Synchrotron-Based Methods for Investigating Degradation of BP Macondo Oil

Daniel Duarte, Edward Overton, Amitava Roy, Gregory Merchan, Henning Lichtenberg, Kyuingmin Ham, Eizi Morikawa, Orhan Kizilkaya, Axita Gupta, Annette Summer Engel, Josef Hormes and Richard Kurtz

J. Bennett Johnston, Sr., Center for Advanced Microstructures and Devices, Louisiana State University, Baton Rogue, LA 70803

Chemistry of Crude Oil

- Crude oil is composed of many molecular compounds of different molecular weights
- It is divided into different types based on API specific gravity, solubility in different liquids, etc. These are operationally defined. SARA: saturates, aromatics, resins, and asphaltenes.
- Geologically more recent oil has higher level of vanadium than nickel.
- About half of these metals are present as porphyrins; the rest have very similar structures but are not porphyrins.

Crude Oil Composition

C	83 – 87%
H	10 – 14%
N	0.1 – 2.0%
O	0.05 – 1.5%
S	0.05 – 6.0 %
V	< 2000 ppm
Ni	< 1000 ppm

Aromatic Rings and Asphaltene

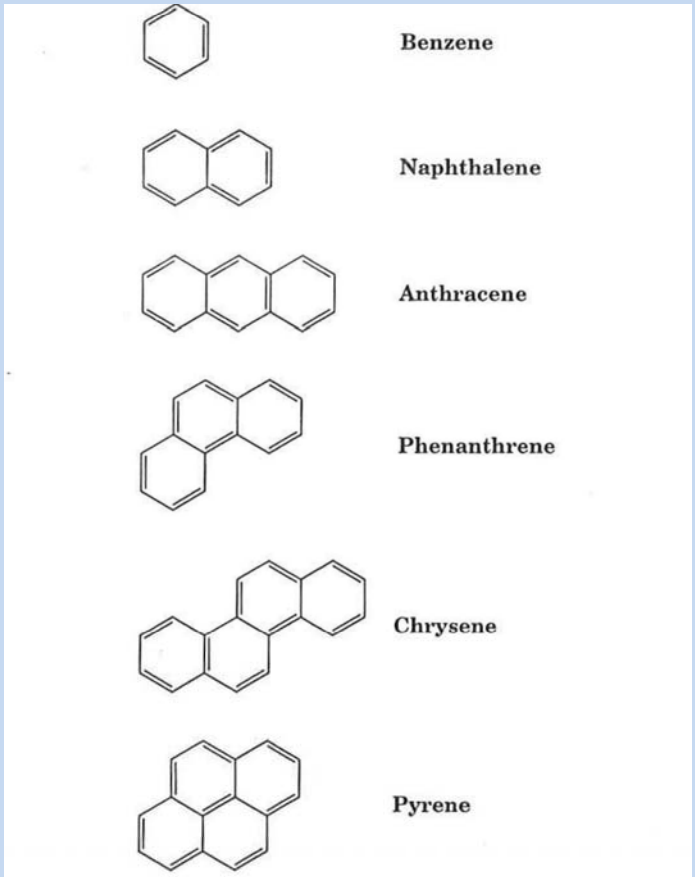
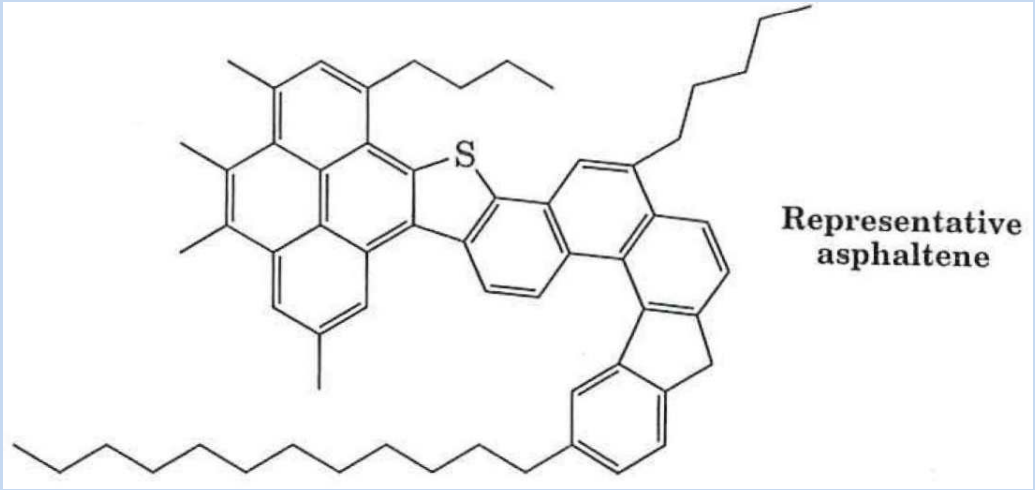


Figure 3. Some six-member ring aromatic constituents of crude oils. Benzenes, naphthalenes, phenanthrenes, and chrysenes are usually most abundant in crude oils.

