ENVIRONMENTAL FORENSIC ANALYSIS OF CRUDE AND REFINED PETROLEUM PRODUCTS UTILIZING GC×GC-FID, GC×GC-TOF-MS, AND GC×GC-HRT-MS

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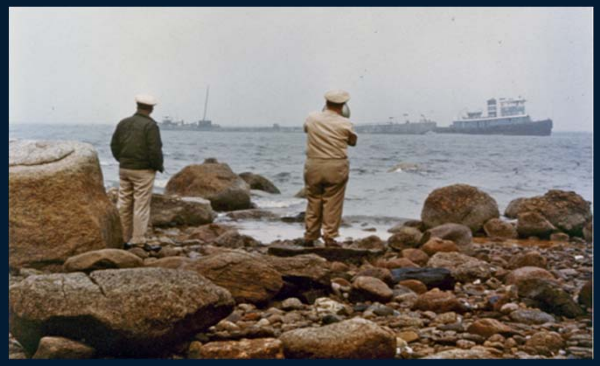
August 7, 2018

2018 National Environmental Monitoring Conference
New Orleans, LA

Goals – To Forensically Identify Crude Oil and Refined Petroleum Products Released Into The Environment

- Study the ultimate fate of spilled petroleum products – can we predict how spilled products will weather?
- Can we provide useful an timely information to spill response and damage assessment professionals?
- By comparing results from spills that have occurred over the past 40 years can we forecast and hindcast complex petroleum weathering effects such as biodegradation, photooxidation, evaporation, and dissolution.
- Utilize traditional and non-traditional biomarker compounds to identify release sources. *Adding new forensic compounds to our arsenal.
- To do this, we seek to compare and contrast the composition of spilled products in order to identify molecular insights that expand our traditional approaches to studying spills.

We Study Crude Oil and Refined Petroleum Product Spills



Florida; Buzzards Bay, MA (1969)

Bouchard 65; Buzzards Bay, MA (1974)

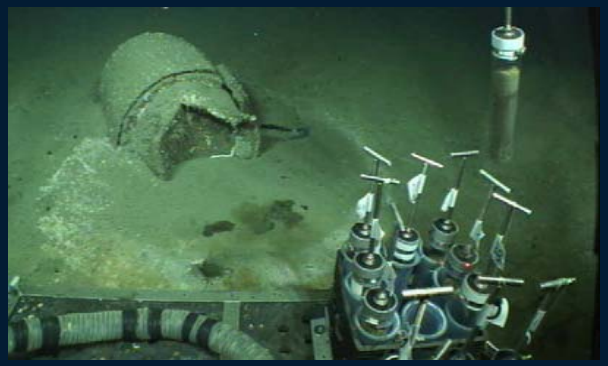
Bouchard 120; Buzzards Bay, MA (2003)

Hebei Spirit; South Korea (2007)

Exxon Valdez (1989)

Prestige; Portugal (2002)

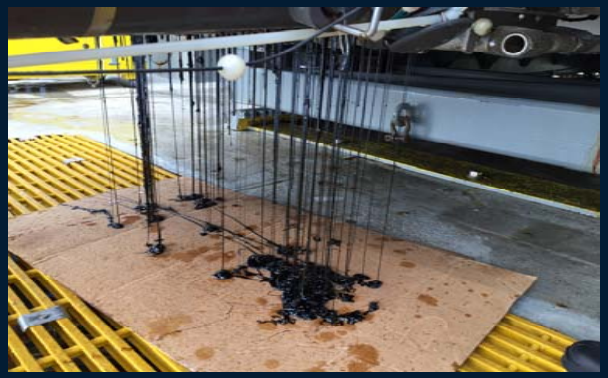
We Study Crude Oil and Refined Petroleum Product Spills



DDT/oil residues; CA coast (1950s/1960s)

Unknown samples; Gulf of Mexico (2014)

Texas City (Kirby); Galveston, TX (2014)



Natural oil seeps; Gulf of Mexico (everyday)

Natural oil seeps; Santa Barbara, CA (everyday)

Sundarbans; Bangladesh (2014)

We Study Crude Oil and Refined Petroleum Product Spills

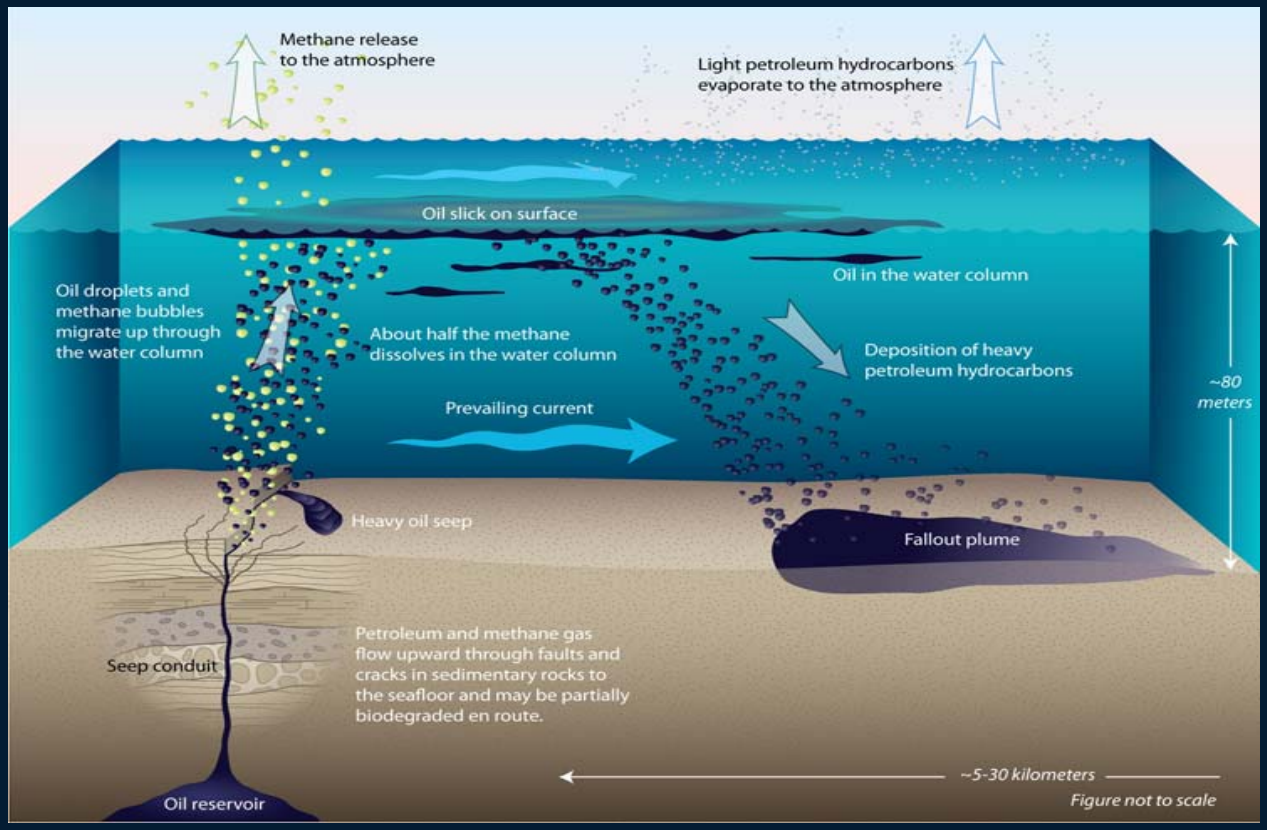
Yellowstone River; Montana (2015)

Kalamazoo River; Michigan (2010)

Sanchi Tanker; Condensate, East China Sea (2018)

Refugio pipeline; Highway 101, CA (2015)

What happens to petroleum in the environment?



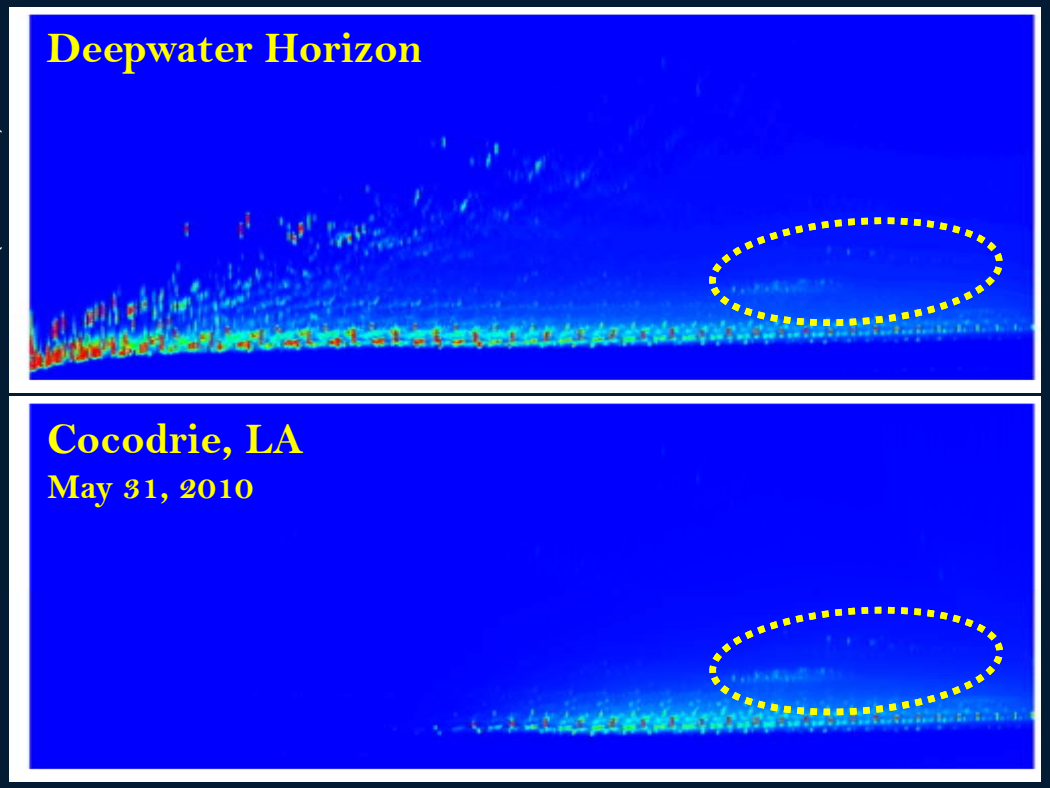
GC×GC Facility at WHOI

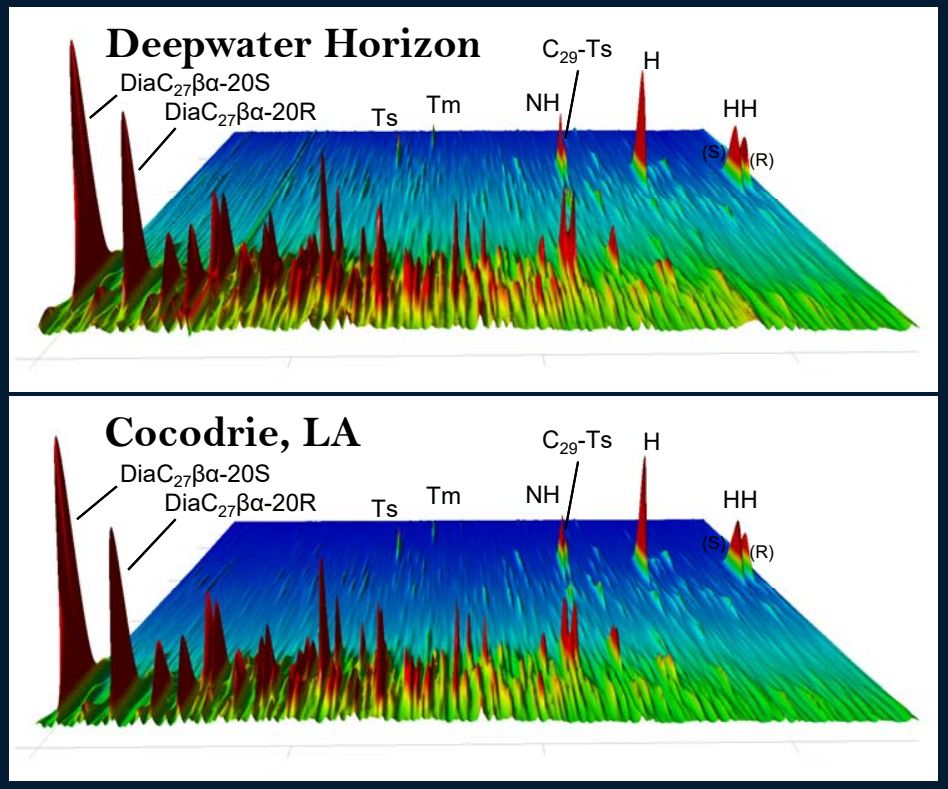
https://www2.whoi.edu/site/gcxgcfacility/

