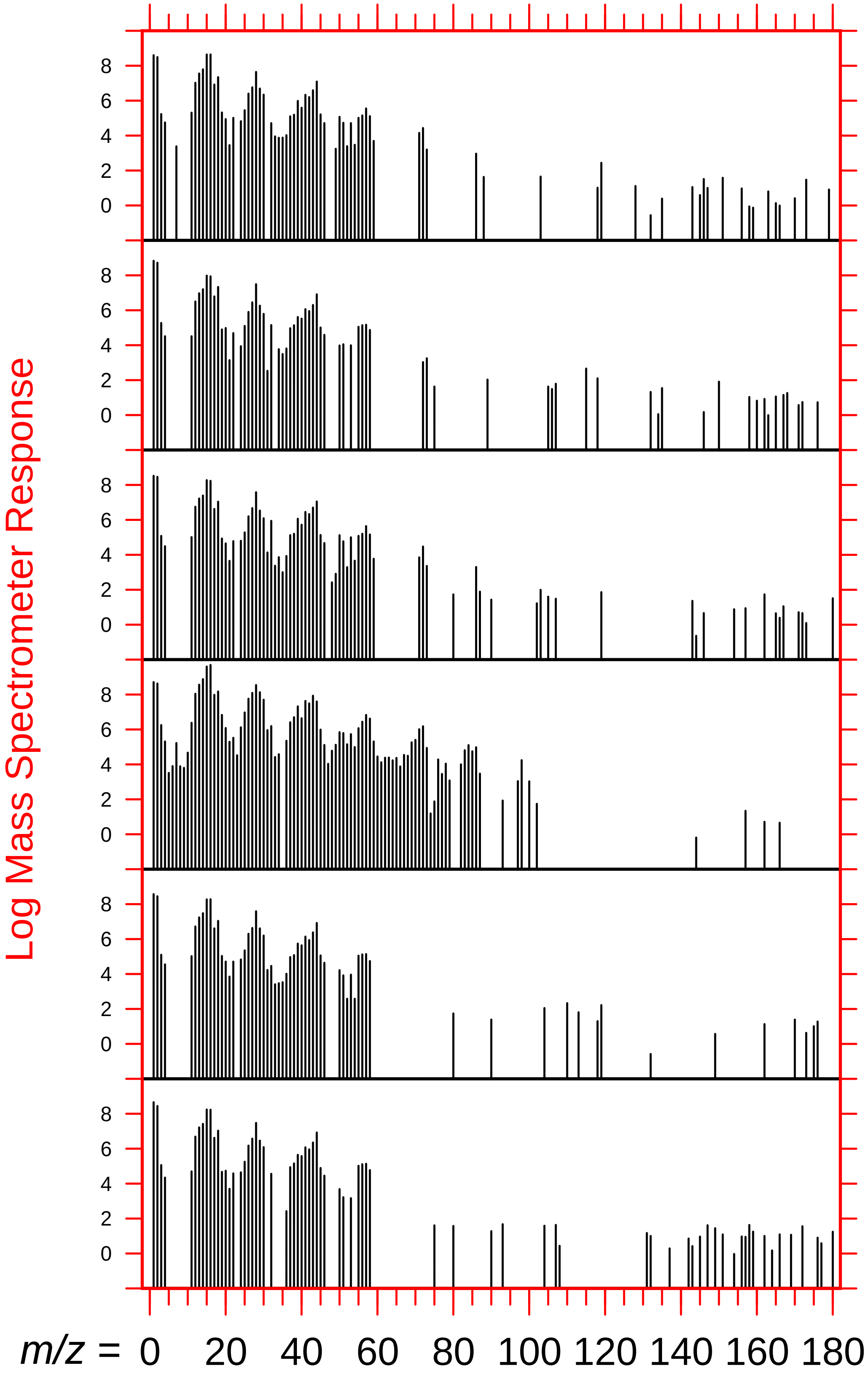
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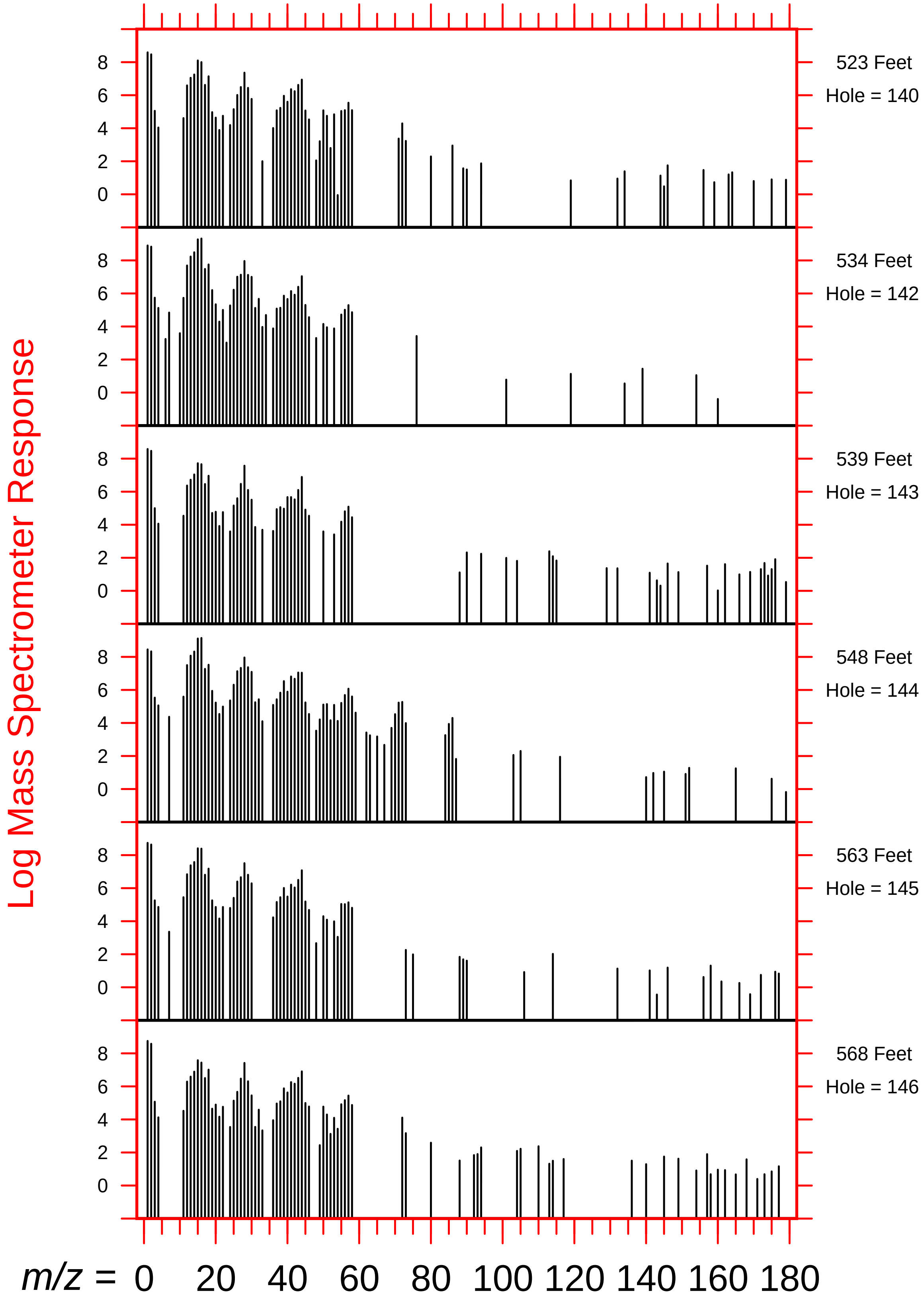

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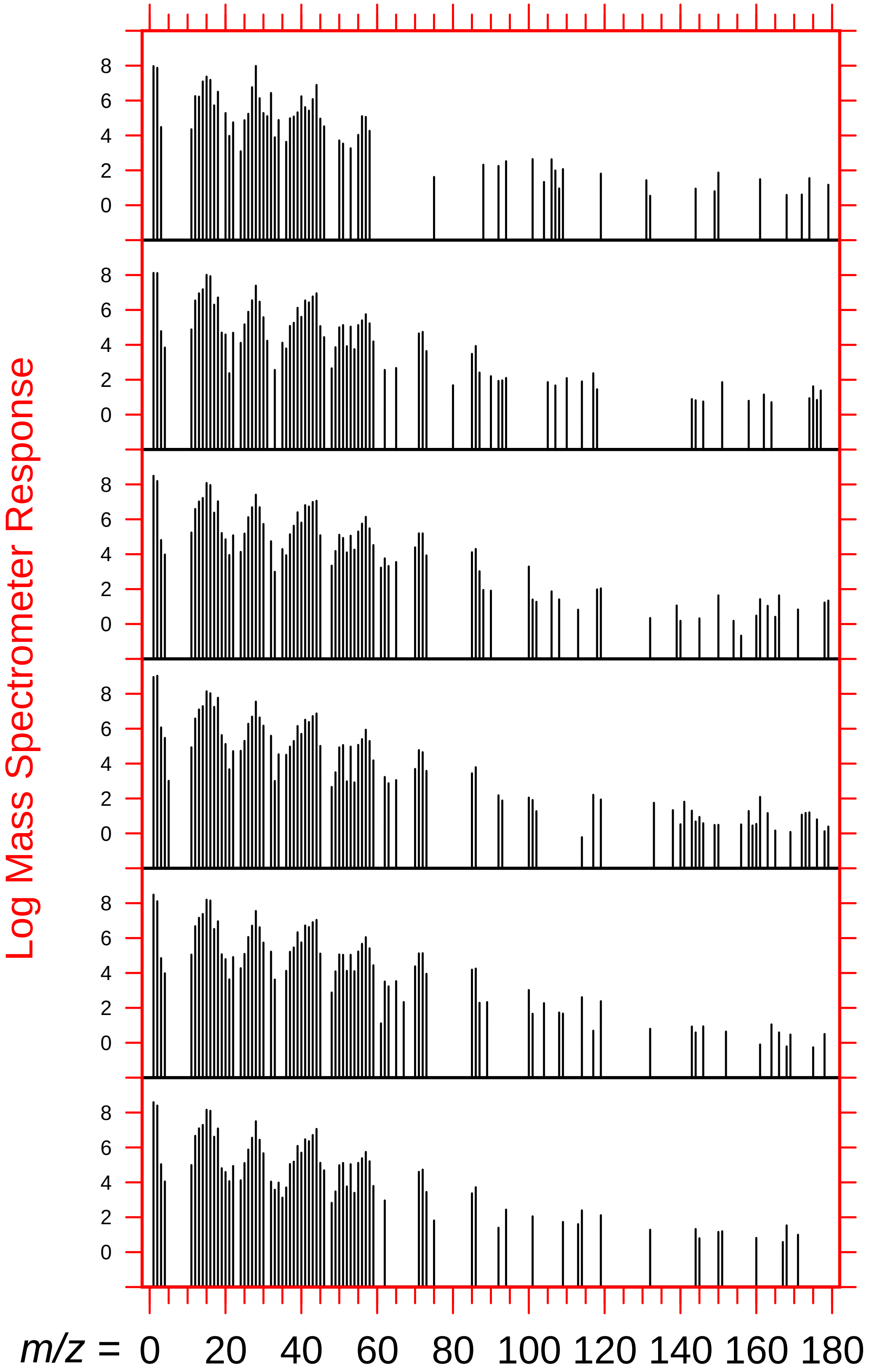
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618 Feet
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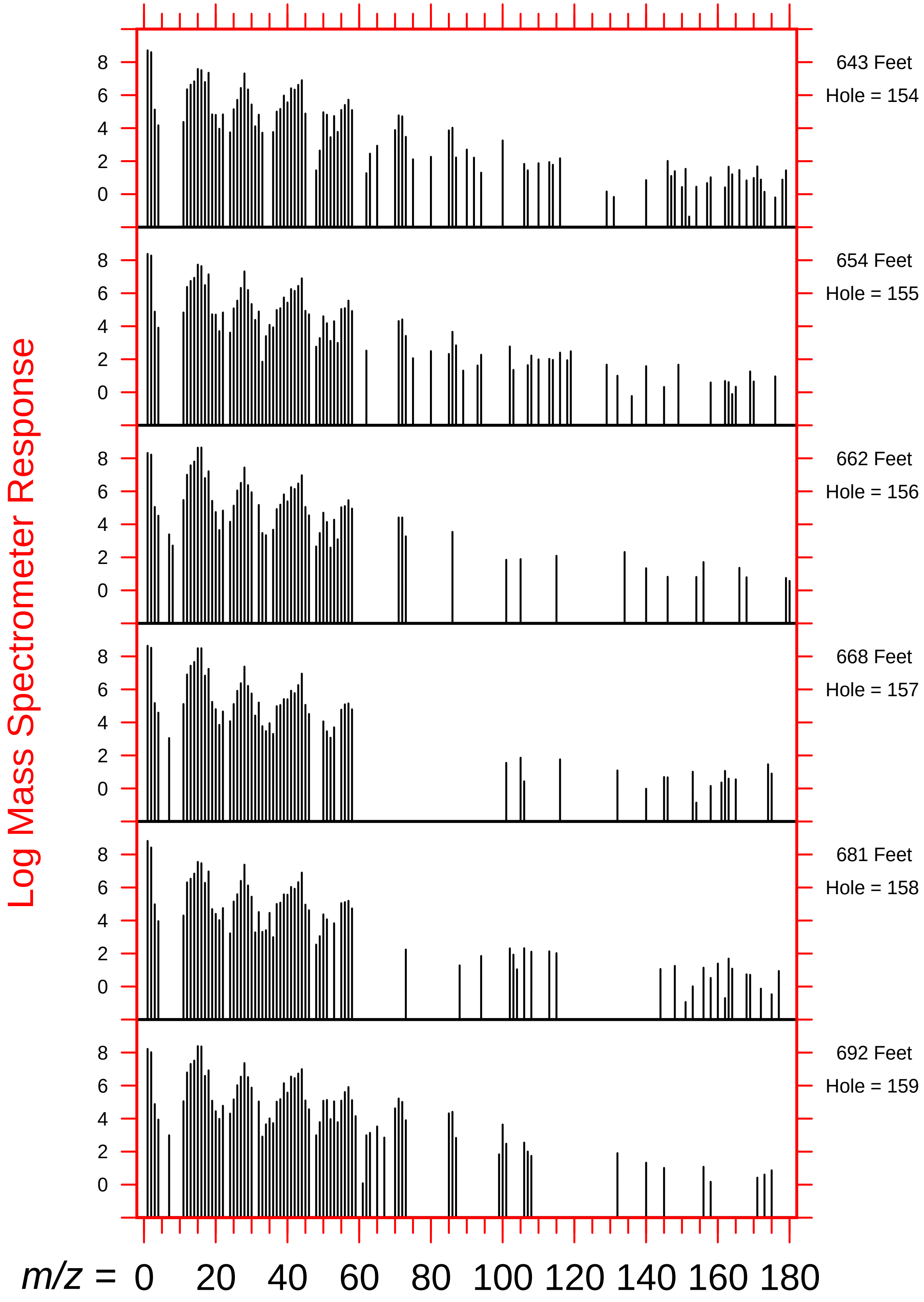
80
100
120
140
160
180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681 Feet
Hole = 158
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Hole = 159
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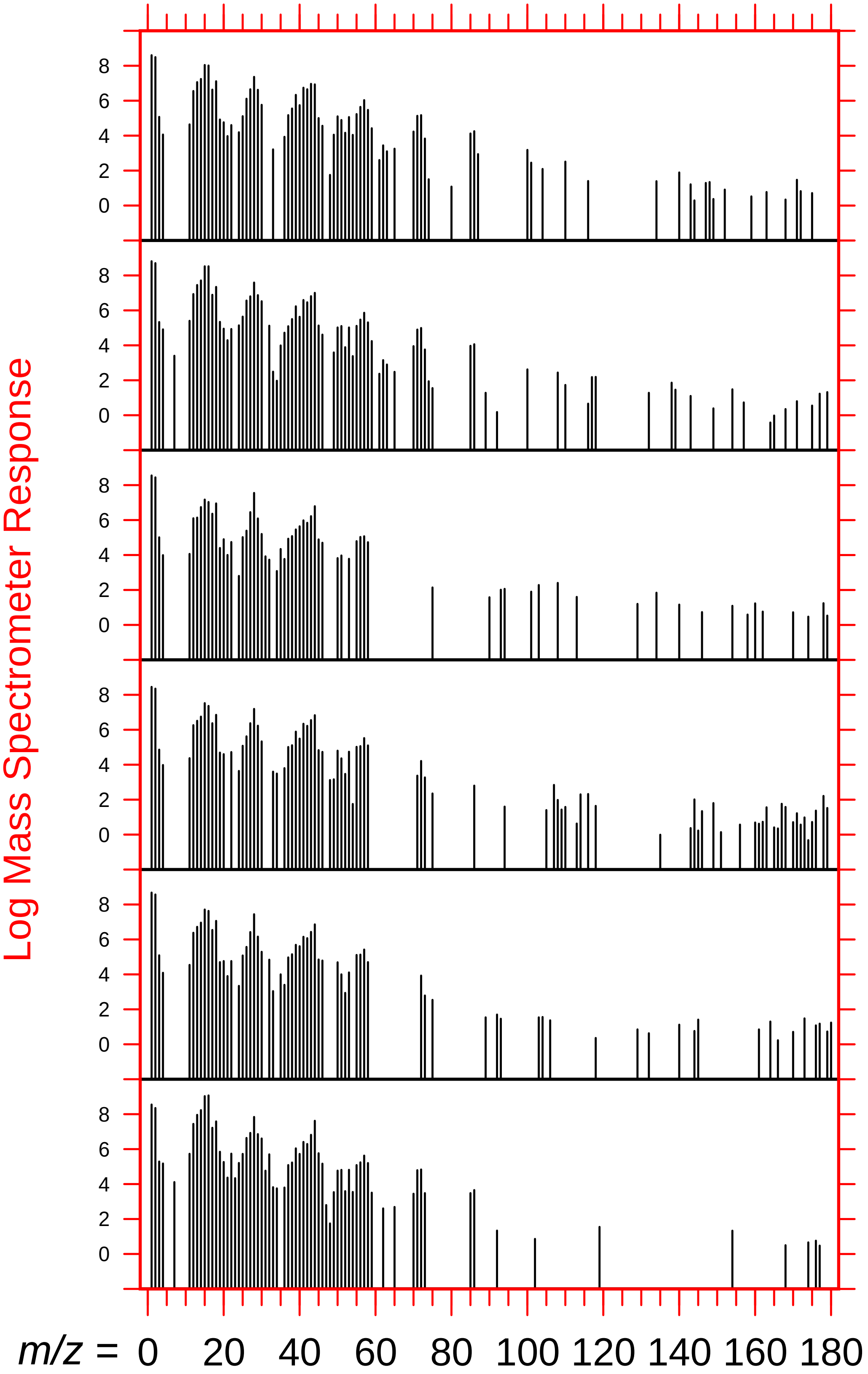
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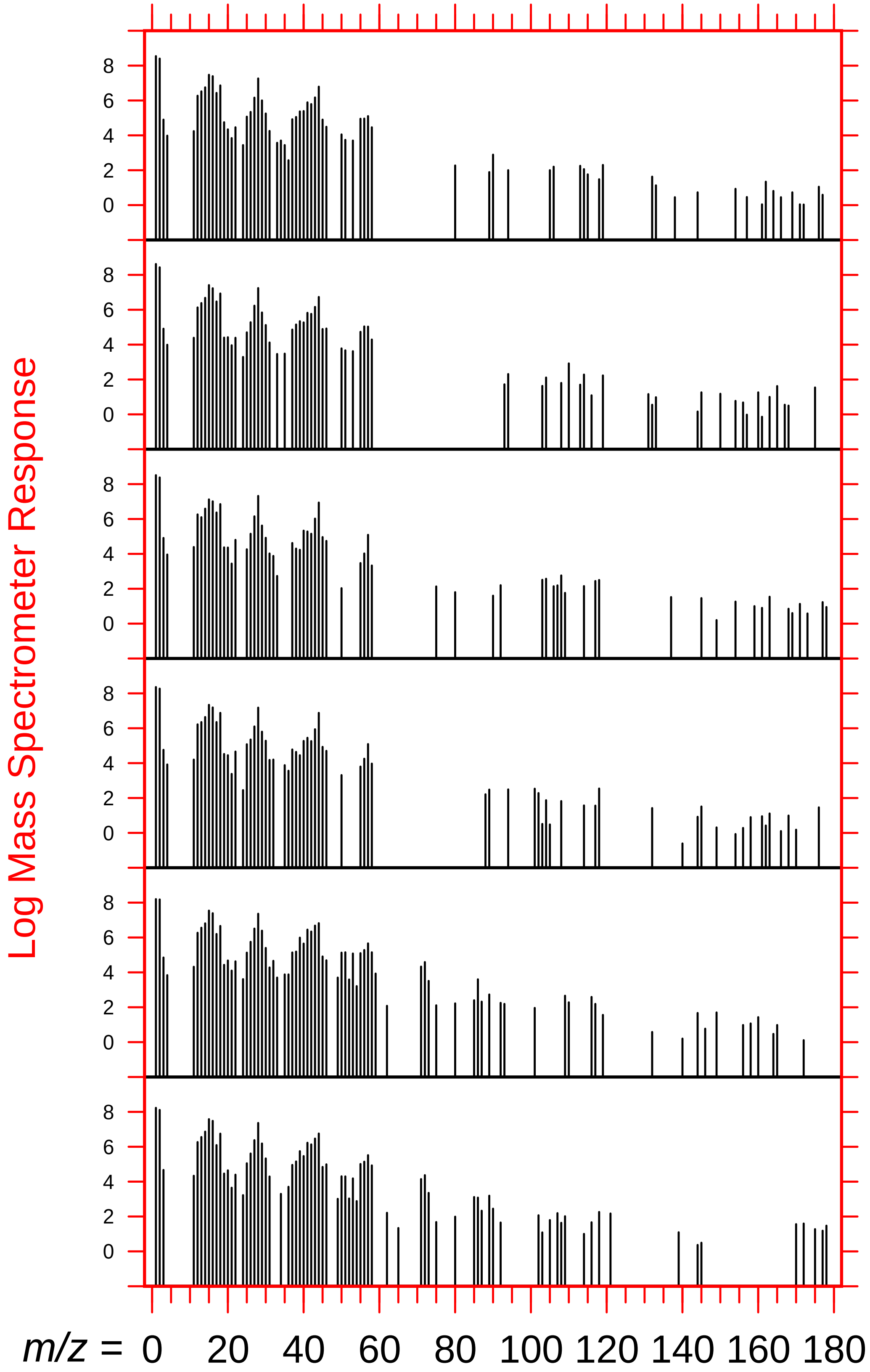
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781 Feet
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798 Feet
Hole = 172
806 Feet
Hole = 173
m/z = 0 20 40 60 80 100 120 140 160 180

Appendix 3

“A stratigraphic reconstruction of bulk volatile chemistry from fluid inclusions in: SO-C-01-15 and 1A,” Fluid Inclusion Technologies, Inc. report FIS# FI160559g prepared August 4, 2016 for the North Carolina Geological Survey, 79p.

UWI# 999999999999
FIS# FI160559g

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

SO-C-1-15 and 1A

Prepared August 4, 2016 for

NC Geological Survey

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

SO-C-1-15 and 1A

Prepared August 4, 2016
by
FIT
A Schlumberger Company

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Executive Summary for well: SO-C-1-15 and 1A

1 FIS Summary for SO-C-1-15 and 1A-15

Wells SO-C-1-15 and 1A-15 were drilled by the North Carolina Geologic Survey in 2015. The main hole, SO-C-1-15, was drilled to metamorphic basement and reached the basal conglomerate in the Pine Hall Fm, unfortunately a significant portion of coal and organic-rich sections were lost. SO-C-1A-15 is a sidetrack. Core samples at 197.3 ft and 204.5 ft from well SO-C-1-15 record fizzing/gas release. Weak petroleum odors were noted in core samples from well SO-C-1A-15 at 225 ft and 275 ft. Substantial de-gassing was noted in the lower portion of the core (Walnut Cove Fm) from SO-C-1A-15. This well was drilled with Insta-VIS Plus, a liquid drilling polymer. The product contains a petroleum solvent, a surfactant and poly oil. Wells SO-C-1-15 and SO-C-1A-15 were merged into a single FIS run and subsequent report. FIS analysis was performed on 6 core samples from well SO-C-1-15 at depths 197.3-204.5 ft and 1290-1432 ft. FIS analysis was performed on 40 core samples from 10-275 ft from well SOC-1A-15 as well. This study is performed in conjunction with three other wells (SO-C-1-81 in report FI160559a; SO-C-2-81 in report FI160559c; RC-C-1-81 in report FI160559e). The primary goals of the analysis were to study the Dan River Basin using FIS in order to determine the gas chemistry and hydrocarbon potential of the region. The areas of particular interest are the Walnut Cove Formation and the overlying Dry Fork Formation.

FIS data from the interval above 98 ft (Dry Fork Formation) give dry gas responses with a single wet gas spectrum at 89.5 ft. Stronger methane or liquid hydrocarbon signals are recorded at 41.5 ft and 89.5 ft. Gas and liquids are decoupled, suggesting either local contribution from kerogen or a two-stage charging history involving dry gas and a heavier fluid. CS2 of probable bacterial origin is noted at 41.5 ft and 89.5 ft, along with minor SO2 and H2S. SO2 can be accentuated in porous rock that has high water saturation and a source of sour gas components. Helium concentrations are elevated at 89.5 ft, but only at 30 ppm with respect to methane. Helium can indicate an ancient fraction of arkosic detritus, a deep sourced component of hydrocarbon gas, or diagenetic involvement of deep basin brines. A thin section prepared from 89.5 ft contains several occurrences of yellow, blue, and white-fluorescent, high gravity wet gas inclusions in porous sandstone. Some inclusions have what appear to be bitumen-dusted internal surfaces, possibly indicating post-entrapment thermal alteration. Porosity appears to be predominantly secondary, and to have occurred post-stylolitization, but some quartz cement clearly post-dates porosity development, as quartz euhedra are found to occupy secondary pore space. A charged deeper equivalent of this interval may represent an attractive conventional target. Shale contains minor gas-prone kerogen. Appreciable dead petroleum stain (pyrobitumen?) is also noted.

The section at 102.5-275 ft (Walnut Cove Formation) displays dry gas FIS responses with a single wet gas signal at 110 ft. Higher methane or liquid hydrocarbon concentrations are documented intermittently at 110-154 ft, 228 ft, and 245.5 ft. CS2 of possible thermal origin is identified intermittently at 110-275 ft. SO2 +/- S2 is detected at 224.5-245.5 ft. Helium spikes are identified at 224.5 ft and 245.5 ft, but only reach about 100 ppm with respect to methane. An elevated CO2 signal is noted at 224.5 ft. Three thin sections were evaluated. A sample from 275 ft contains several, white and pale-blue-fluorescent, high gravity wet gas inclusions in tight sandstone, indicating low petroleum saturation or migration. No visible petroleum inclusions were identified in the other two thin sections from 197.3 ft (ostracod-rich, carbonate-rich shale; possibly with some barite and phosphate) and 228 ft (sandy carbonate rich shale). Shale contains moderate to high abundance of gas-prone (or overmature) kerogen (most prominent at 228 ft and 275 ft). Moderate to high abundance of dead stain (possible pyrobitumen) is identified at 275 ft.

The lowermost analyzed section at 1290-1432 ft (Pine Hall Formation) shows mostly weak dry gas FIS spectra with slight enrichment in benzene. No thin sections were prepared in this interval.

2 FIS Chemical Zonation

10 ft to 98 ft :

Dry gas: 90%

Wet gas: 10%

Hydrocarbon species to C7 are observed in this zone. No proximity to pay signal is indicated. Sulfur species are extensively recorded.

Slide @ 89.5 ft: Population 1: Several, high gravity petroleum inclusions are indicated. Population 2: Rare, high gravity petroleum inclusions are preserved. Population 3: Rare, high gravity petroleum inclusions are observed. Several occurrences of gas prone kerogen are found. Common occurrences of dead stain are indicated.

102.5 ft to 275 ft :

Dry gas: 97%

Wet gas: 3%

Hydrocarbon species to C6 are documented in this zone. No proximity to pay signal is observed. Sulfur species are extensively observed.

Slide @ 197.3 ft: Several occurrences of gas prone kerogen are present.

Slide @ 228 ft: Common occurrences of gas prone kerogen are indicated.

Slide @ 275 ft: Population 1: Several, high gravity petroleum inclusions are present. Abundant occurrences of gas prone kerogen are found. Several occurrences of dead stain are found.

1290 ft to 1432 ft :

Dry gas: 83%

Low hydrocarbon responses: 17%

Hydrocarbon species to C1 are found in this section. No proximity to pay signal is recorded. Sulfur species are not documented.

Summary of Results for well: SO-C-1-15 and 1A

This report contains Fluid Inclusion Stratigraphy and Fluid Inclusion Petrography results for SO-C-1-15 and 1A and was prepared for NC Geological Survey by *Fluid Inclusion Technologies, 2217 N. Yellowood Ave., Broken Arrow, OK 74133; ph: (918) 461-8984; fax: (918) 461-2085; www.fittulsa.com.*

Table I: Logistical Information

Client:	**NC Geological Survey**	Analyzed Depth:	**10 - 1432 Feet**
Well:	**SO-C-1-15 and 1A**	Sample Spacing:	**See Individual Spectra**
		Sample Total:	**46**

Table II: Fluid Inclusion Petrography from SO-C-1-15 and 1A

Well Name: SO-C-1-15 and 1A																					
Sample Depth	**Rock Type**		**Petroleum Fluid Inclusion Populations**												**Kerogen (possible source rk)**					**Bitu-men**	
			Population 1				**Population 2**				**Population 3**										
Units: **(Feet)**	***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***
89.5	ss,sh,mu,bi		wt	h	dq	sv	bl	h	dq	r	yl	h	dq	r	sh	gp		sv		ds	c
197.3	sdmish														sh	gp		sv			
228	cbsh,tr ss														sh	gp		c			
275	sdcbsh		wt	h	dq	sv									sh	gp		a		ds	sv

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: mu = muscovite,
an: anhydrite	wt: white	qc: quartz cement	go: oil and gas prone	bi = bioite, sdmish =
ch: chert	bl: blue	df: frac detrital feldspar	op: oil prone	sand, mica-rich sh, cbsh
co: coal	l: low	cm: matrix carbonate	gp: gas prone	= cb-rich sh, sdcbsh =
ig: igneous rock	ul: upper-low	cc: carbonate cement	ls: live petroleum stain	sand, cb-rich sh

Table III: FIS Terminology: Abbreviations and Acronyms

HC Type & Quality		Anomalous HC Zones		Fluid Contacts	
NHC	non-hydrocarbon	**MP**	migration pathway	**OWC**	oil-water contact
DG	dry gas	**PC**	present day ptrlm column	**GWC**	gas-water contact
WG	wet gas	**PPC**	paleo-ptrlm column	**GOC**	gas-oil contact
GC	gas condensate	**RI**	recycled ptrlm inclusions	**POWC**	paleo-oil-water contact
VO	volatile oil	**SR**	source rock	**PGWC**	paleo-gas-water contact
O	oil	**GP**	gas prone kerogen	**PGOC**	paleo-gas-oil contact
BD	biodegraded	**OP**	oil prone kerogen		
TA	thermally altered	**OGP**	oil and gas prone kerogen		
		CNT	contamination		

Water-Soluble Anomalies		Miscellaneous	
WS	undifferentiated water-soluble anomaly	**SL**	seal
WSSR	source rock related water-soluble anomaly	**MS**	microseep
WSTA	water-soluble anomaly sourced from thermal alteration		
PTPL	proximity to oil or gas-condensate		
PTPG	proximity to gas		

Petrographic Observations					
A	abundant	**IG**	igneous rock	**SA**	salt
AN	anhydite	**L**	low	**SH**	shale
BL	blue	**LG**	large	**SI**	siltstone
BR	brown	**M**	moderate	**SM**	small
C	common	**MD**	medium	**SS**	sandstone
CB	carbonate	**MT**	metamorphic rock	**ST**	petroleum stain
CC	carbonate cement	**NO**	none	**SV**	several
CH	chert	**OR**	orange	**UL**	upper-low
CM	matrix carbonate	**PB**	pyrobitumen	**UM**	upper-moderate
CO	coal	**PF**	pore filling bitumen	**V**	variable
DF	detrital feldspar	**PR**	pore rimming bitumen	**W**	weak
DQ	detrital quartz	**QC**	quartz cement	**WT**	white
DR	quartz dust rim	**R**	rare	**XA**	extremely abundant
H	high	**S**	strong	**YL**	yellow

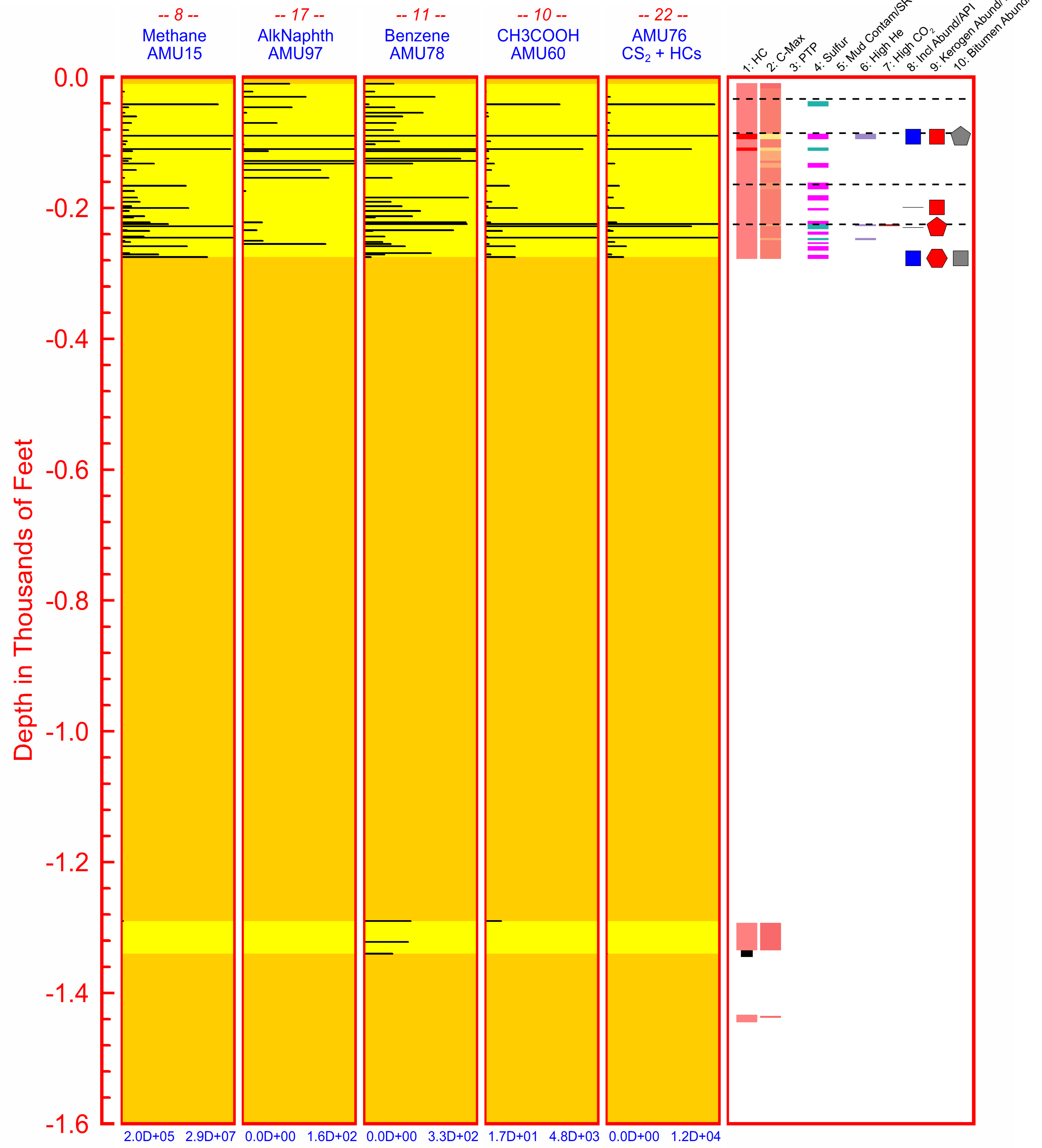
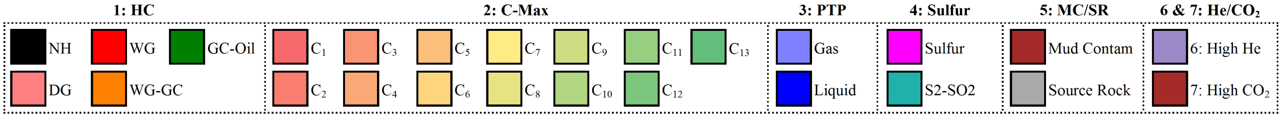