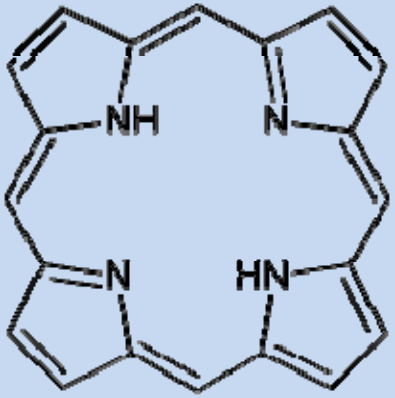


X-Ray Based Methods

- X-Ray Fluorescence Spectrometry
- X-Ray Diffractometry
- Small Angle X-Ray Scattering
- X-Ray Absorption Spectroscopy

Advantages of X-ray based methods:
Non destructive
little or no sample preparation
Liquid or solid samples can be easily studied

Petroporphyrins in Crude Oil



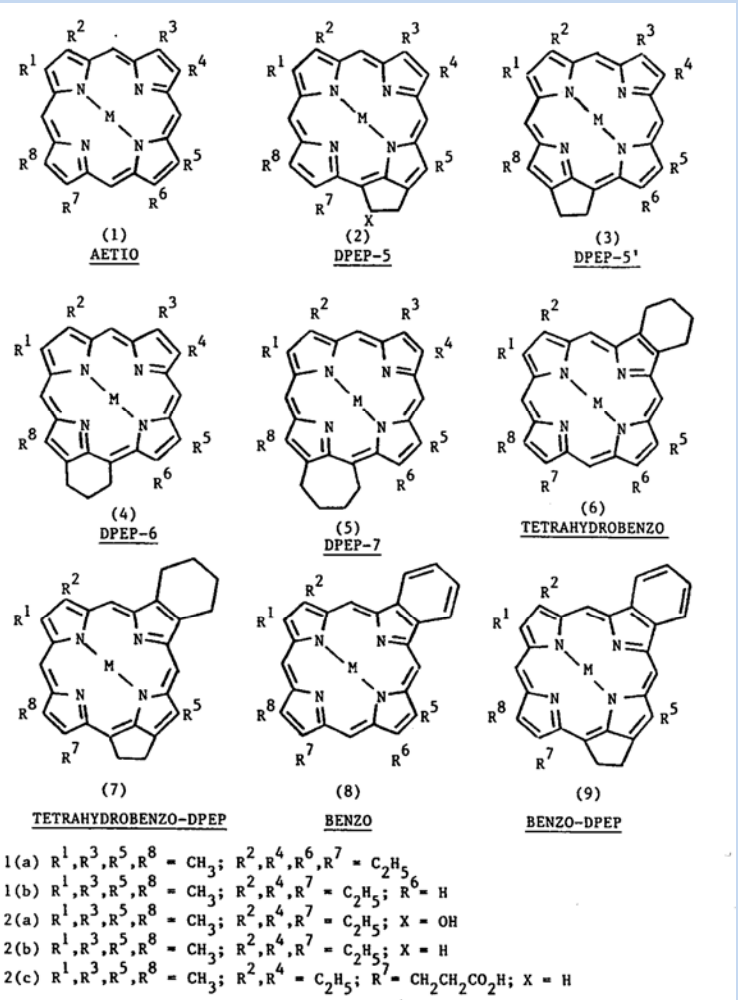
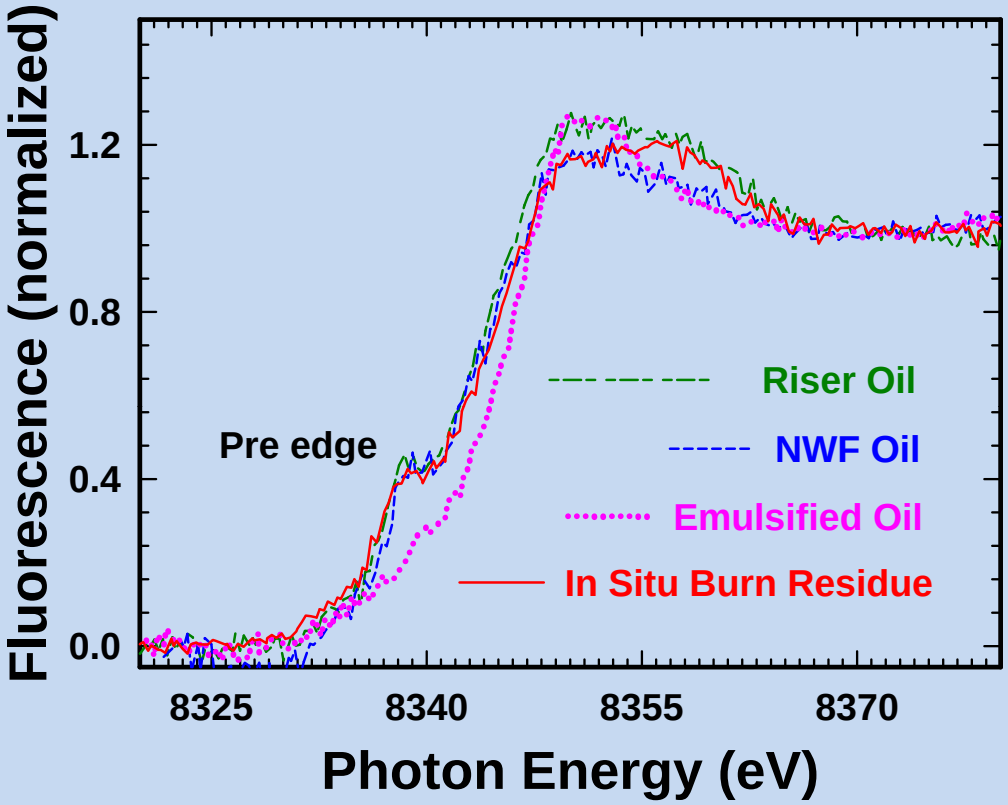
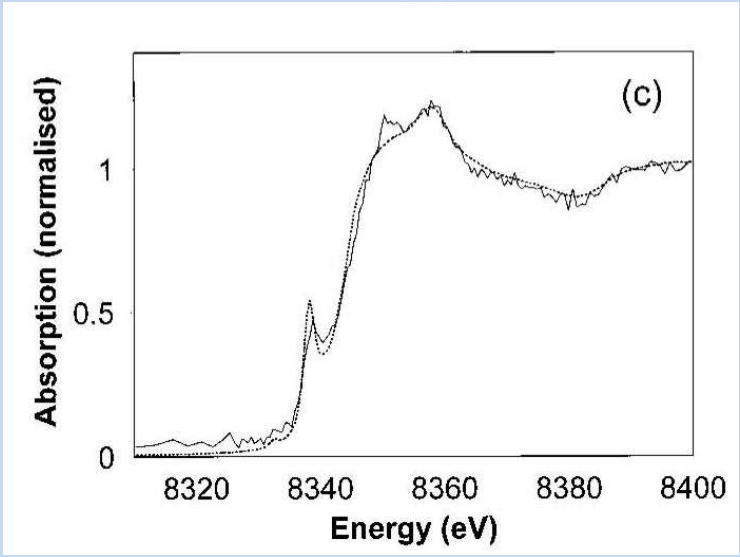