Forensically Useful Petroleum Biomarkers

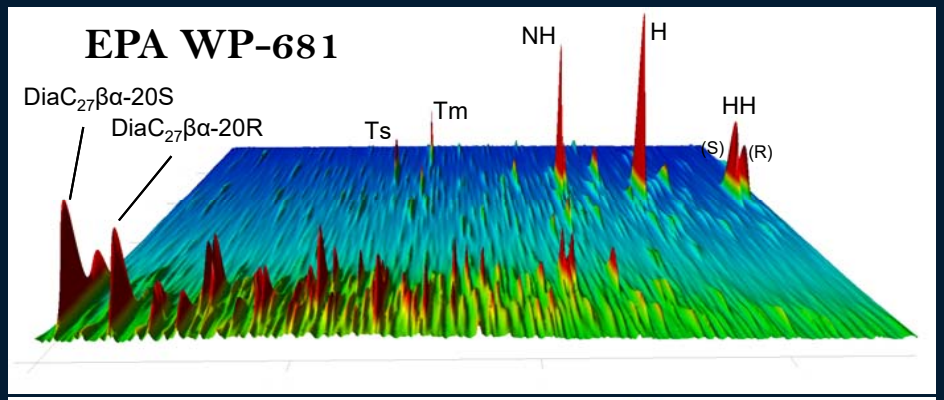
- Environmentally recalcitrant molecules are the most useful compounds for fingerprinting petroleum products.
- These molecules should ***NOT*** be susceptible to:
  - Evaporation
  - Photooxidation
  - Dissolution (water-washing)
  - Biodegradation

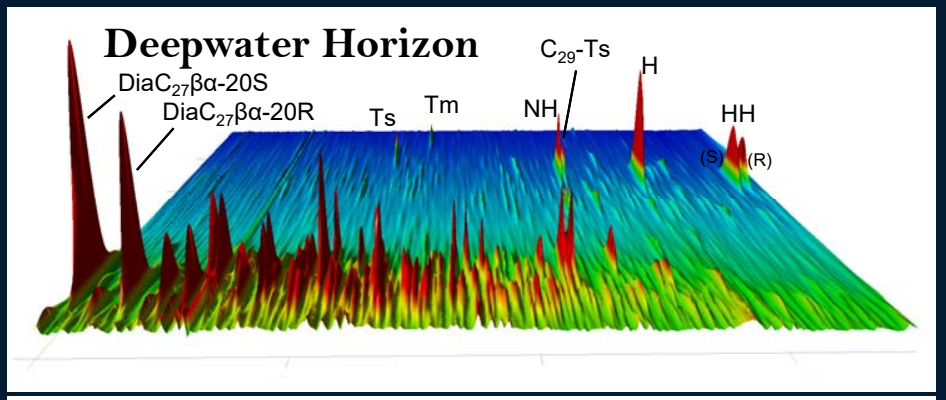
Deepwater Horizon
Sterane, Diasterane, Hopanoid Biomarkers

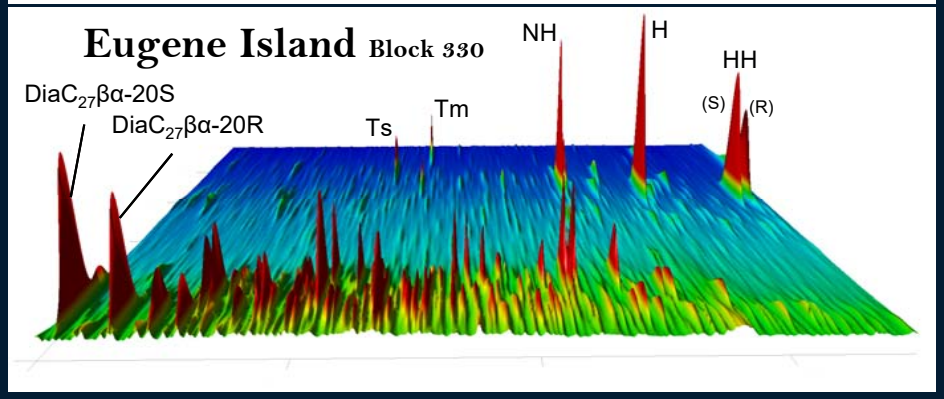


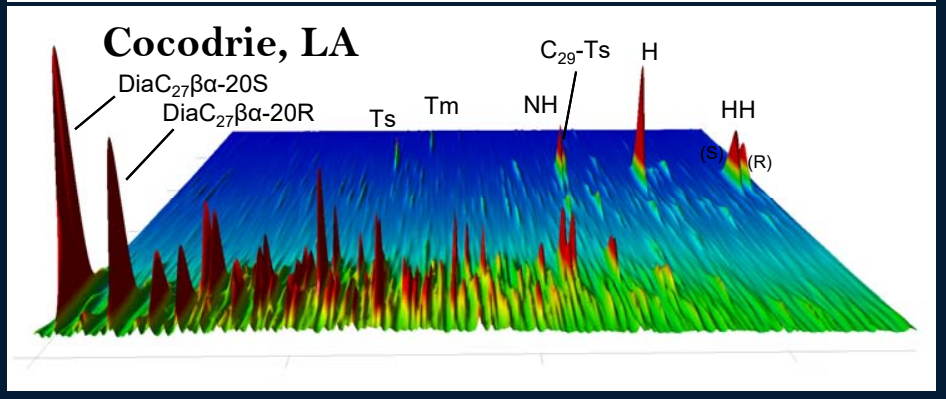


Biomarker Comparison – Louisiana Crudes

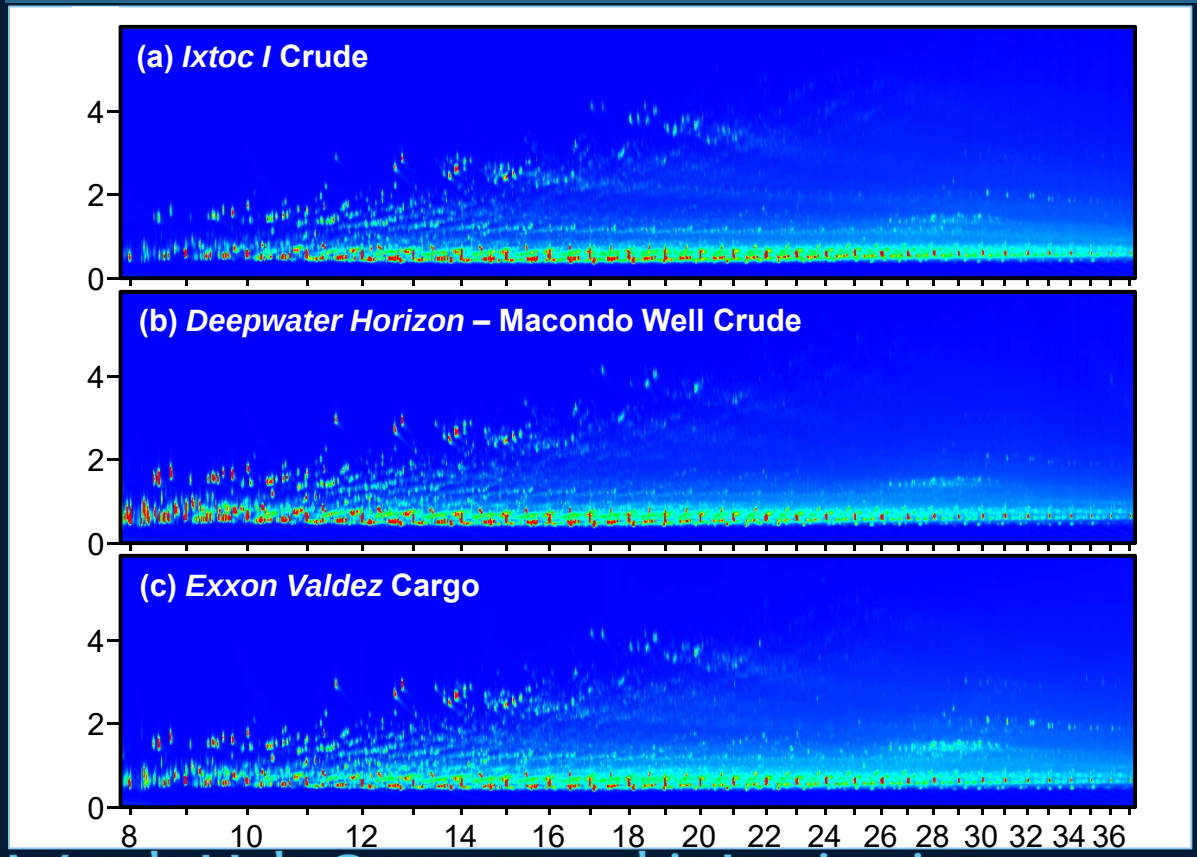


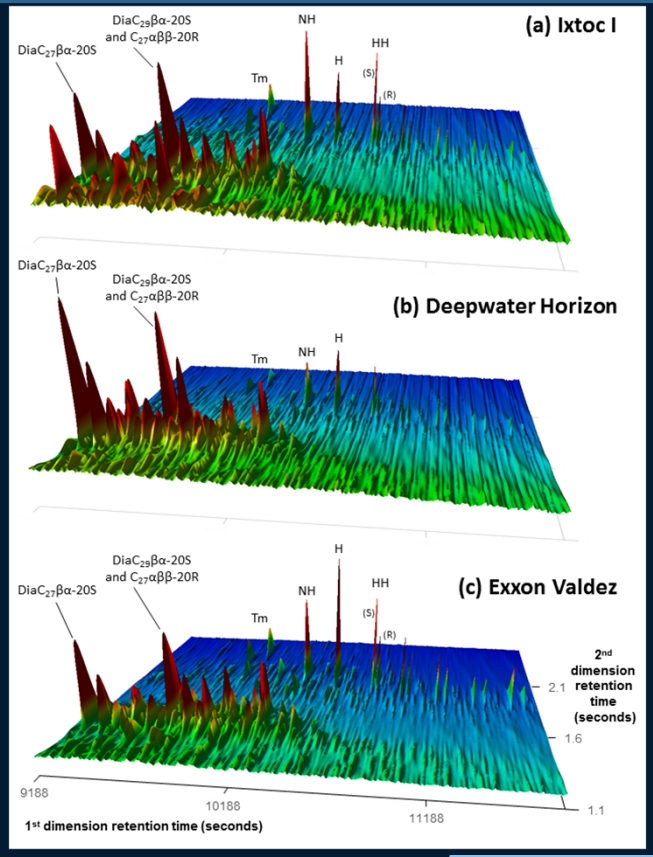






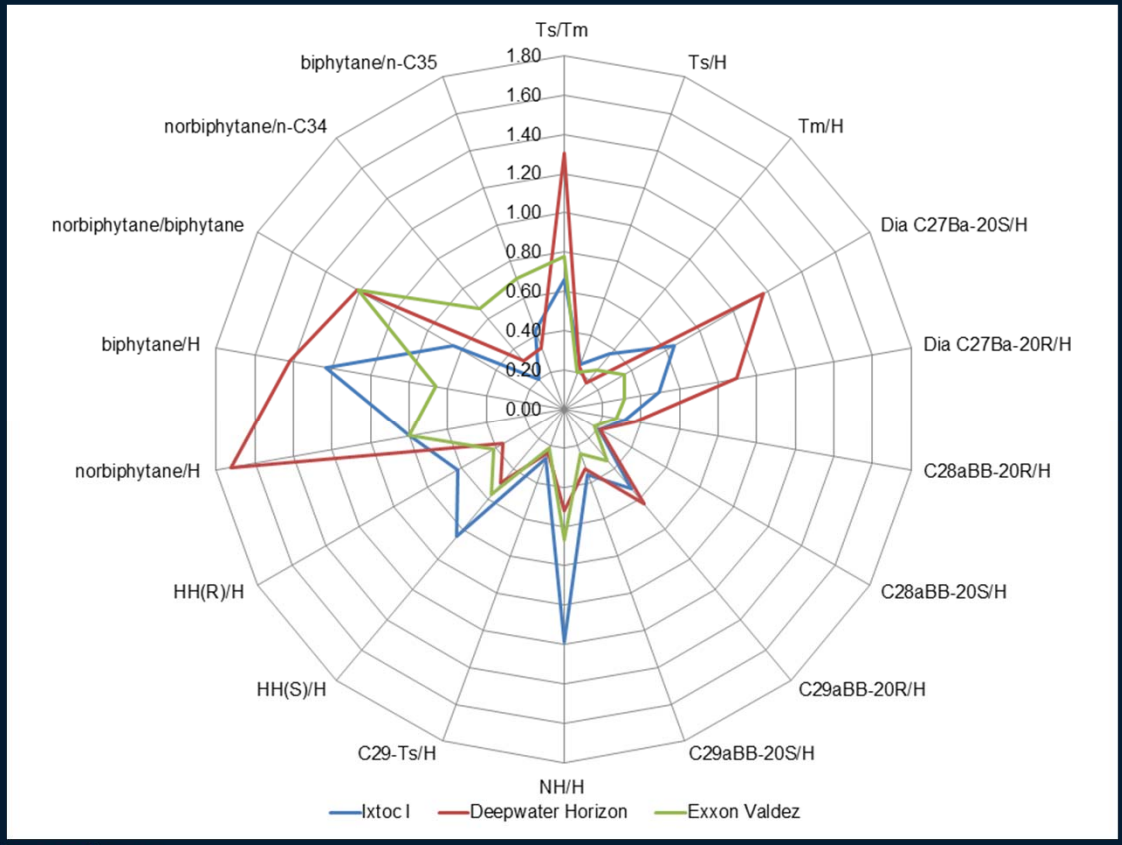
Biomarker Comparison
Ixtoc I, Deepwater Horizon, and Exxon Valdez