Figure 1: FIS Summary Tracks (see Sect. A for further explanation)



Legend (cont)

8: Colors for Inclusion Abundance/API describe the API gravity of the liquid hydrocarbon inclusions:

- ▲ **Triangle:** Rare abundance **Brown:** Low Gravity
- 🟧 **Square:** Several abundance **Orange:** Upper Low gravity
- ⬟ **Pentagon:** Common abundance **Yellow:** Moderate gravity
- ⬢ **Hexagon:** Abundant **Light blue:** Upper Moderate gravity
- 🔵 **Circle:** Extra Abundant **Blue:** High gravity

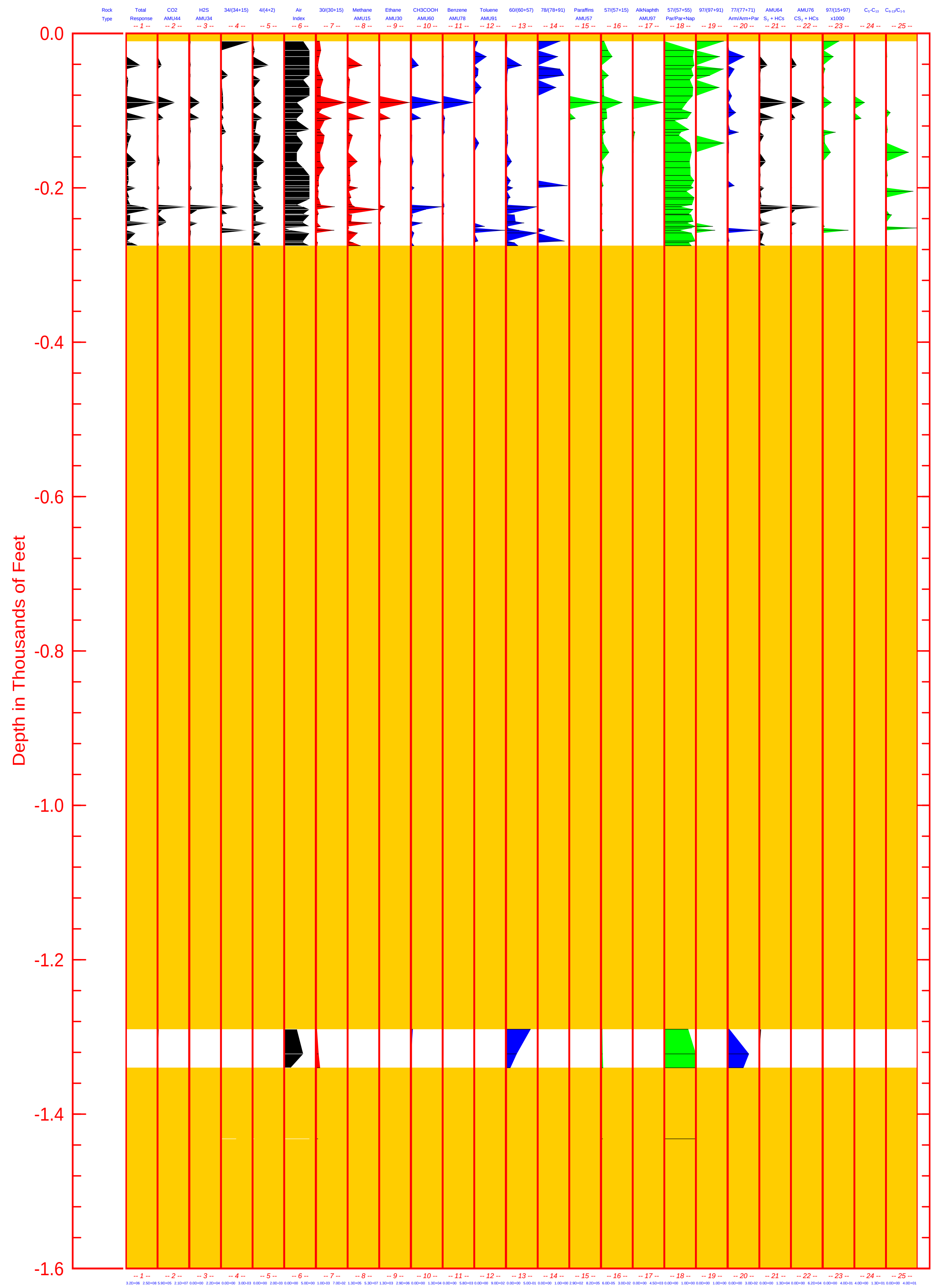
9: Colors for Kerogen indicate if the kerogen are oil prone, gas prone, or both

- 🔺 **Triangle:** Rare kerogen abundance **Red:** Gas prone
- 🟧 **Square:** Several abundance **Orange:** Both oil and gas
- ⬟ **Pentagon:** Common kerogen abundance **Green:** Oil prone
- ⬢ **Hexagon:** Abundant **Red:** Gas prone
- 🟠 **Circle:** Extra Abundant kerogen **Orange:** Both oil and gas

10: Colors for Bitumen indicate the bitumen type:

- ▲ **Triangle:** Rare bitumen abundance **Green:** Live stain
- ■ **Square:** Several bitumen **Gray:** Dead stain
- ⬟ **Pentagon:** Common kerogen abundance **Green:** Live stain
- ⬢ **Hexagon:** Abundant bitumen **Black:** Pore occluding
- ● **Circle:** Extra Abundant bitumen **Magenta:** Pyrobitumen

SO-C-1-15 and 1A : All FIS Data



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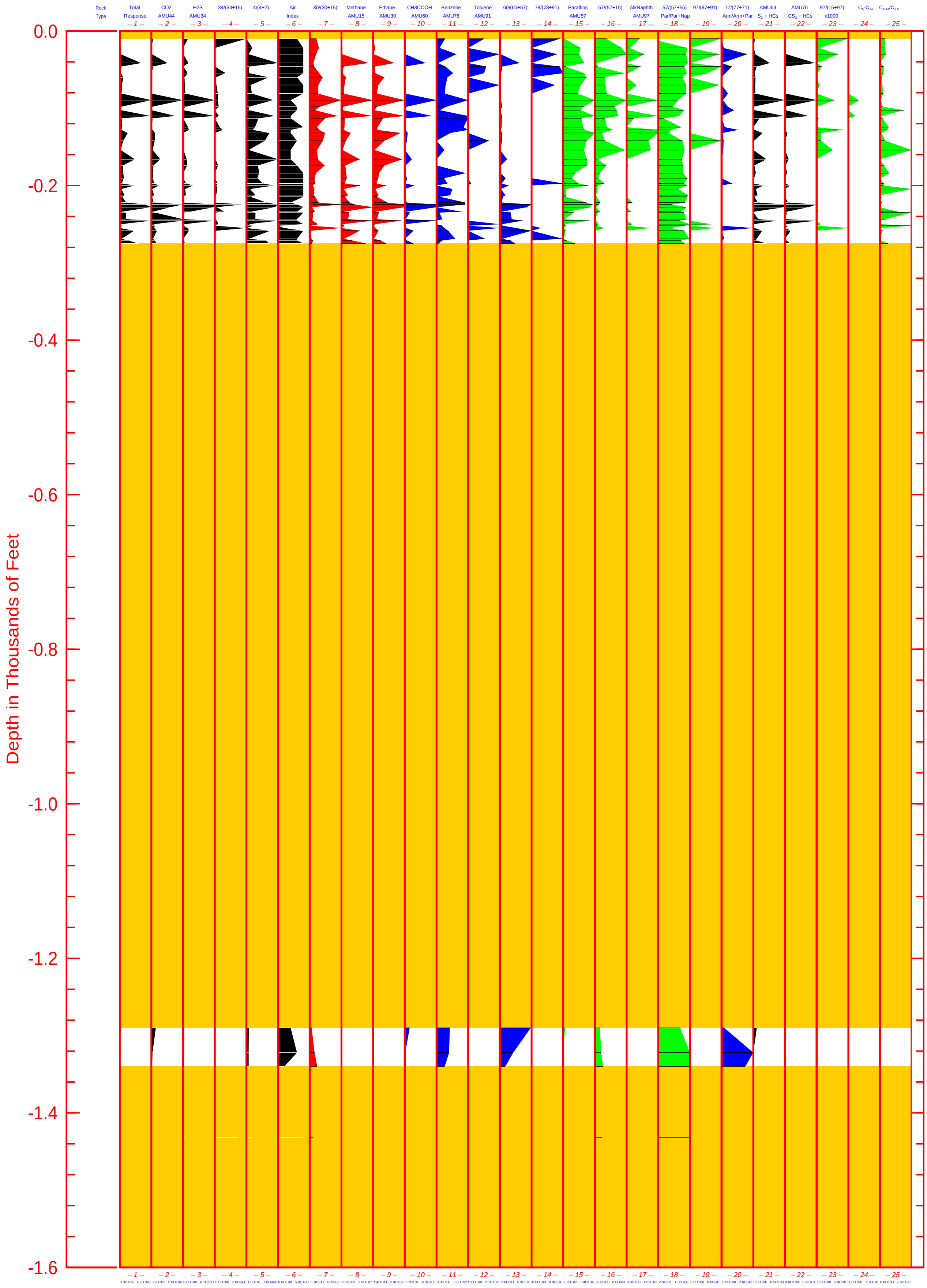
UWI# 999999999999
FIS# *FI*160559*g*

SO-C-1-15 and 1A : 90% of all FIS Data



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UWI$^{\#}$999999999999
FIS$^{\#}$FI160559g

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Appendices

List of Tables

List of Figures

3 Overview of FIT, Inc. and Fluid Inclusion Stratigraphy

FIT, a Schlumberger Company, is a laboratory-based petroleum service organization established in 1997 and acquired by Schlumberger in November, 2015, 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 FIT 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 Compartmentallization** 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".

3.1 General Logistics of Initiating an FIS Analysis

To Initiate an FIS Analysis: contact FIT[1] 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 FIT for sample preparation including any necessary crushing/sieving, subsampling and washing.

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), 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

---

[1] FIT Inc., a Schlumberger Company affiliate, 2217 N. Yellowood Ave., Broken Arrow, 74012, USA., phone (918) 461-8984

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 SO-C-1-15 and 1A 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. FI160559g-1.las – LAS-format, 26-column file containing recorded depth and Tracks 1-25 from the *FIT Analysis* of SO-C-1-15 and 1A
2. FI160559g-2.las – LAS-format, 181-column file containing recorded depth and background corrected, normalized, standardized individual mass spectra (m/z 2-180) from the *FIT Analysis* of SO-C-1-15 and 1A
3. FI160559g-s.pdf – PDF format, electronic file of the summary tracks from the *FIT Analysis* of SO-C-1-15 and 1A
4. FI160559g-t.pdf – PDF format, electronic file of the petrography table from the *FIT Analysis* of SO-C-1-15 and 1A
5. FI160559g-1.pdf – PDF format, electronic file of the final report (entire document) of the *FIT Analysis* of SO-C-1-15 and 1A

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 (H_2^+)
4	helium ($^4He^+$)
15	C_1 fragment (CH_3^+); largely methane
30	C_2 fragment ($C_2H_6^+$); largely ethane
34	hydrogen sulfide (H_2S^+)
44	dominantly carbon dioxide (CO_2^+); possible C_3 fragment overlap
55	contribution from C_4 and greater naphthenes
57	contribution from C_4 and greater paraffins
60	dominantly acetic acid (CH_3COOH^+); possible dominance by carbonyl sulfide (COS^+) in some cases
64	S_2 or SO_2 plus hydrocarbons
71	contribution from C_5 and greater paraffins
76	CS_2 plus hydrocarbons
77	contribution from aromatic species
78	benzene ($C_6H_6^+$) with possible contribution by carbon disulfide (CS_2^+)
91	toluene ($C_7H_7^+$)
97	C_7 alkylated naphthene fragment

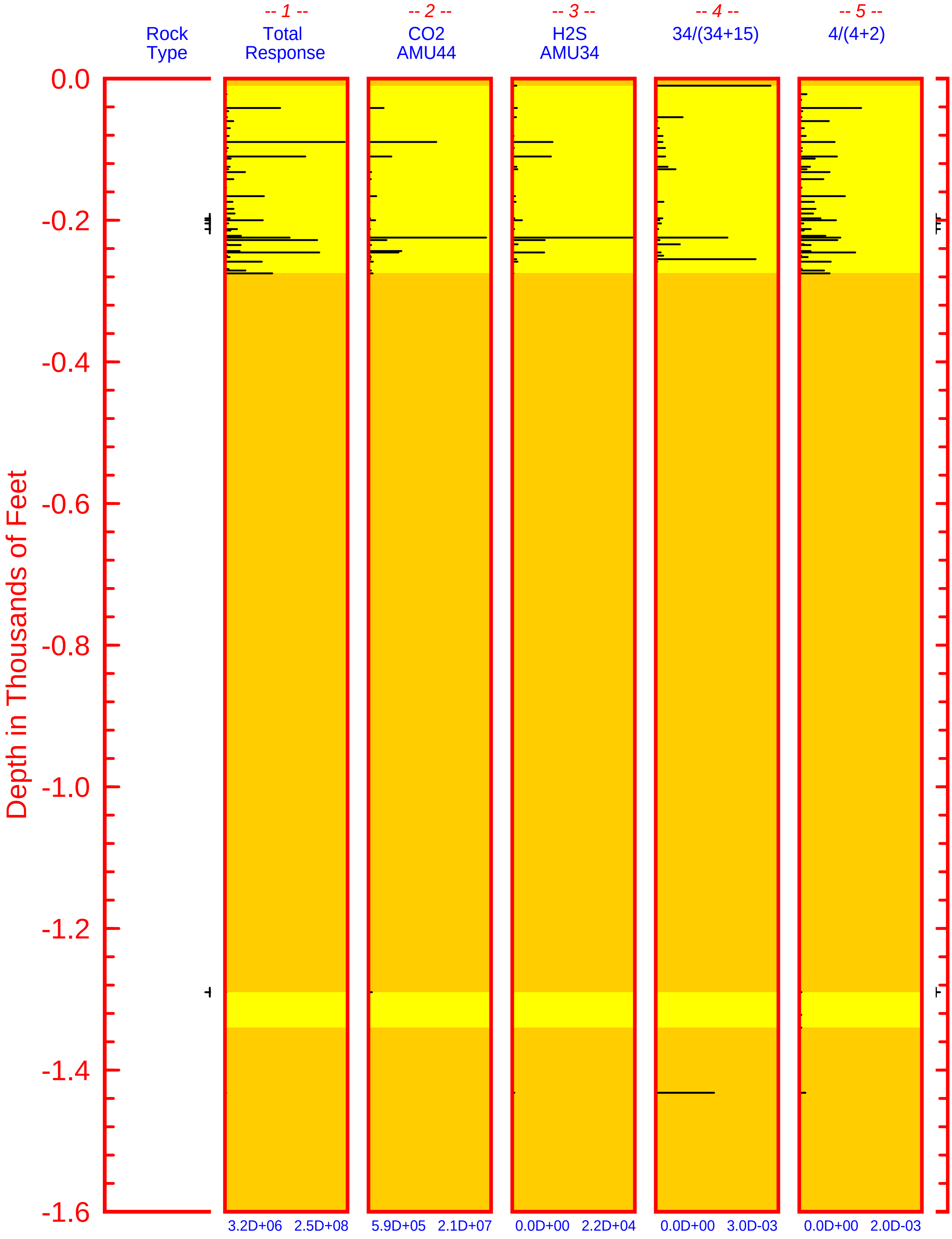


Figure 2: All FIS Data: Tracks 1 – 5 (see Sect. A.3 for explanation)

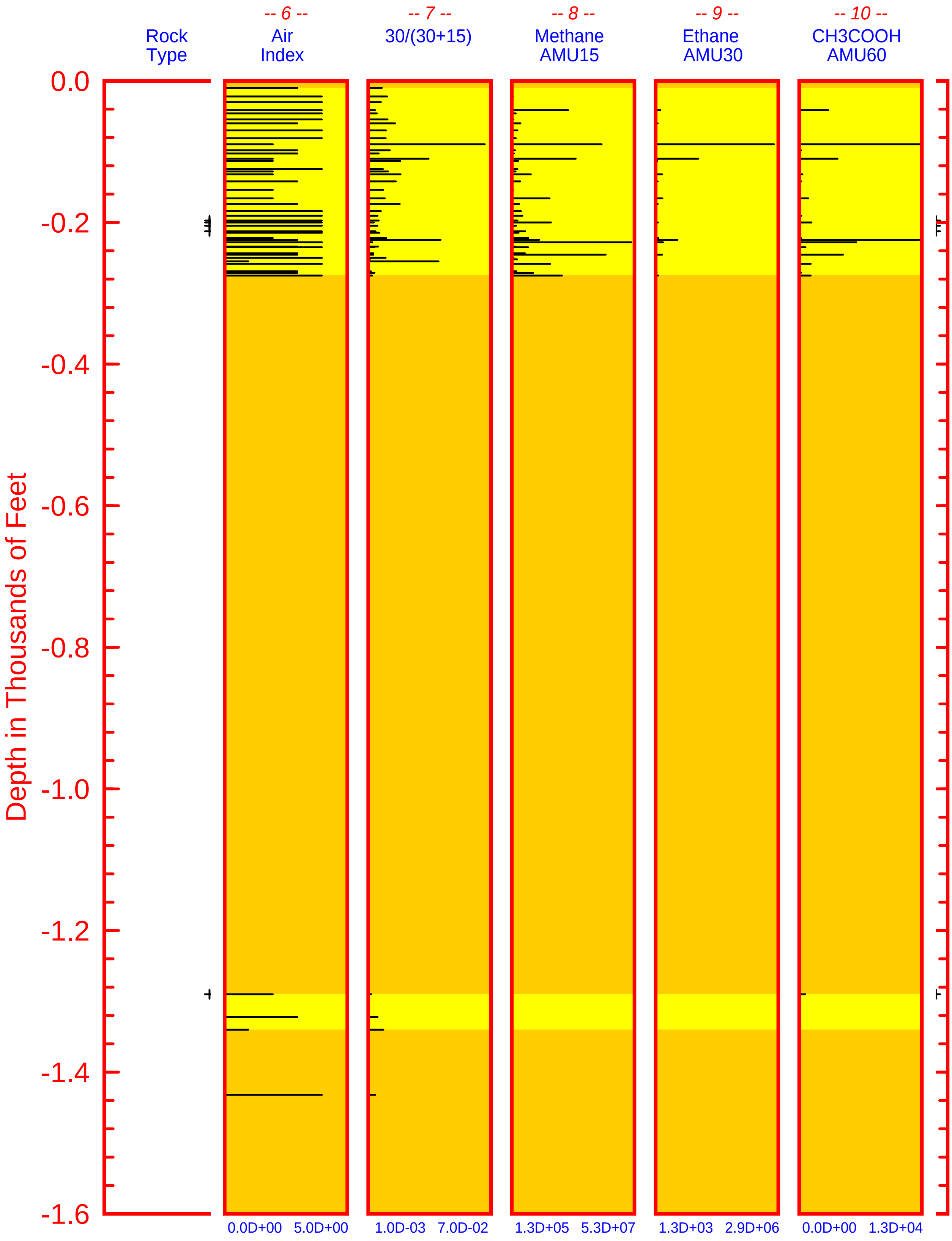


Figure 3: All FIS Data: Tracks 6 – 10 (see Sect. A.3 for explanation)

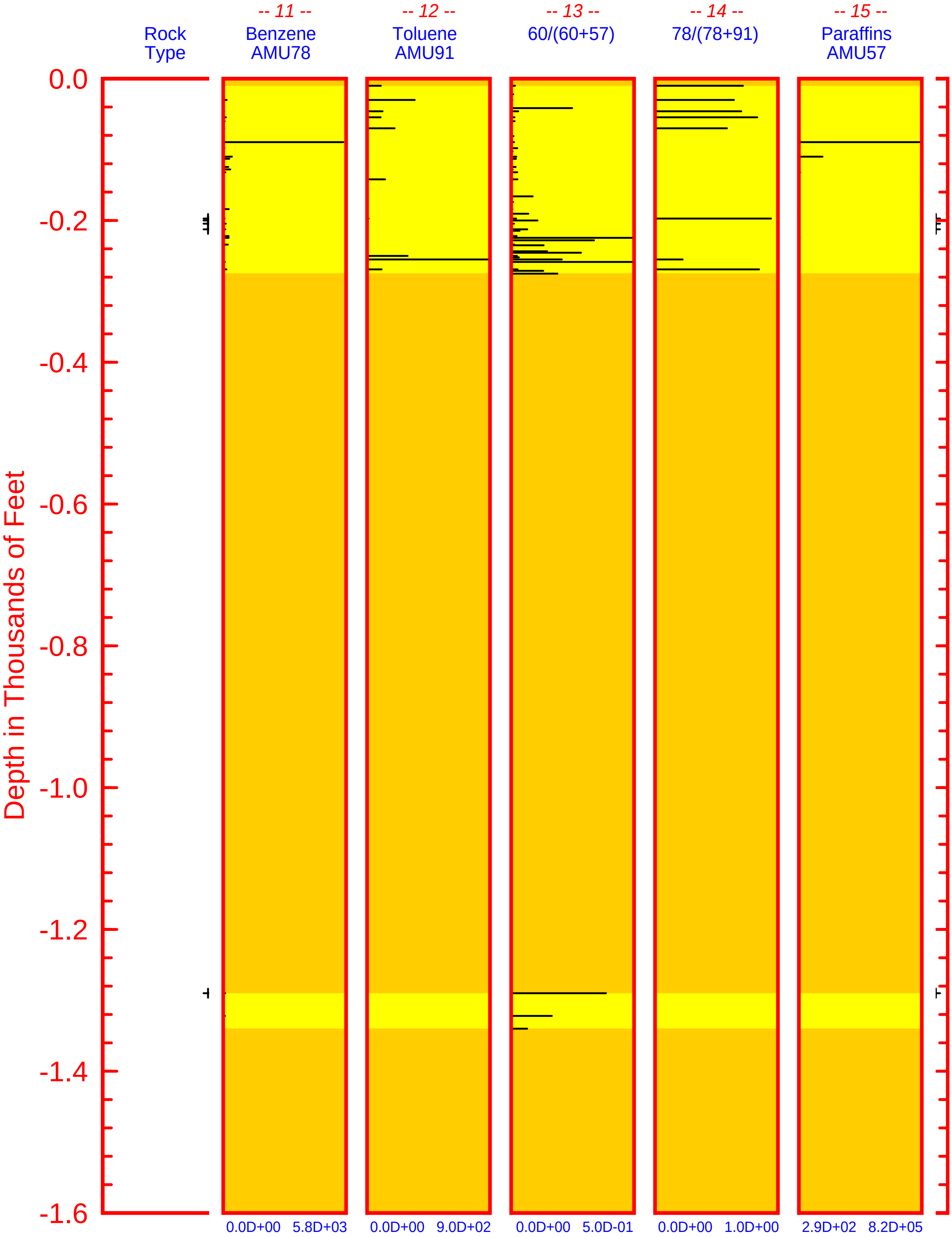


Figure 4: All FIS Data: Tracks 11 – 15 (see Sect. A.3 for explanation)

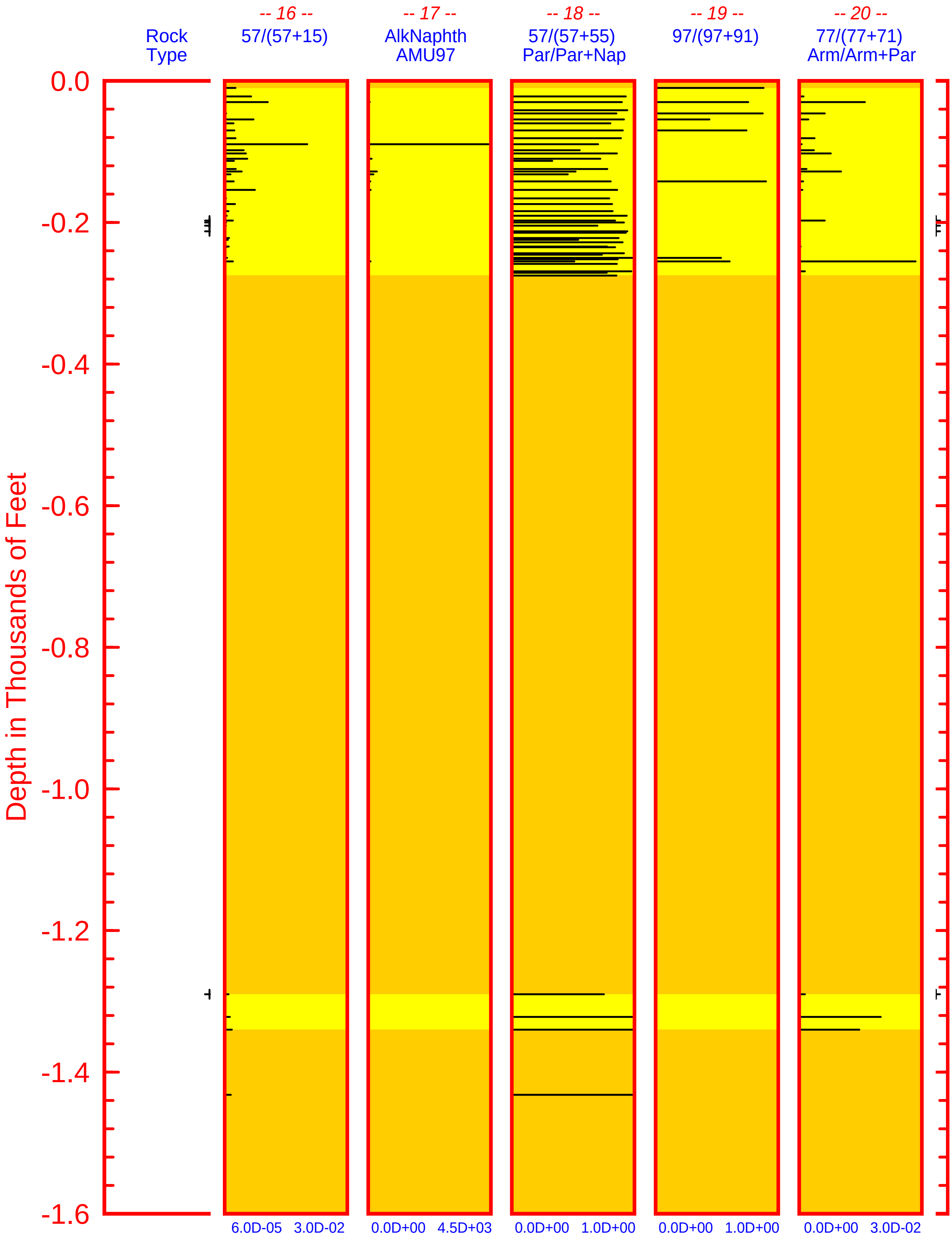


Figure 5: All FIS Data: Tracks 16 – 20 (see Sect. A.3 for explanation)

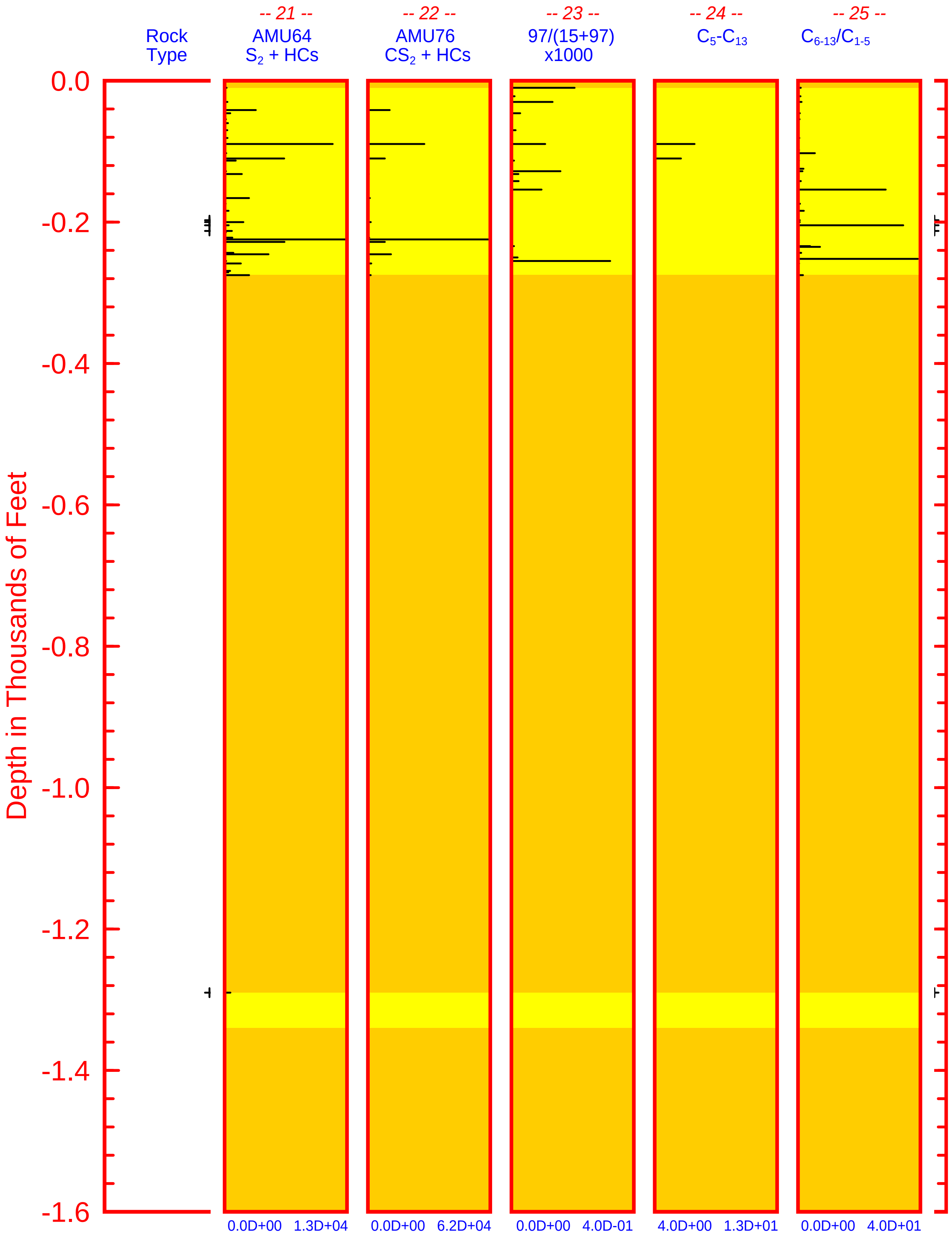


Figure 6: All FIS Data: Tracks 21 – 25 (see Sect. A.3 for explanation)

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.