Figure 3-16. Structure of metallo-porphyrins found in fossil fuels (Quirke, 1988. Copyright American Chemical Society. Reproduced with permission).

Speight (1998)

Nickel K Edge XANES

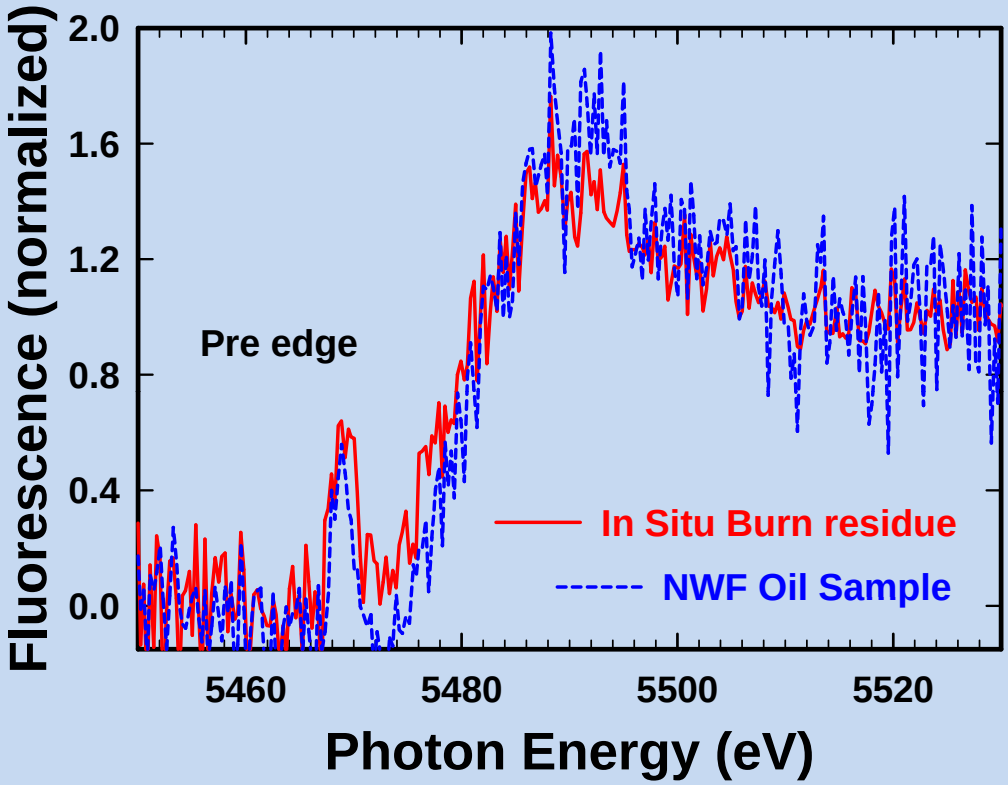


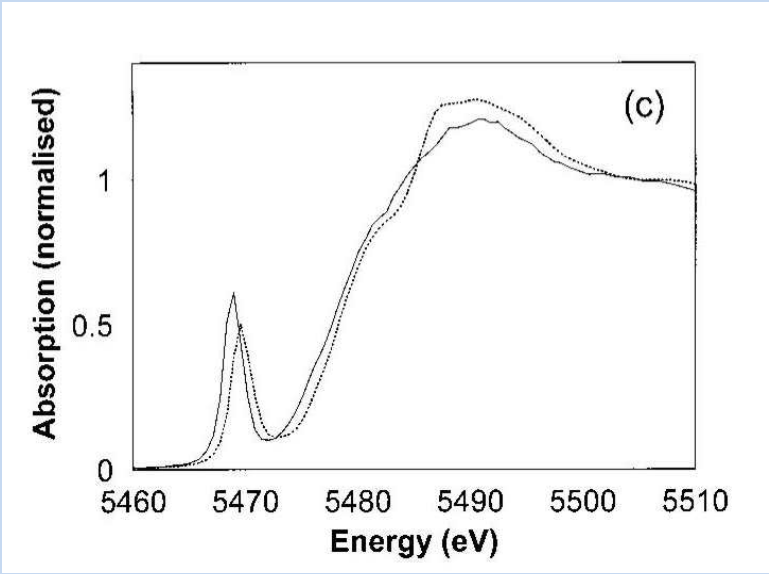


Miller et al. 1999

Miller, J. T., R. B. Fisher, van der Eerden, A. M. J., Koningsberger, D. C (1999). "Structural Determination by XAFS Spectroscopy of Non-Porphyrin Nickel and Vanadium in Maya Residuum, Hydrocracked Residuum, and Toluene-Insoluble Solid." Energy & Fuels 13(3): 719-727.