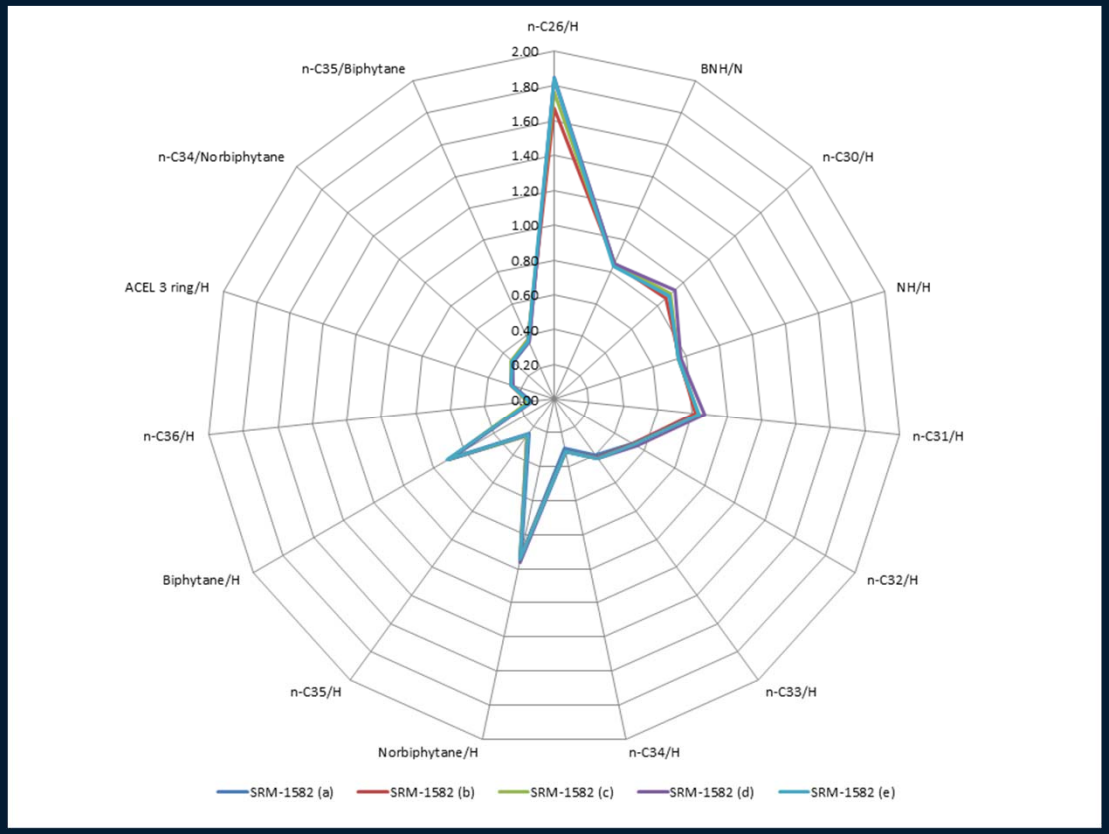


Biomarker Comparison
Ixtoc I, Deepwater Horizon, and Exxon Valdez

Biomarker Ratio	Ixtoc I	Deepwater Horizon	Exxon Valdez
Ts/Tm	0.66	1.30	0.78
Ts/H	0.24	0.23	0.20
Tm/H	0.37	0.18	0.26
Dia C27Ba-20S/H	0.65	1.18	0.36
Dia C27Ba-20R/H	0.50	0.90	0.31
C28aBB-20R/H	0.32	0.37	0.27
C28aBB-20S/H	0.21	0.21	0.18
C29aBB-20R/H	0.53	0.64	0.35
C29aBB-20S/H	0.36	0.32	0.25
NH/H	1.19	0.52	0.67
C29-Ts/H	0.27	0.24	0.22
HH(S)/H	0.85	0.50	0.57
HH(R)/H	0.63	0.36	0.41
norbiphytane/H	0.80	1.72	0.80
biphytane/H	1.23	1.42	0.66
norbiphytane/biphytane	0.65	1.22	1.21
norbiphytane/n-C34	0.20	0.32	0.67
biphytane/n-C35	0.43	0.33	0.71



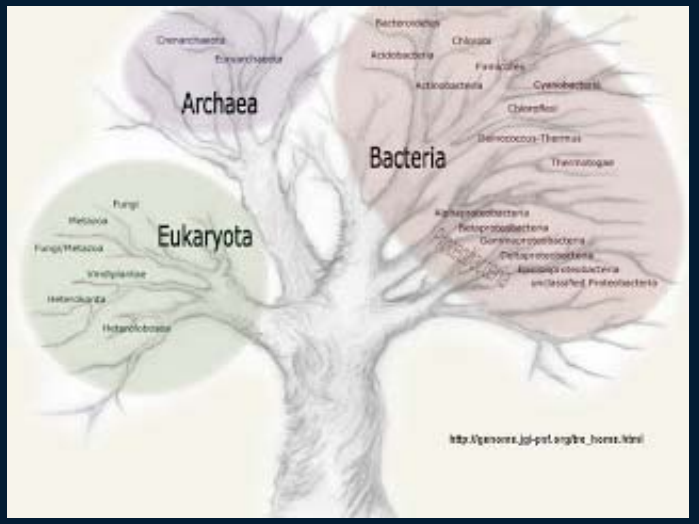
Biomarker Comparison
NIST SRM-1582 (crude oil) Replicate Analysis



What are:
ACEL *3* ring,
Norbiphytane,
and Biphytane?

Side Track: Non-traditional Biomarkers for Environmental Forensics

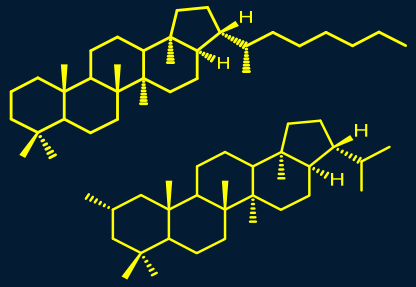
Archeal Core Ether Lipids



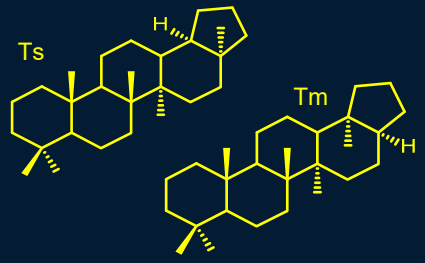
Traditional & Non-traditional Biomarkers

Prokaryotic

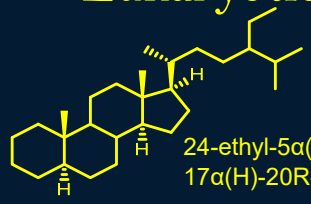
17α(H),21β(H)-22S-pentakishomohopane



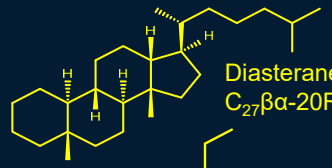
2α-methyl-17α(H),21β(H)-hopane
(cyanobacterial origin)



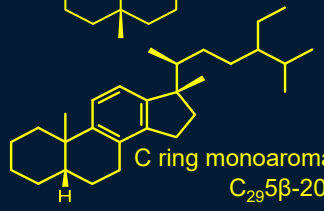
Eukaryotic



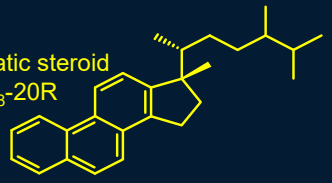
24-ethyl-5α(H),14α(H),
17α(H)-20R-cholestane



Diasterane
C_{27}βα-20R



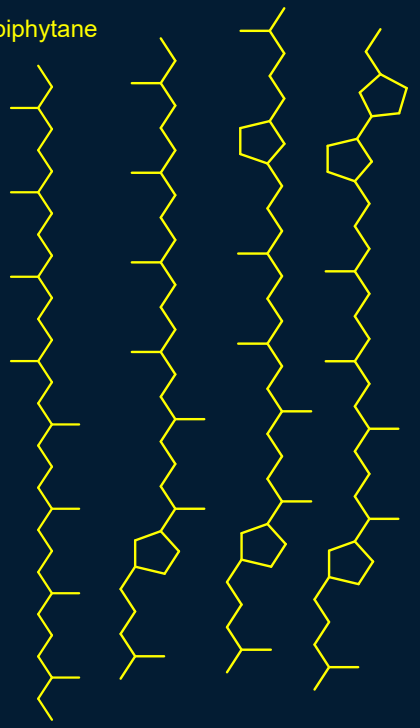
C ring monoaromatic steroid
C_{29}5β-20S



triaromatic steroid
C_{28}-20R

Archeal

biphytane



Archeal Core Ether Lipids PNAS 2007

PNAS PNAS PNAS

Molecular evidence of Late Archean archaea and the presence of a subsurface hydrothermal biosphere

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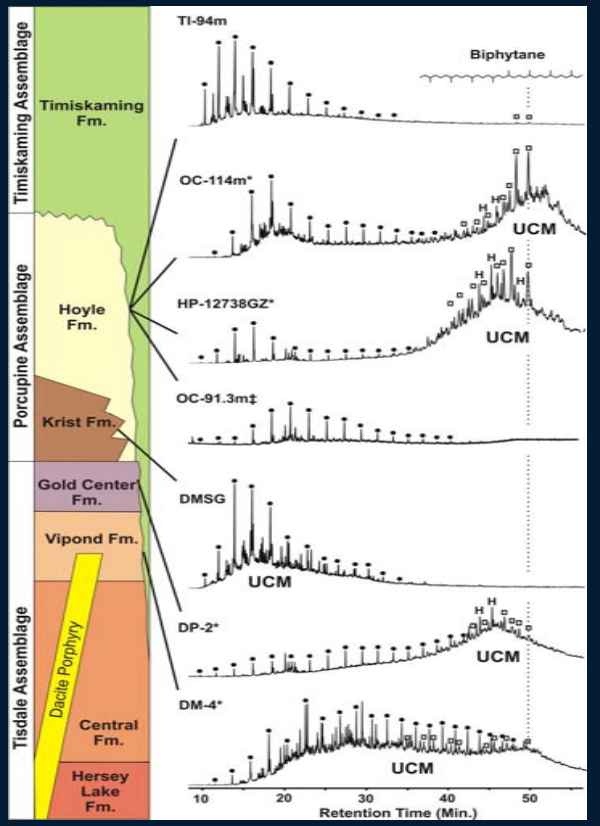
Edited by John M. Hayes, Woods Hole Oceanographic Institution, Falmouth, MA, and approved July 20, 2007 (received for review December 13, 2006)

Highly cracked and isomerized archaeal lipids and bacterial lipids, structurally changed by thermal stress, are present in solvent extracts of 2,707- to 2,685-million-year-old (Ma) metasedimentary rocks from Timmins, ON, Canada. These lipids appear in conventional gas chromatograms as unresolved complex mixtures and include cyclic and acyclic biphytanes, C_{36}–C_{39} derivatives of the biphytanes, and C_{31}–C_{35} extended hopanes. Biphytane and extended hopanes are also found in high-pressure catalytic hydrogenation products released from solvent-extracted sediments, indicating that archaea and bacteria were present in Late Archean sedimentary environments. Postdepositional, hydrothermal gold mineralization and graphite precipitation occurred before metamorphism (≈2,665 Ma). Late Archean metamorphism significantly reduced the kerogen's adsorptive capacity and severely restricted sediment porosity, limiting the potential for post-Archean additions of organic matter to the samples. Argillites exposed to hydrothermal gold mineralization have disproportionately high concentrations of extractable archaeal and bacterial lipids relative to what is releasable from their respective high-pressure catalytic hydrogenation product and what is observed for argillites deposited away from these hydrothermal settings. The addition of these lipids to the sediments likely results from a Late Archean subsurface hydrothermal biosphere of archaea and bacteria.