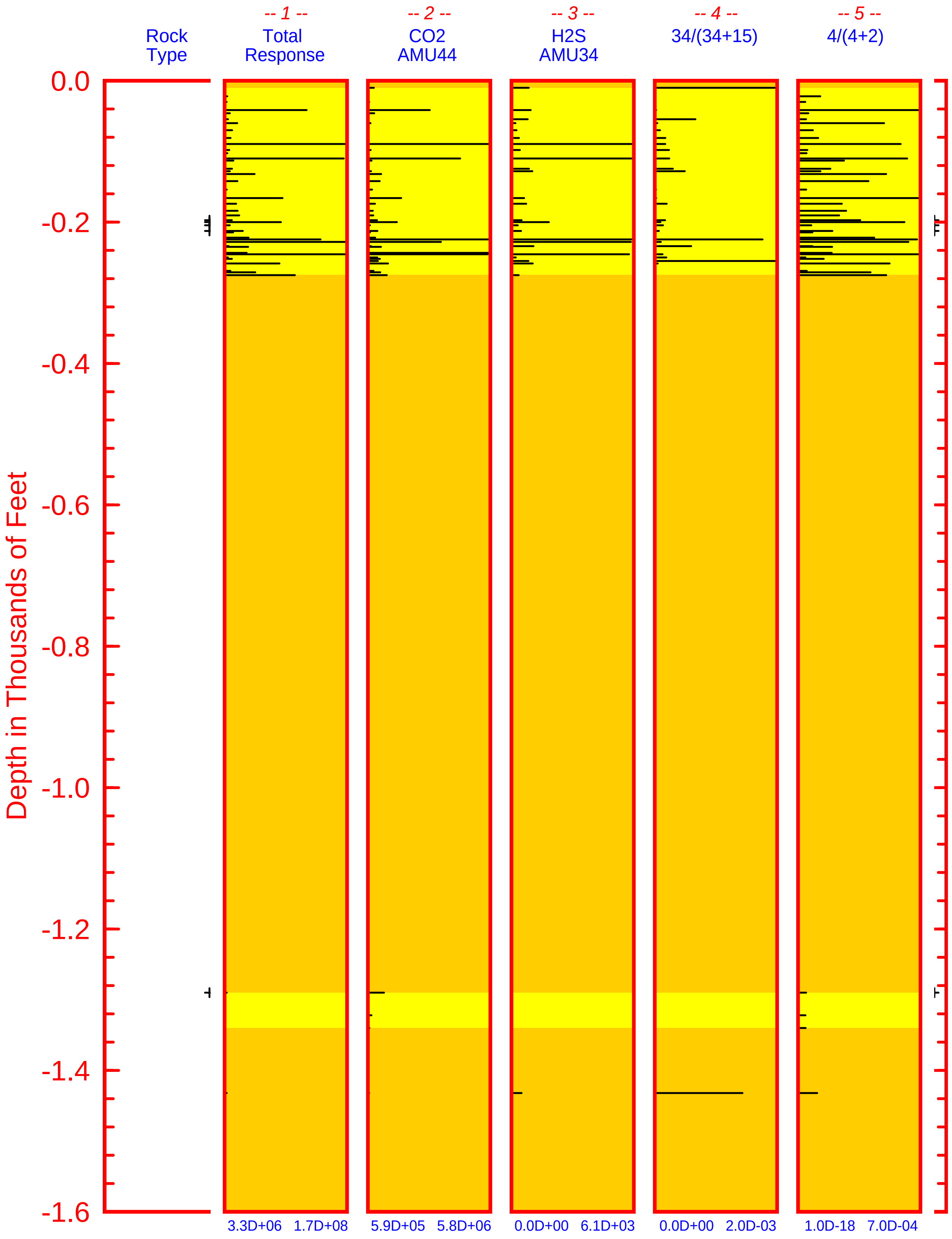


Figure 7: 90% of all FIS Data: Tracks 1 – 5 (see Sect. A.3 for explanation)

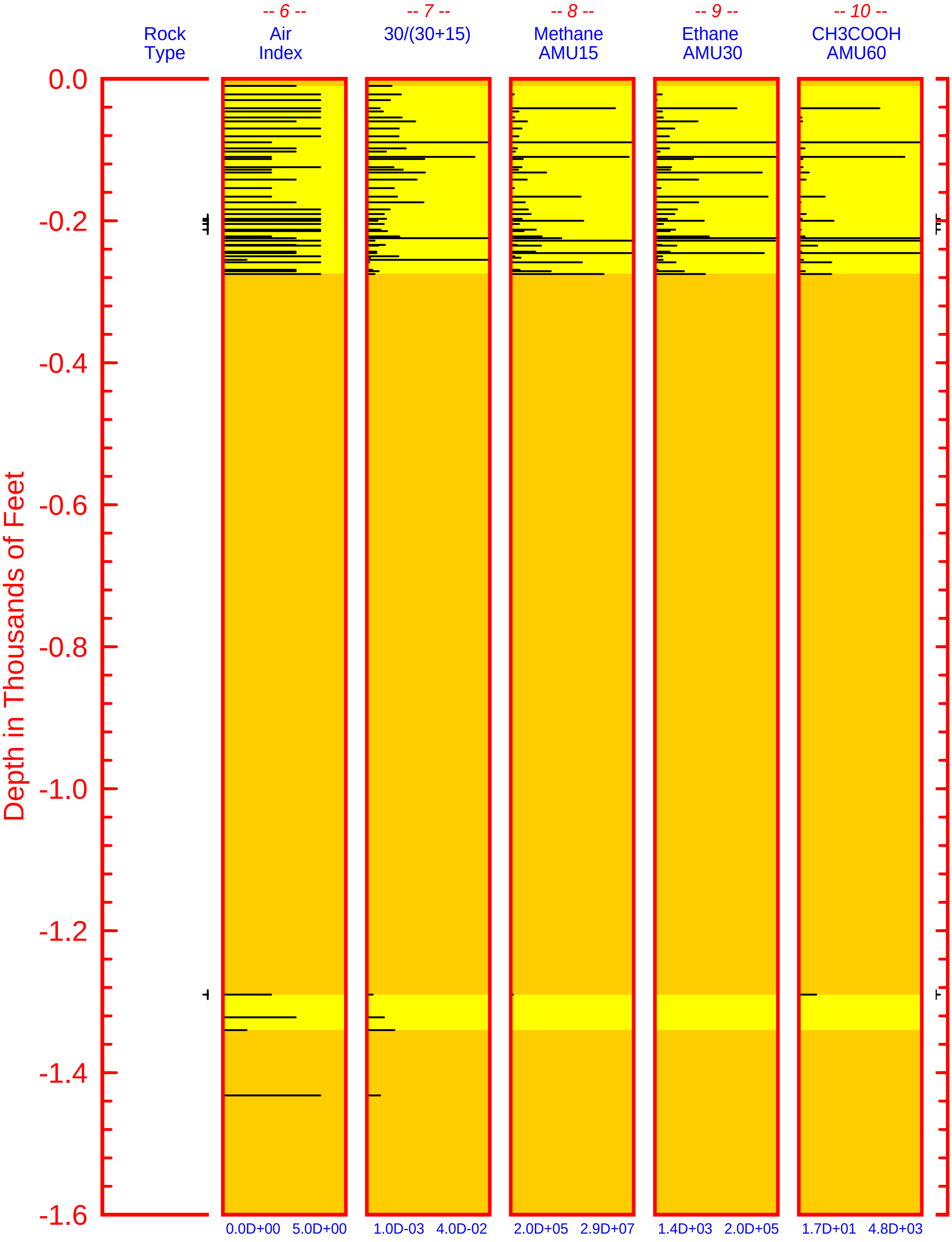


Figure 8: 90% of all FIS Data: Tracks 6 – 10 (see Sect. A.3 for explanation)

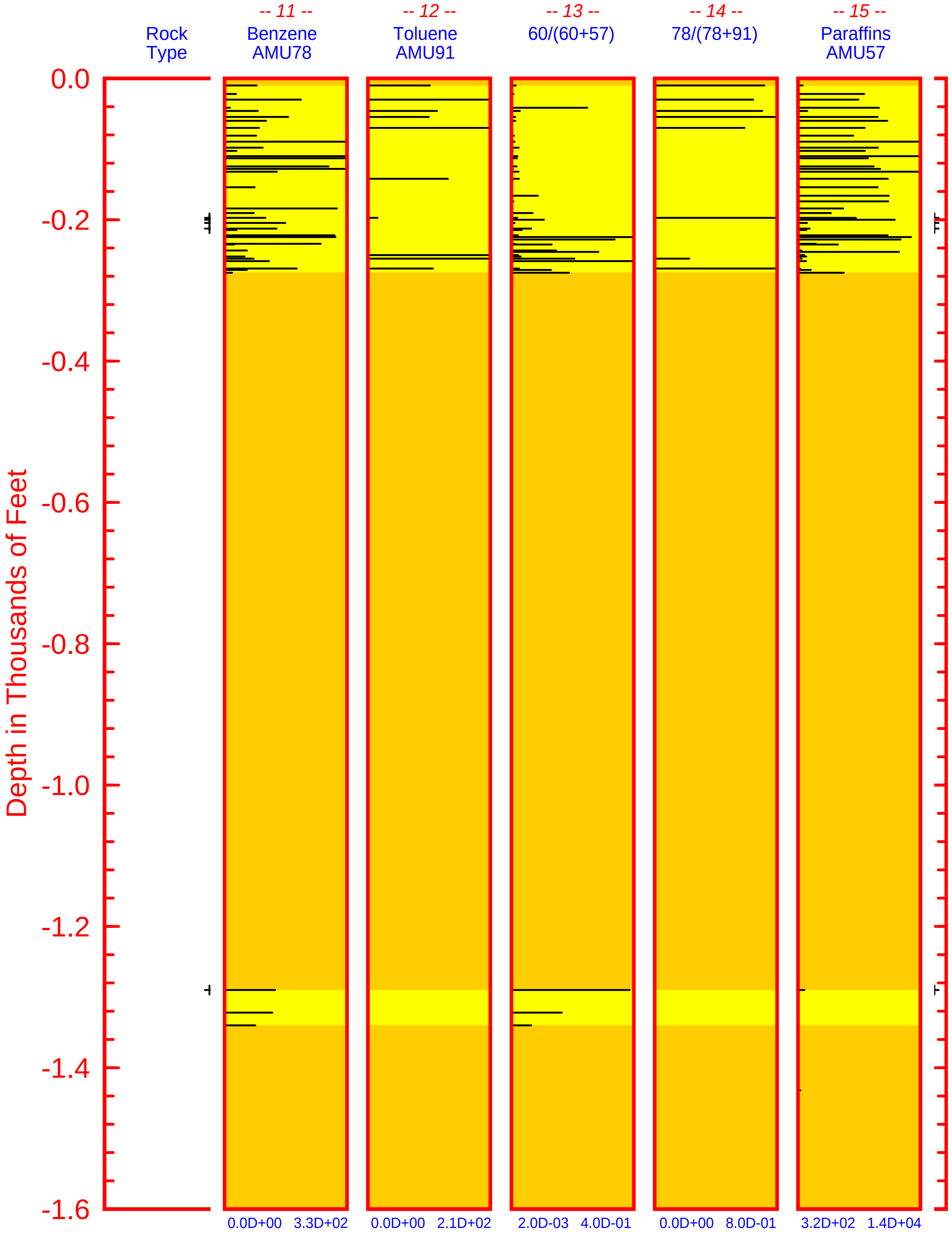


Figure 9: 90% of all FIS Data: Tracks 11 – 15 (see Sect. A.3 for explanation)

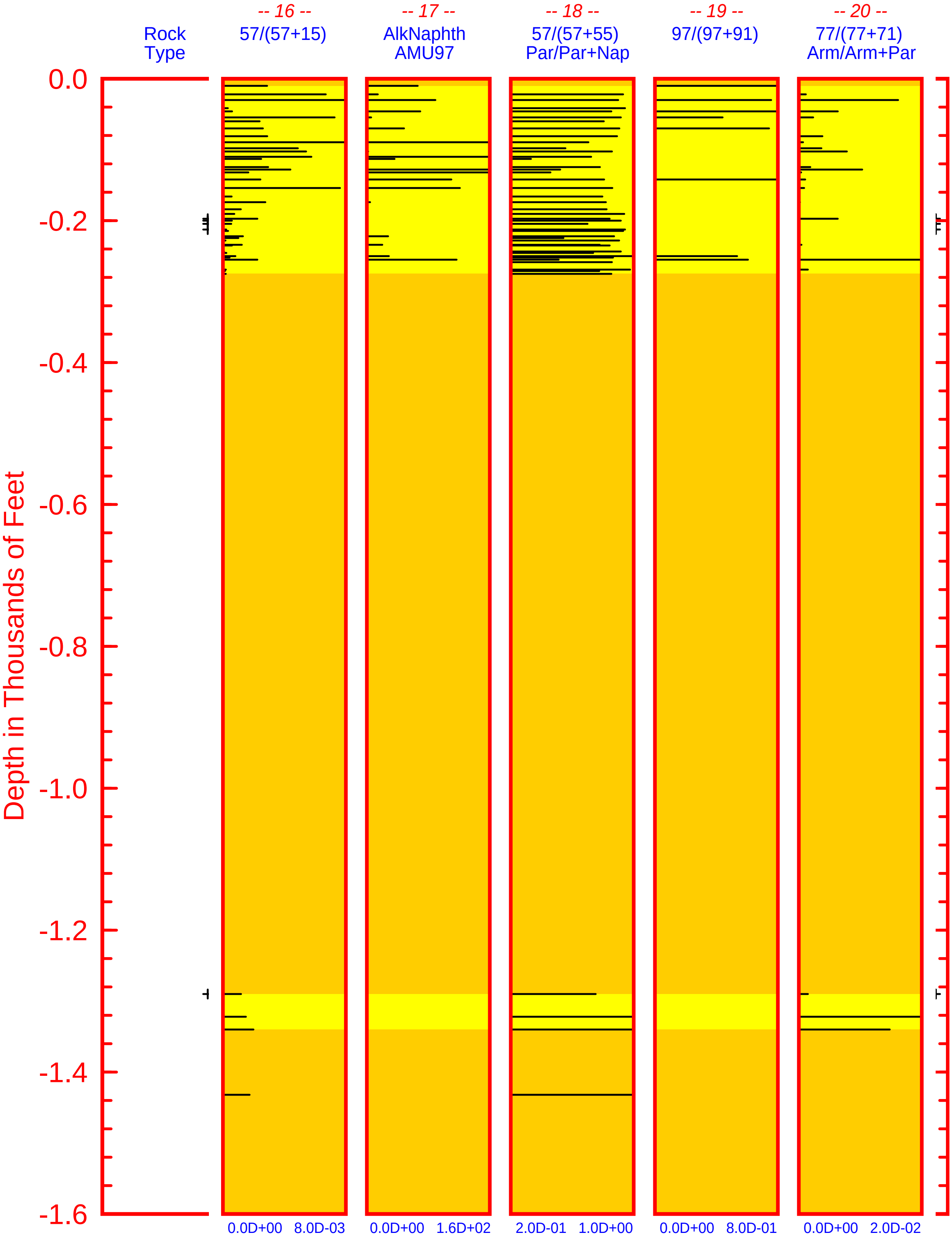


Figure 10: 90% of all FIS Data: Tracks 16 – 20 (see Sect. A.3 for explanation)

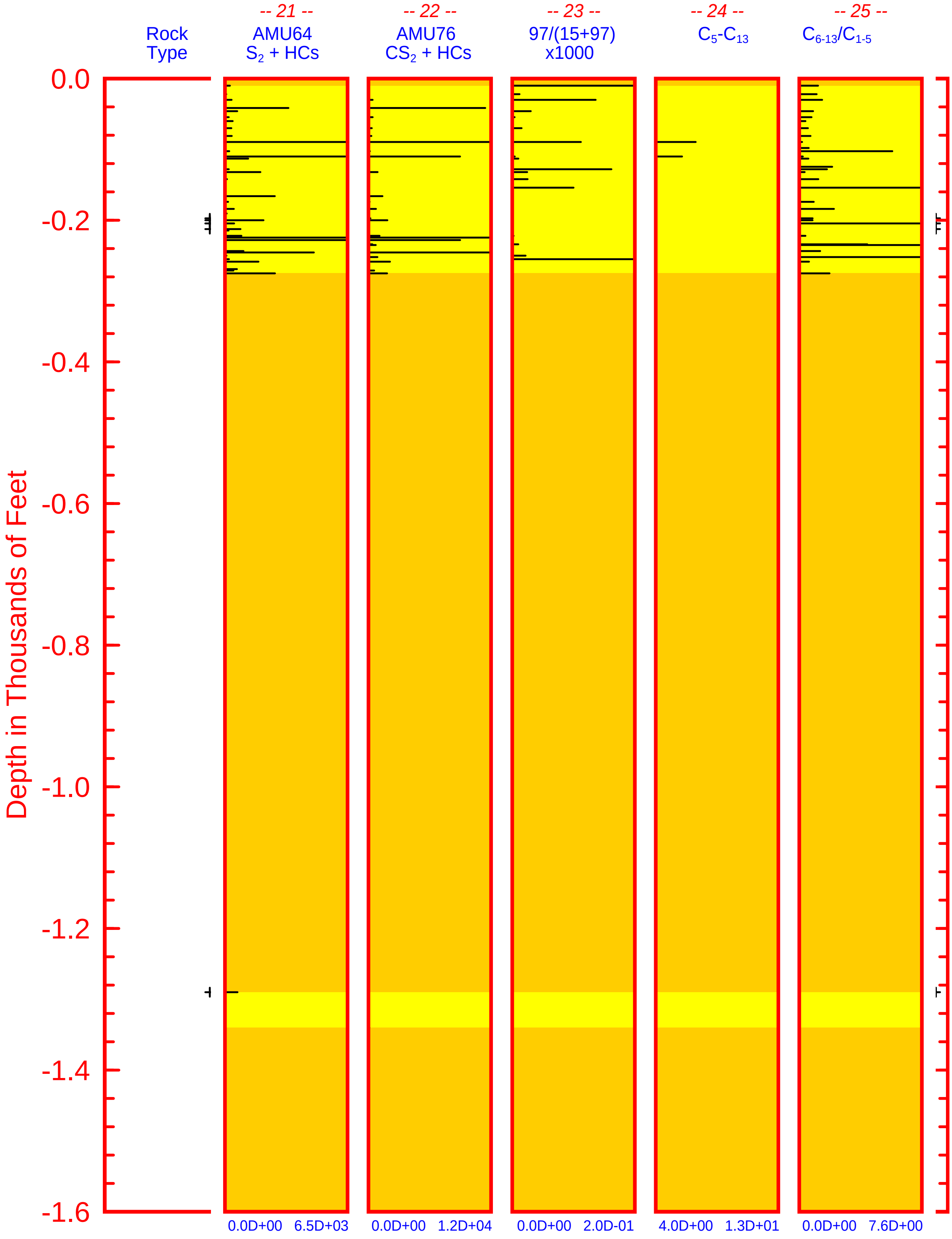


Figure 11: 90% of all FIS Data: Tracks 21 – 25 (see Sect. A.3 for explanation)

5 Photomicroscopy

Thin sections were prepared from SO-C-1-15 and 1A 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 SO-C-1-15 and 1A at the depths indicated.

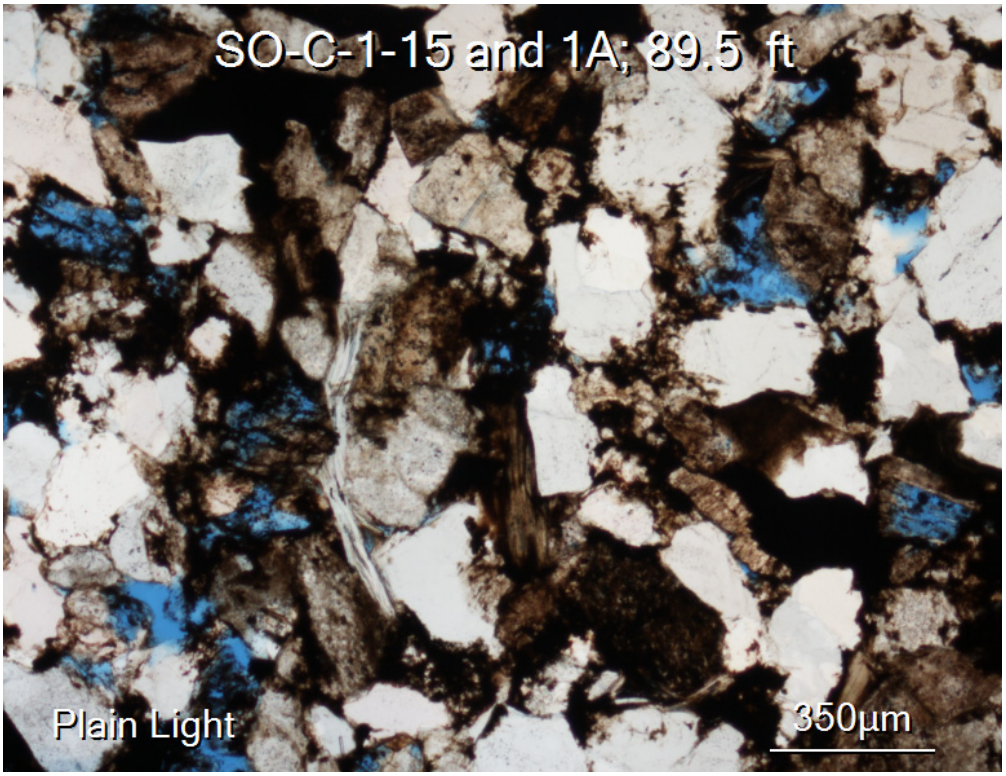


Figure 12: Photomicroscopy from SO-C-1-15 and 1A

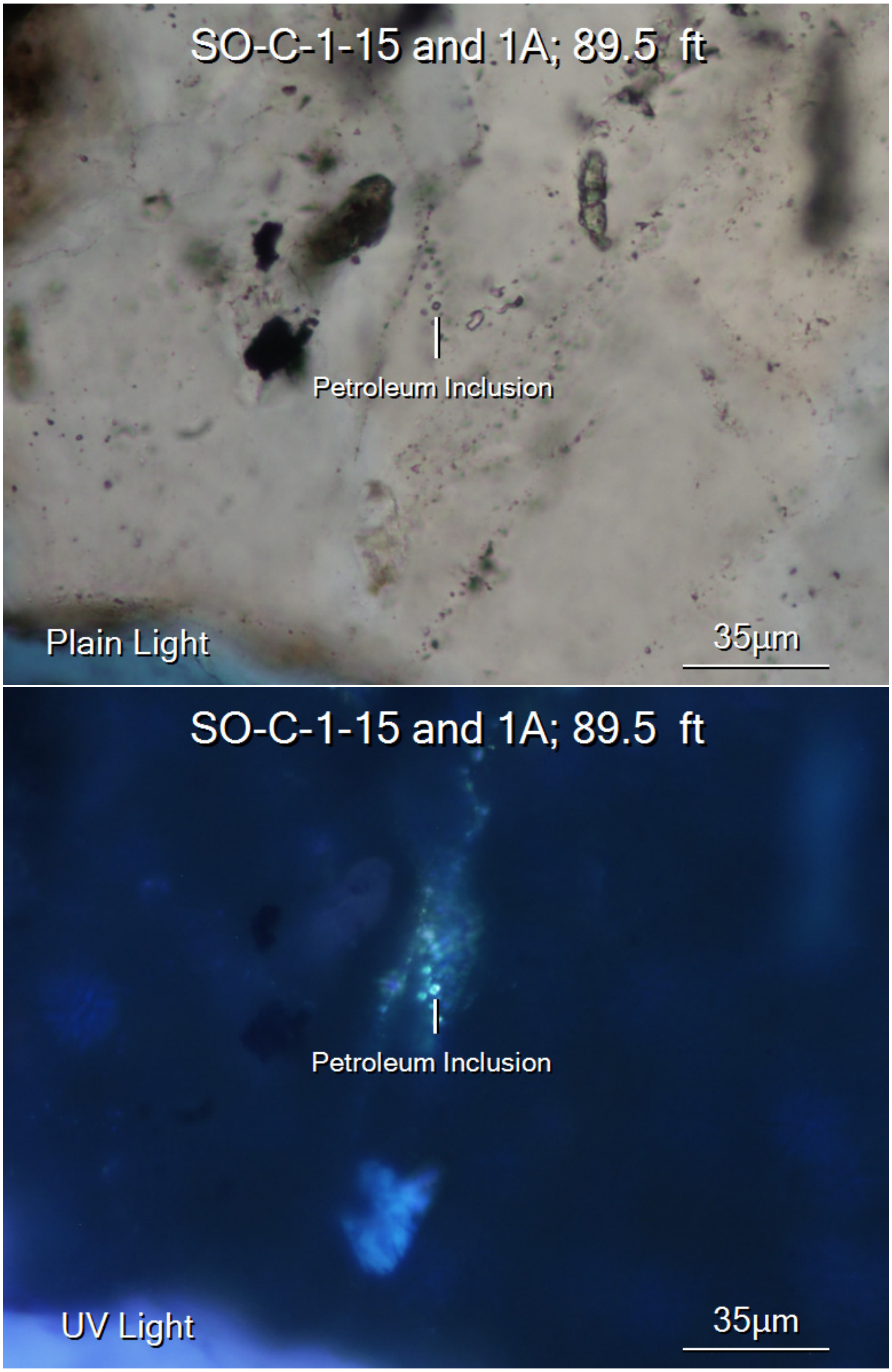


Figure 13: Photomicroscopy from SO-C-1-15 and 1A

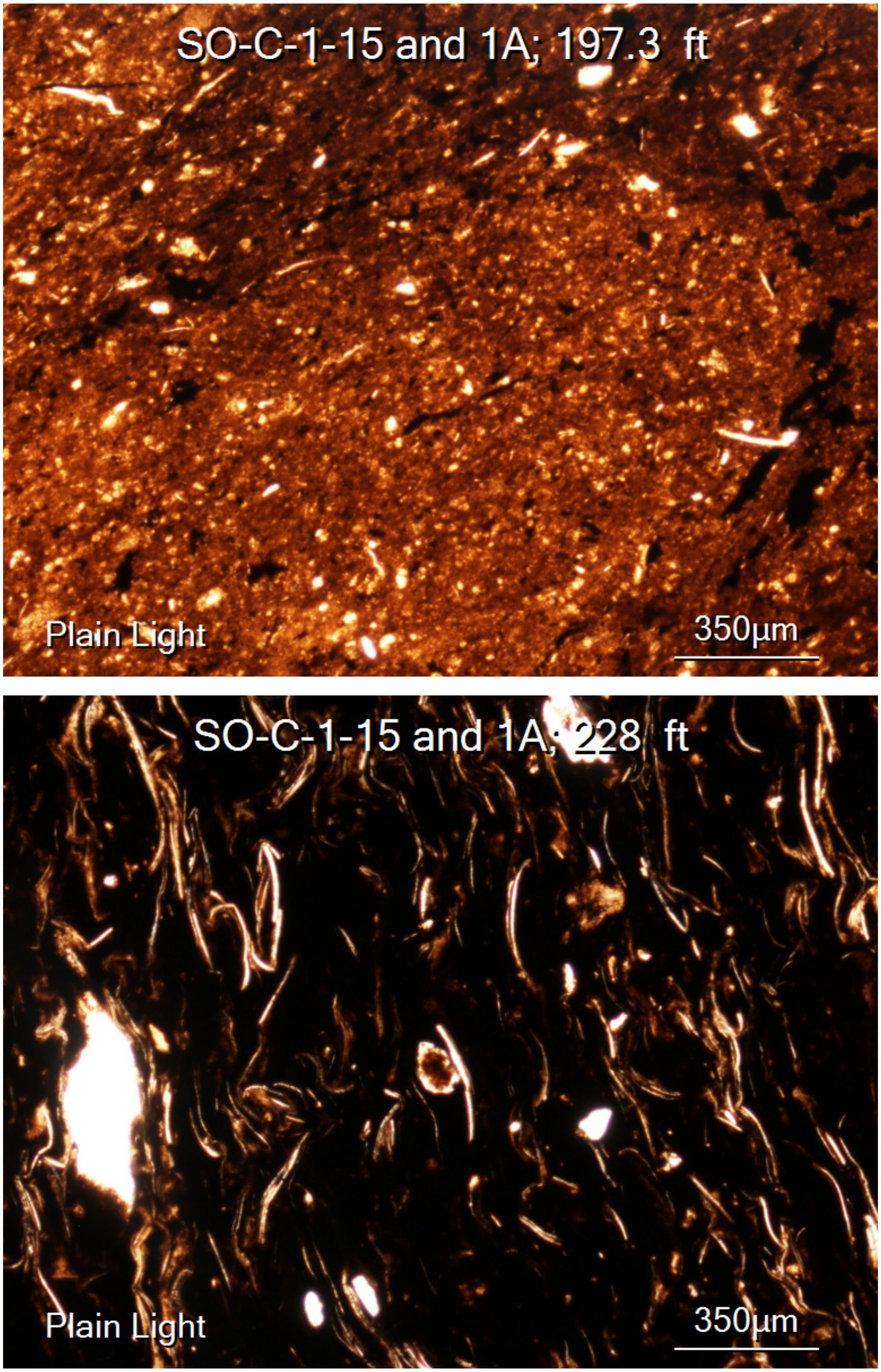


Figure 14: Photomicroscopy from SO-C-1-15 and 1A

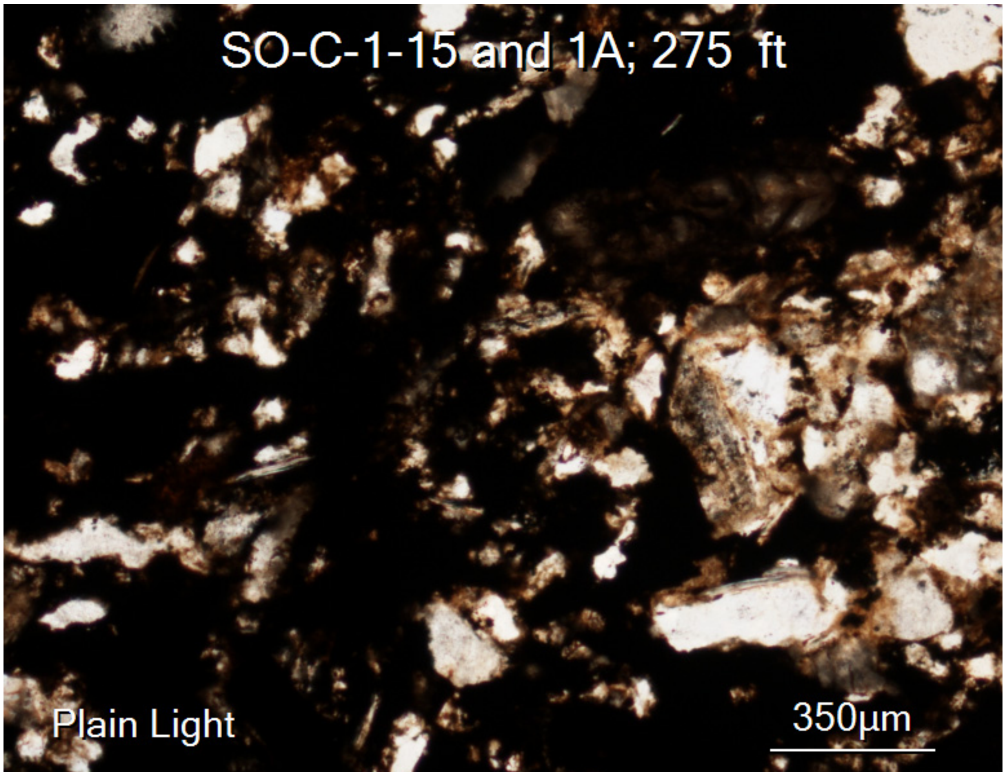


Figure 15: Photomicroscopy from SO-C-1-15 and 1A

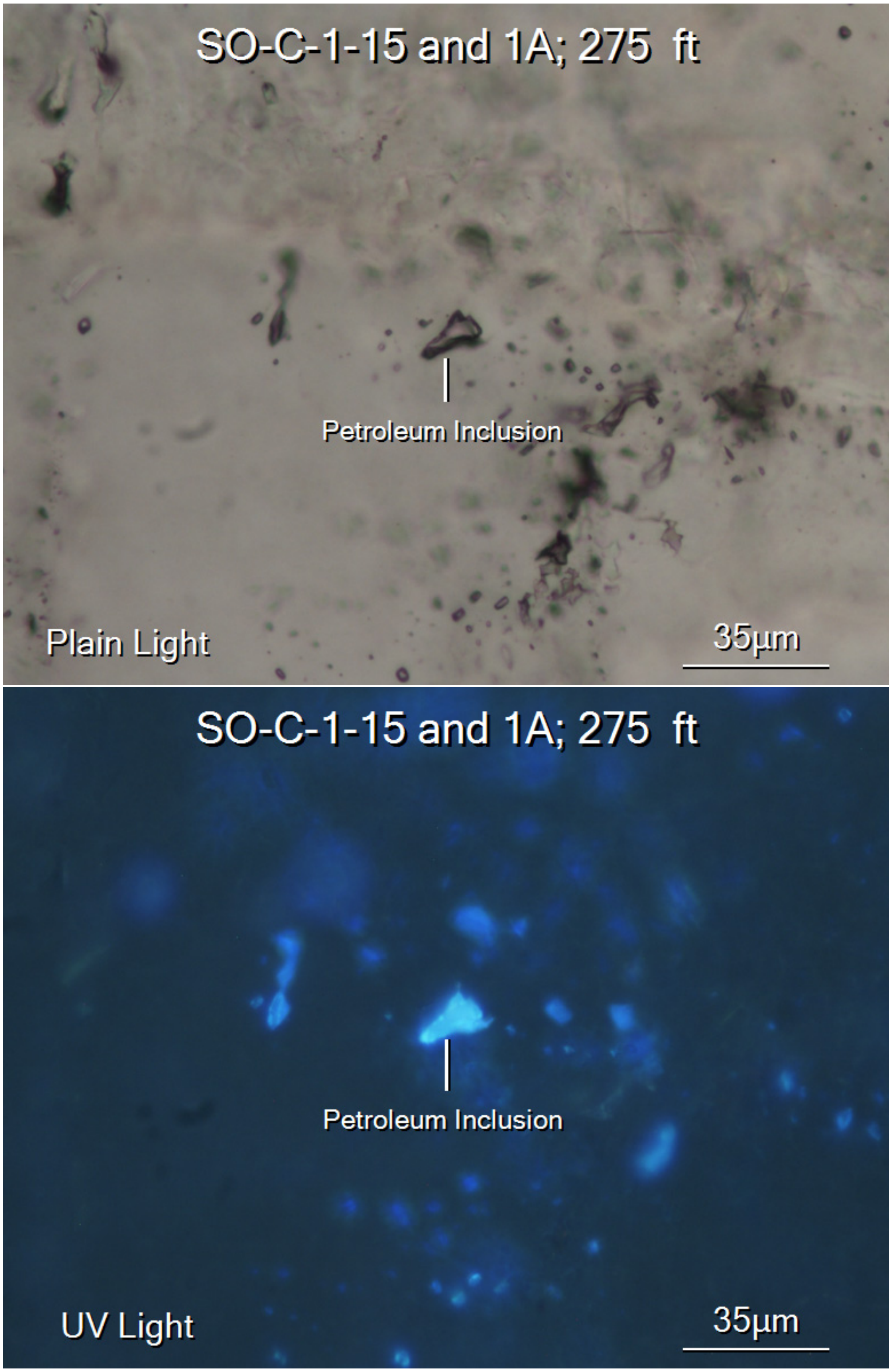


Figure 16: Photomicroscopy from SO-C-1-15 and 1A

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 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. HD^+ and $^3He^+$ 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:* C_nH_{2n+2}
2. *Naphthenes:* C_nH_{2n}
3. *Aromatics:* C_nH_{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 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 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 C_1-C_5 hydrocarbons with dwindling responses in the C_6-C_8 range, and essentially no response in the C_9+ range. Drier gases may exhibit responses only in the C_1-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_4-C_6 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_2 and water, nitrogen and minor hydrocarbon contributions). The distinction lies in the relative proportion of these species. Gases can typically contain 90% C_1 and 95% C_1-C_3. Hence, FIS gas spectra typically have prominent C_1-C_3 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_4+ paraffins / C_4+ 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_7-C_{13} 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, 71	156(4%)
C12	165-171	57, 43, 71	170(8%)
C13	179-185	43, 57, 71	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_7-C_{13} paraffins are usually the same, and represent some of the most intense peaks previously identified for the C_4-C_6 gas-range paraffins.

Only normal (straight-chain) paraffins have been considered in the above table. Typical C_6-C_{10} (gasoline) fractions contain 40% paraffins, 50% naphthenes and 10% aromatics by volume. Typical C_{11}-C_{13} (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_7 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_1-C_{13} 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_2, 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 though 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 indictor species include light hydrocarbons, CO_2, possibly organic acids and aromatic compounds, and sulfurous volatiles, including H_2S, COS, CS_2, S_2 (+/- SO_2) and in some cases thiols. H_2S 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 downdip.

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 (CO_2^+), with possible minor contribution from C_3^+ hydrocarbon fragments and acetic acid. Anomalous values have been noted associated with pan-evaporative dolomitization of limestones in China and Oman. CO_2 response is often

high in proximity samples which show elevated levels of acetic acid. CO_2 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_2S^+). Anomalous values associated with petroleum may indicate sour oil or gas. H_2S is also noted at times in association with shallow dry gas of probable biogenic origin (including FIS microseeps) and with some proximity zones. H_2S is probably not quantitatively analyzed due to rapid scavenging by metallic surfaces of the analytical system.

Track 4: 34/(34+15) - $H_2S/(H_2S$+methane). Not frequently used, but ratio tends to be elevated in sour gas zones.

Track 5: 4/(4+2) - Helium fraction $^4He^+/(^4He^+ + H_2^+)$; 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_3^+; mostly derived from methane, with minor contributions from all other paraffins and NH_2^+, 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 ($C_2H_6^+$). Use similar to that of methane ($m/z = 15$).