Vanadium K Edge XANES

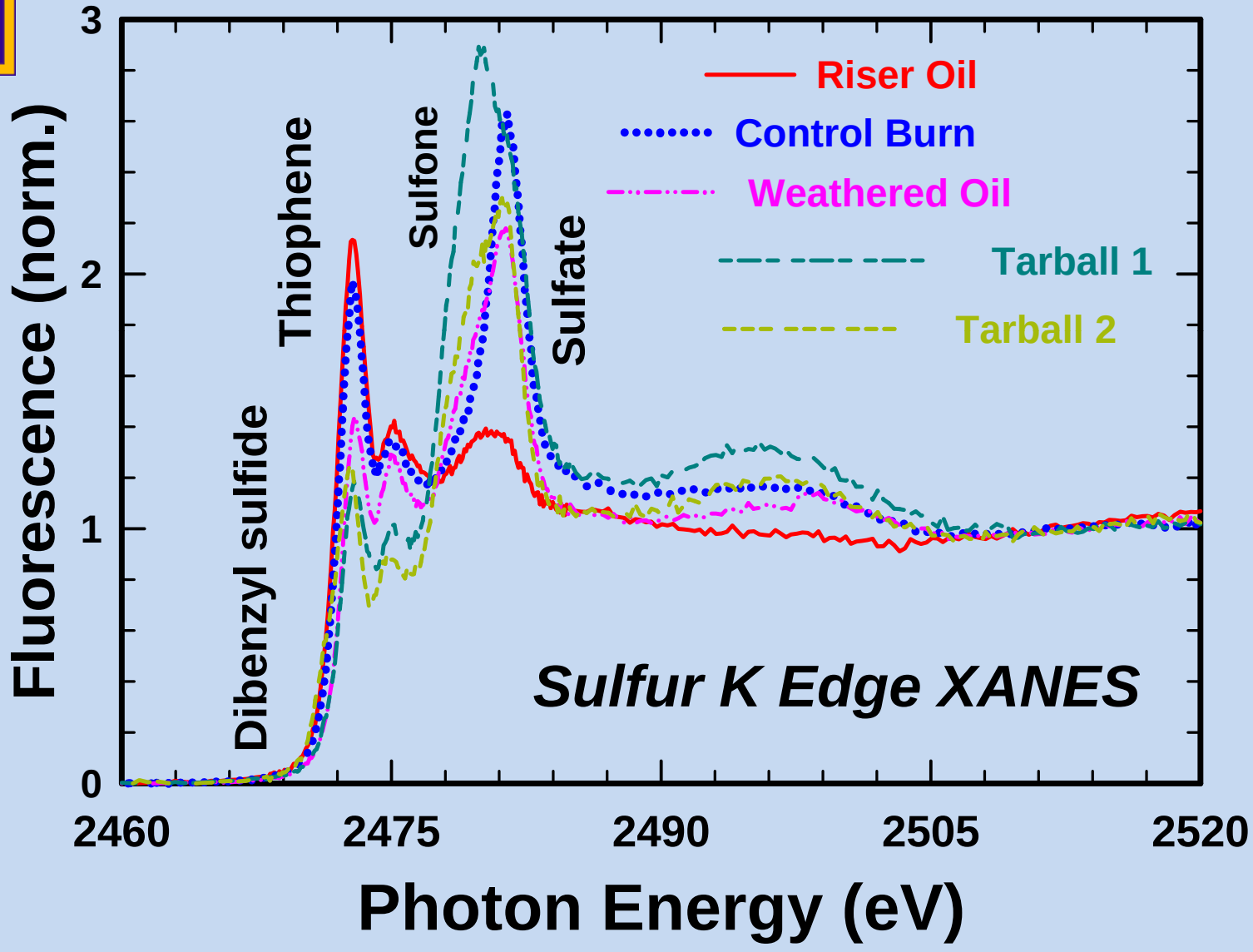




Miller et al. 1999

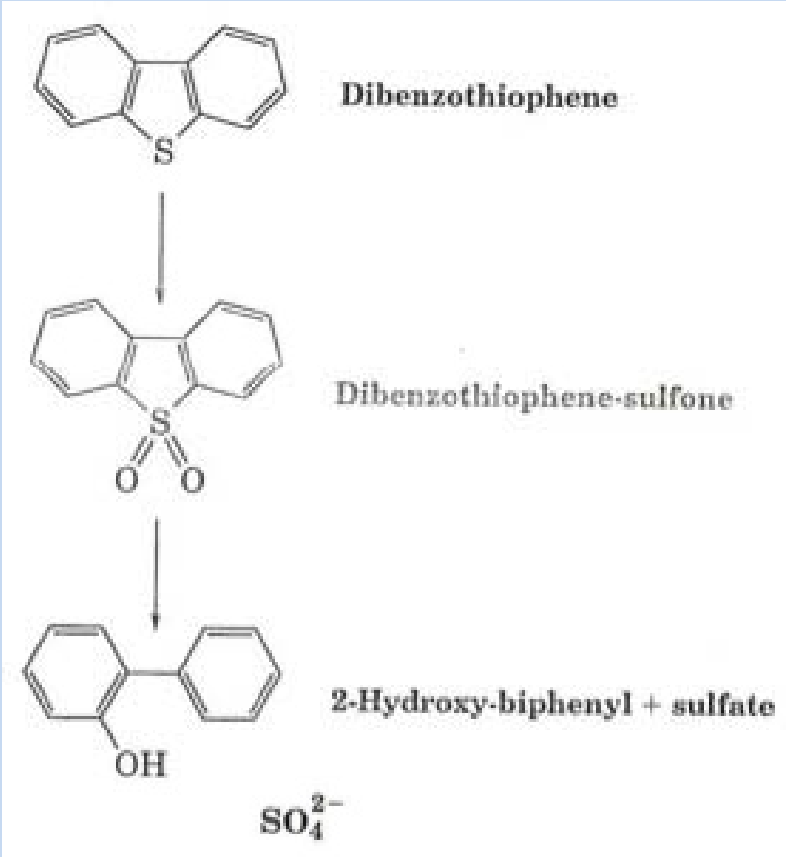
Miller, J. T., R. B. Fisher, van der Eerden, A. M. J., Koningsberger, D. C (1999). "Structural Determination by XAFS Spectroscopy of Non-Porphyrin Nickel and Vanadium in Maya Residuum, Hydrocracked Residuum, and Toluene-Insoluble Solid." Energy & Fuels 13(3): 719-727.