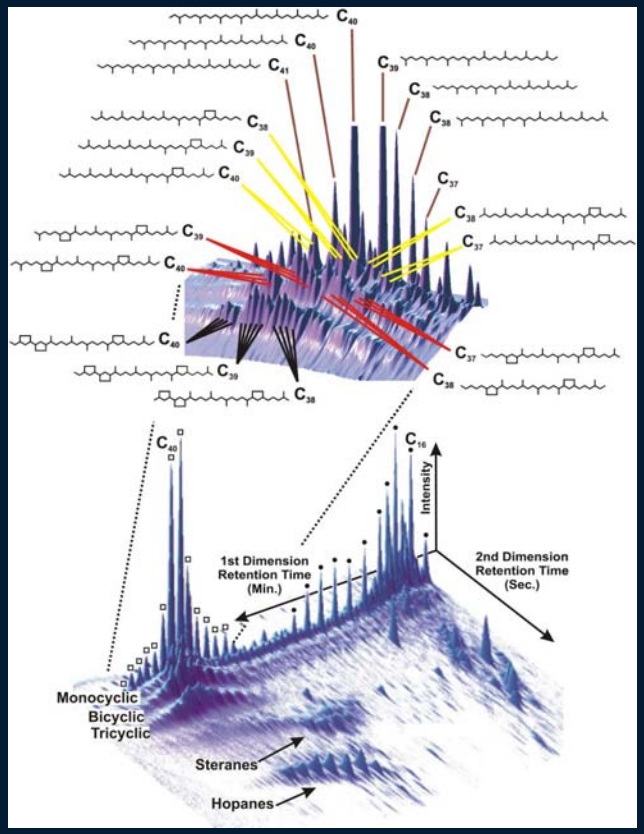
fossils diagnostic of bacteria and eukarya have been extracted from 2,700-Ma sediments of the Hammersley Basin of Western Australia and provide direct evidence for a Late Archean existence of these two domains of life (18). Hydrothermal settings further may enhance the potential for Archean molecular fossils to survive because high-pressure and -temperature aqueous solutions suppress the thermal destruction of hydrocarbons (19).

This investigation was conducted to assess the abundance and preservation of molecular fossils within Late Archean hydrothermal environments and hydrothermally altered sediments. Samples were collected from the lower greenschist metasediments (20, 21) of the Tisdale and Porcupine Assemblage (≈2,707–2,685 Ma) from the southern Abitibi greenstone belt near Timmins, ON, Canada. Here we report the occurrence of hydrocarbon molecular fossils diagnostic of archaea and bacteria among the solvent-extractable lipids and high-pressure catalytic hydrogenation (HPCH) products (22) of these samples. We provide evidence that these lipids are of Archean age and that a portion of the organic matter trapped in these sediments was derived from a subsurface hydrothermal biosphere.

Results and Discussion



Archeal Core Ether Lipids PNAS 2007



GC×GC-FID chromatograms (mountain plots) of the solvent extract from sample OC-114m of the Hoyle Formation.

(*Upper*) Enlargement of region with archaeal core lipids. Multiple peaks joined to a single molecular structure are diastereomers.

(*Lower*) Complete chromatograph.

2015 Refugio Oil Spill

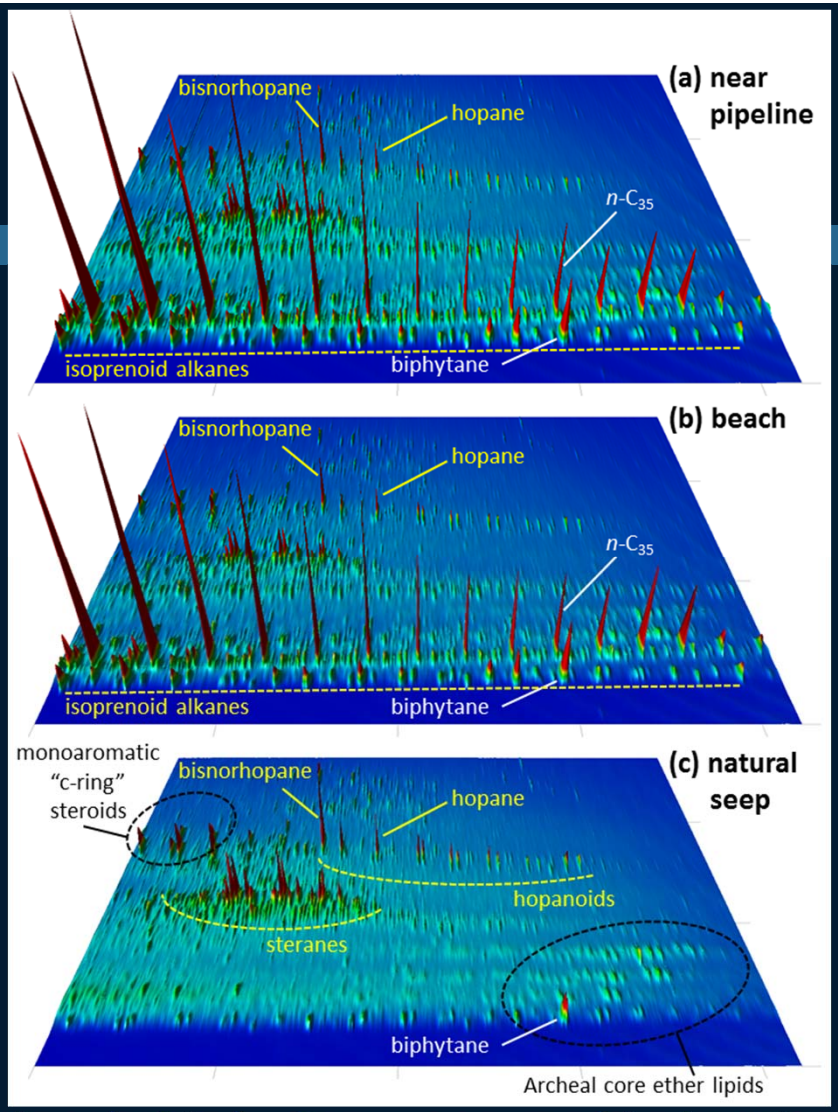
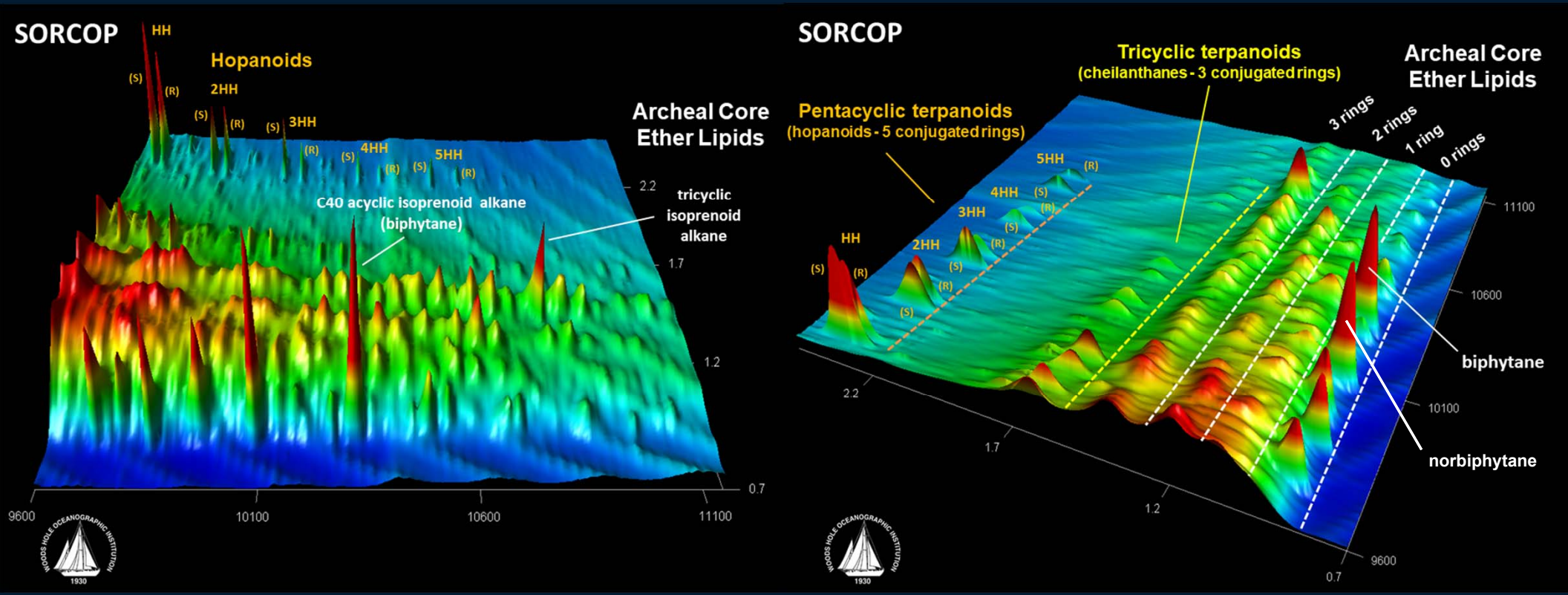
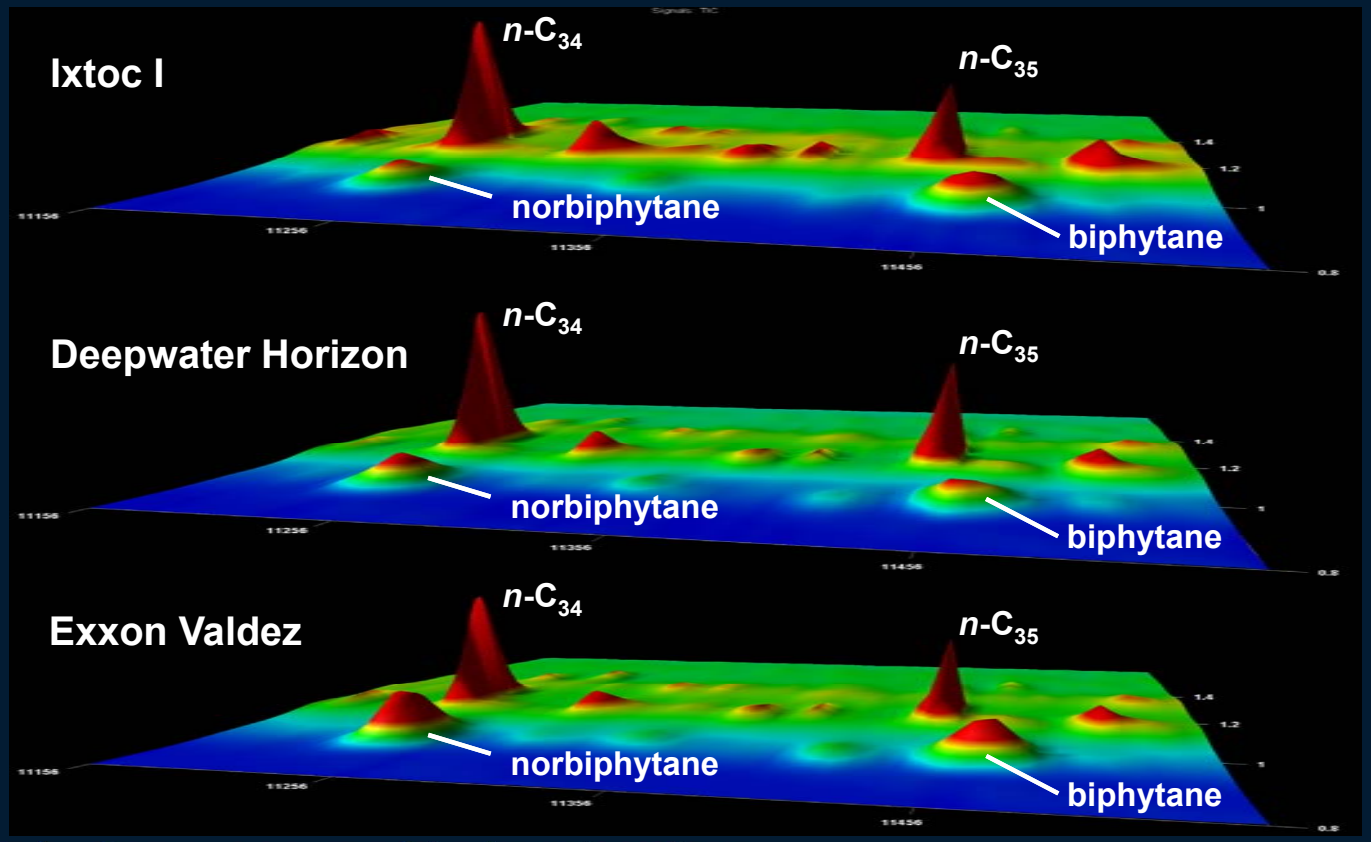


Figure 8.21 GC × GC–FID biomarker regions of (A) fresh oil collected 150 m from the ruptured pipeline on May 20, 2015; (B) fresh oil collected on May 19, 2015, on the beach and ~450 m down current from the location where the oil first entered the ocean; and (C) naturally seeped oil collected in 2005 directly at Coal Oil Point, Santa Barbara, CA.