Track 10: $m/z = 60$ - Acetic aid (CH_3COOH), 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 ($C_6H_6^+$). 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 ($C_7H_7^+$). 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: $m/z = 76$ - CS_2 and C_6^+ hydrocarbons. 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: $C_5 - C_{13}$ 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 C_5 group is the highest molecular weight range hydrocarbon group present in a given sample, a ranking of 5 is assigned; if 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 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: C_{6-13}/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 (H_2^+); largely from H_2O, which makes up most of the evolved fluid in almost all samples.

- $m/z = 3$ - Deuterated hydrogen and helium-3 (HD and $^3He^+$).

- $m/z = 12$ - Carbon (C^+).

- $m/z = 14$ - Nitrogen (N^+) and 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. CH_2^+ will generally be accompanied by relatively larger responses on $m/z = 15$ (CH_3^+), and $m/z = 16$ (CH_4^+) (due to it's fragmentation origin from 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 (CH_4^+), but major interference by O^+ fragment of water.

- $m/z = 17$ - Dominated by OH^+ fragment from water
- $m/z = 18$ - Dominated by water parent peak (H_2O^+)
- $m/z = 22$ - Doubly charged carbon dioxide ($CO2^{2+}$); minor contribution from neon ($^{22}Ne^+$)
- $m/z = 28$ - Dominated by diatomic nitrogen (N_2^+) and CO^+ fragment from carbon dioxide. Minor C_2^+ hydrocarbon contribution
- $m/z = 32$ - Oxygen (O^+) and sulfur (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 $m/z = 34$ (H_2S), $m/z = 48$ (SO^+) and $m/z = 64$ (S_2^+, 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 (Ar^+) with possible significant interference by 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 (SO^+); also, C_4^+
- $m/z = 55$ - Naphthene fragment ($C_4H_7^+$). 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 ($C_5H_{11}^+$). Same use as $m/z = 57$.
- $m/z = 77$ - Aromatic fragment ($C_6H_5^+$). Same general use as for benzene and toluene.
- $m/z = 85$ - Paraffin fragment ($C_6H_{13}^+$). Same use as $m/z = 57$.
- $95 \leq m/z \leq 103$ - peaks centered within this range are mostly $C_7 - C_8$ fragments
- $110 \leq m/z \leq 115$ - peaks centered within this range are mostly $C_8 - C_9$ fragments
- $122 \leq m/z \leq 126$ - peaks centered within this range are mostly $C_9 - C_{10}$ fragments
- $134 \leq m/z \leq 138$ - peaks centered within this range are mostly $C_{10} - C_{11}$ fragments
- $148 \leq m/z \leq 152$ - peaks centered within this range are mostly $C_{11} - C_{12}$ fragments
- $160 \leq m/z \leq 164$ - peaks centered within this range are mostly $C_{12} - C_{13}$ fragments
- $175 \leq m/z \leq 180$ - peaks centered within this range are mostly $C_{13} - C_{14}$ 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 17. 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 inhomogenieties 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 18 and 19. 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 20. 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.

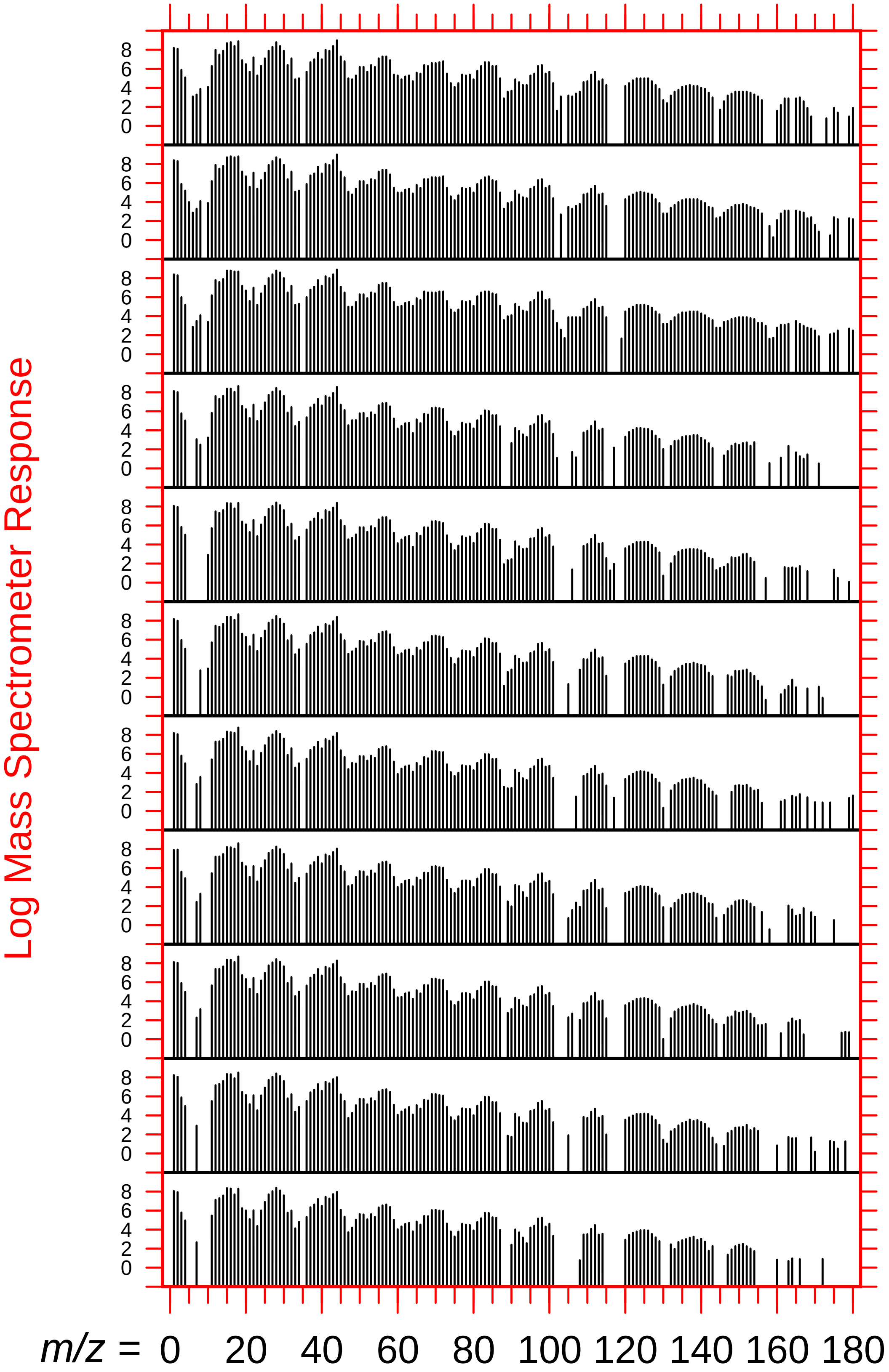


Figure 17: Oil Spectra

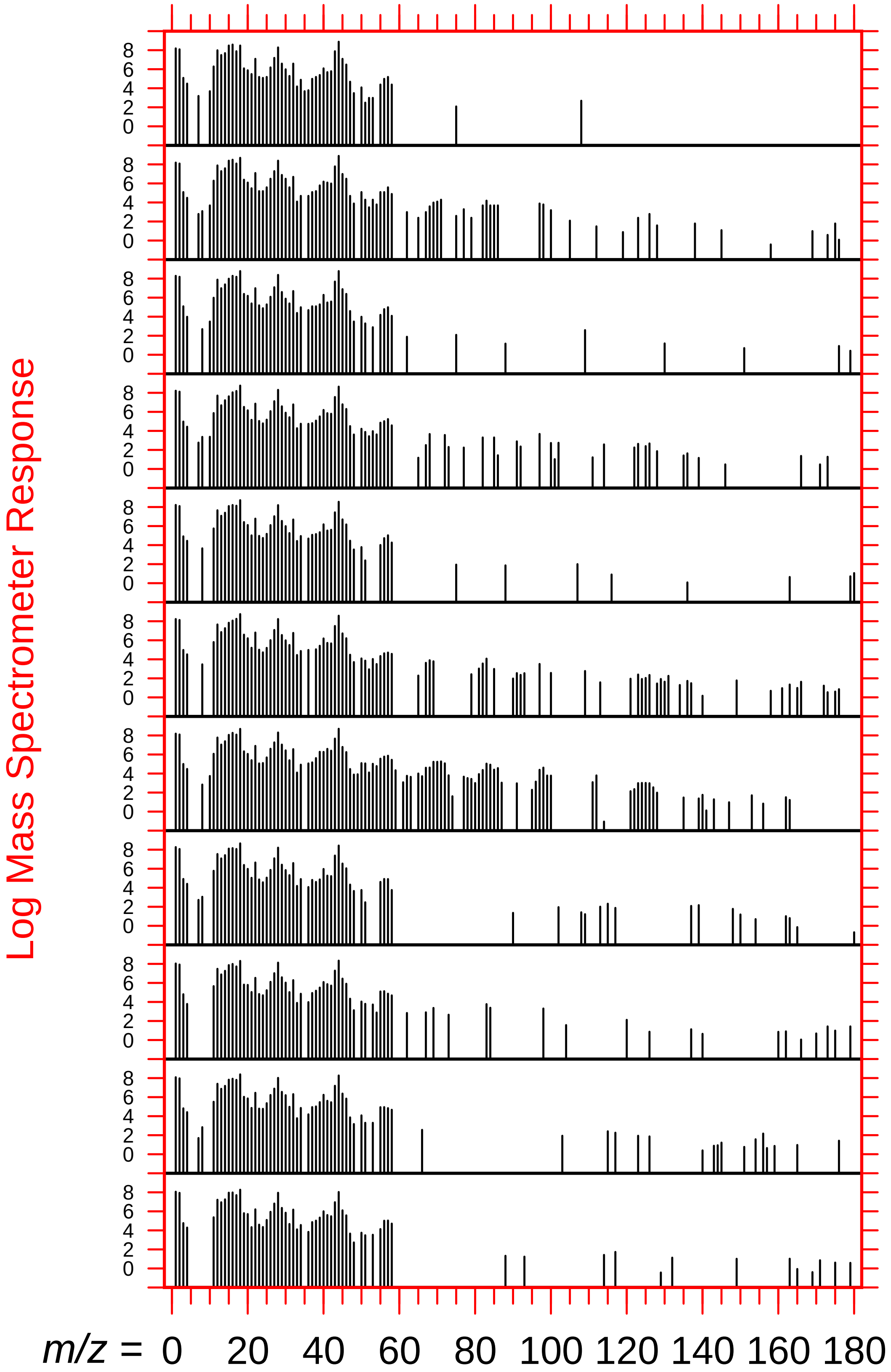


Figure 18: Frac Sand Spectra

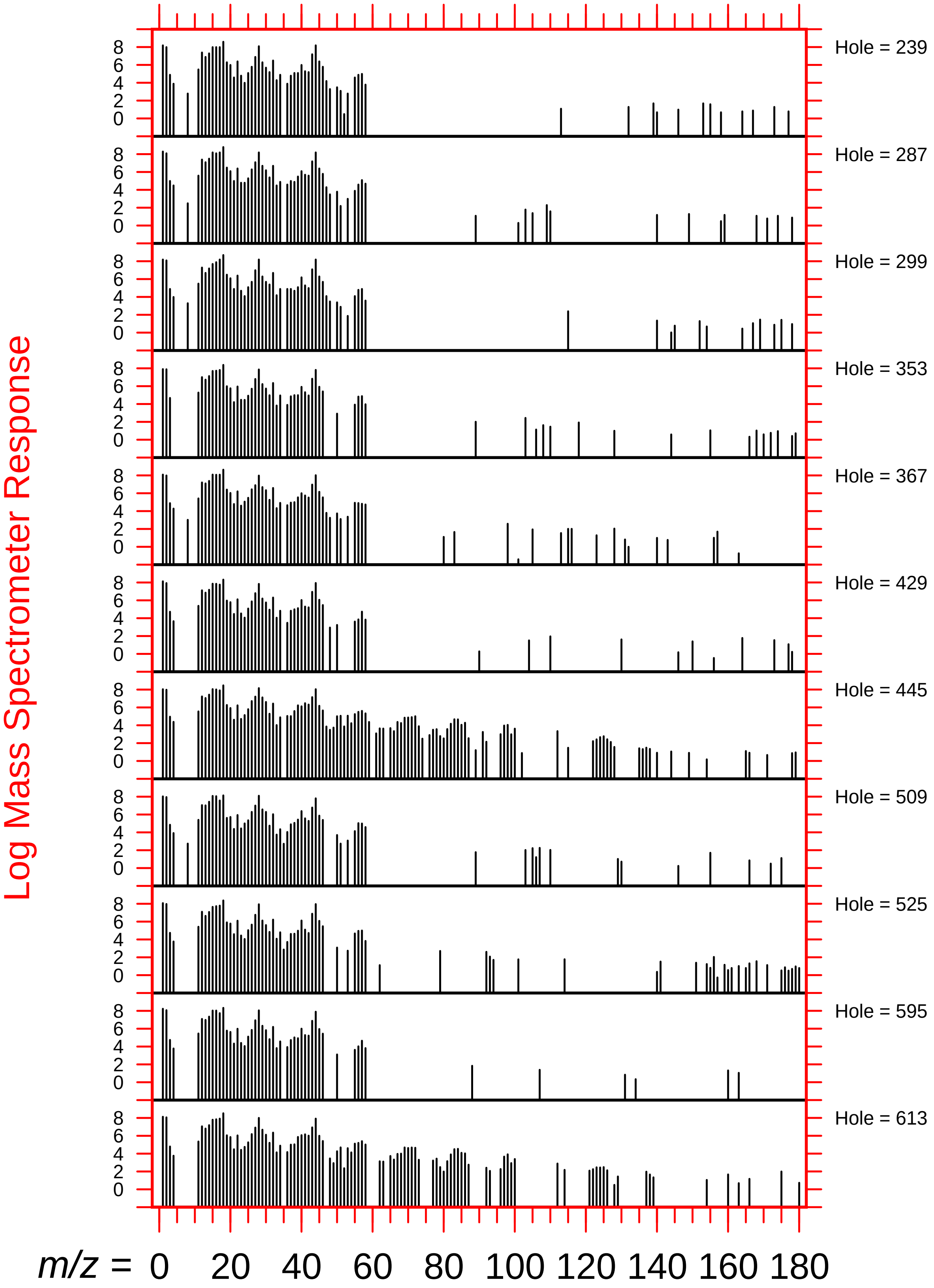


Figure 19: Frac Sand Spectra

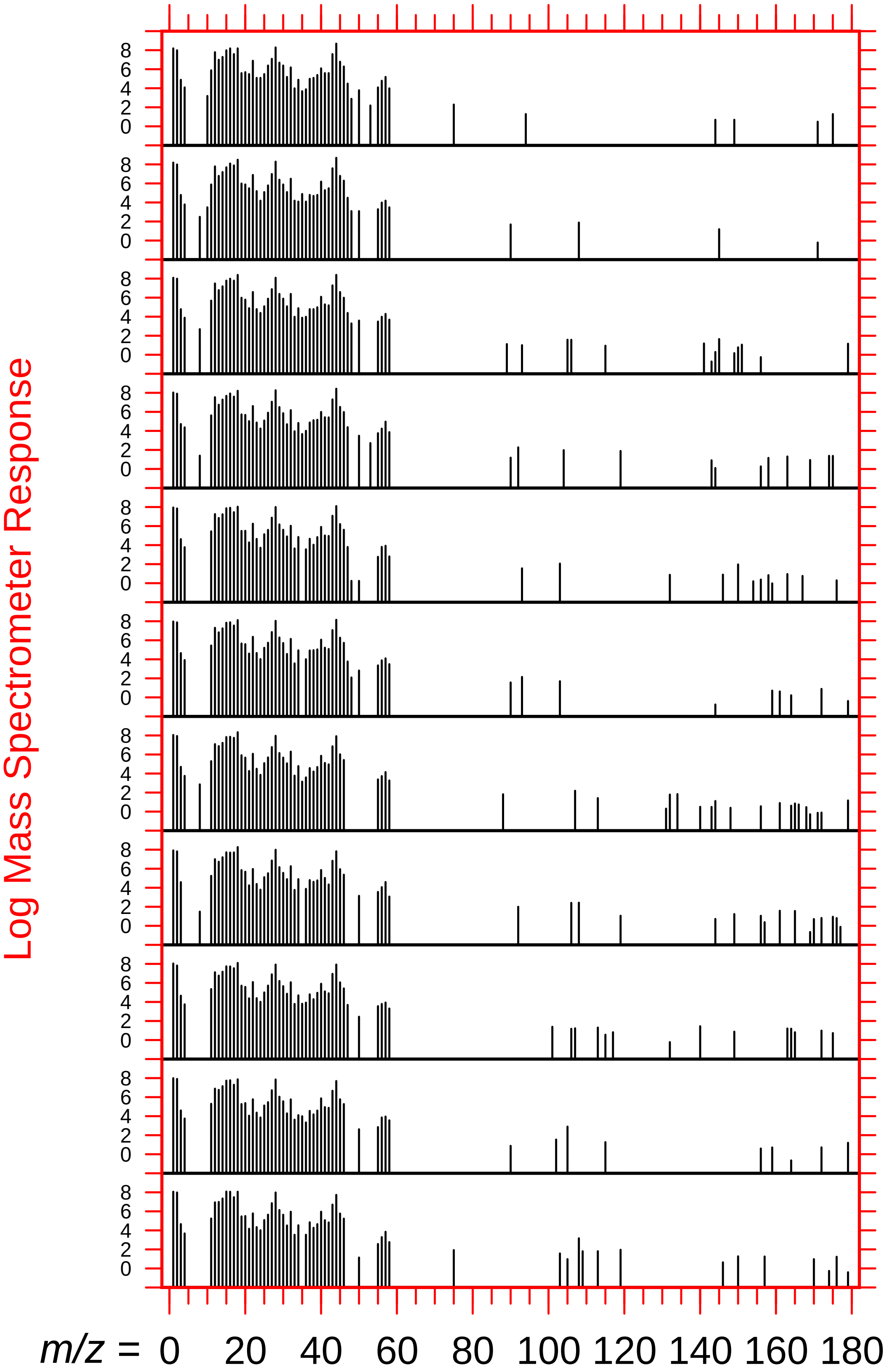


Figure 20: Cooked Frac Sand Spectra

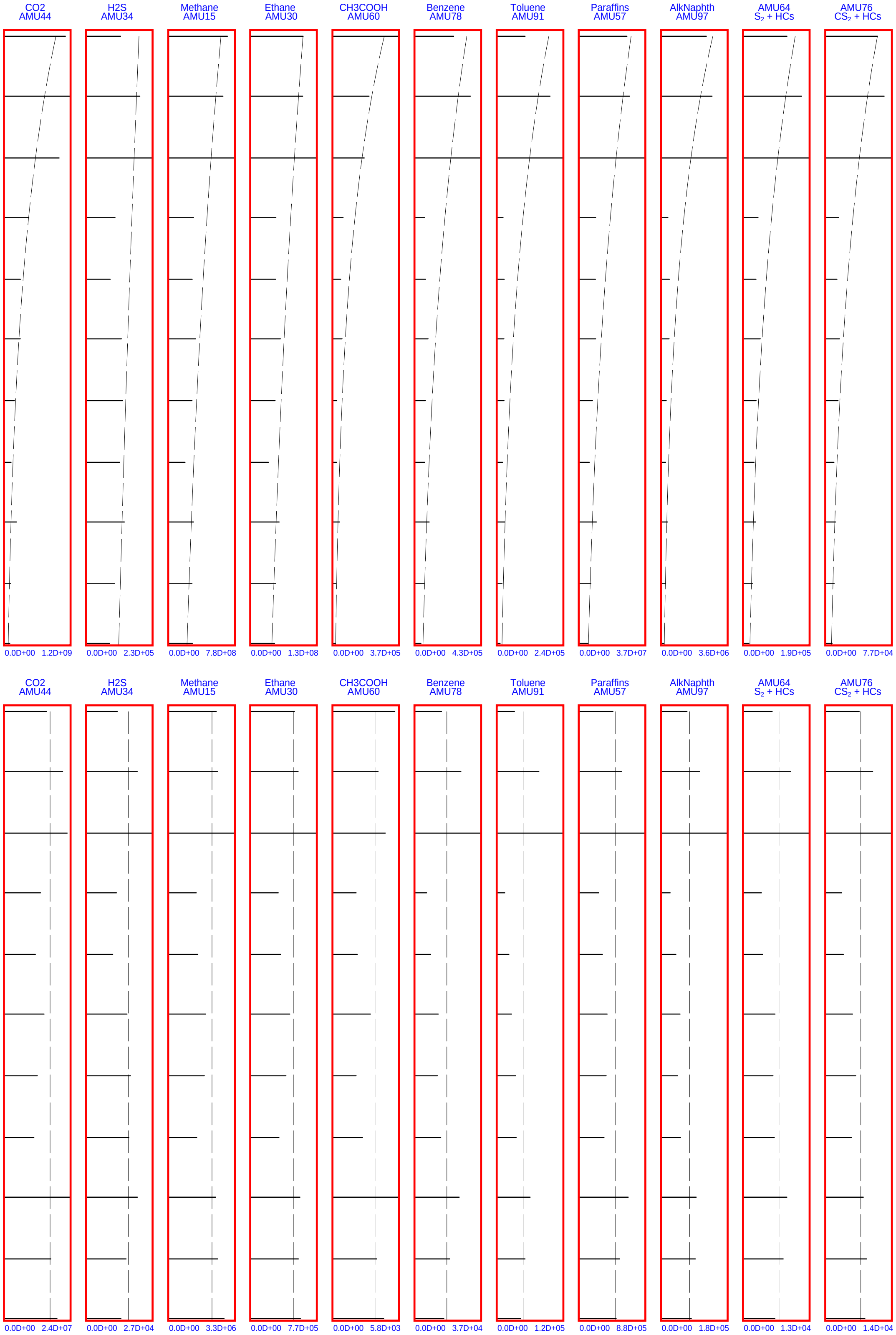
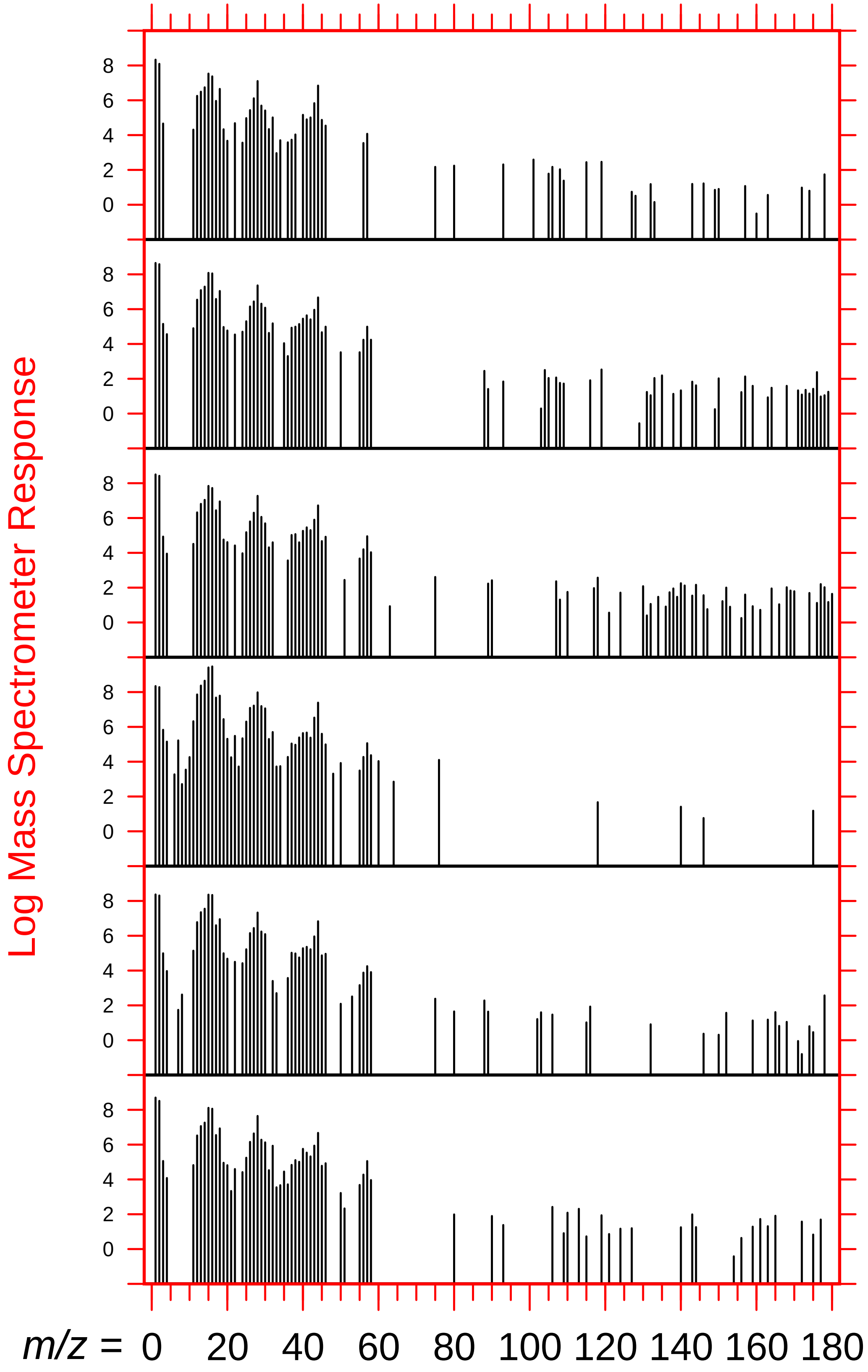
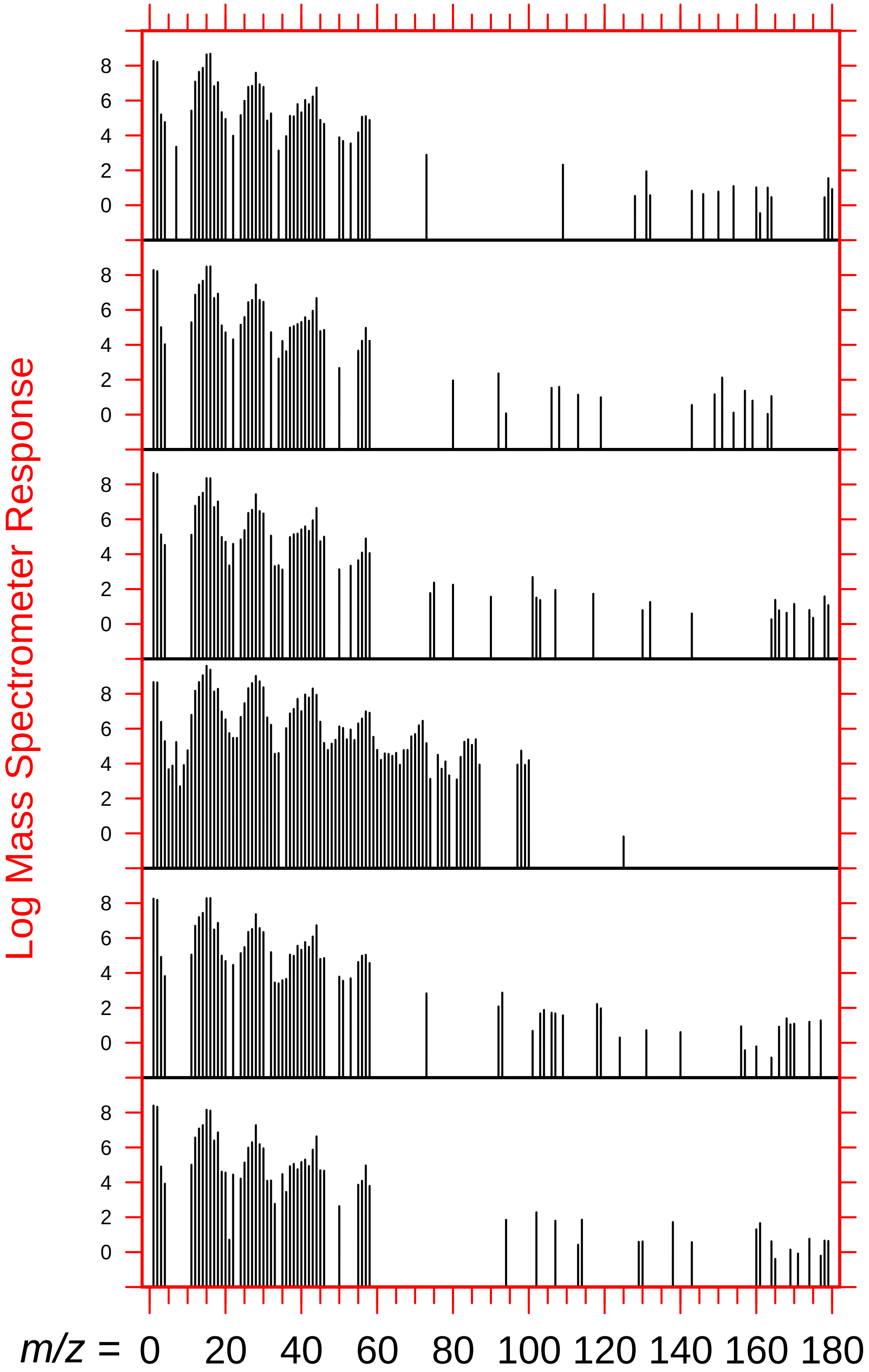


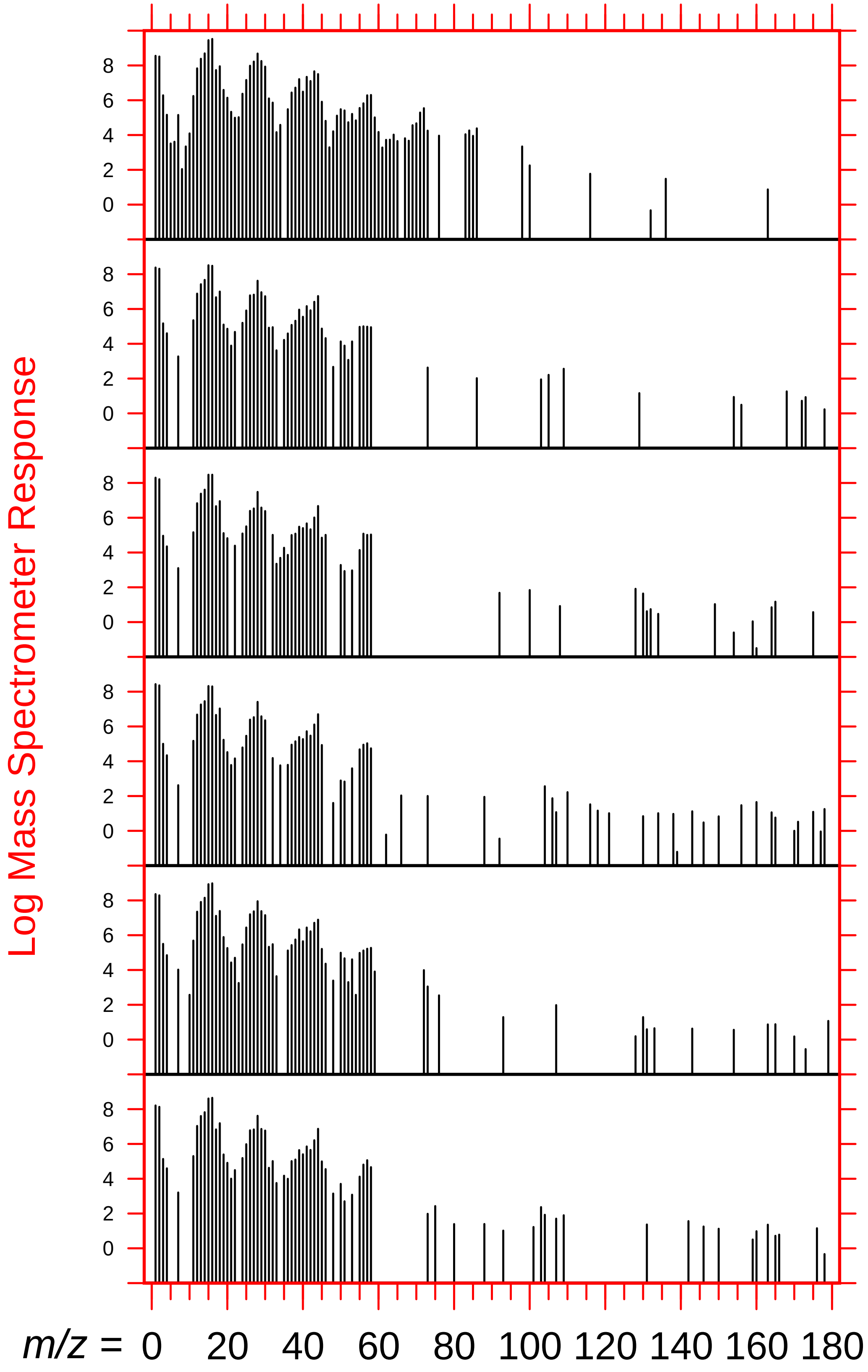
Figure 21: Kindblade Oil Standards Before (top) and After (bottom) Correction

C Individual Spectra

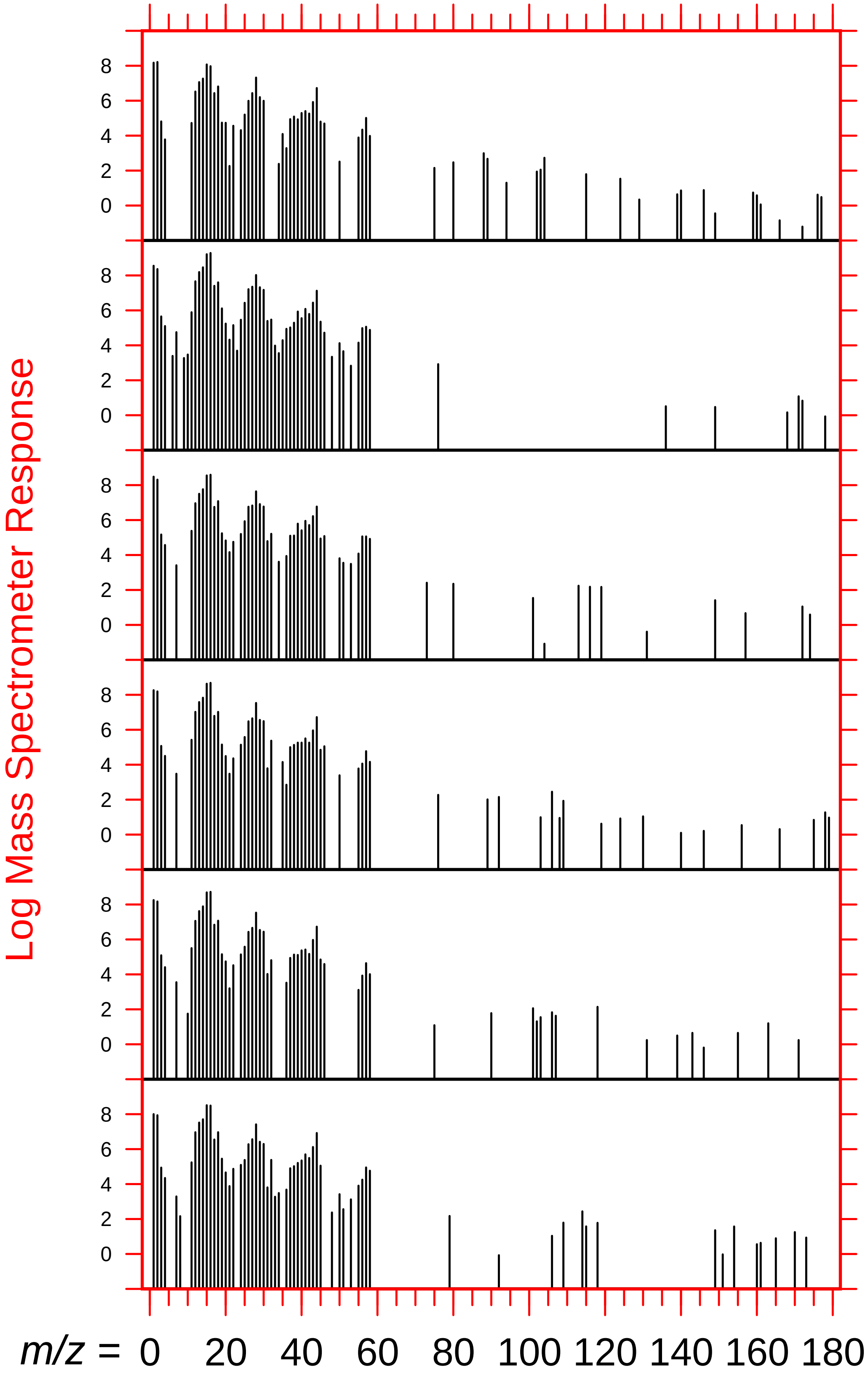
Individual spectra for each sample from SO-C-1-15 and 1A are shown on the following pages. Each spectrum is indexed according to depth and indicates the log of the millivolt response for atomic mass units (AMU, m/z) from $2 \leq m/z \leq 180$.