Degradation Products of BP Crude Oil



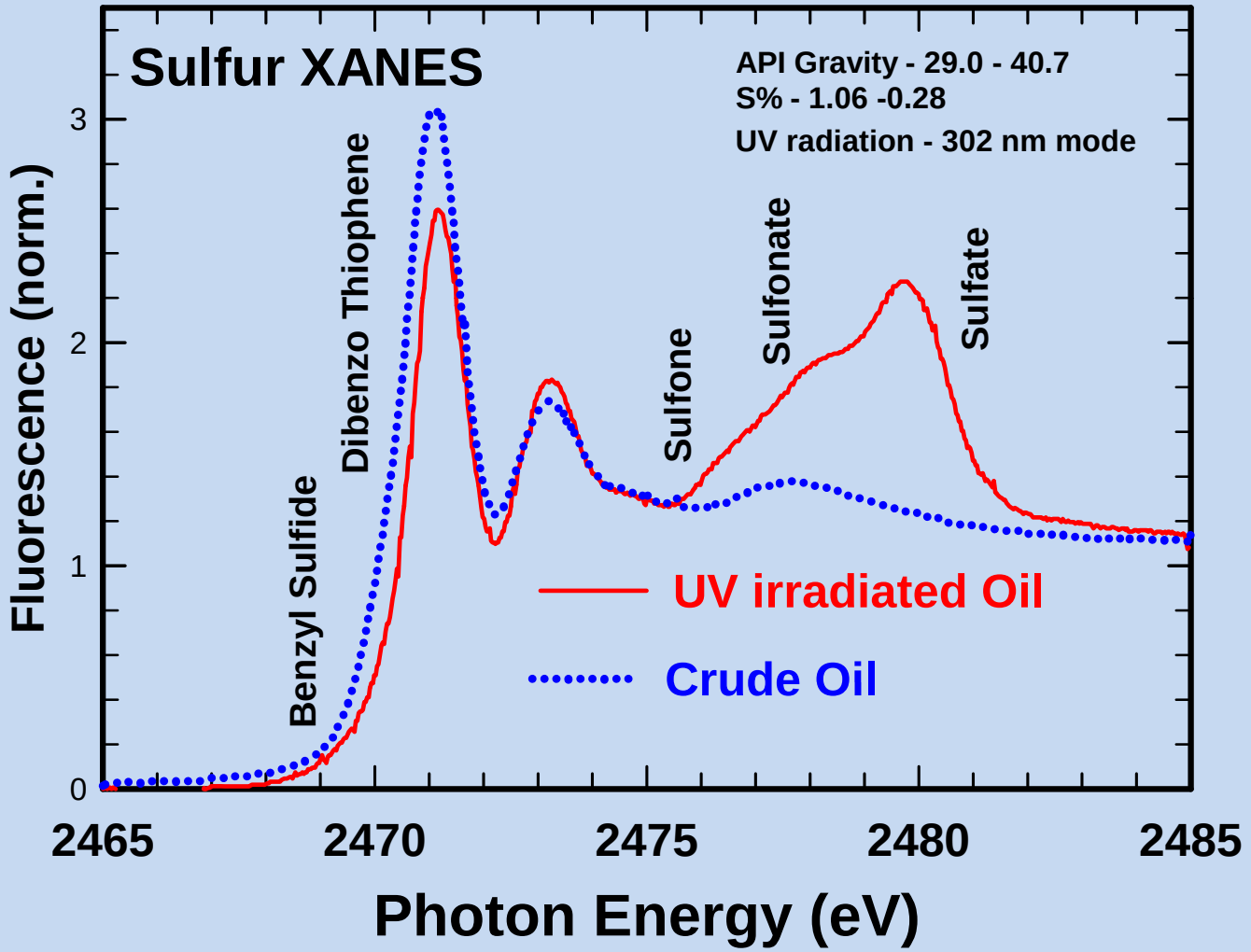
Possible Biodegradation Pathway for Dibenzohiophene (by *Brevibacterium sp*.)