Archeal Core Ether Lipid Biomarkers

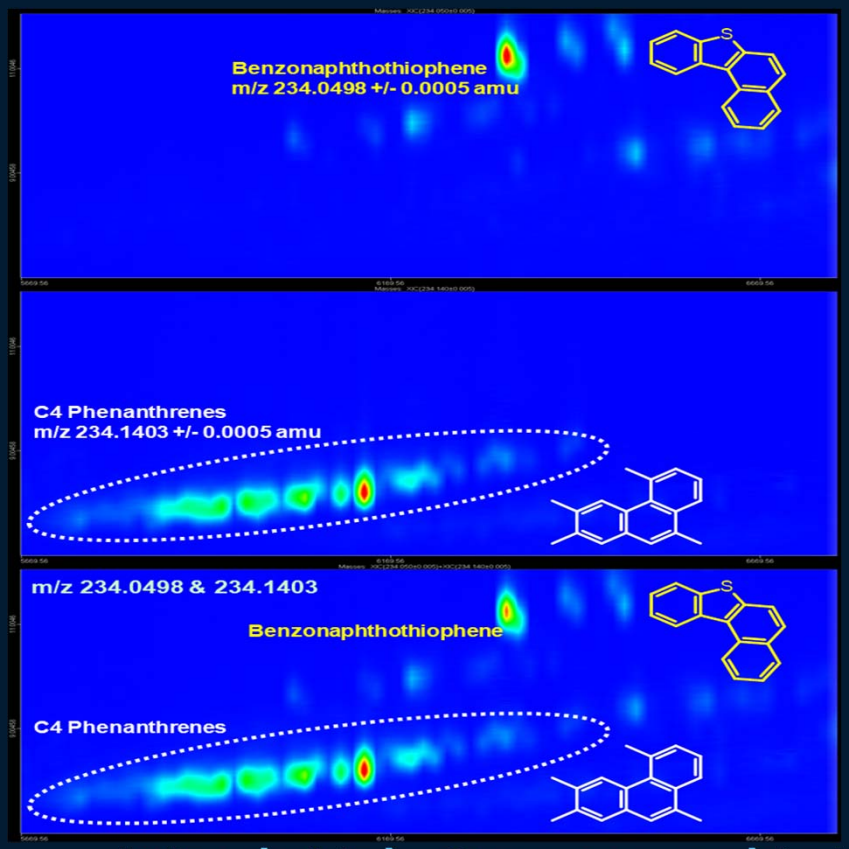


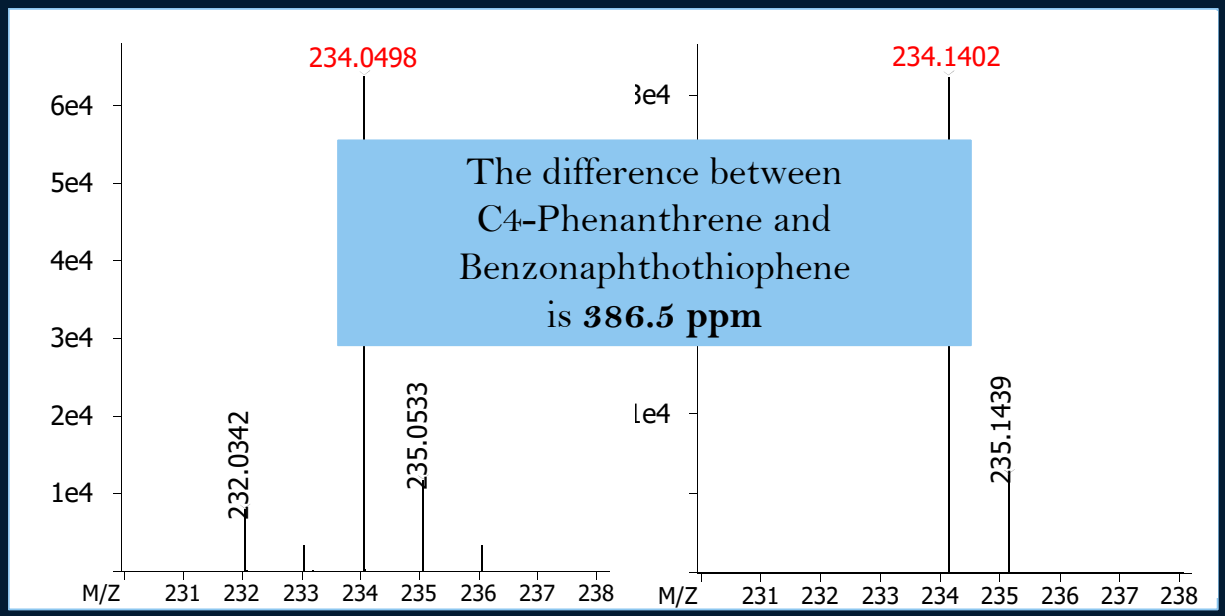
Archeal Core Ether Lipid Biomarkers – Other Examples



Back on Track
GC×GC-HRT-MS

Confidence - The Power of High Resolution TOF Coupled with GC×GC: m/z 234 compounds



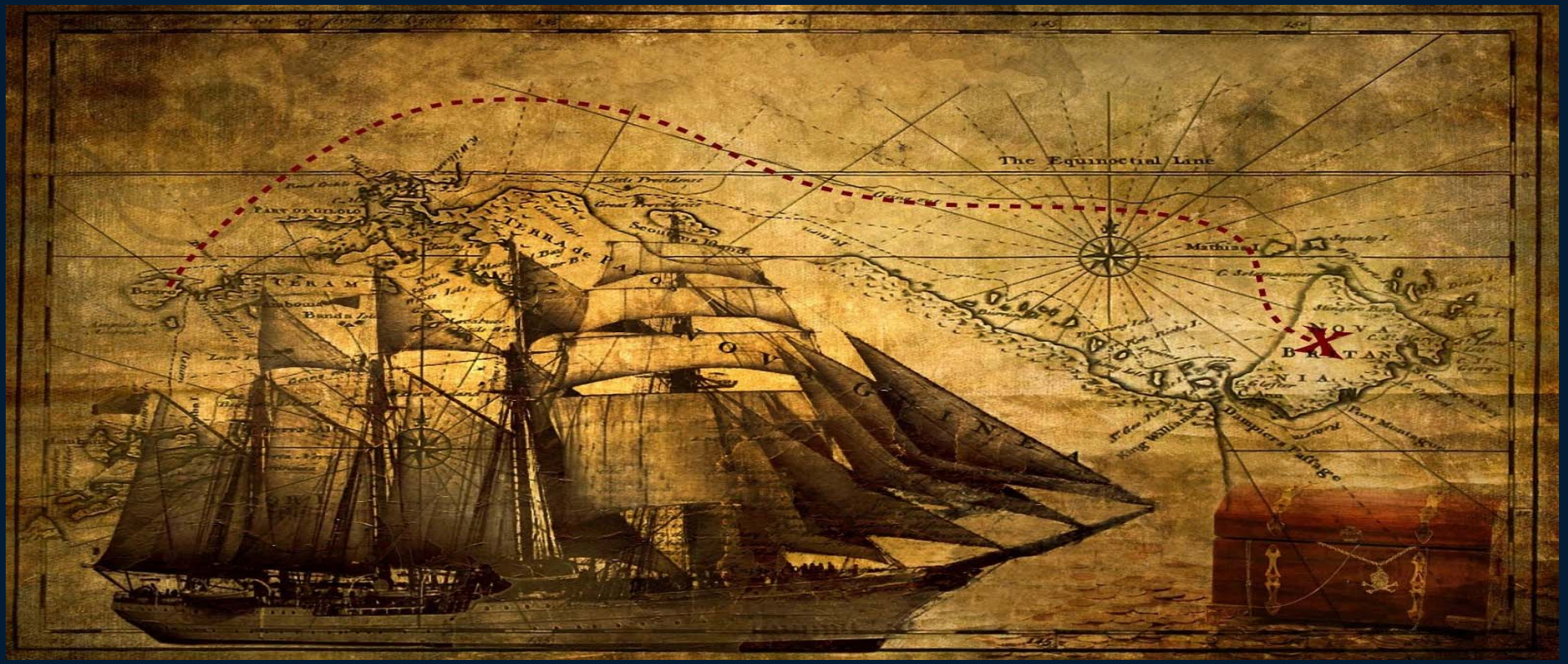


Benzonaphthothiophene
$C_{16}H_{10}S$
Theoretical mass: 234.0498
Observed mass: 234.0498
Mass error: 0 ppm

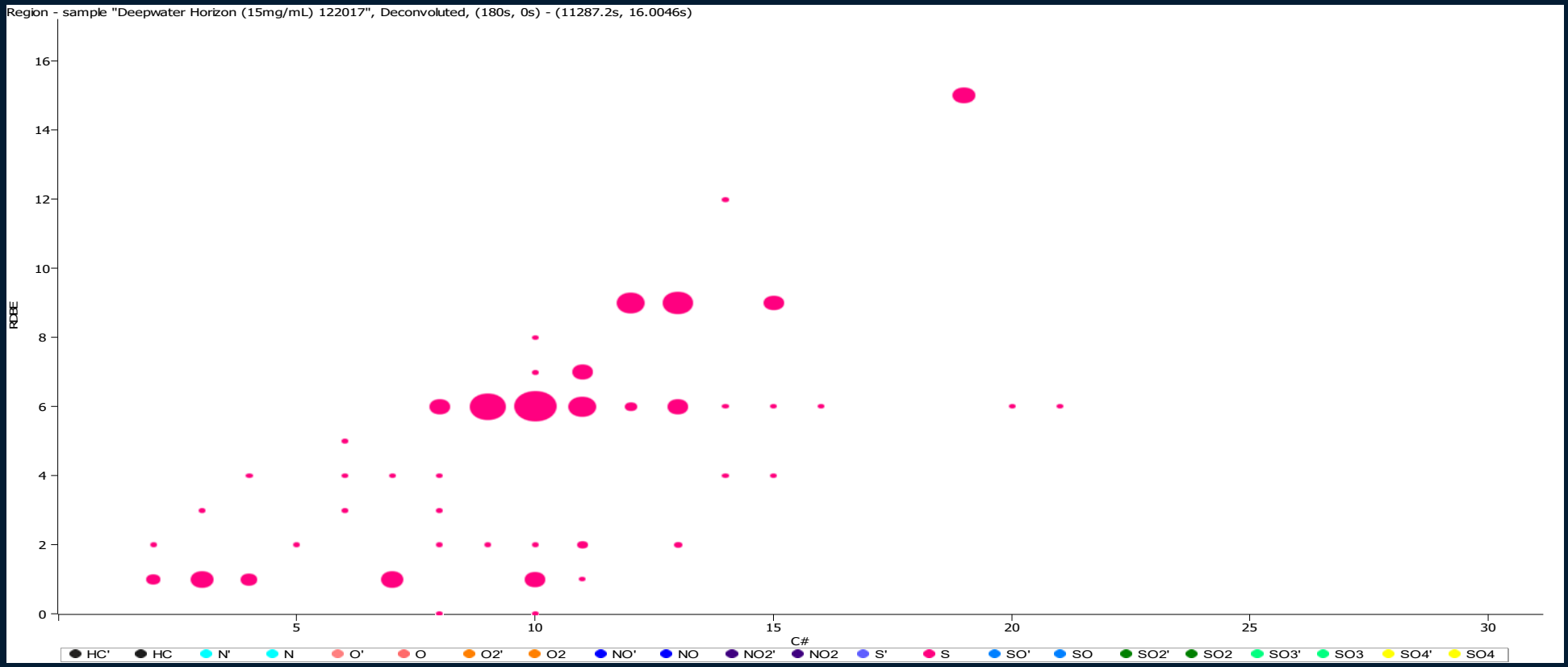
C4-Phenanthrene
$C_{18}H_{18}$
Theoretical mass: 234.1403
Observed mass: 234.1402
Mass error: -0.43 ppm