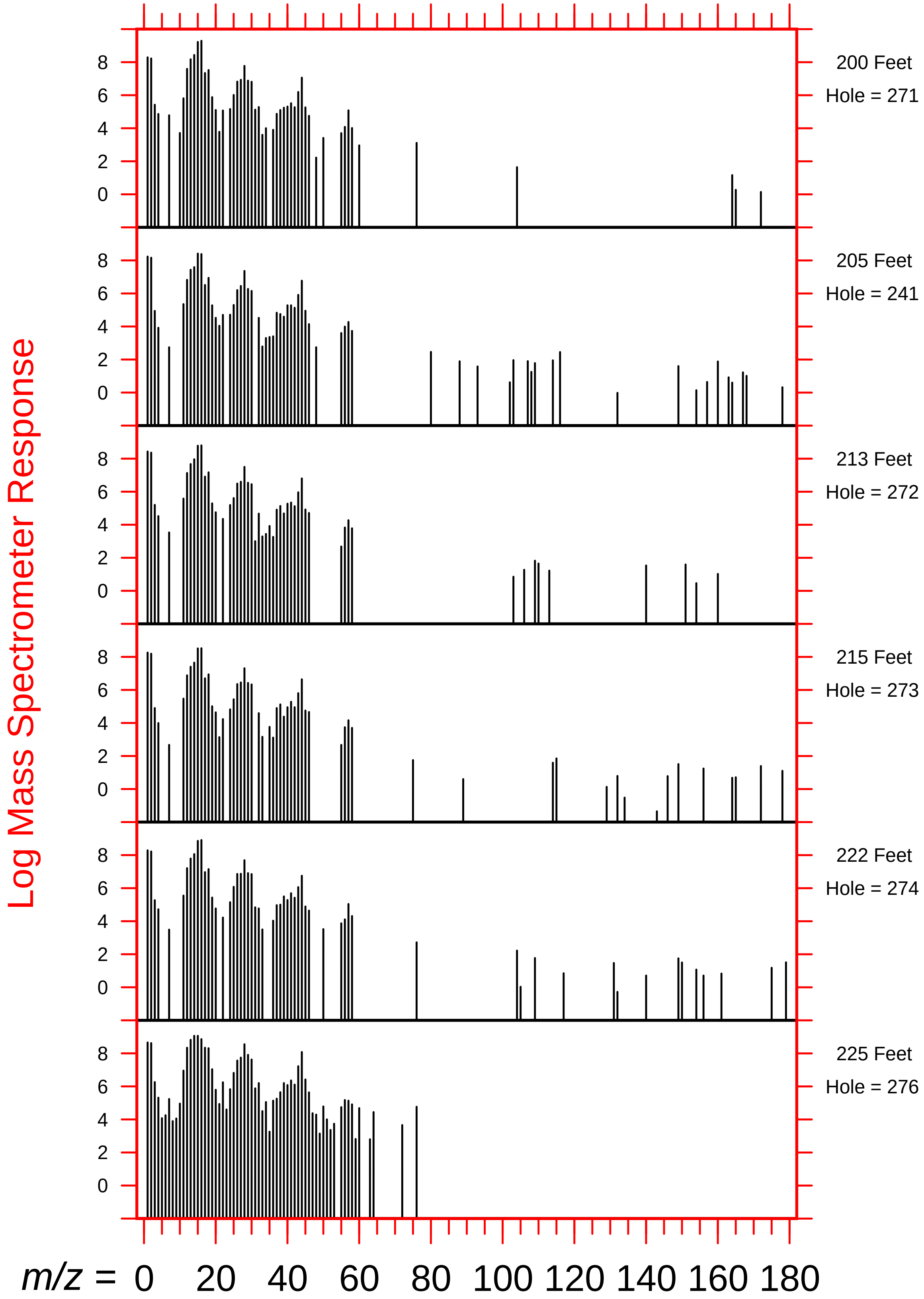

Log Mass Spectrometer Response
8
6
4
2
0
10 Feet
Hole = 246
22 Feet
Hole = 247
30 Feet
Hole = 248
42 Feet
Hole = 249
46 Feet
Hole = 250
55 Feet
Hole = 252
m/z = 0 20 40 60 80 100 120 140 160 180

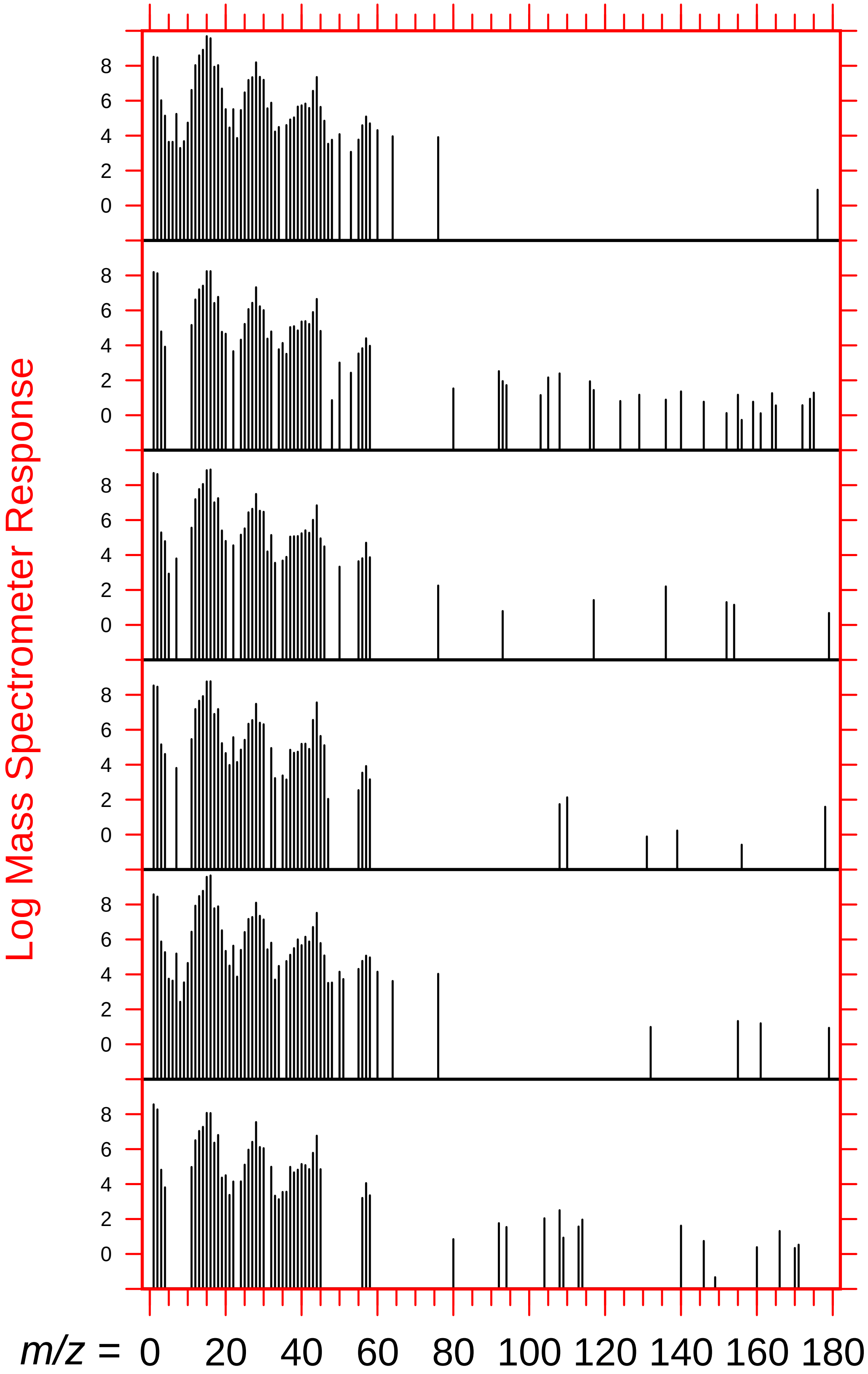

Log Mass Spectrometer Response
8
6
4
2
0
60 Feet
Hole = 253
70 Feet
Hole = 254
81 Feet
Hole = 255
90 Feet
Hole = 256
98 Feet
Hole = 257
103 Feet
Hole = 258
m/z = 0 20 40 60 80 100 120 140 160 180

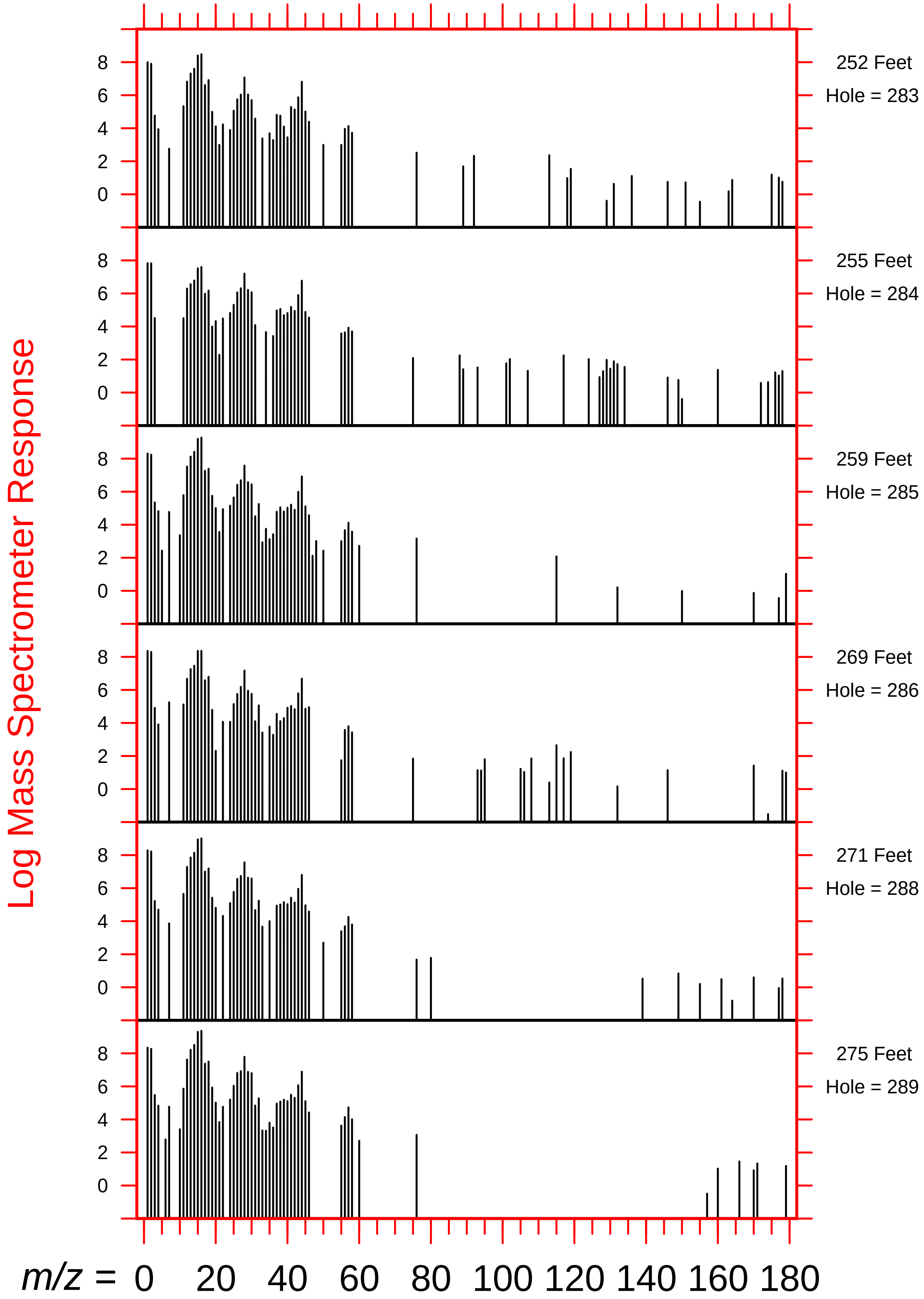


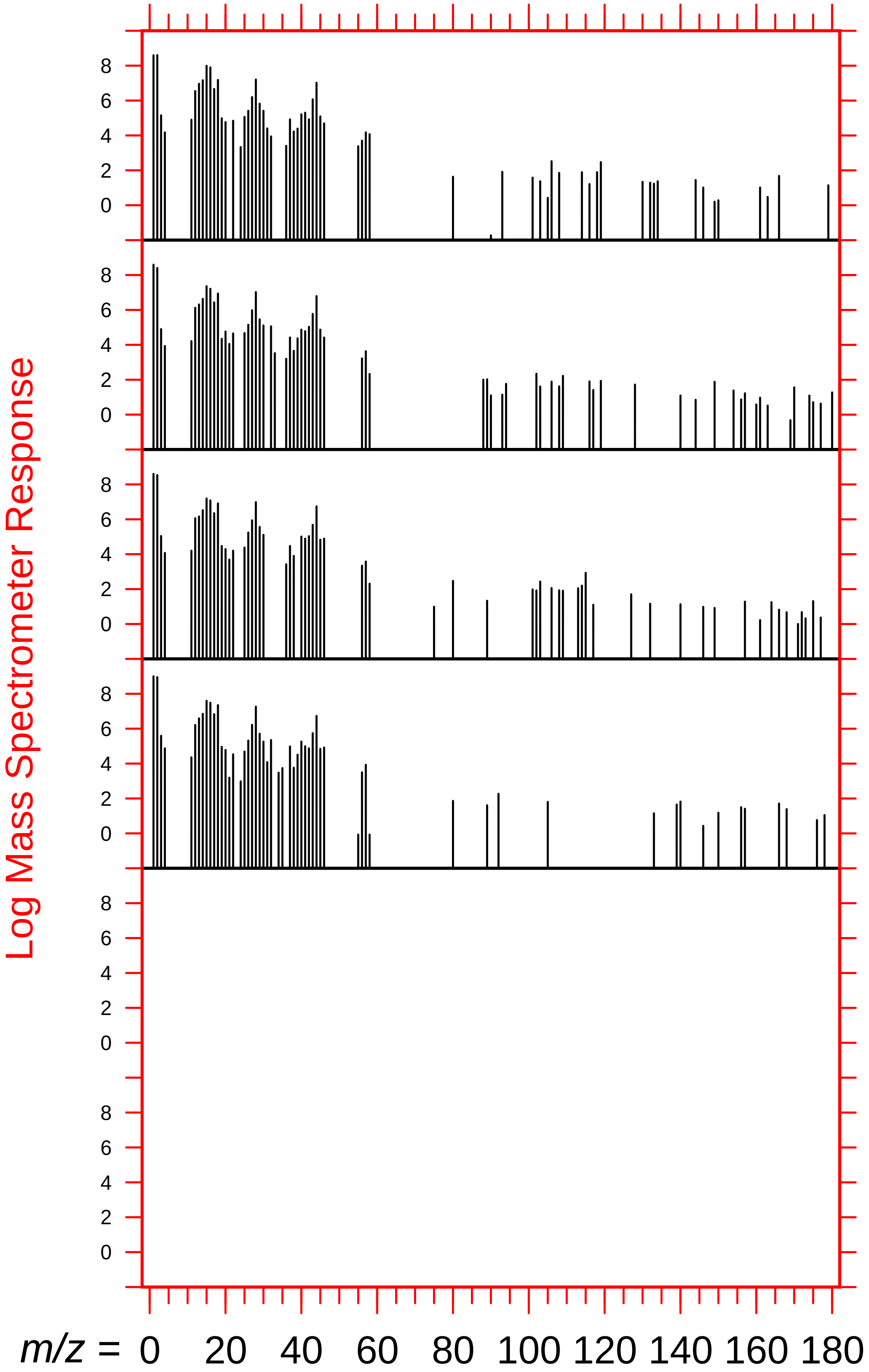
Log Mass Spectrometer Response
8
6
4
2
0
110 Feet
Hole = 259
113 Feet
Hole = 260
125 Feet
Hole = 261
128 Feet
Hole = 262
132 Feet
Hole = 264
142 Feet
Hole = 265
m/z = 0 20 40 60 80 100 120 140 160 180


Log Mass Spectrometer Response
8
6
4
2
0
154 Feet
Hole = 266
166 Feet
Hole = 267
174 Feet
Hole = 268
184 Feet
Hole = 269
191 Feet
Hole = 270
197 Feet
Hole = 240
m/z = 0 20 40 60 80 100 120 140 160 180


Log Mass Spectrometer Response
8
6
4
2
0
200 Feet
Hole = 271
205 Feet
Hole = 241
213 Feet
Hole = 272
215 Feet
Hole = 273
222 Feet
Hole = 274
225 Feet
Hole = 276
m/z = 0 20 40 60 80 100 120 140 160 180


Log Mass Spectrometer Response
8
6
4
2
0
228 Feet
Hole = 277
234 Feet
Hole = 278
235 Feet
Hole = 279
244 Feet
Hole = 280
246 Feet
Hole = 281
250 Feet
Hole = 282
m/z = 0 20 40 60 80 100 120 140 160 180


Log Mass Spectrometer Response
8
6
4
2
0
252 Feet
Hole = 283
255 Feet
Hole = 284
259 Feet
Hole = 285
269 Feet
Hole = 286
271 Feet
Hole = 288
275 Feet
Hole = 289
m/z = 0 20 40 60 80 100 120 140 160 180


Log Mass Spectrometer Response
8
6
4
2
0
1290 Feet
Hole = 242
1322 Feet
Hole = 243
1340 Feet
Hole = 244
1432 Feet
Hole = 245
m/z = 0 20 40 60 80 100 120 140 160 180

Appendix 4

"A stratigraphic reconstruction of bulk volatile chemistry from fluid inclusions in: RC-C-01-81," Fluid Inclusion Technologies, Inc. report FIS# FI160559e prepared August 4, 2016 for the North Carolina Geological Survey, 74p.

UWI# 999999999999
FIS# FI160559e

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

RC-C-1-81

Prepared August 4, 2016 for

NC Geological Survey

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

RC-C-1-81

Prepared August 4, 2016
by
FIT
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Executive Summary for well: RC-C-1-81

1 FIS Summary for RC-C-1-81

RC-C-1-81 is a shallow legacy core hole drilled in the Dan River Basin in 1981. FIS analysis was performed on a total of 40 core samples from 88-479 ft. This study was completed in conjunction with three other wells (SO-C-1-81 in report FI160559a; SO-C-2-81 in report FI160559c; SO-C-1-15 and 1A-15 in report FI160559g). The primary goals of the analysis were to use FIS to determine the gas chemistry and hydrocarbon potential of this area. The stratigraphic zones of particular interest are the Walnut Cove Formation and the overlying Dry Fork Formation.

The upper interval at 88-287 ft (Walnut Cove Formation?) exhibits dry gas to wet gas FIS responses. Methane concentrations are elevated at 161 ft, 193 ft, 271 ft, and 287 ft. Methane and trace liquid hydrocarbons signals do not covary, indicating possible dual hydrocarbon migration (dry gas versus wetter hydrocarbons). CS2 of probable thermal origin is identified at 161 ft and 287 ft, along with trace sulfate. H2S is slightly elevated above 143 ft. Helium is intermittently elevated at 161-287 ft and partially covaries with methane. Values are low, however, and generally less than 100 ppm with respect to methane. No visible petroleum inclusions were observed in three sandstone samples prepared from 149 ft, 249 ft, and 287 ft. Sandstone is arkosic with detrital heavy metamorphic minerals (epidote, garnet) as well as detrital muscovite and biotite, indicating a metamorphic or meta-igneous source terrain. The sample from 287 ft contains fracture-fill quartz and barite(?). No visible porosity is noted. Shale at 249 ft and 287 ft contains trace gas-prone kerogen.

The lower section at 303-479 ft (Walnut Cove Formations) displays dry gas FIS responses above 345 ft and intermittent dry gas, wet gas to gas-condensate below 361 ft. Higher liquid hydrocarbon signals (but relatively depleted in methane) are recorded at 361 ft, 399 ft, and 410 ft. Several occurrences of gas inclusions were identified in late compactional microfractures in the sample from 410 ft. These fluids are interpreted to represent migrated components, considering the low organic content of the host rocks.

2 FIS Chemical Zonation

88 ft to 287 ft :

Dry gas: 70%

Wet gas: 25%

Low hydrocarbon responses: 6%

Hydrocarbon species to C5 are present in this zone. No proximity to pay signal is recorded. Sulfur species are intermittently observed.

Slide @ 149 ft: No liquid petroleum inclusions, significant stain or kerogen are observed.

Slide @ 249 ft: Rare occurrences of gas prone kerogen are present.

Slide @ 287 ft: Rare occurrences of gas prone kerogen are indicated.

303 ft to 479 ft :

Dry gas: 39%

Wet gas: 19%

WG-GC: 7%

Low hydrocarbon responses: 36%

Hydrocarbon species to C9 are documented in this zone. No proximity to pay signal is recorded. Sulfur species are not recorded.

Slide @ 410 ft: Population 1: Several, indeterminate gravity petroleum inclusions are found.

Summary of Results for well: RC-C-1-81

This report contains Fluid Inclusion Stratigraphy and Fluid Inclusion Petrography results for RC-C-1-81 and was prepared for NC Geological Survey by *Fluid Inclusion Technologies, 2217 N. Yellowood Ave., Broken Arrow, OK 74133; ph: (918) 461-8984; fax: (918) 461-2085; www.fittulsa.com.*

Table I: Logistical Information

Client:	**NC Geological Survey**	Analyzed Depth:	**88 - 479 Feet**
Well:	**RC-C-1-81**	Sample Spacing:	**See Individual Spectra**
		Sample Total:	**40**

Table II: Fluid Inclusion Petrography from RC-C-1-81

Well Name: RC-C-1-81																					
Sample Depth	**Rock Type**		**Petroleum Fluid Inclusion Populations**												**Kerogen (possible source rk)**					**Bitu-men**	
			Population 1				**Population 2**				**Population 3**										
***Units:* (Feet)**	***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***
149	ss,tr cb,sh																				
249	ss,mu,tr sh														sh	gp		r			
287	ss,mu,bi,sh														sh	gp		r			
410	ss,mu,bi		no		dq	sv															

ss: sandstone
si: siltstone
sh: shale
cb: carbonate
sa: salt
an: anhydrite
ch: chert
co: coal
ig: igneous rock

mt: metamorphic rock
no: none
br: brown
or: orange
yl: yellow
wt: white
bl: blue
l: low
ul: upper-low

m: moderate
um: upper-moderate
h: high
dq: frac in detrital quartz
dr: quartz dust rim
qc: quartz cement
df: frac detrital feldspar
cm: matrix carbonate
cc: carbonate cement

r: rare
sv: several
c: common
a: abundant
xa: very abundant
go: oil and gas prone
op: oil prone
gp: gas prone
ls: live petroleum stain

ds: dead petroleum stain
po: pore-occluding bitmn
pb: pyrobitumen

Notes: mu = muscovite, bi = biotite

Table III: FIS Terminology: Abbreviations and Acronyms

HC Type & Quality		Anomalous HC Zones		Fluid Contacts	
NHC	non-hydrocarbon	**MP**	migration pathway	**OWC**	oil-water contact
DG	dry gas	**PC**	present day ptrlm column	**GWC**	gas-water contact
WG	wet gas	**PPC**	paleo-ptrlm column	**GOC**	gas-oil contact
GC	gas condensate	**RI**	recycled ptrlm inclusions	**POWC**	paleo-oil-water contact
VO	volatile oil	**SR**	source rock	**PGWC**	paleo-gas-water contact
O	oil	**GP**	gas prone kerogen	**PGOC**	paleo-gas-oil contact
BD	biodegraded	**OP**	oil prone kerogen		
TA	thermally altered	**OGP**	oil and gas prone kerogen		
		CNT	contamination		

Water-Soluble Anomalies		Miscellaneous	
WS	undifferentiated water-soluble anomaly	**SL**	seal
WSSR	source rock related water-soluble anomaly	**MS**	microseep
WSTA	water-soluble anomaly sourced from thermal alteration		
PTPL	proximity to oil or gas-condensate		
PTPG	proximity to gas		

Petrographic Observations					
A	abundant	**IG**	igneous rock	**SA**	salt
AN	anhydite	**L**	low	**SH**	shale
BL	blue	**LG**	large	**SI**	siltstone
BR	brown	**M**	moderate	**SM**	small
C	common	**MD**	medium	**SS**	sandstone
CB	carbonate	**MT**	metamorphic rock	**ST**	petroleum stain
CC	carbonate cement	**NO**	none	**SV**	several
CH	chert	**OR**	orange	**UL**	upper-low
CM	matrix carbonate	**PB**	pyrobitumen	**UM**	upper-moderate
CO	coal	**PF**	pore filling bitumen	**V**	variable
DF	detrital feldspar	**PR**	pore rimming bitumen	**W**	weak
DQ	detrital quartz	**QC**	quartz cement	**WT**	white
DR	quartz dust rim	**R**	rare	**XA**	extremely abundant
H	high	**S**	strong	**YL**	yellow

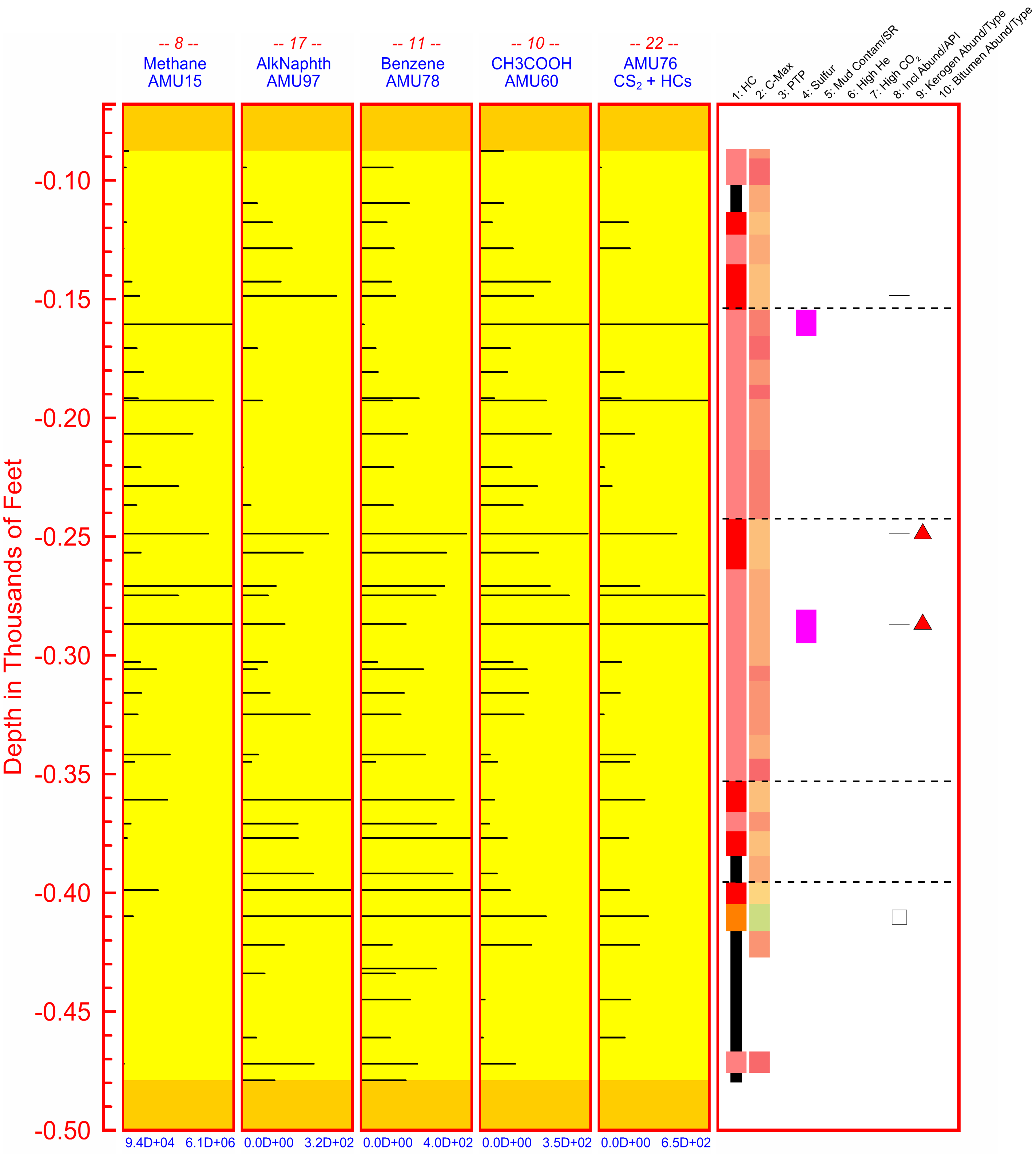
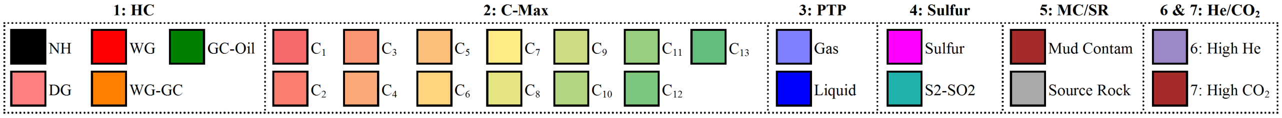


Figure 1: FIS Summary Tracks (see Sect. A for further explanation)

*FIS$^{\#}$FI*160559*e* – **RC-C-1-81** – *www.fittulsa.com*



Legend (cont)

8: Colors for Inclusion Abundance/API describe the API gravity of the liquid hydrocarbon inclusions:

▲ **Triangle:** Rare abundance **Brown:** Low Gravity

■ **Square:** Several abundance **Orange:** Upper Low gravity

⬟ **Pentagon:** Common abundance **Yellow:** Moderate gravity

⬢ **Hexagon:** Abundant **Light blue:** Upper Moderate gravity

● **Circle:** Extra Abundant **Blue:** High gravity

9: Colors for Kerogen indicate if the kerogen are oil prone, gas prone, or both

▲ **Triangle:** Rare kerogen abundance **Red:** Gas prone

■ **Square:** Several abundance **Orange:** Both oil and gas

⬟ **Pentagon:** Common kerogen abundance **Green:** Oil prone

⬢ **Hexagon:** Abundant **Red:** Gas prone

● **Circle:** Extra Abundant kerogen **Orange:** Both oil and gas

10: Colors for Bitumen indicate the bitumen type:

▲ **Triangle:** Rare bitumen abundance **Green:** Live stain

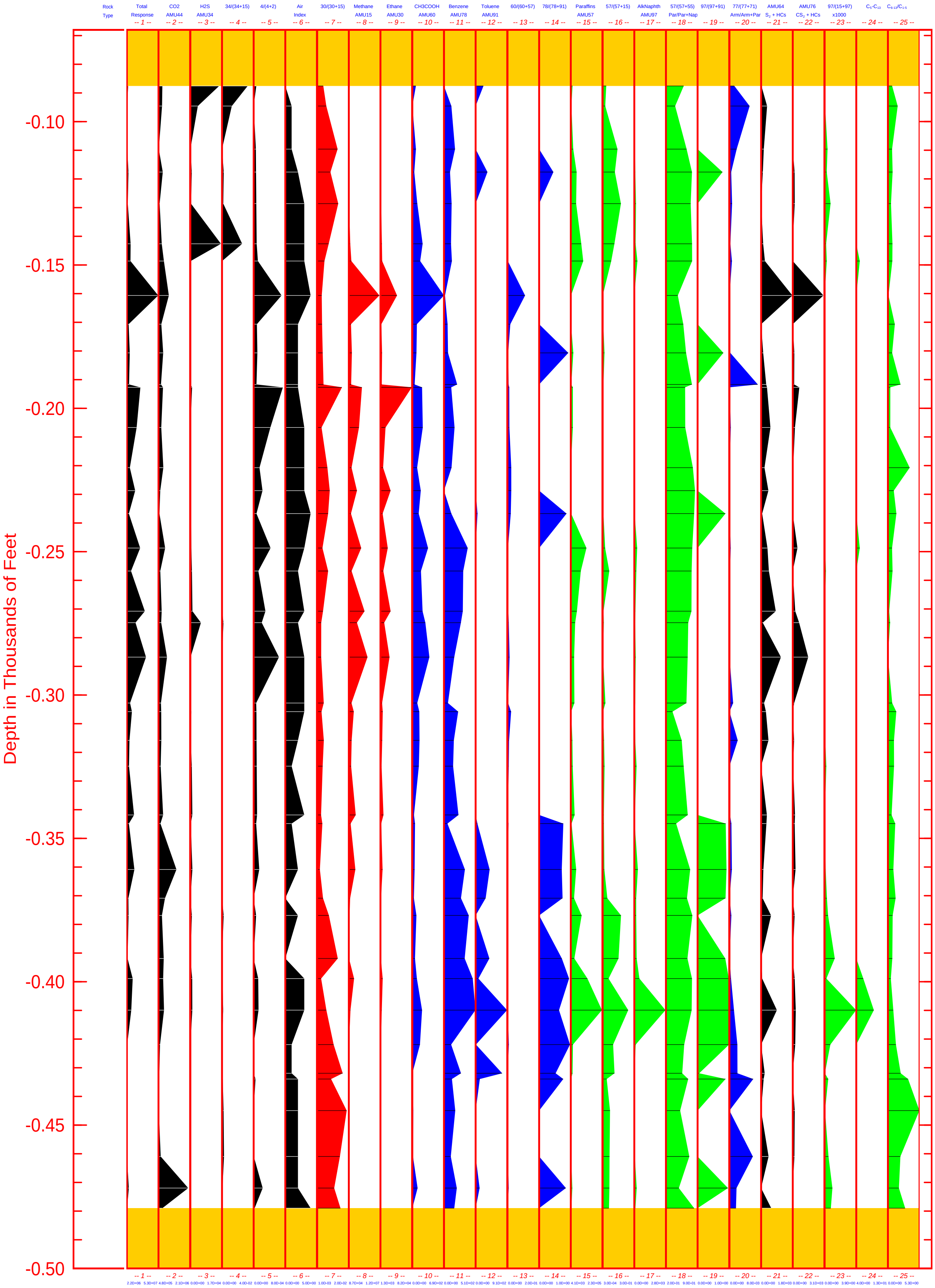
■ **Square:** Several bitumen **Gray:** Dead stain

⬟ **Pentagon:** Common kerogen abundance **Green:** Live stain

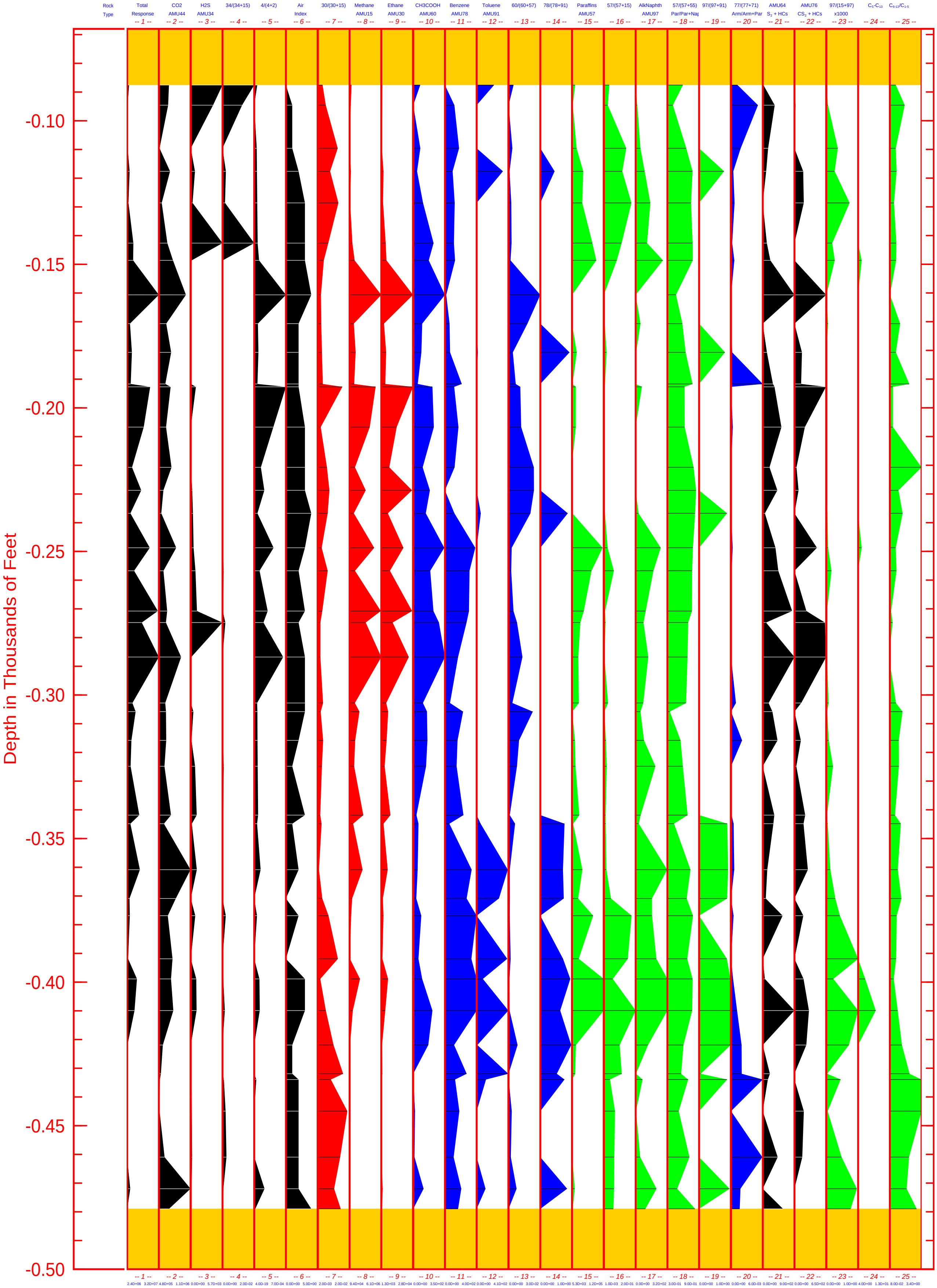
⬢ **Hexagon:** Abundant bitumen **Black:** Pore occluding

● **Circle:** Extra Abundant bitumen **Magenta:** Pyrobitumen

RC-C-1-81 : All FIS Data



RC-C-1-81 : 90% of all FIS Data



Fluid Inclusion Technologies, Inc.
http://www.fittulsa.com

A Schlumberger Company

UWI# 999999999999
FIS# *FI*160559*e*

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3 Overview of FIT, Inc. and Fluid Inclusion Stratigraphy

FIT, a Schlumberger Company, is a laboratory-based petroleum service organization established in 1997 and acquired by Schlumberger in November, 2015, 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 FIT 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 Compartmentallization** 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".