van Afferden et al. 1990



Photodegradation of Crude Oil

Garrett et al. 1998

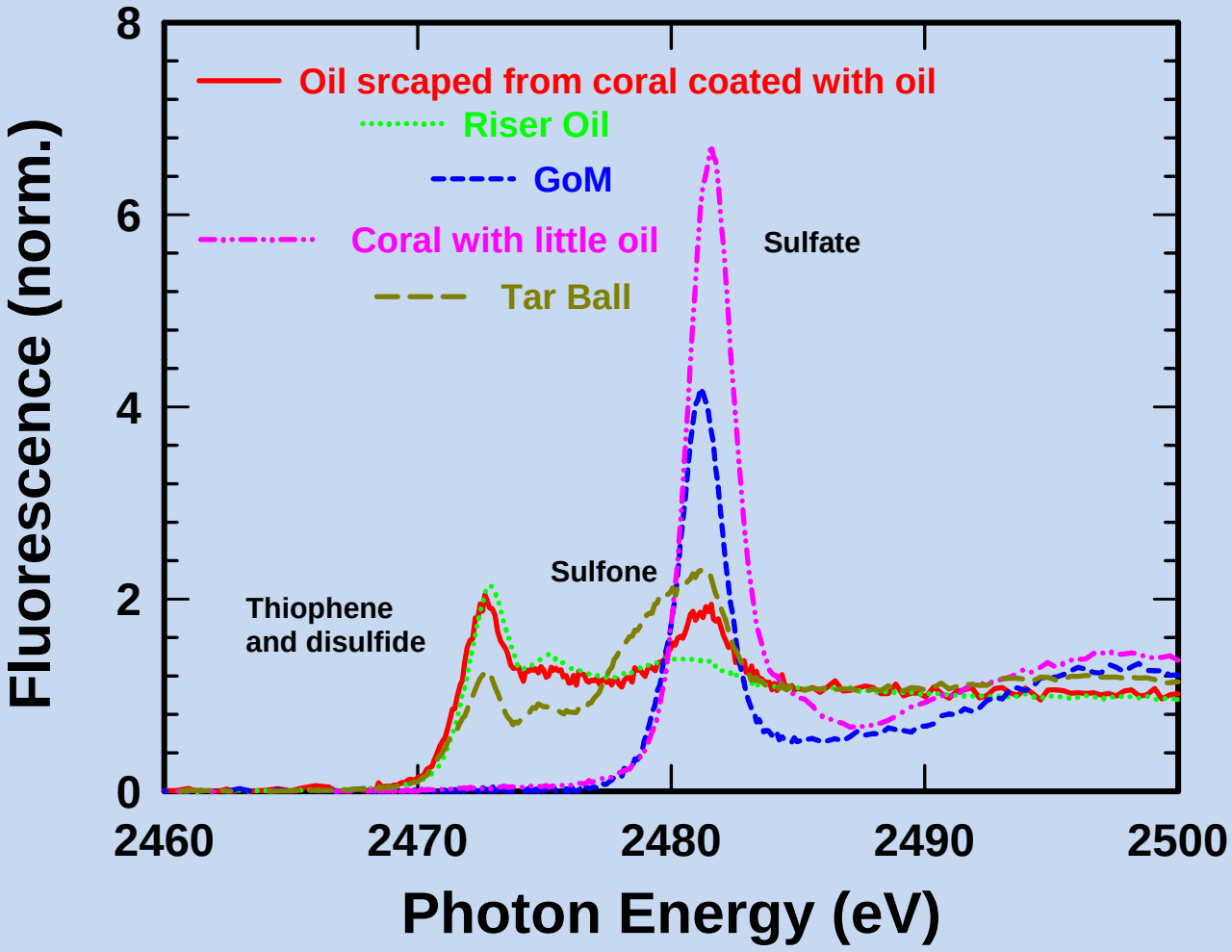


Coral sample collected 140 miles west of Deepwater Horizon Spill site