GC×GC - High Resolution - TOF

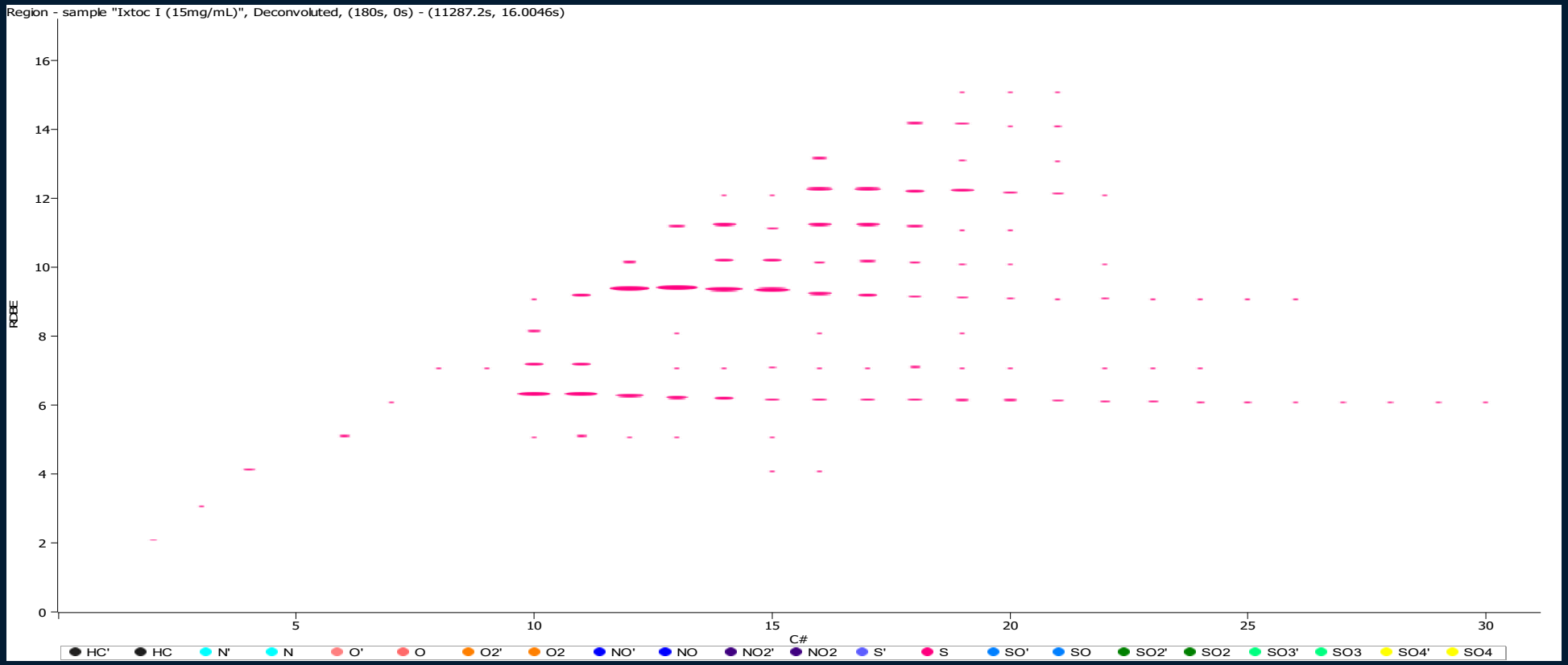
How Dou You Rapidly Find and Identify Compounds of Forensic Interest? You Need a Map!



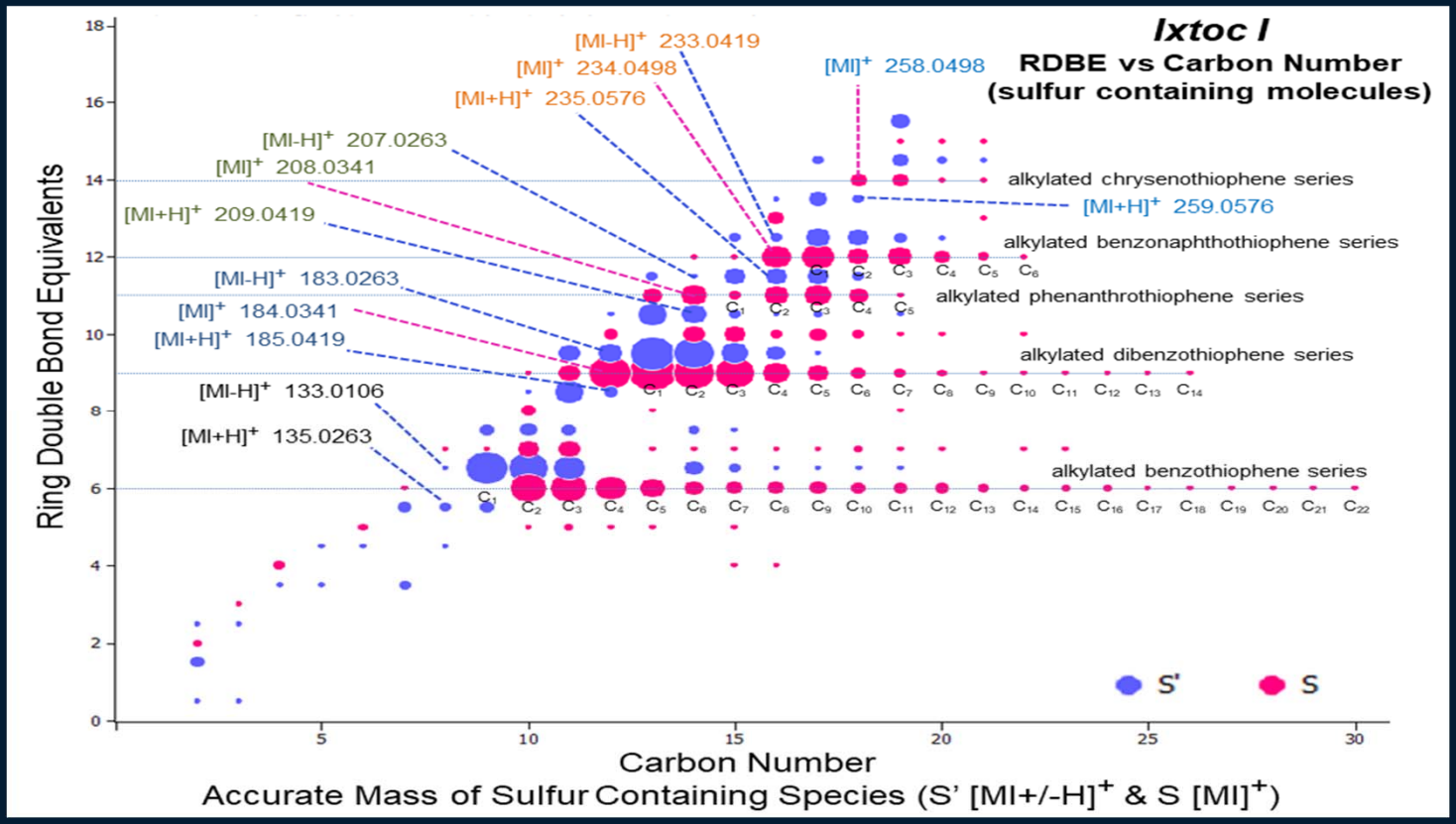
DWH Ring Double Bond Equivalents (RDBE) vs Carbon Number for Molecules Containing a Sulfur Atom



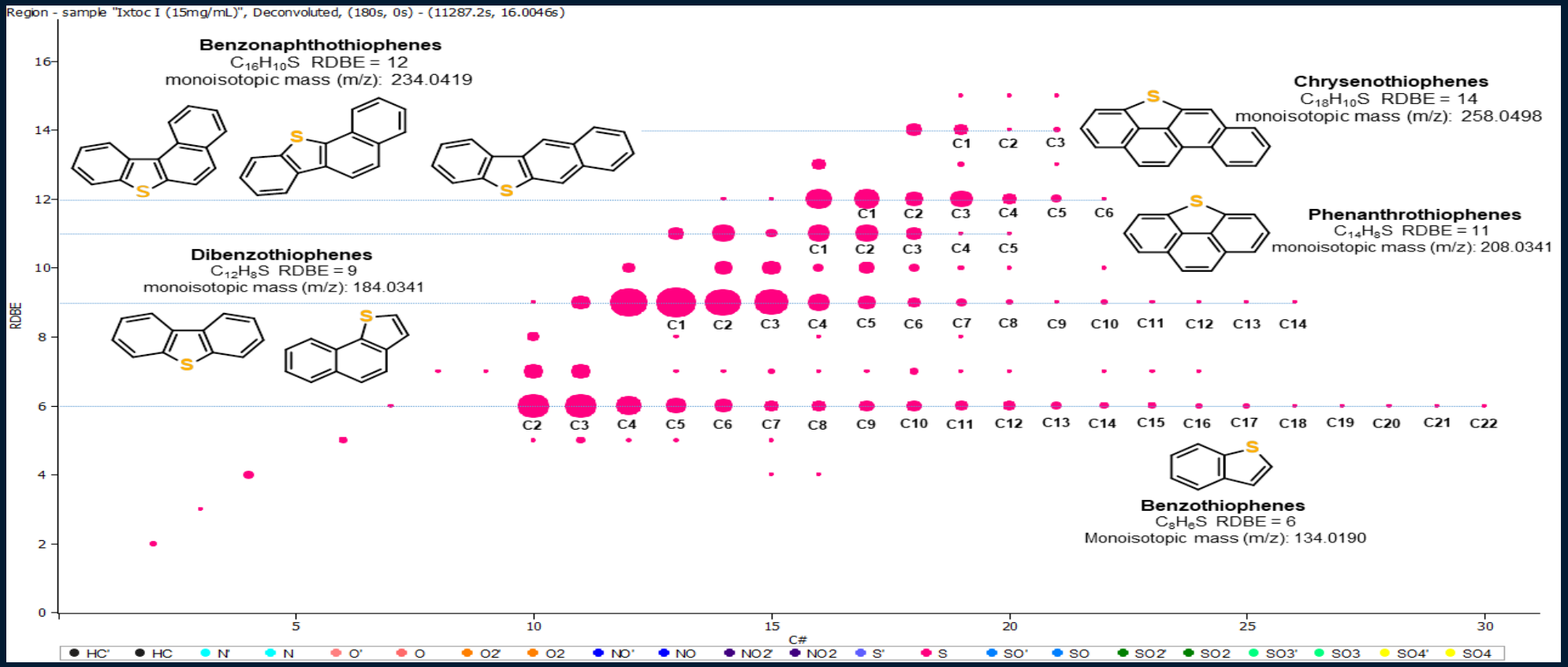
Ixtoc I Ring Double Bond Equivalents (RDBE) vs Carbon Number for Molecules Containing a Sulfur Atom