3.1 General Logistics of Initiating an FIS Analysis

To Initiate an FIS Analysis: contact FIT[1] 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 FIT for sample preparation including any necessary crushing/sieving, subsampling and washing.

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), 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

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[1] FIT Inc., a Schlumberger Company affiliate, 2217 N. Yellowood Ave., Broken Arrow, 74012, USA., phone (918) 461-8984

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 RC-C-1-81 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. FI160559e-1.las – LAS-format, 26-column file containing recorded depth and Tracks 1-25 from the *FIT Analysis* of RC-C-1-81
2. FI160559e-2.las – LAS-format, 181-column file containing recorded depth and background corrected, normalized, standardized individual mass spectra (m/z 2-180) from the *FIT Analysis* of RC-C-1-81
3. FI160559e-s.pdf – PDF format, electronic file of the summary tracks from the *FIT Analysis* of RC-C-1-81
4. FI160559e-t.pdf – PDF format, electronic file of the petrography table from the *FIT Analysis* of RC-C-1-81
5. FI160559e-1.pdf – PDF format, electronic file of the final report (entire document) of the *FIT Analysis* of RC-C-1-81

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 (H_2^+)
4	helium ($^4He^+$)
15	C_1 fragment (CH_3^+); largely methane
30	C_2 fragment ($C_2H_6^+$); largely ethane
34	hydrogen sulfide (H_2S^+)
44	dominantly carbon dioxide (CO_2^+); possible C_3 fragment overlap
55	contribution from C_4 and greater naphthenes
57	contribution from C_4 and greater paraffins
60	dominantly acetic acid (CH_3COOH^+); possible dominance by carbonyl sulfide (COS^+) in some cases
64	S_2 or SO_2 plus hydrocarbons
71	contribution from C_5 and greater paraffins
76	CS_2 plus hydrocarbons
77	contribution from aromatic species
78	benzene ($C_6H_6^+$) with possible contribution by carbon disulfide (CS_2^+)
91	toluene ($C_7H_7^+$)
97	C_7 alkylated naphthene fragment

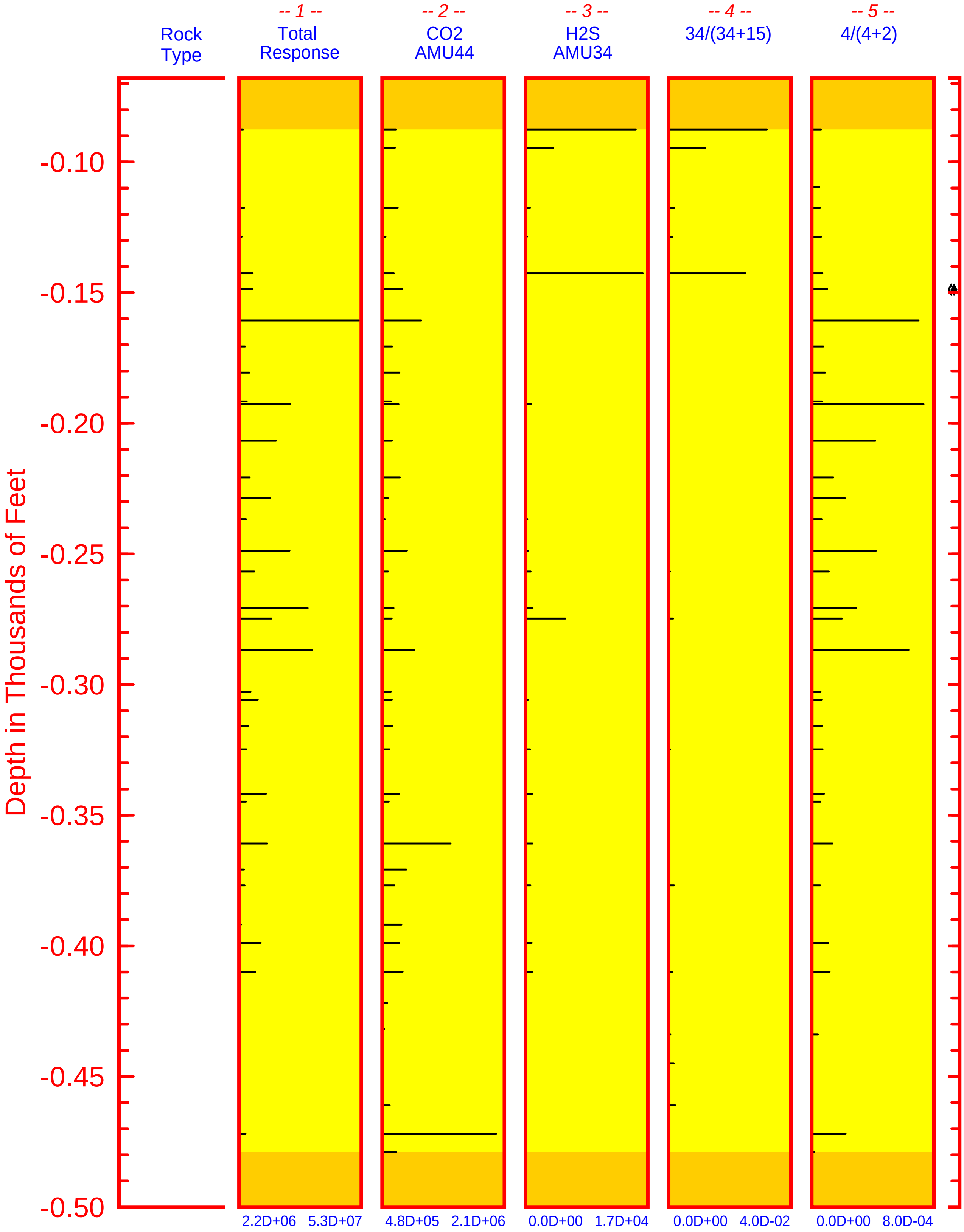


Figure 2: All FIS Data: Tracks 1 – 5 (see Sect. A.3 for explanation)

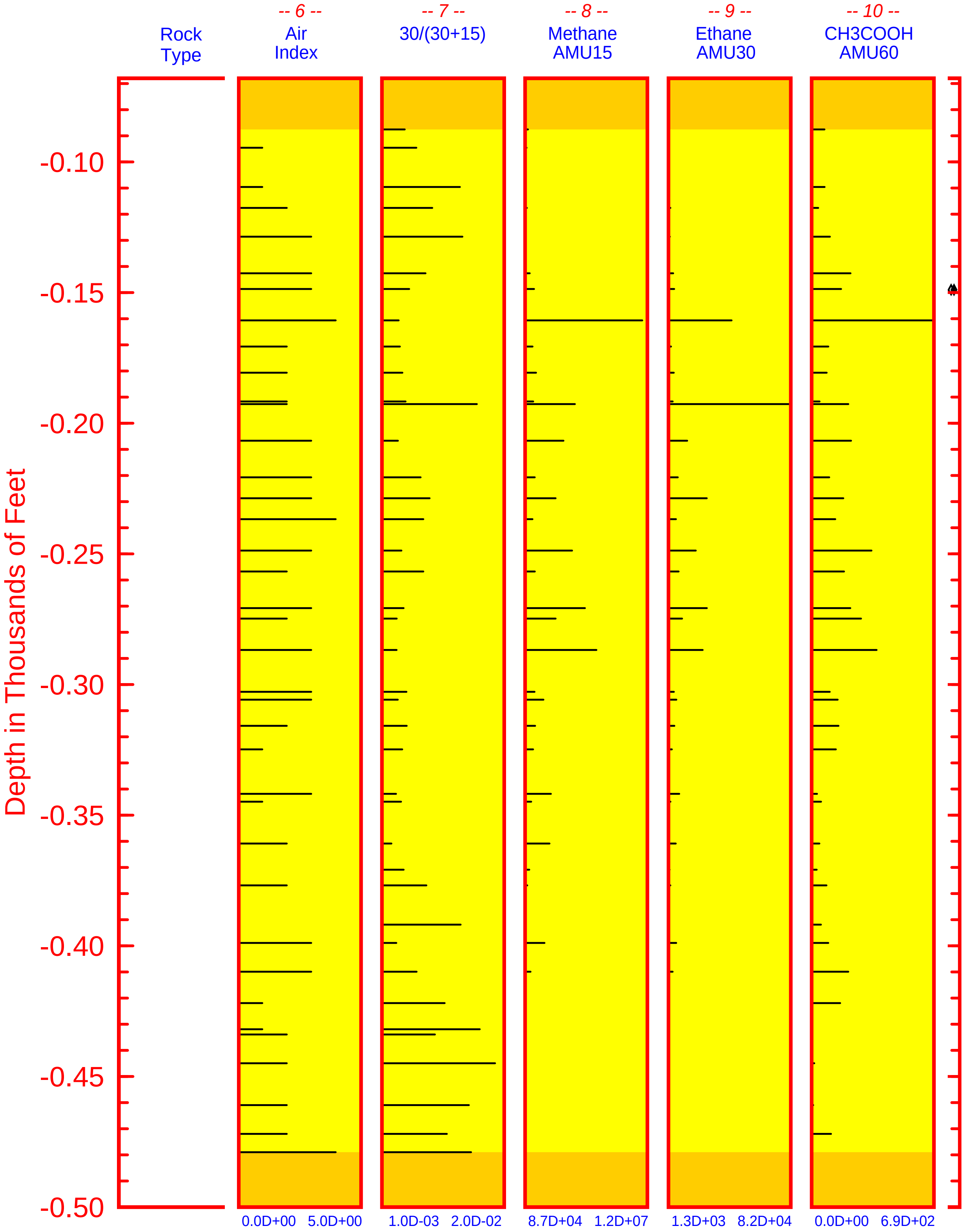


Figure 3: All FIS Data: Tracks 6 – 10 (see Sect. A.3 for explanation)

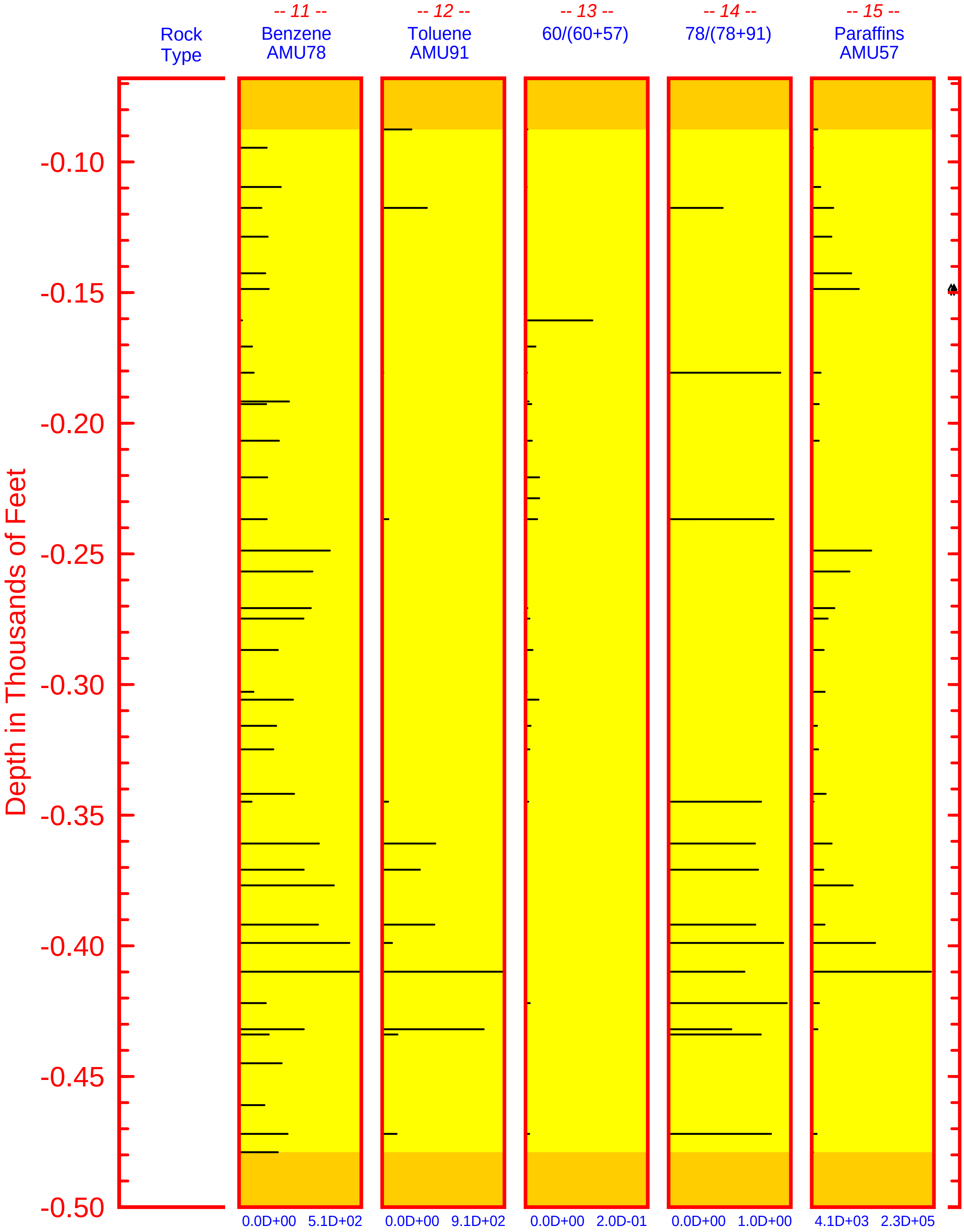


Figure 4: All FIS Data: Tracks 11 − 15 (see Sect. A.3 for explanation)

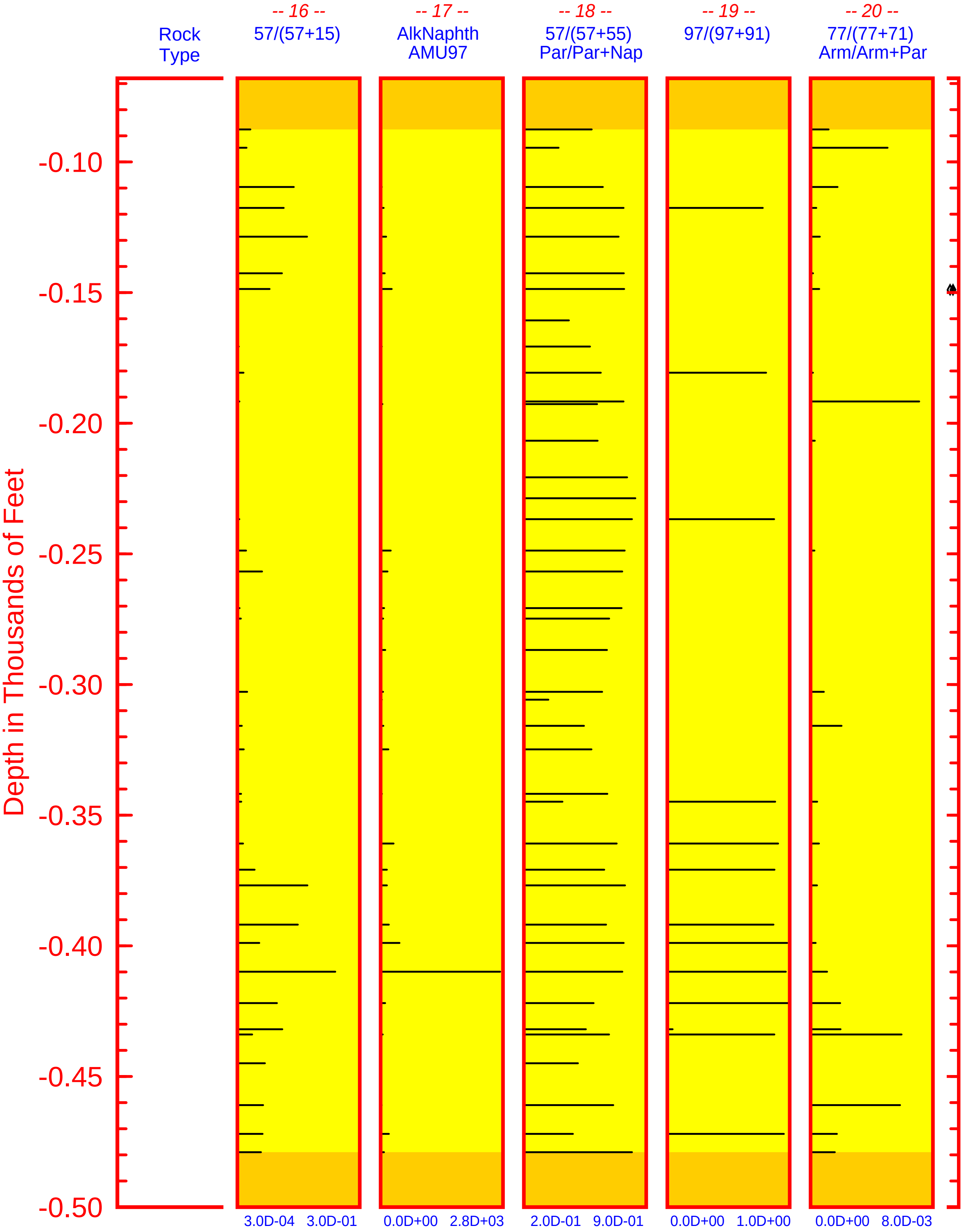


Figure 5: All FIS Data: Tracks 16 – 20 (see Sect. A.3 for explanation)

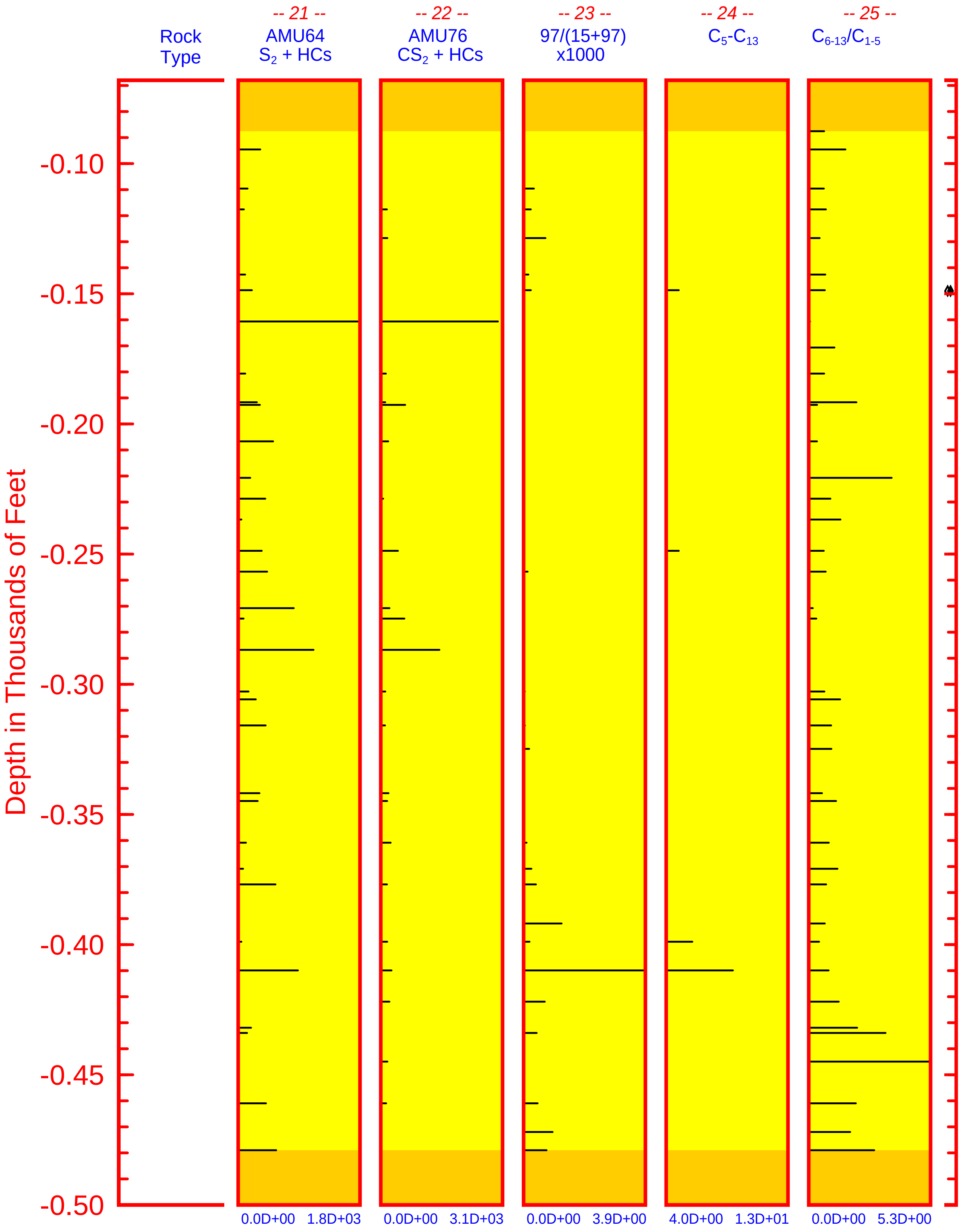


Figure 6: All FIS Data: Tracks 21 – 25 (see Sect. A.3 for explanation)

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.

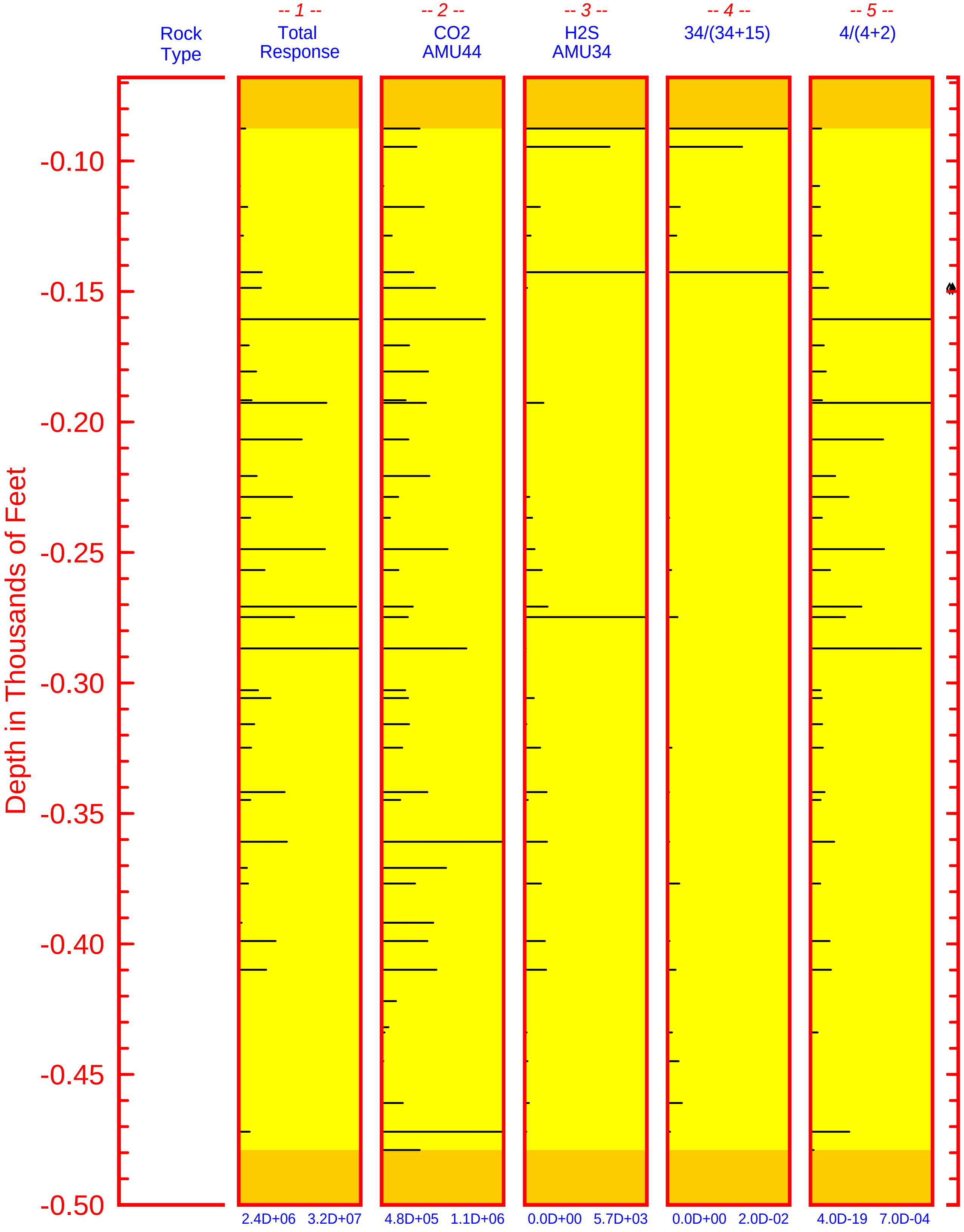


Figure 7: 90% of all FIS Data: Tracks 1 – 5 (see Sect. A.3 for explanation)

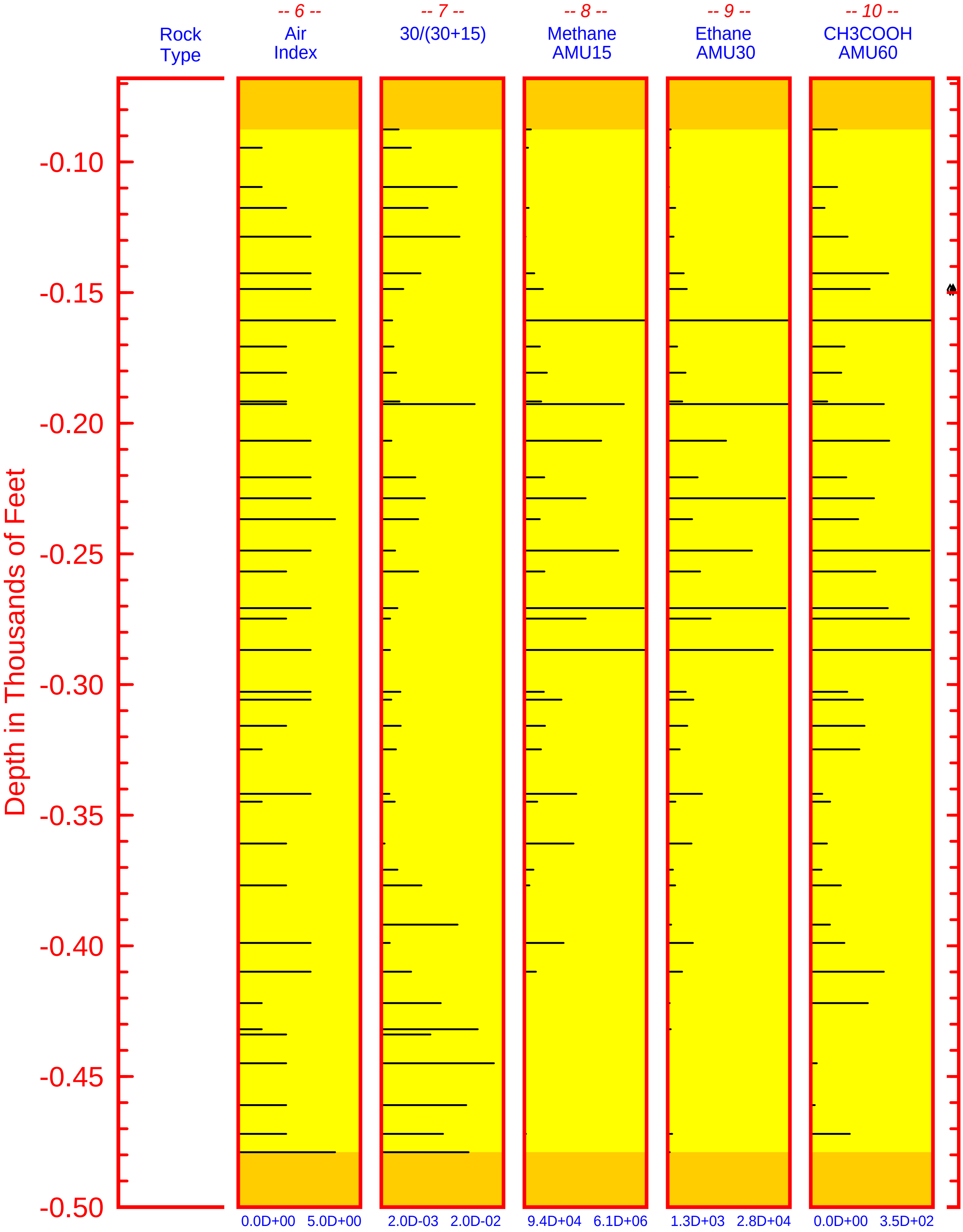


Figure 8: 90% of all FIS Data: Tracks 6 – 10 (see Sect. A.3 for explanation)