collected by Suzanne Fredericq, ULL, on December 4th, 2010

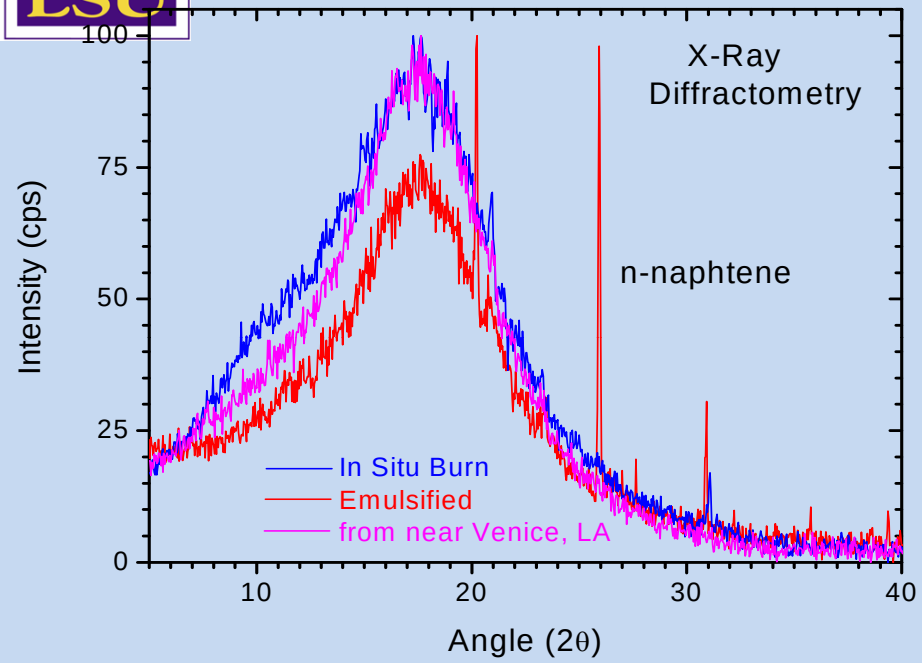
Is This BP Oil?

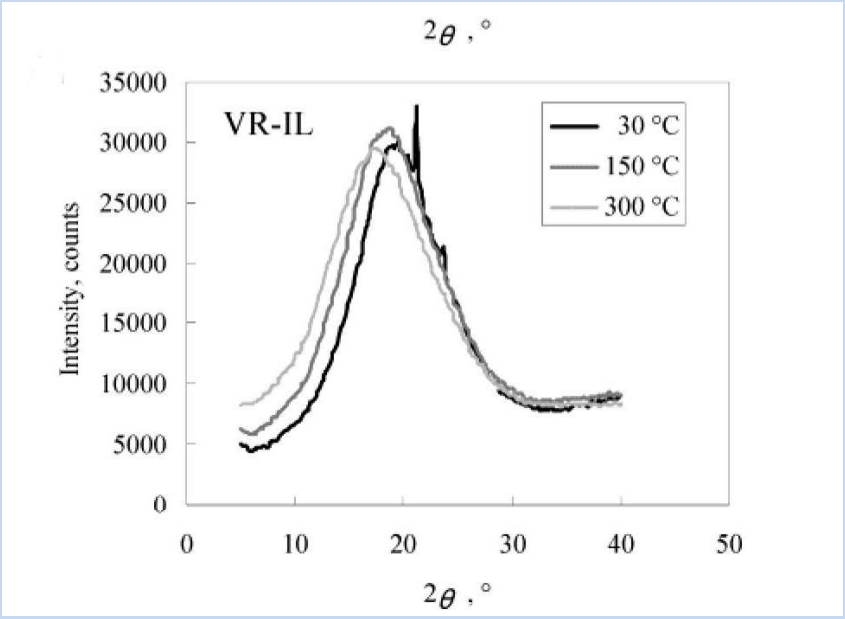
Chromatographic methods produced no signal