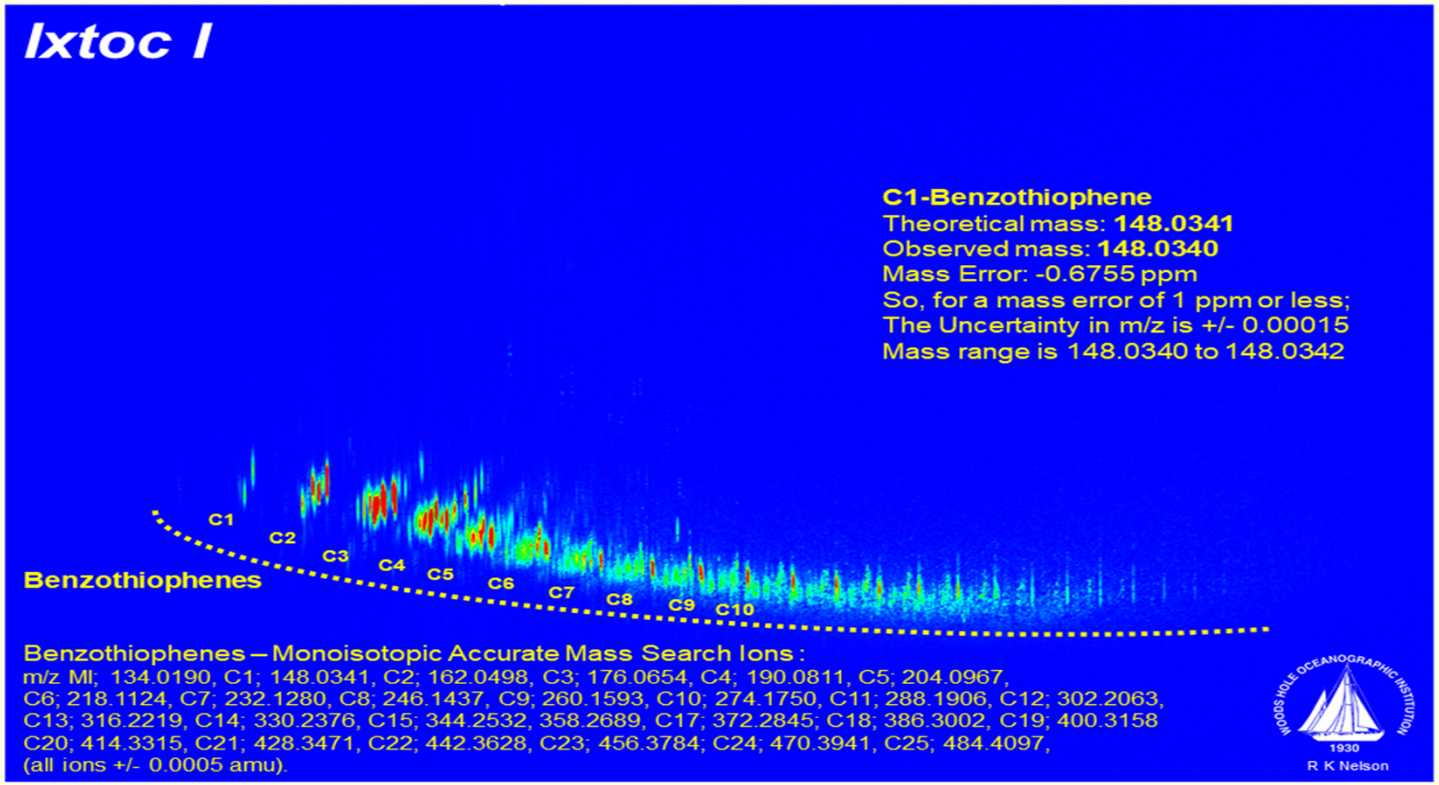
Ixtoc I Ring Double Bond Equivalents (RDBE) vs Carbon Number for Molecules Containing a Sulfur Atom

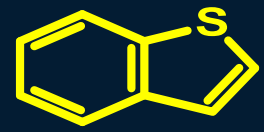


Ixtoc I Ring Double Bond Equivalents (RDBE) vs Carbon Number for Molecules Containing a Sulfur Atom

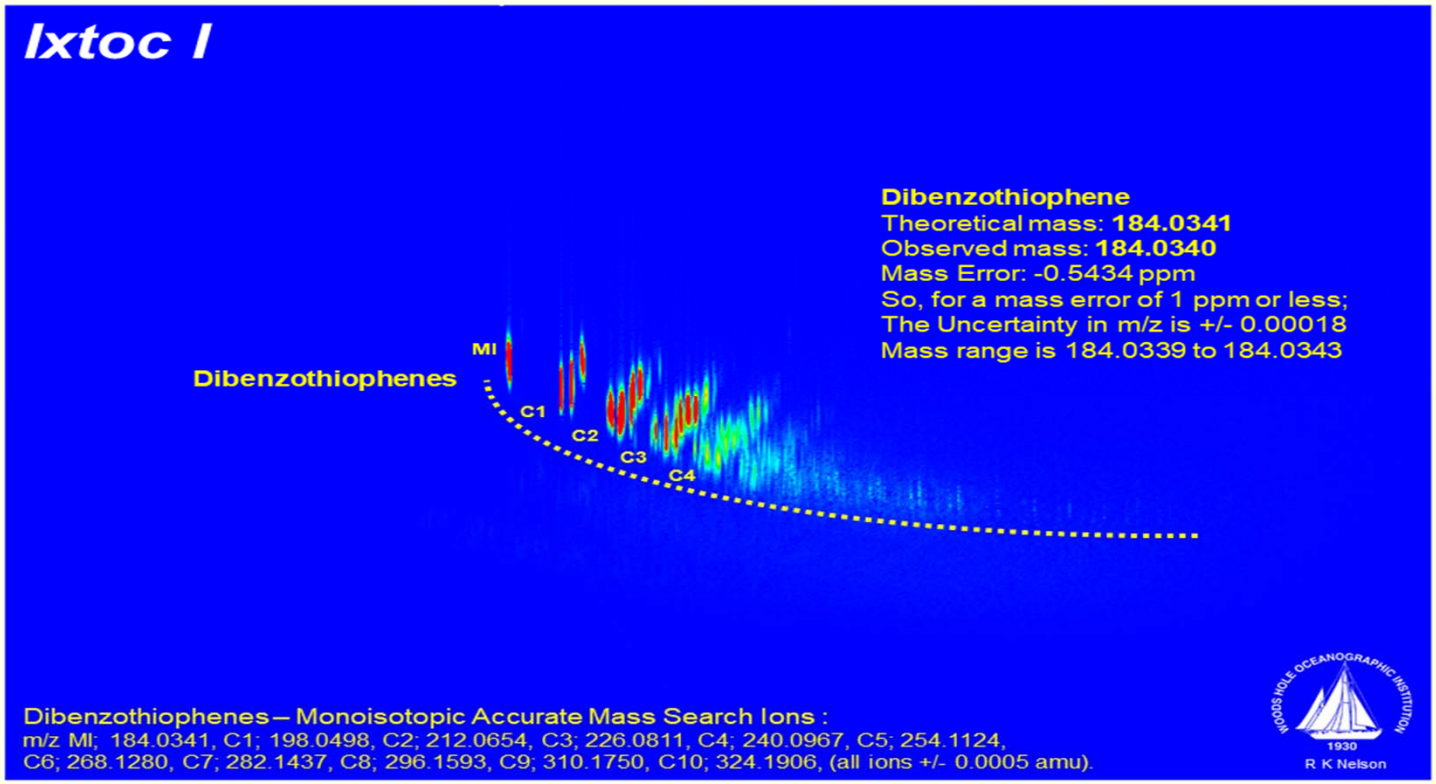


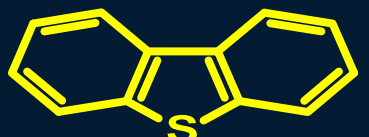
Ixtoc I – GC×GC-HRT
Benzothiophene Suite

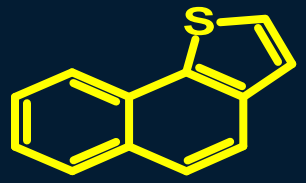




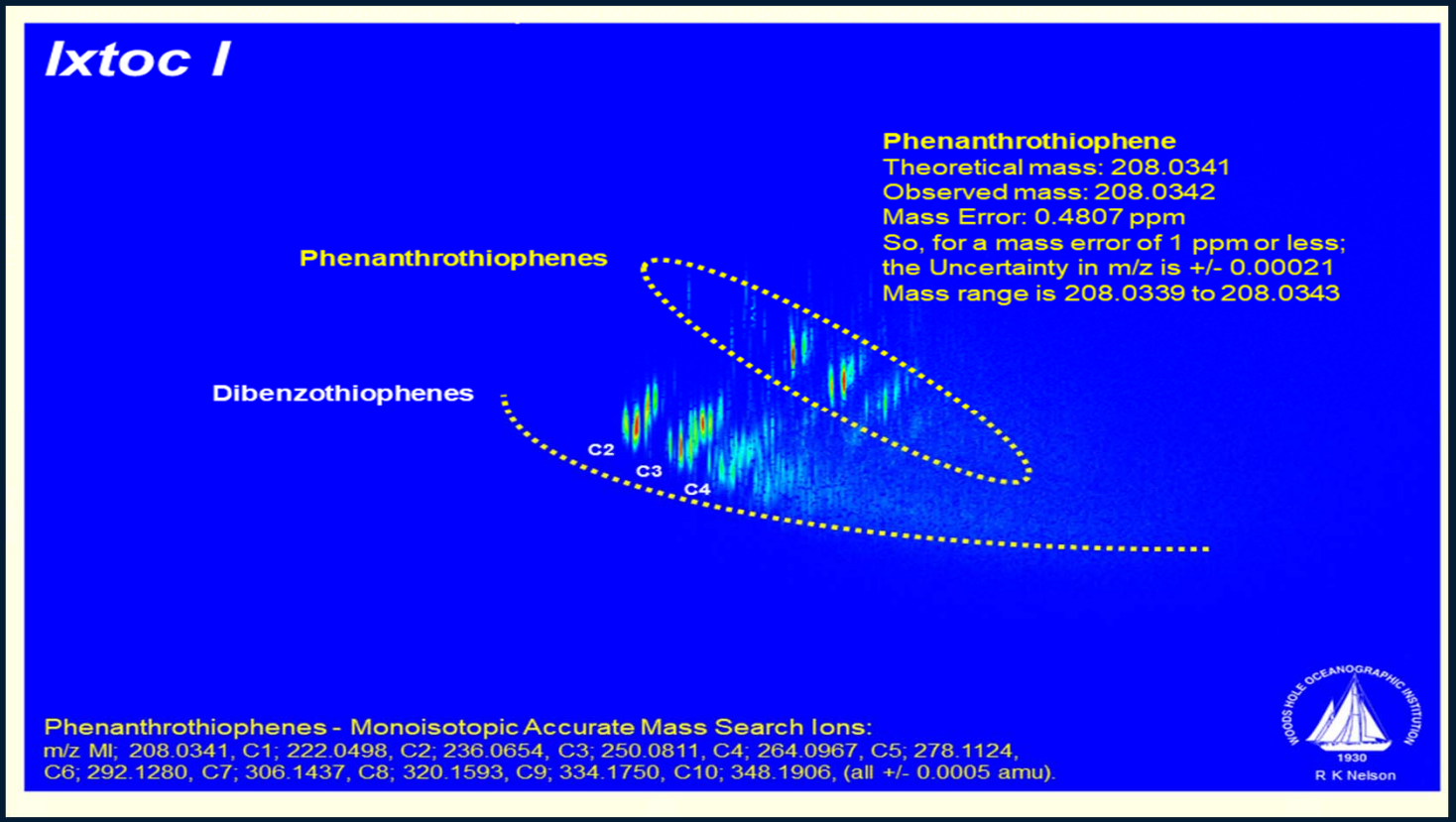
Ixtoc I – GC×GC-HRT
Dibenzothiophene Suite