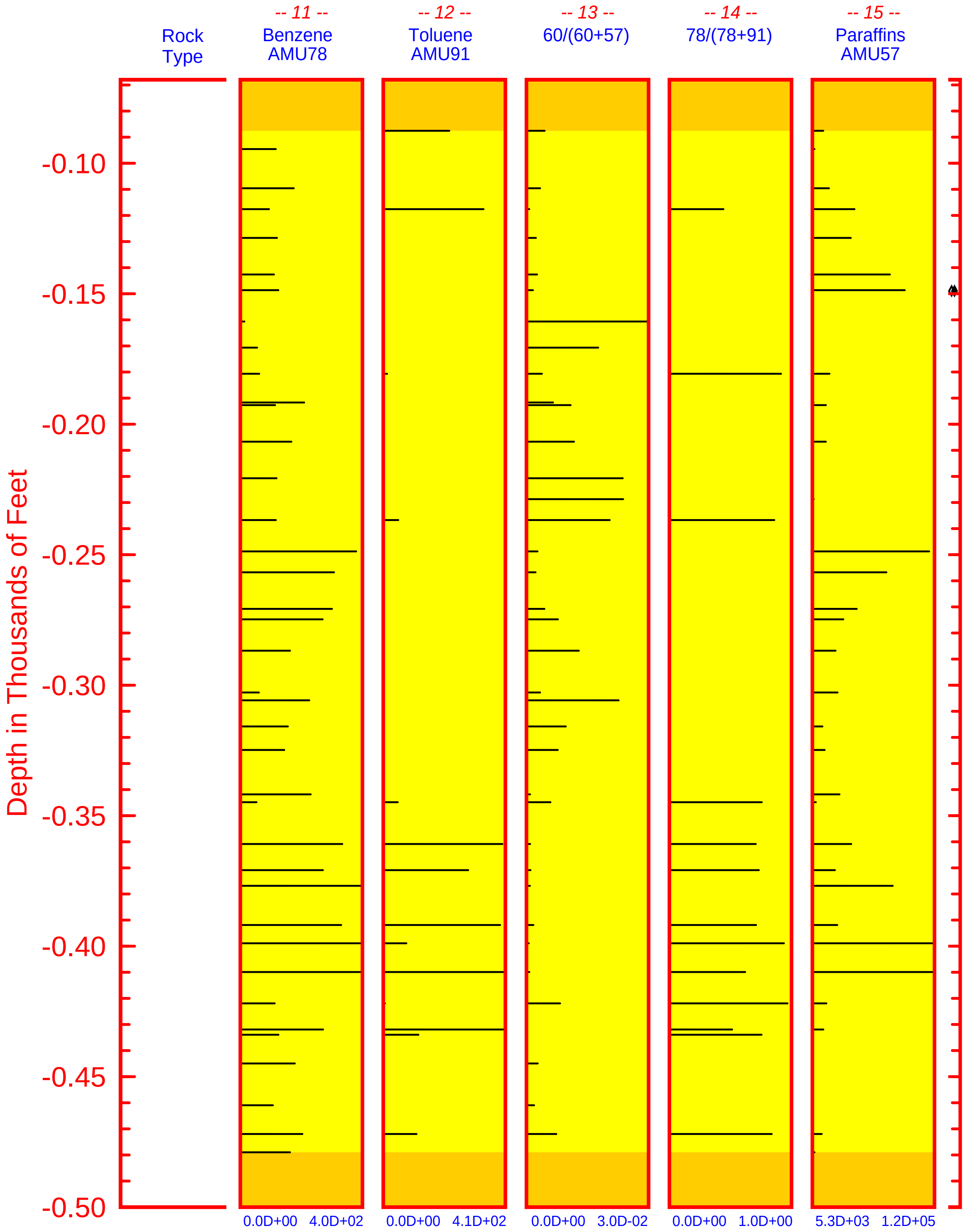


Figure 9: 90% of all FIS Data: Tracks 11 – 15 (see Sect. A.3 for explanation)

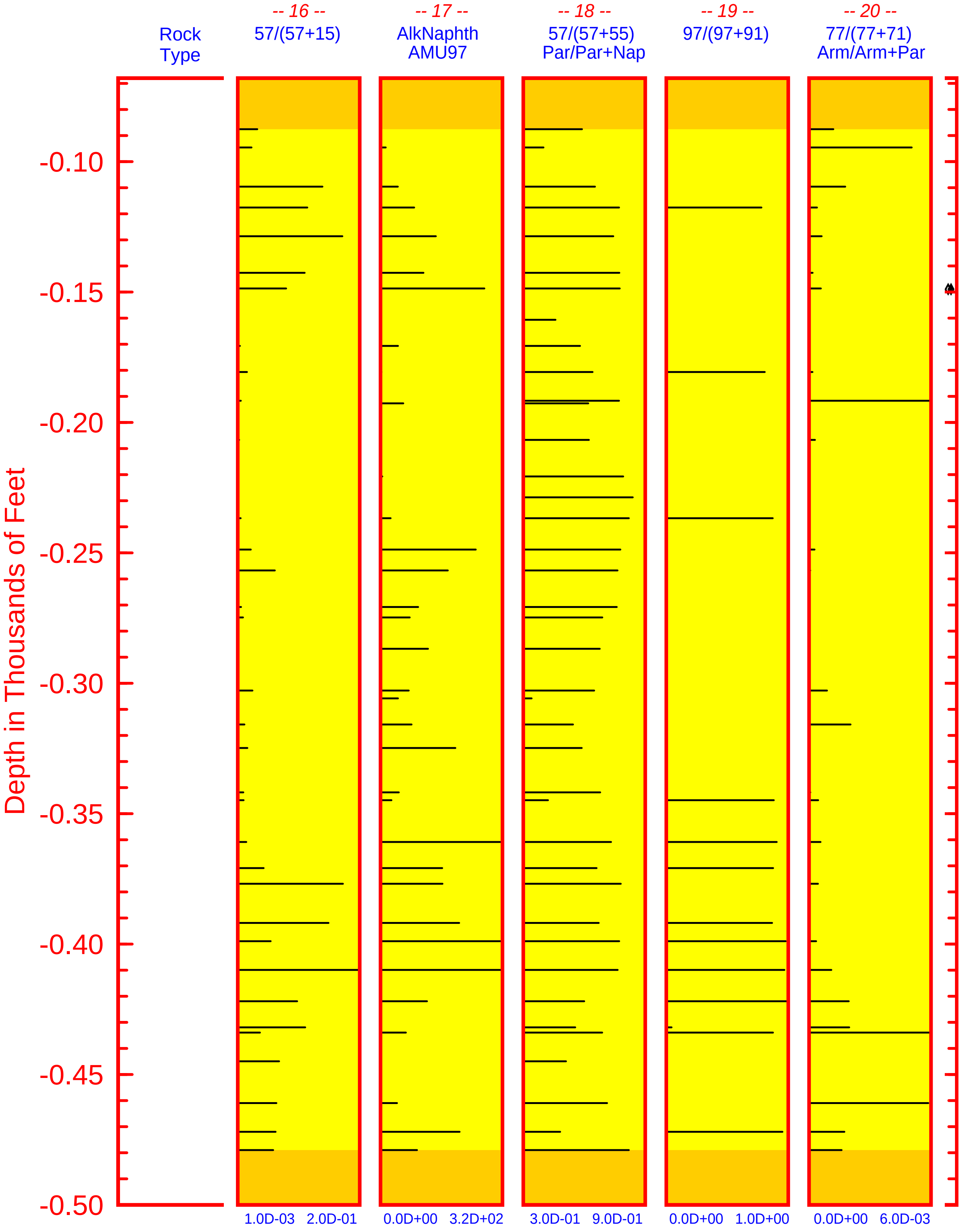


Figure 10: 90% of all FIS Data: Tracks 16 – 20 (see Sect. A.3 for explanation)

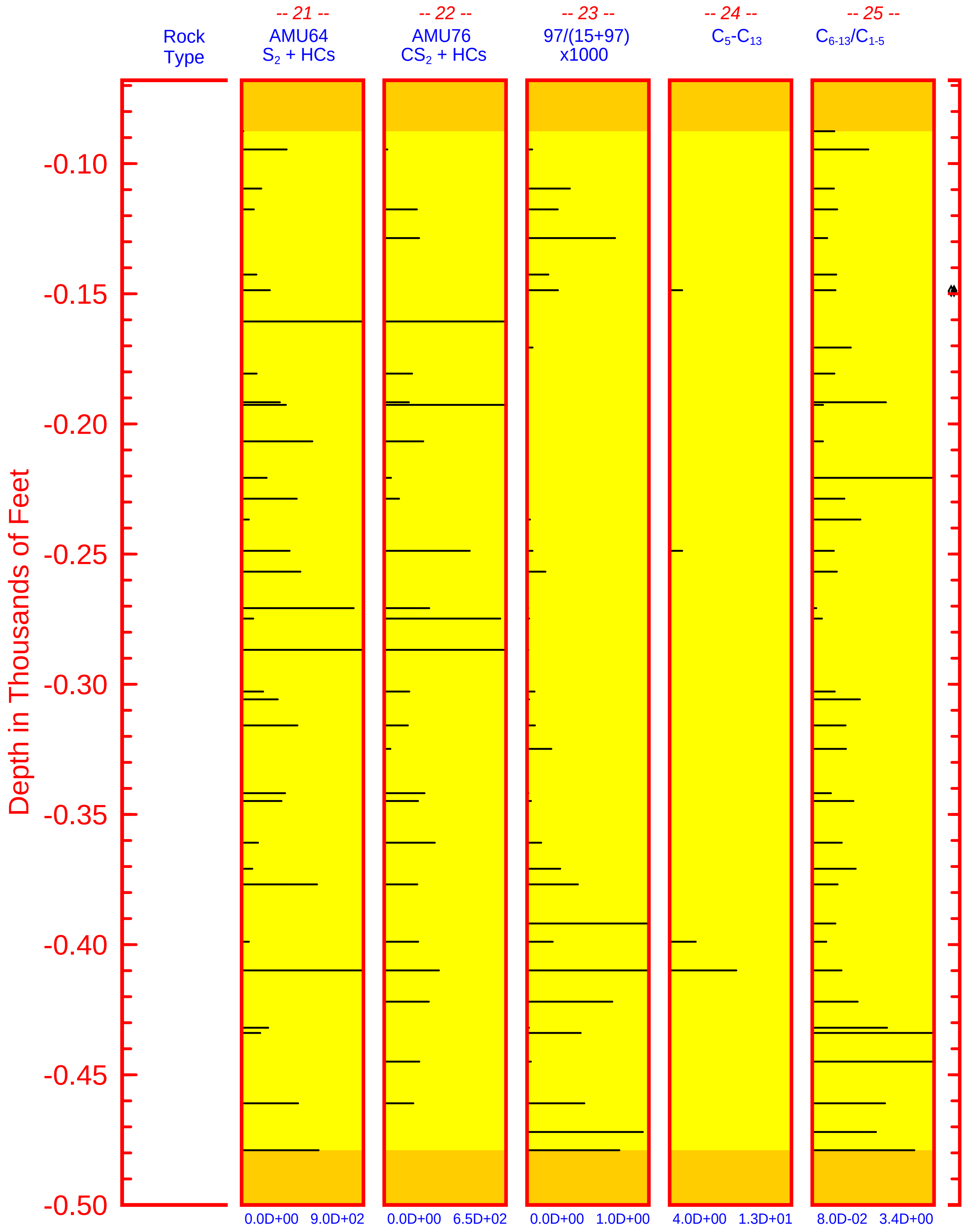


Figure 11: 90% of all FIS Data: Tracks 21 – 25 (see Sect. A.3 for explanation)

5 Photomicroscopy

Thin sections were prepared from RC-C-1-81 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 RC-C-1-81 at the depths indicated.

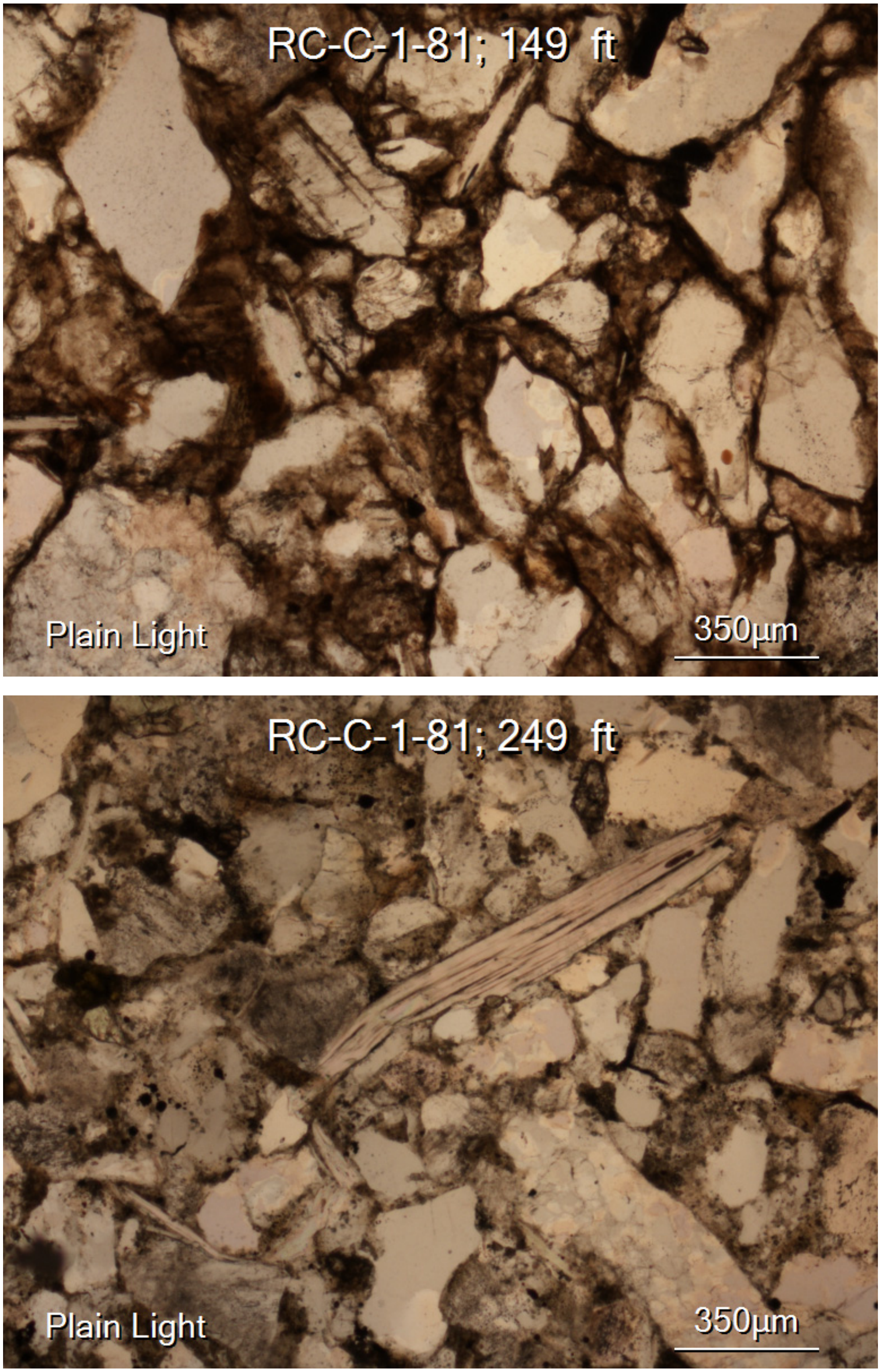


Figure 12: Photomicroscopy from RC-C-1-81

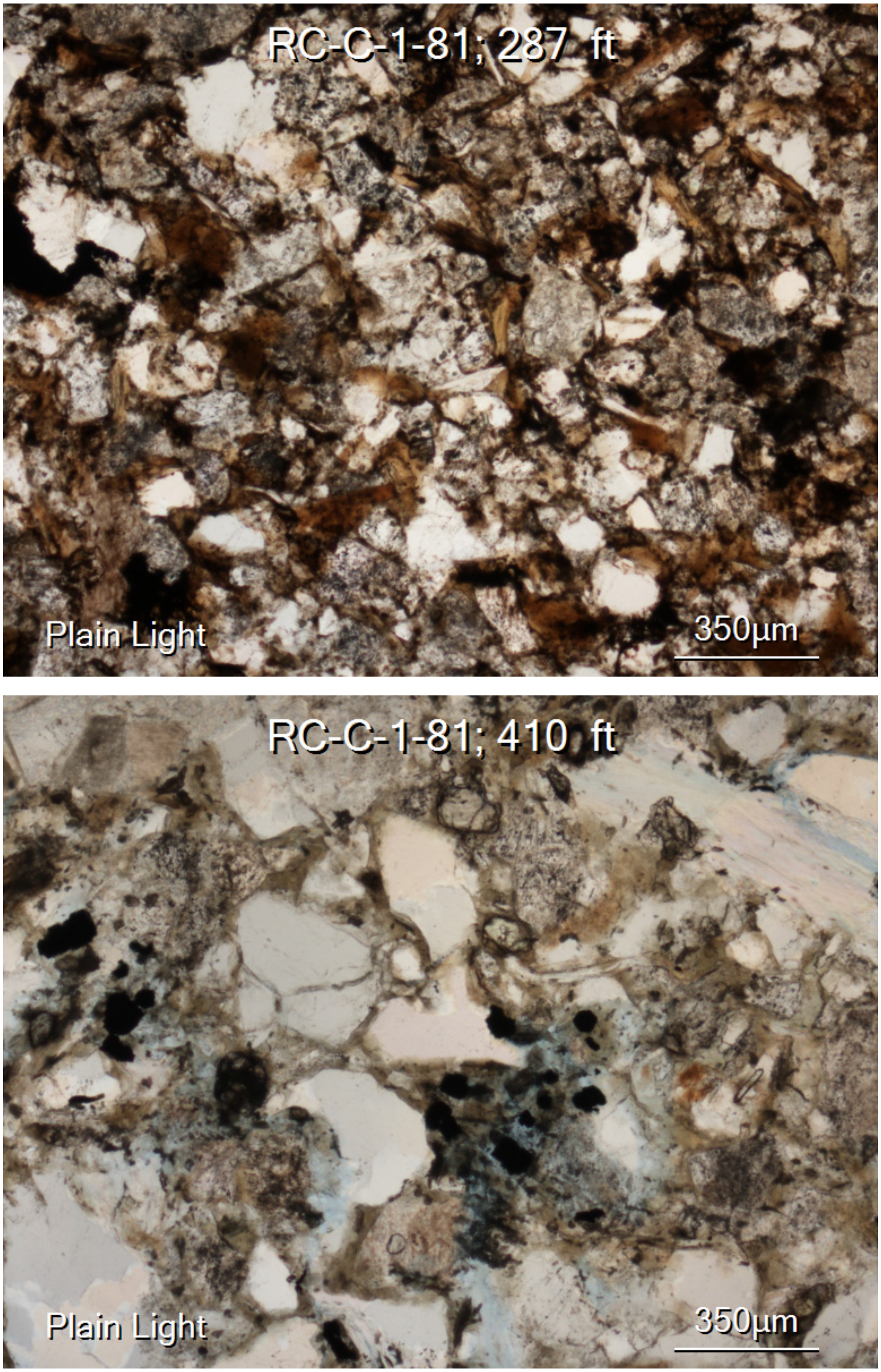


Figure 13: Photomicroscopy from RC-C-1-81

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 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. HD^+ and $^3He^+$ 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:* C_nH_{2n+2}
2. *Naphthenes:* C_nH_{2n}
3. *Aromatics:* C_nH_{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 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 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 C_1-C_5 hydrocarbons with dwindling responses in the C_6-C_8 range, and essentially no response in the C_9+ range. Drier gases may exhibit responses only in the C_1-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_4-C_6 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_2 and water, nitrogen and minor hydrocarbon contributions). The distinction lies in the relative proportion of these species. Gases can typically contain 90% C_1 and 95% C_1-C_3. Hence, FIS gas spectra typically have prominent C_1-C_3 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_4+ paraffins / C_4+ 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_7-C_{13} 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, 71	156(4%)
C12	165-171	57, 43, 71	170(8%)
C13	179-185	43, 57, 71	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_7-C_{13} paraffins are usually the same, and represent some of the most intense peaks previously identified for the C_4-C_6 gas-range paraffins.

Only normal (straight-chain) paraffins have been considered in the above table. Typical C_6-C_{10} (gasoline) fractions contain 40% paraffins, 50% naphthenes and 10% aromatics by volume. Typical C_{11}-C_{13} (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_7 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_1-C_{13} 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_2, 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 though 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 indictor species include light hydrocarbons, CO_2, possibly organic acids and aromatic compounds, and sulfurous volatiles, including H_2S, COS, CS_2, S_2 (+/- SO_2) and in some cases thiols. H_2S 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 downdip.

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 (CO_2^+), with possible minor contribution from C_3^+ hydrocarbon fragments and acetic acid. Anomalous values have been noted associated with pan-evaporative dolomitization of limestones in China and Oman. CO_2 response is often

high in proximity samples which show elevated levels of acetic acid. CO_2 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_2S^+). Anomalous values associated with petroleum may indicate sour oil or gas. H_2S is also noted at times in association with shallow dry gas of probable biogenic origin (including FIS microseeps) and with some proximity zones. H_2S is probably not quantitatively analyzed due to rapid scavenging by metallic surfaces of the analytical system.

Track 4: 34/(34+15) - H_2S/(H_2S+methane). Not frequently used, but ratio tends to be elevated in sour gas zones.

Track 5: 4/(4+2) - Helium fraction ${}^4He^+/({}^4He^+ + H_2^+)$; 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_3^+; mostly derived from methane, with minor contributions from all other paraffins and NH_2^+, 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 ($C_2H_6^+$). Use similar to that of methane ($m/z = 15$).

Track 10: $m/z = 60$ - Acetic aid (CH_3COOH), 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 ($C_6H_6^+$). 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 ($C_7H_7^+$). 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: $m/z = 76$ - CS_2 and C_6^+ hydrocarbons. 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: $C_5 - C_{13}$ 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 C_5 group is the highest molecular weight range hydrocarbon group present in a given sample, a ranking of 5 is assigned; if 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 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: C_{6-13}/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 (H_2^+); largely from H_2O, which makes up most of the evolved fluid in almost all samples.
- $m/z = 3$ - Deuterated hydrogen and helium-3 (HD and $^3He^+$).
- $m/z = 12$ - Carbon (C^+).
- $m/z = 14$ - Nitrogen (N^+) and 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. CH_2^+ will generally be accompanied by relatively larger responses on $m/z = 15$ (CH_3^+), and $m/z = 16$ (CH_4^+) (due to it's fragmentation origin from 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 (CH_4^+), but major interference by O^+ fragment of water.

- $m/z = 17$ - Dominated by OH^+ fragment from water
- $m/z = 18$ - Dominated by water parent peak (H_2O^+)
- $m/z = 22$ - Doubly charged carbon dioxide ($CO2^{2+}$); minor contribution from neon ($^{22}Ne^+$)
- $m/z = 28$ - Dominated by diatomic nitrogen (N_2^+) and CO^+ fragment from carbon dioxide. Minor C_2^+ hydrocarbon contribution
- $m/z = 32$ - Oxygen (O^+) and sulfur (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 $m/z = 34$ (H_2S), $m/z = 48$ (SO^+) and $m/z = 64$ (S_2^+, 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 (Ar^+) with possible significant interference by 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 (SO^+); also, C_4^+
- $m/z = 55$ - Naphthene fragment ($C_4H_7^+$). 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 ($C_5H_{11}^+$). Same use as $m/z = 57$.
- $m/z = 77$ - Aromatic fragment ($C_6H_5^+$). Same general use as for benzene and toluene.
- $m/z = 85$ - Paraffin fragment ($C_6H_{13}^+$). Same use as $m/z = 57$.
- $95 \leq m/z \leq 103$ - peaks centered within this range are mostly $C_7 - C_8$ fragments
- $110 \leq m/z \leq 115$ - peaks centered within this range are mostly $C_8 - C_9$ fragments
- $122 \leq m/z \leq 126$ - peaks centered within this range are mostly $C_9 - C_{10}$ fragments
- $134 \leq m/z \leq 138$ - peaks centered within this range are mostly $C_{10} - C_{11}$ fragments
- $148 \leq m/z \leq 152$ - peaks centered within this range are mostly $C_{11} - C_{12}$ fragments
- $160 \leq m/z \leq 164$ - peaks centered within this range are mostly $C_{12} - C_{13}$ fragments
- $175 \leq m/z \leq 180$ - peaks centered within this range are mostly $C_{13} - C_{14}$ 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 14. 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 inhomogenieties 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 15 and 16. 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 17. 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.