Sulfur compounds are typical of crude oil and its degradation products

X-Ray Diffractometry





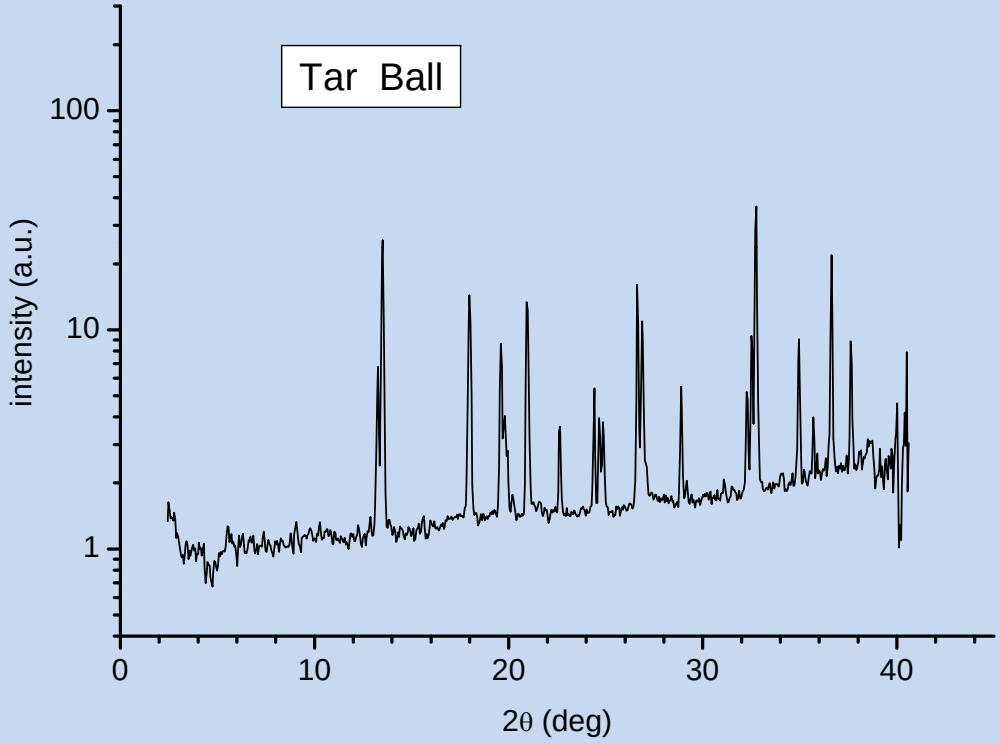
- emulsified oil shows crystallization of a napthene phase.
- The main peak location does not vary.
- There is an additional peak at lower 2θ for the in situ burn sample
- The emulsified oil shows crystallization of a napthene phase.
- Paraffin crystallizes out

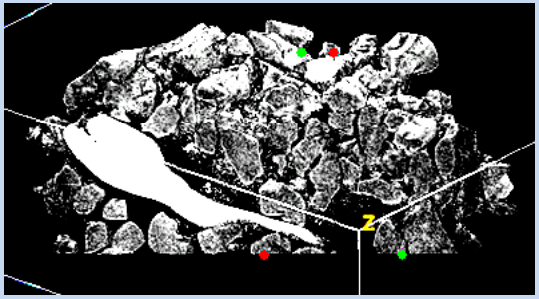
Tanaka et al. 2004

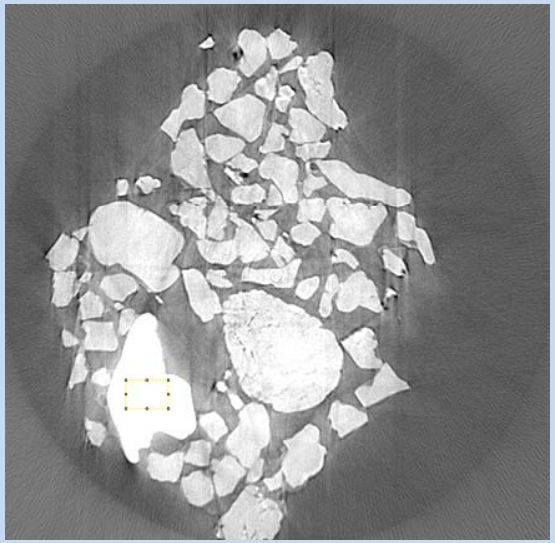
(lab source different wavelength)

Wide Angle X-Ray Scattering

Tarball







Quartz: completely crystalline phase

Conclusions

- Controlled burning does not affect the porphyrin (or porphyrin-like) structure of nickel, however, emulsification does.
- Sulfur-containing compounds in crude oil show variable degree of degradation depending on the fraction.
- Burning of crude oil does not release these metals into the atmosphere
- Emulsified has a different XANES spectrum indicating that the porphyrin-like nickel structure has broken down, possibly due to bacterial action.
- Controlled burning affects the stacking of asphaltene layers.

Acknowledgment

Funding Agencies

LSU/BP Round 1; McNair Program at LSU