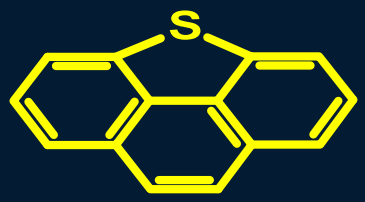




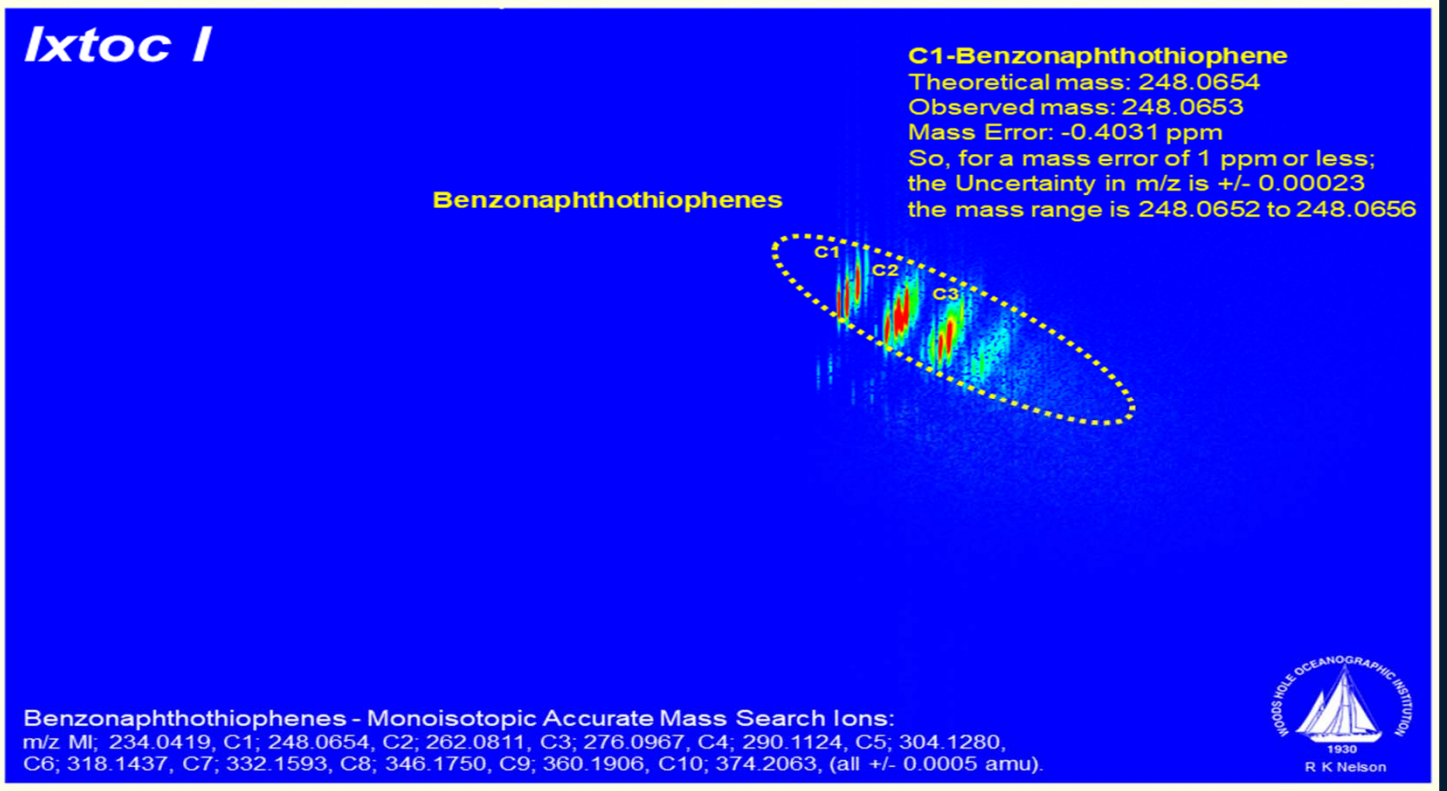


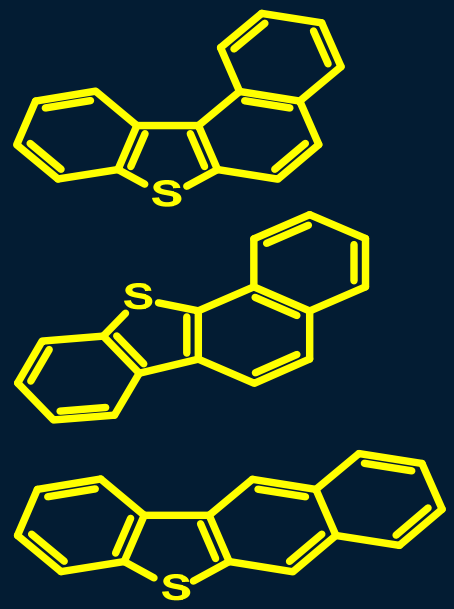
Ixtoc I – GC×GC-HRT
Phenanthrothiophene Suite



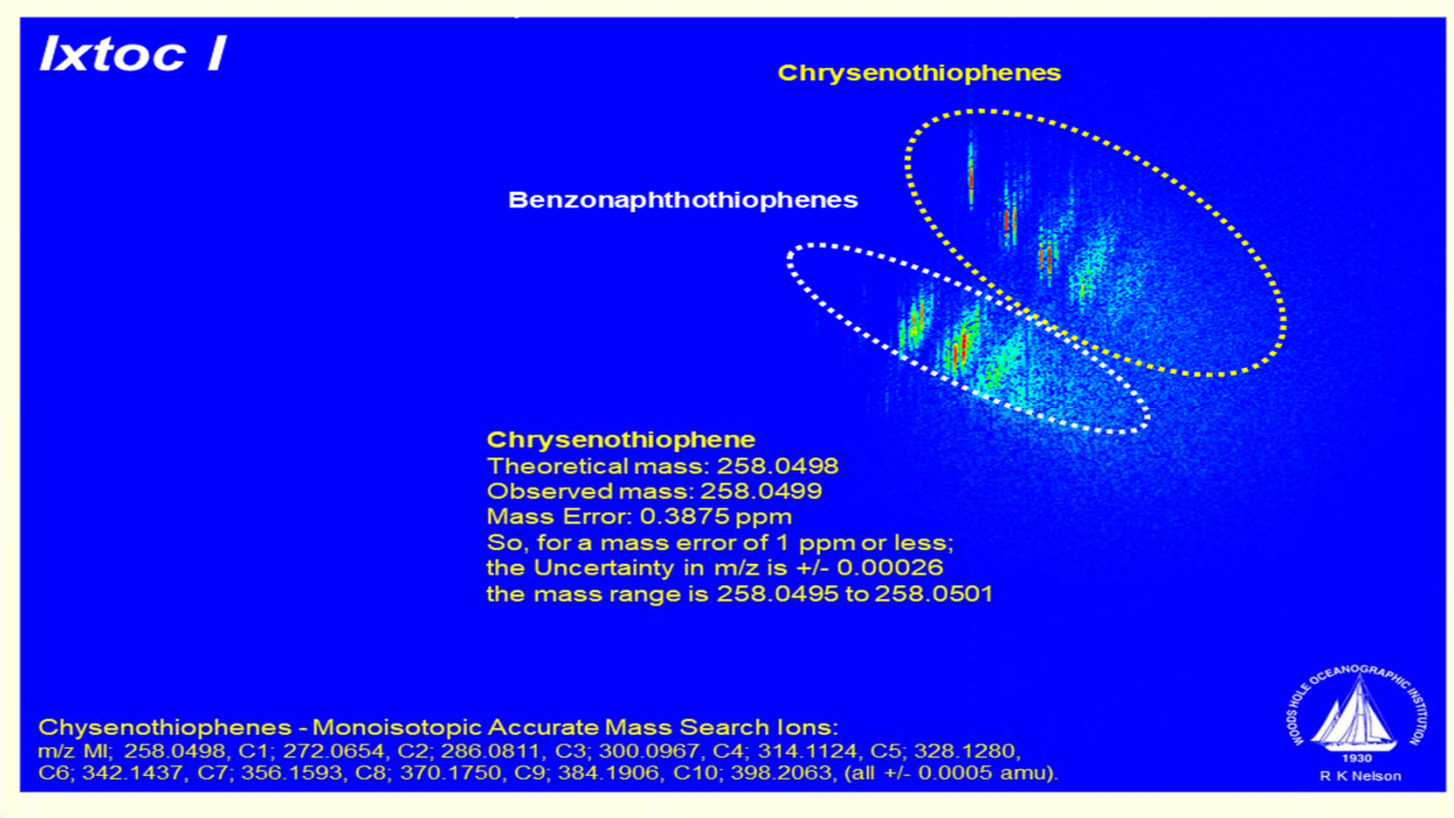


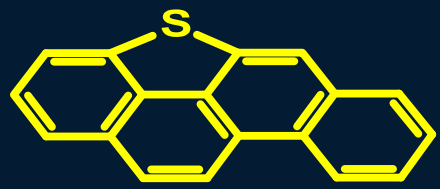
Ixtoc I – GC×GC-HRT
Benzonaphthothiophene Suite



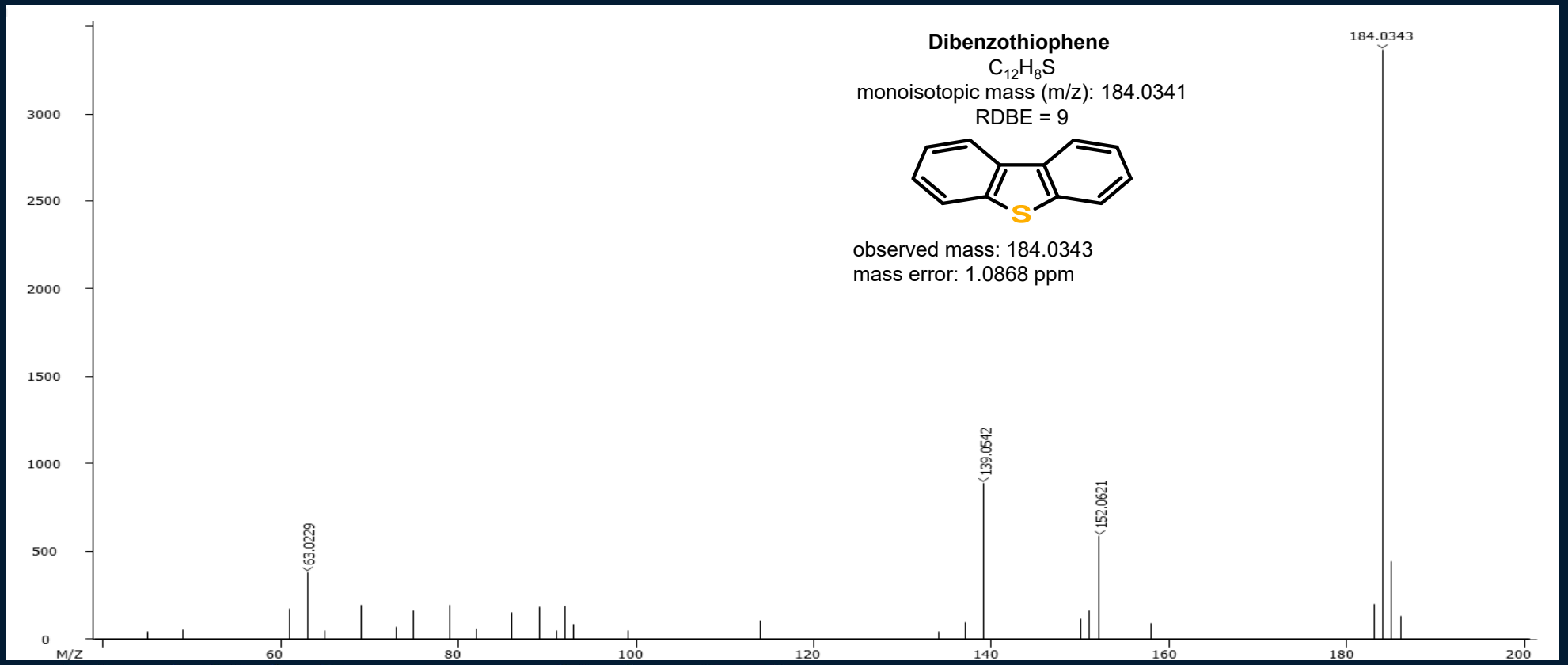


Ixtoc I – GC×GC-HRT
Chrysenothiophene Suite





Ixtoc I Accurate Mass Measurements
Dibenzothiophene Mass Spectrum



Summary

- The combination of GC×GC, high resolution TOF, and petroleomics based mass spectral analysis software tools rapidly provides an extensive inventory of the hydrocarbon compounds found in crude oils.
- HRT accurate mass data provides a high degree of confidence to peak assignments.
- We are well positioned to include Archean biomarkers into environmental forensics.
- GC×GC has matured into a platform that provides superior results capable of delivering a high-level of quality control.
- High resolution data will help to predict the long-term fate of persistent petroleum hydrocarbons in the environment.
- With GC×GC-HRT-MS, we are paving the way for identifying more "forensically useful chemicals" for studying the fate of petroleum in the environment.

Acknowledgements

Thank-you!