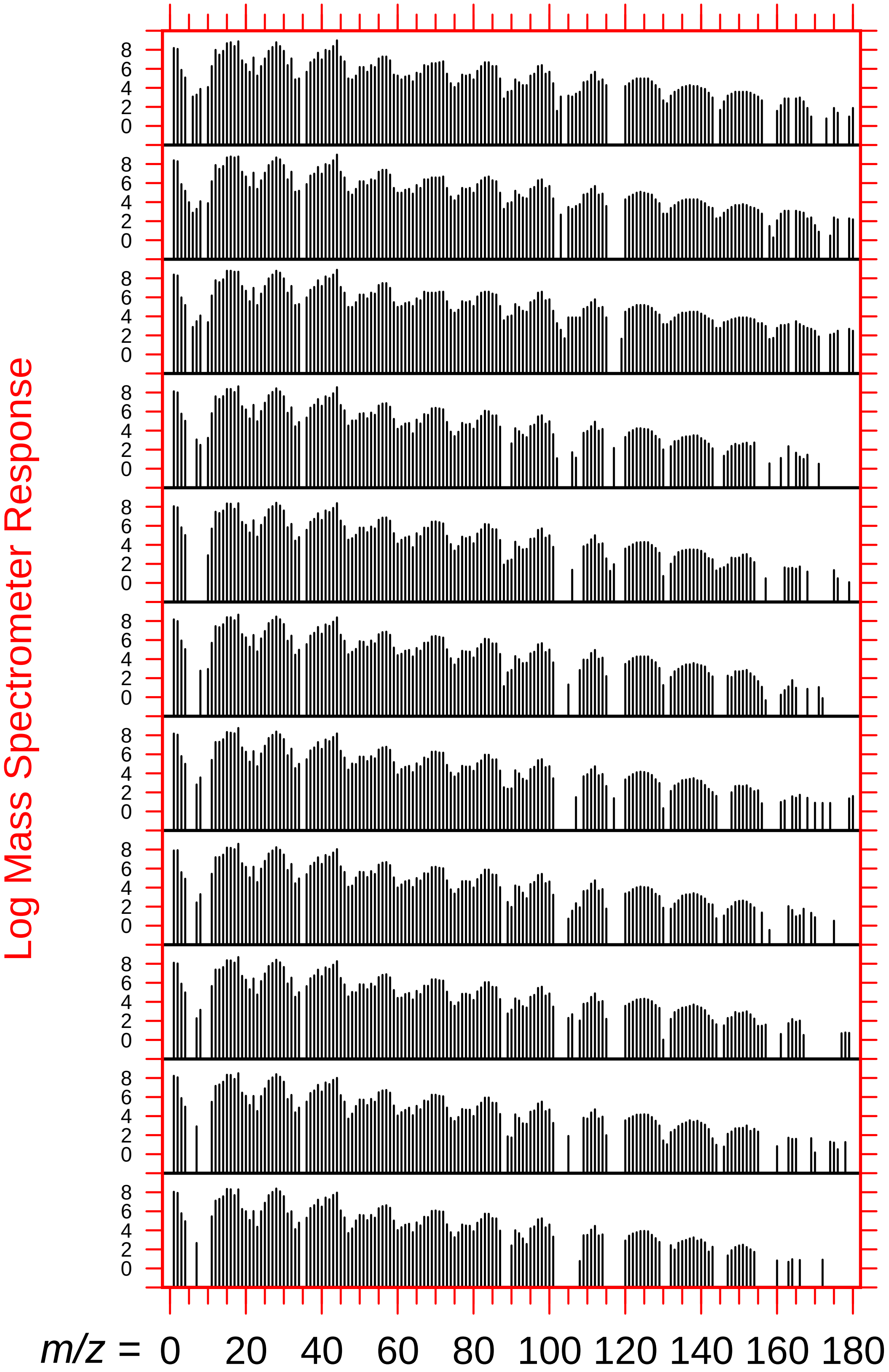


Figure 14: Oil Spectra

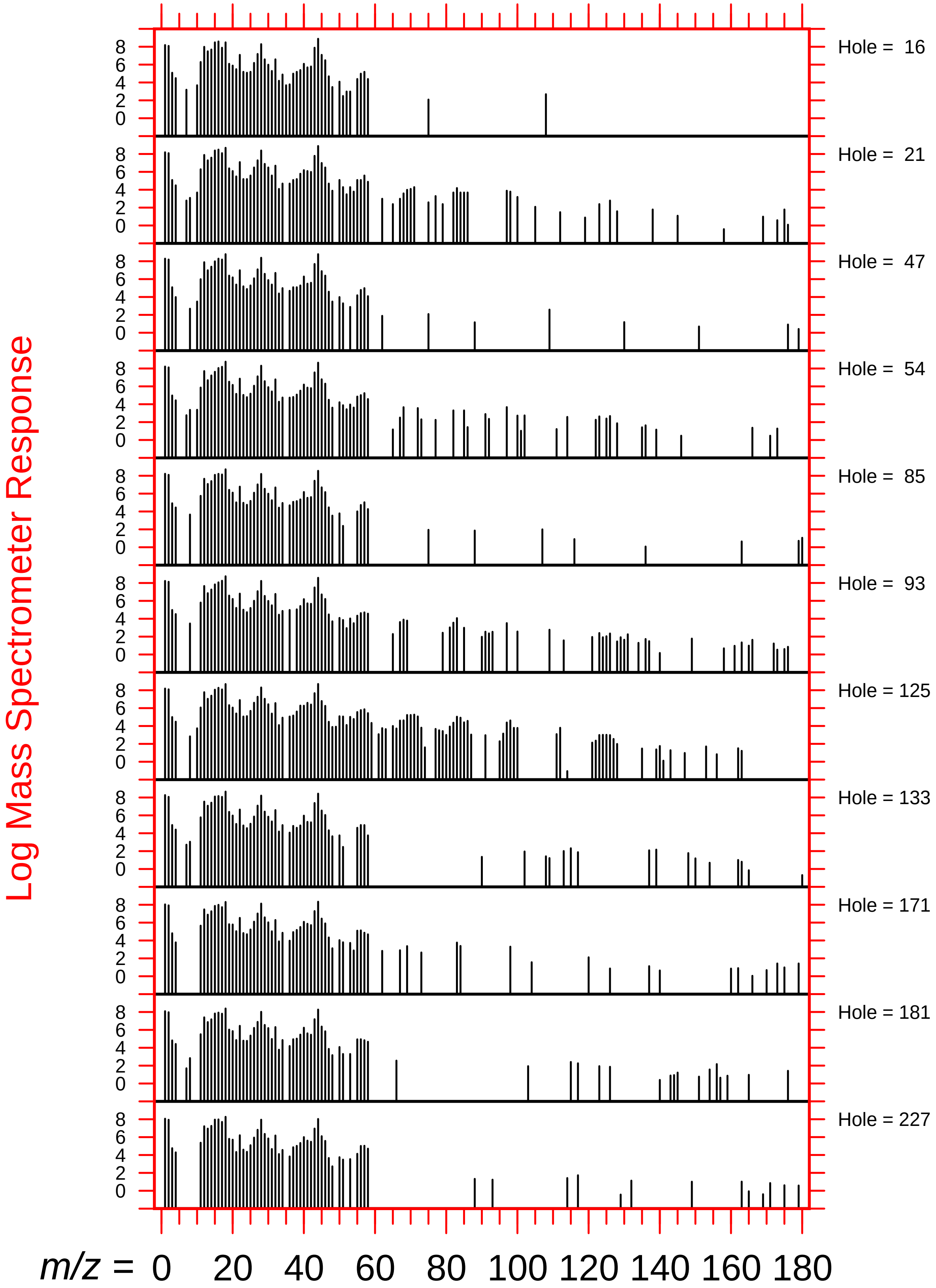


Figure 15: Frac Sand Spectra

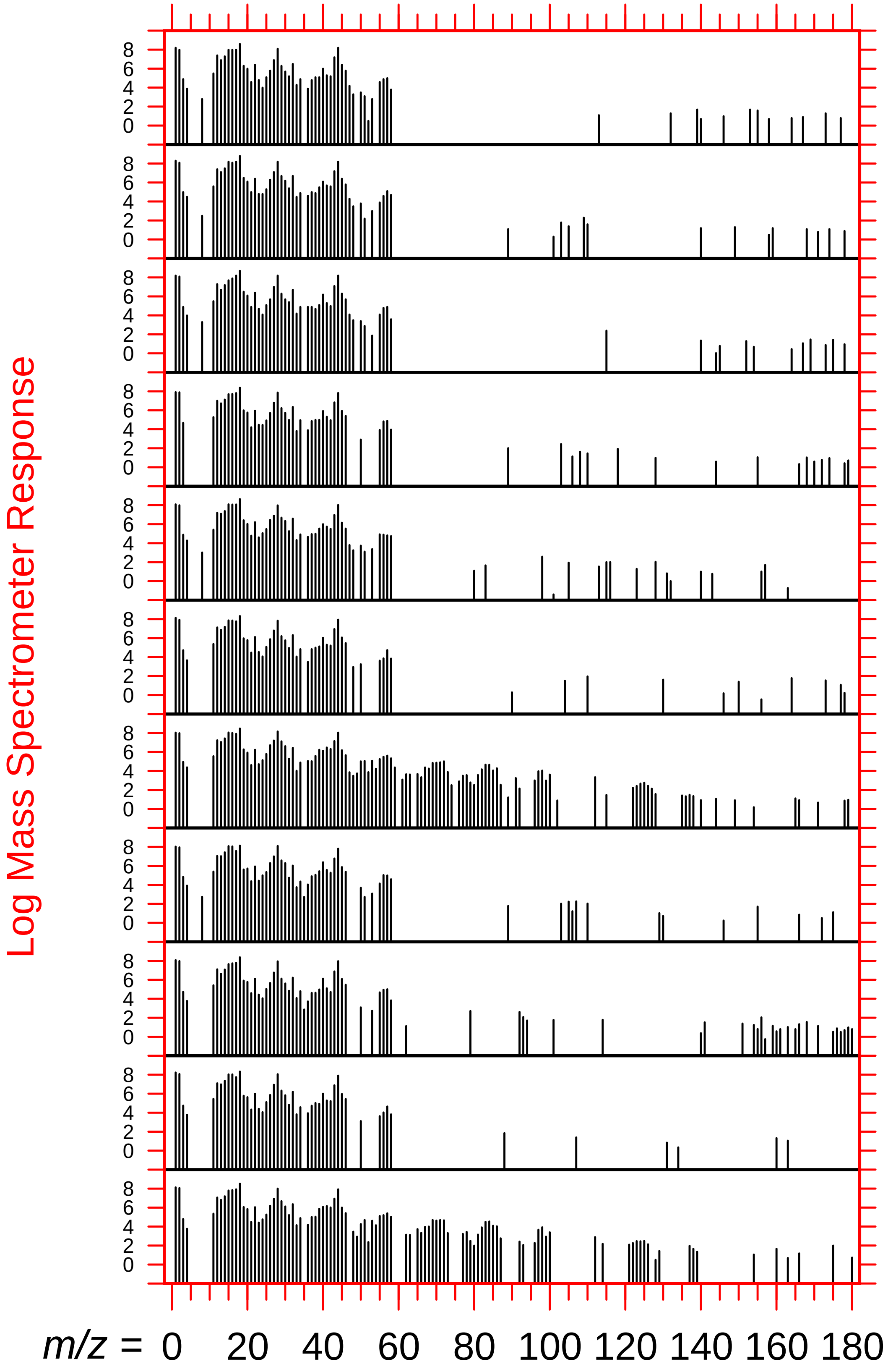


Figure 16: Frac Sand Spectra

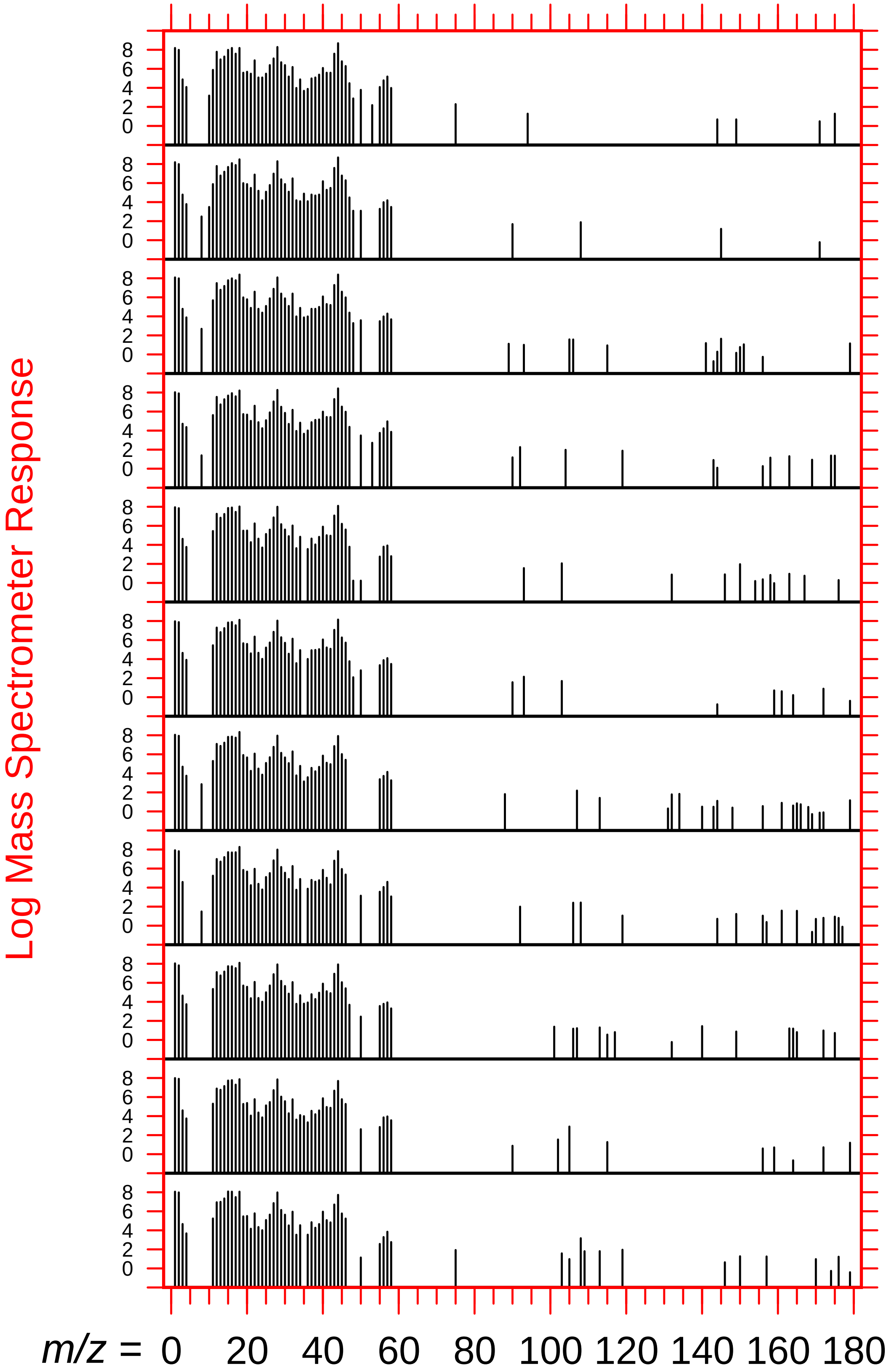


Figure 17: Cooked Frac Sand Spectra

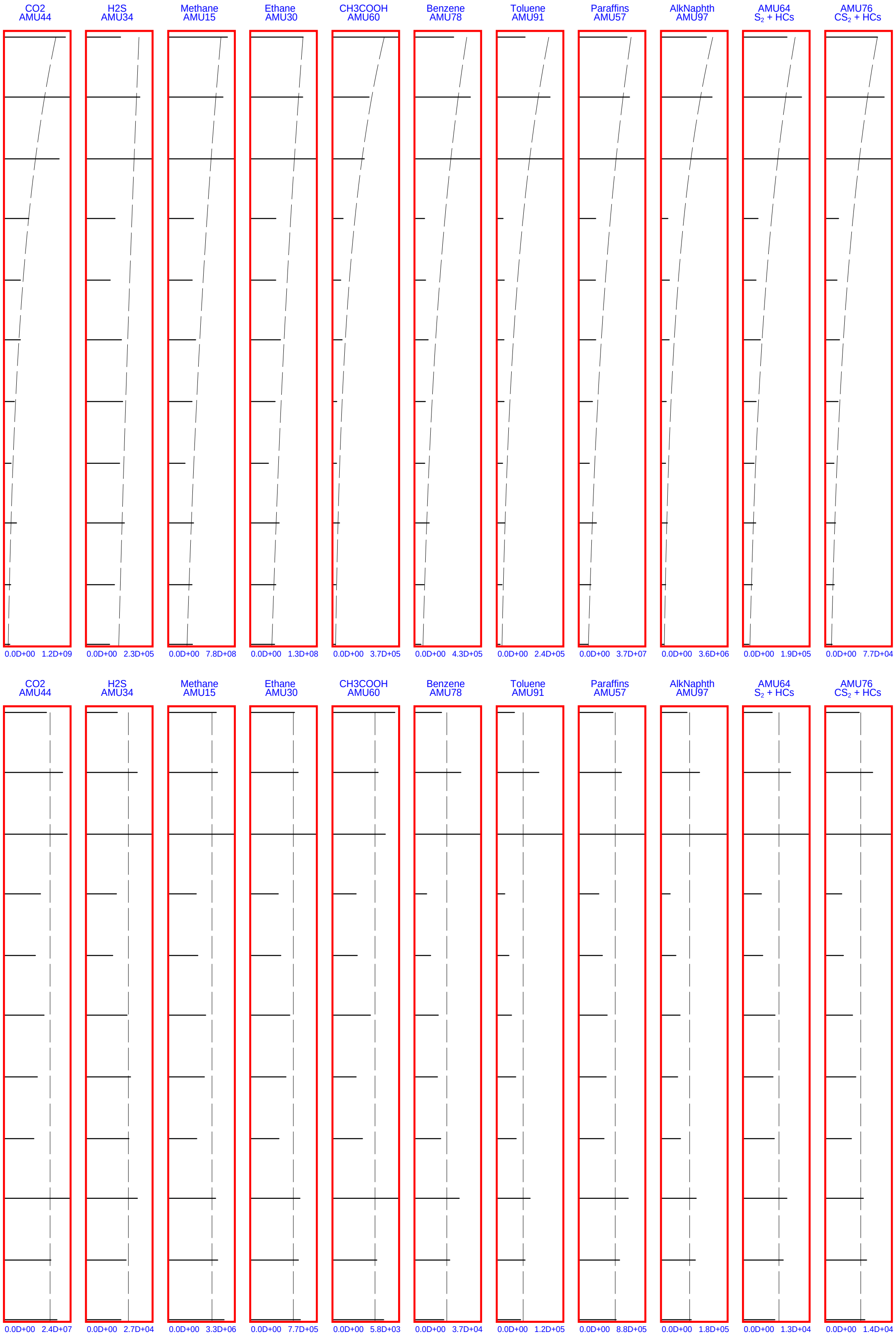
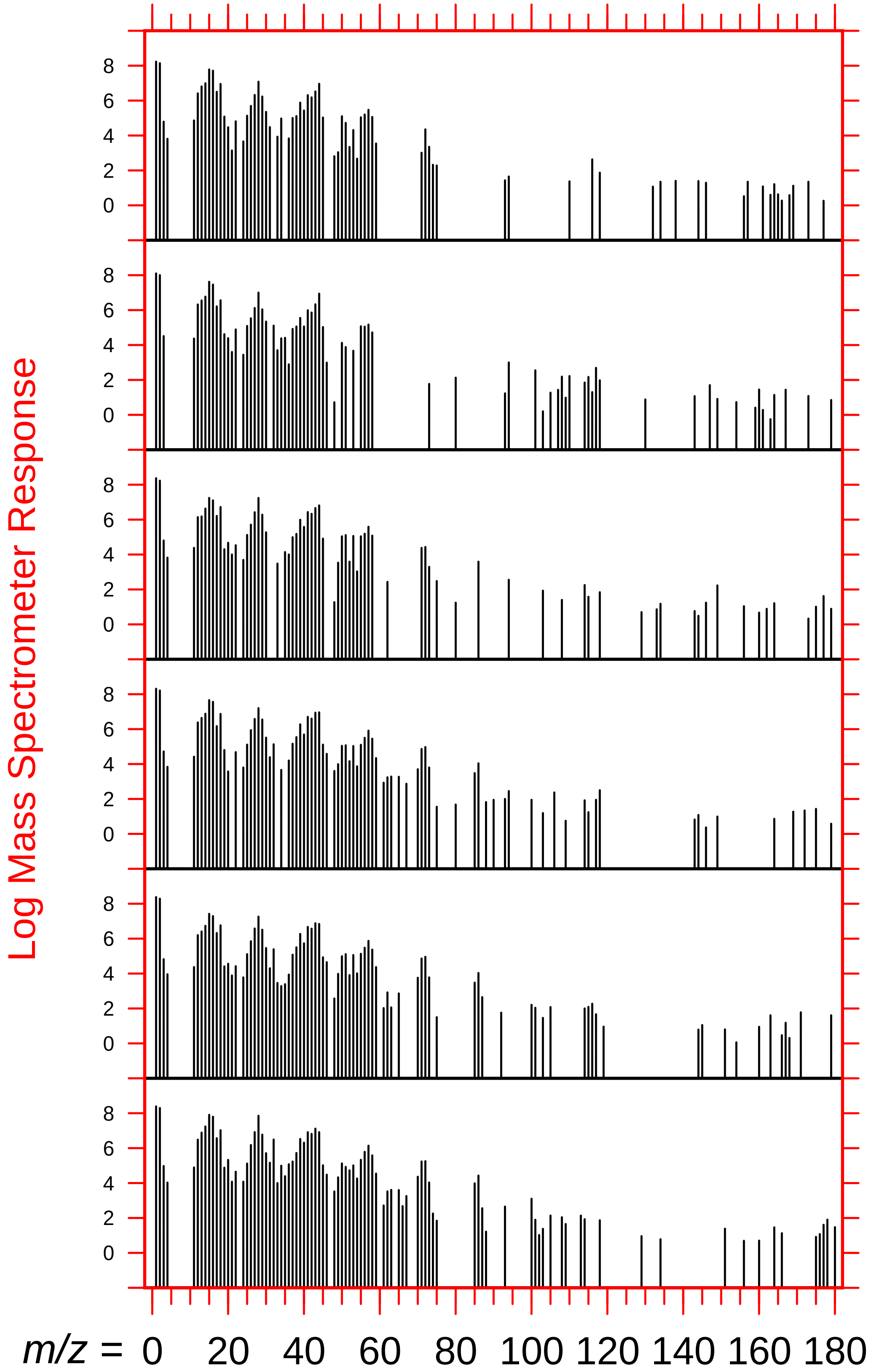
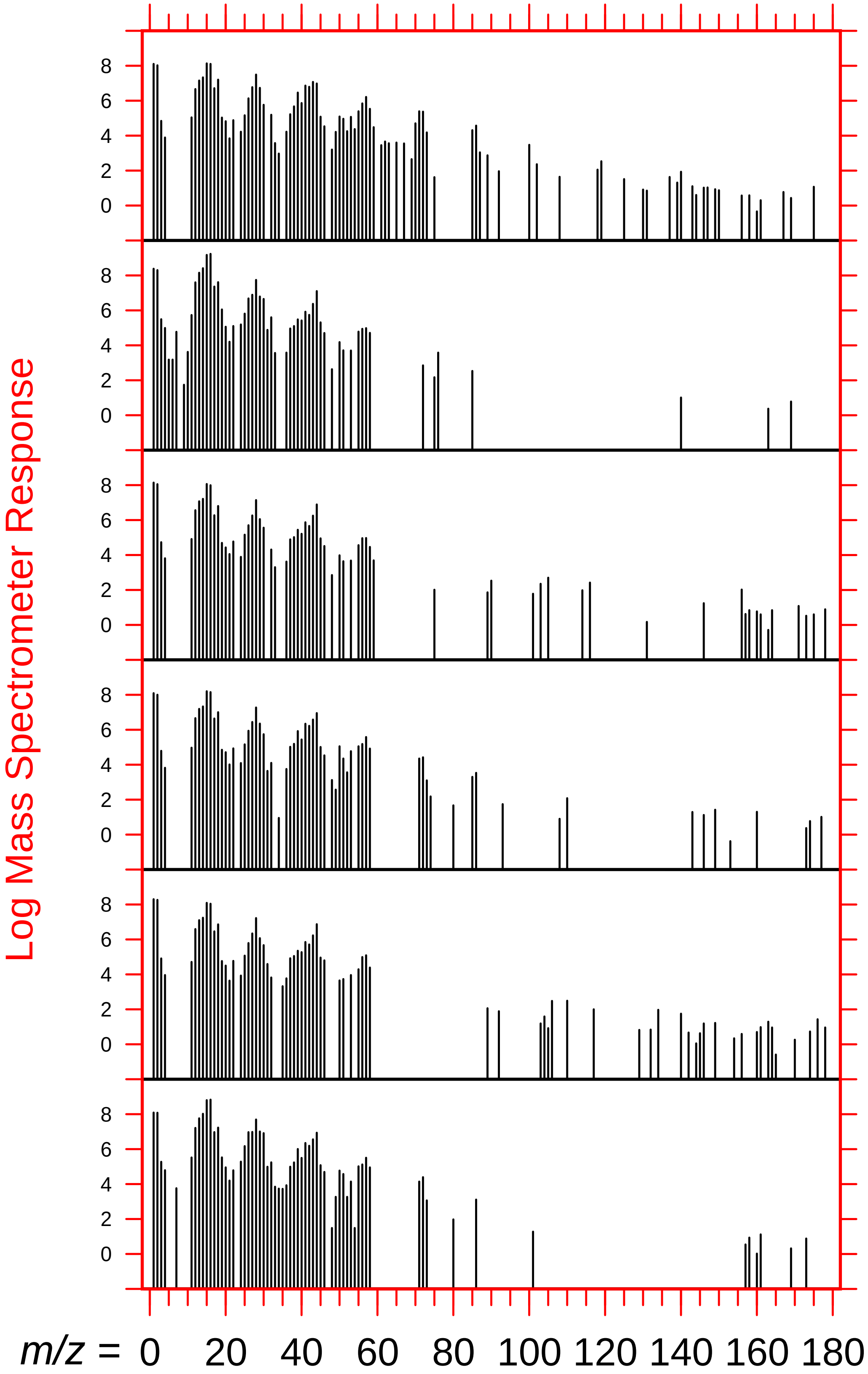


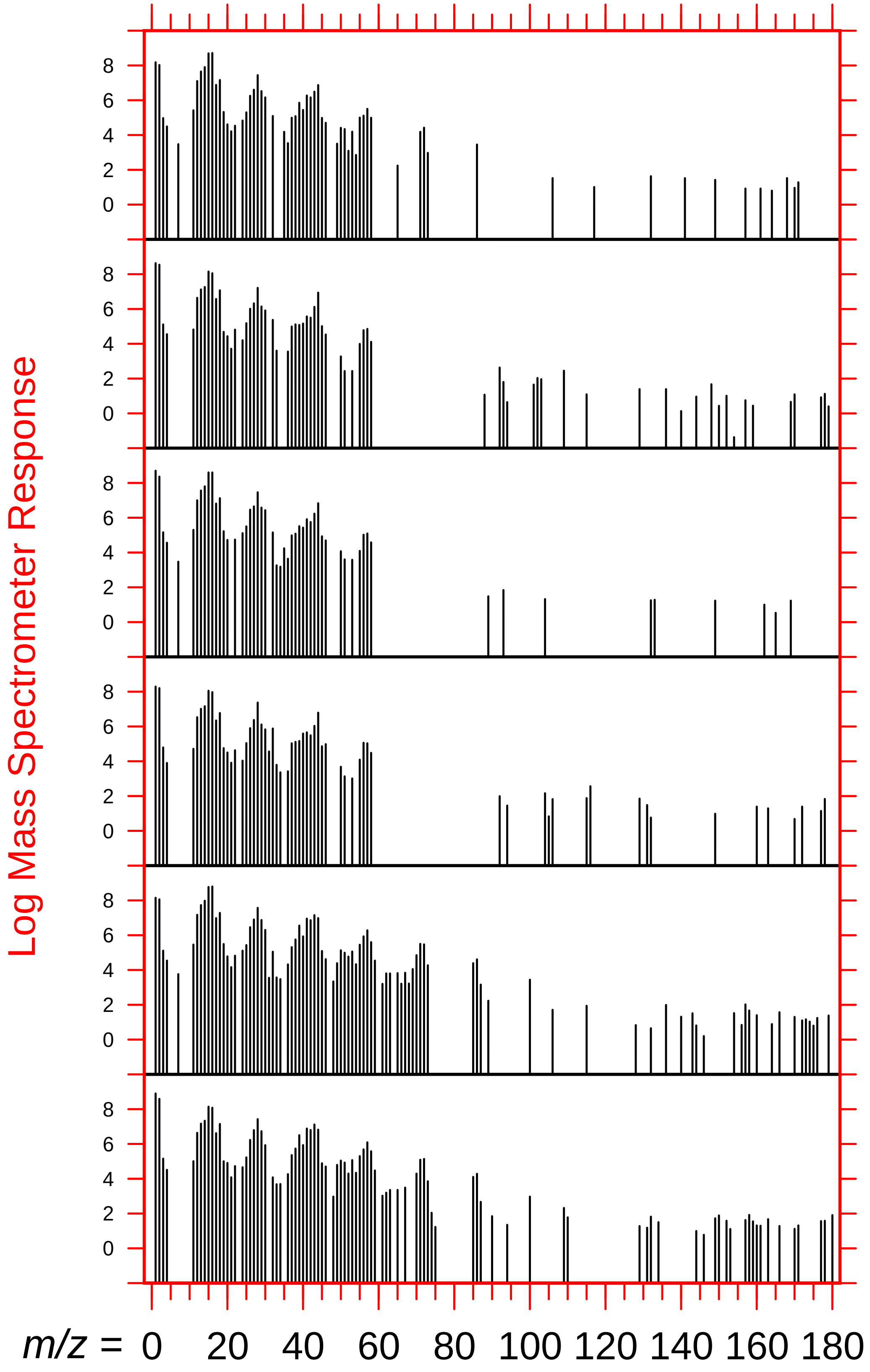
Figure 18: Kindblade Oil Standards Before (top) and After (bottom) Correction

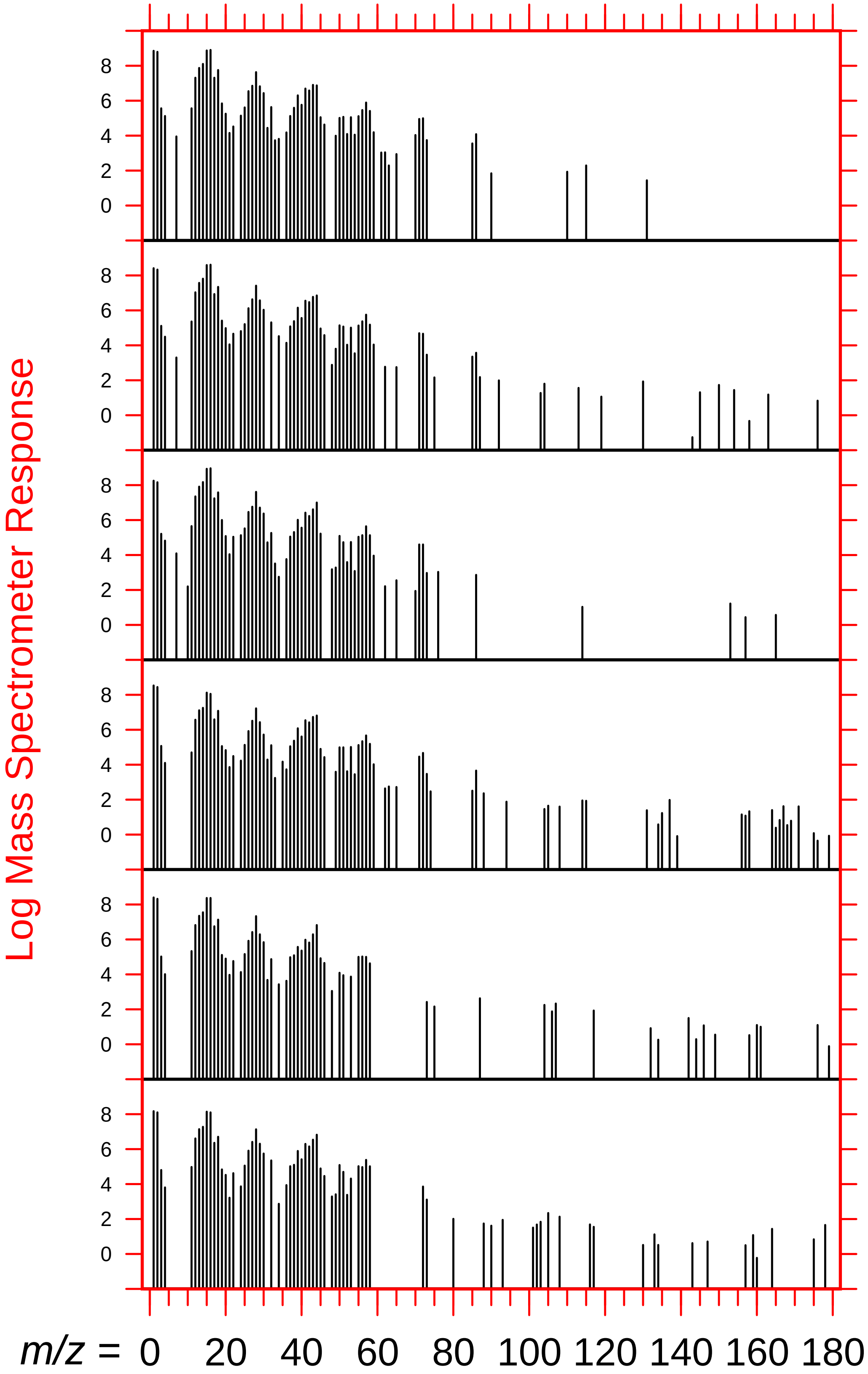
C Individual Spectra

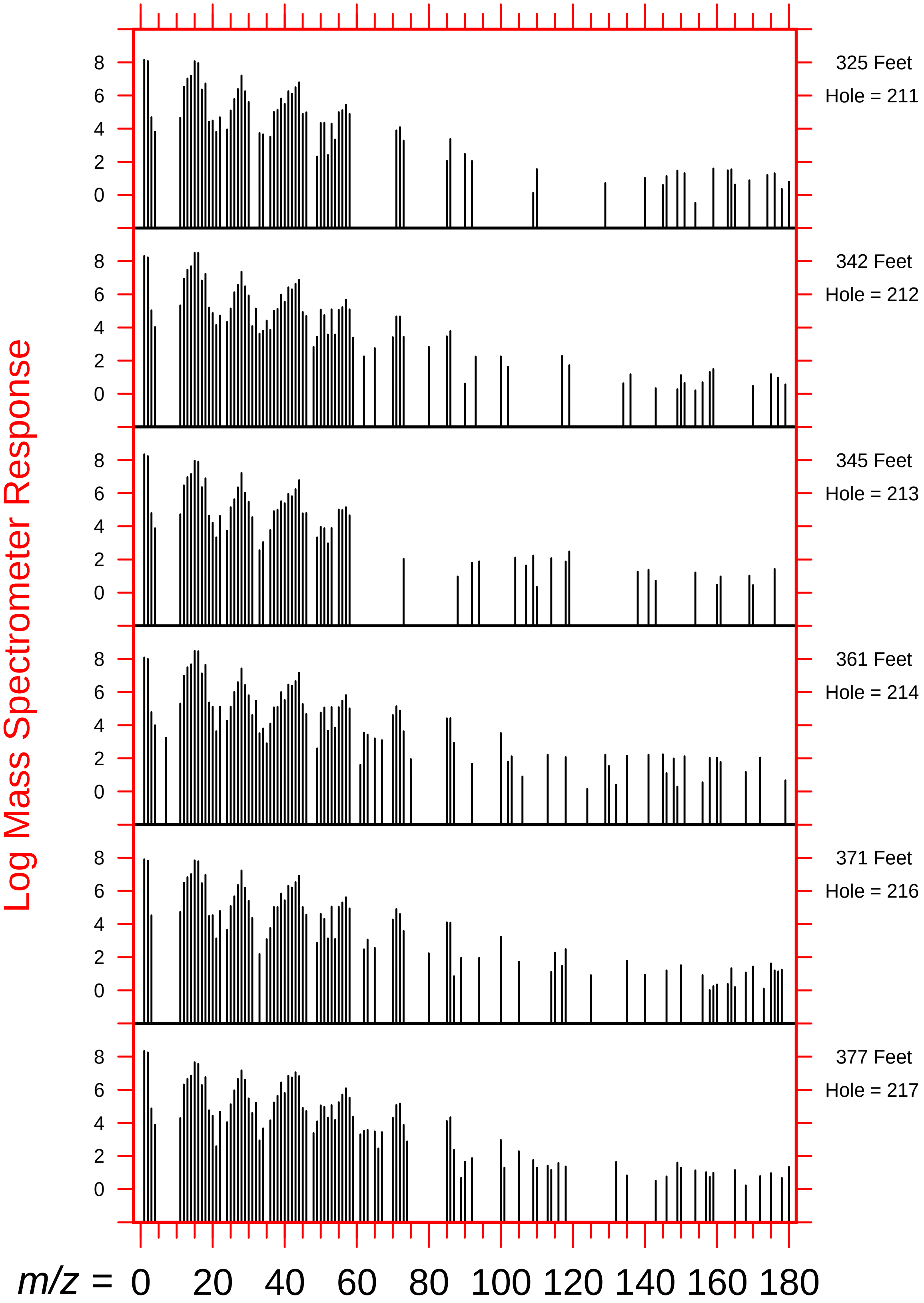
Individual spectra for each sample from RC-C-1-81 are shown on the following pages. Each spectrum is indexed according to depth and indicates the log of the millivolt response for atomic mass units (AMU, m/z) from $2 \leq m/z \leq 180$.

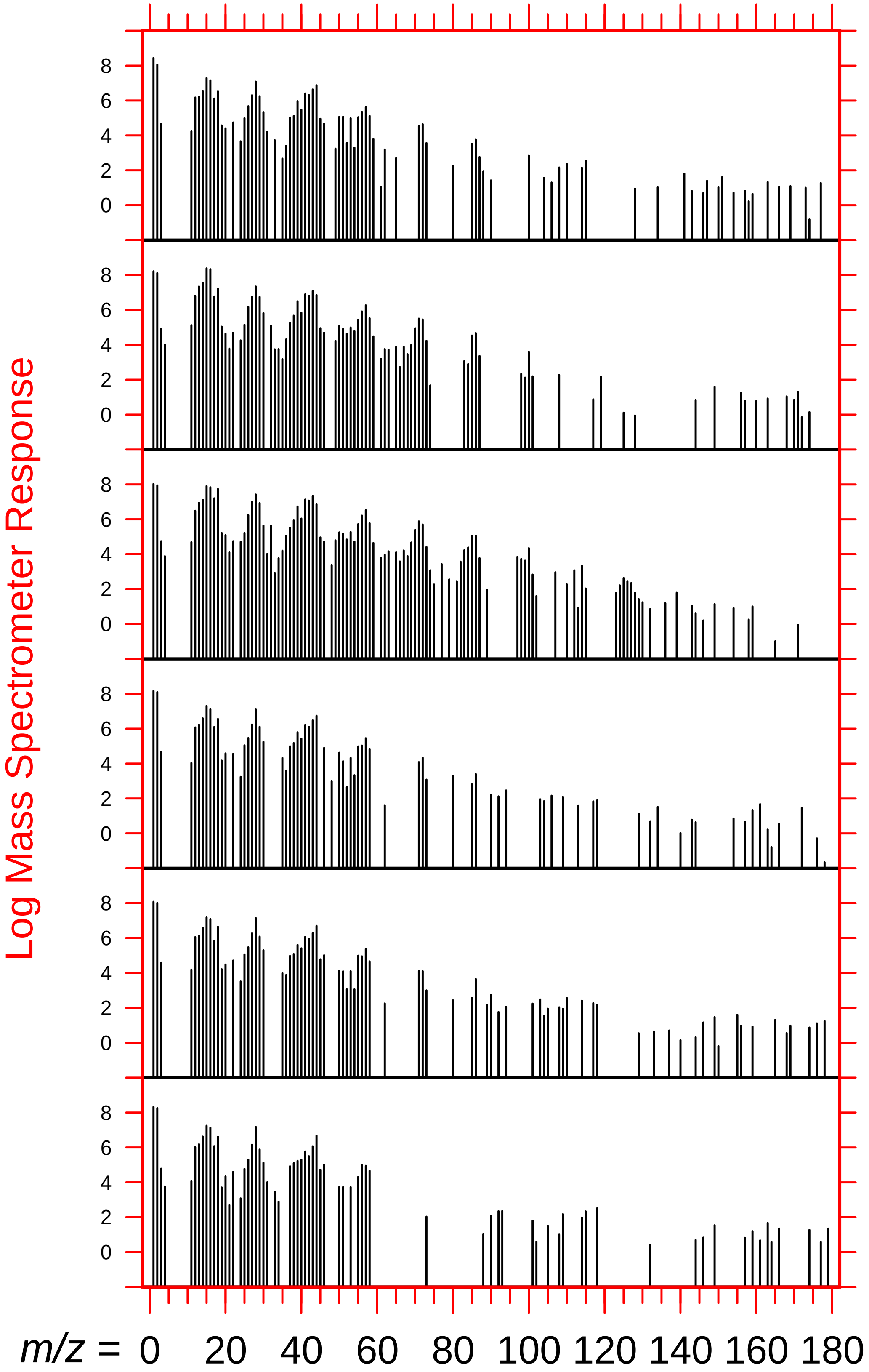

Log Mass Spectrometer Response
8
6
4
2
0
88 Feet
Hole = 185
95 Feet
Hole = 186
110 Feet
Hole = 187
118 Feet
Hole = 188
129 Feet
Hole = 189
143 Feet
Hole = 190
m/z = 0 20 40 60 80 100 120 140 160 180

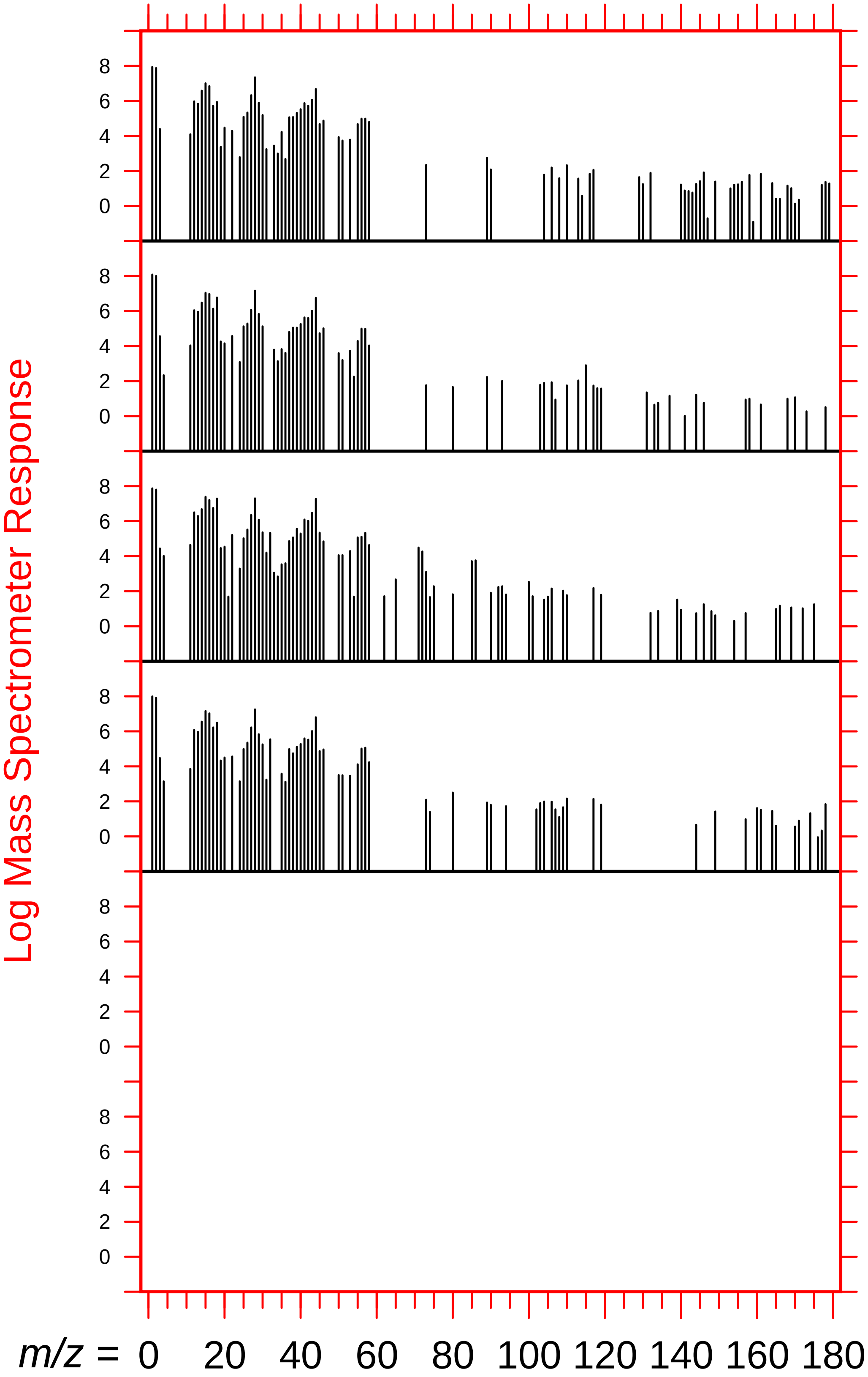

Log Mass Spectrometer Response
8
6
4
2
0
149 Feet
Hole = 192
161 Feet
Hole = 193
171 Feet
Hole = 194
181 Feet
Hole = 195
192 Feet
Hole = 196
193 Feet
Hole = 197
m/z = 0 20 40 60 80 100 120 140 160 180


Log Mass Spectrometer Response
8
6
4
2
0
207 Feet
Hole = 198
221 Feet
Hole = 199
229 Feet
Hole = 200
237 Feet
Hole = 201
249 Feet
Hole = 202
257 Feet
Hole = 204
m/z = 0 20 40 60 80 100 120 140 160 180


Log Mass Spectrometer Response
8
6
4
2
0
271 Feet
Hole = 205
275 Feet
Hole = 206
287 Feet
Hole = 207
303 Feet
Hole = 208
306 Feet
Hole = 209
316 Feet
Hole = 210
m/z = 0
20
40
60
80
100
120
140
160
180


Log Mass Spectrometer Response
8
6
4
2
0
325 Feet
Hole = 211
342 Feet
Hole = 212
345 Feet
Hole = 213
361 Feet
Hole = 214
371 Feet
Hole = 216
377 Feet
Hole = 217
m/z = 0 20 40 60 80 100 120 140 160 180


Log Mass Spectrometer Response
8
6
4
2
0
392 Feet
Hole = 218
399 Feet
Hole = 219
410 Feet
Hole = 220
422 Feet
Hole = 221
432 Feet
Hole = 222
434 Feet
Hole = 223
m/z = 0
20
40
60
80
100
120
140
160
180


Log Mass Spectrometer Response
8
6
4
2
0
445 Feet
Hole = 224
461 Feet
Hole = 225
472 Feet
Hole = 226
479 Feet
Hole = 228
m/z = 0 20 40 60 80 100 120 140 160 180