



Heteroatomic and Aromatic Chemistries Direct the Production of Water-Soluble Pollutants from Fossil Fuels

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Chemical Dark Matter

Ion Cyclotron Resonance

SUMMARY

Fossil fuels contain abundant molecules comprised of multiple aromatic cores linked by alkyl chains, known as “archipelago” structures. Their presence and tendency to undergo photoinduced oxidation, cracking, and polymerization reactions, drive the production of water-soluble species from fossil fuels, which determines their environmental impact.

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INTRODUCTION

FT-ICR MS Uniquely Reveals the Structural Complexity of Fossil Fuels

Asphaltenes are high-boiling and recalcitrant compounds that are enriched in heavy petroleum, weathered oils (spills), and asphalt paving mixtures. They exhibit high structural complexity that was misunderstood (oversimplified) for over five decades; asphaltenes are now known to be comprised predominantly of two polycyclic aromatic hydrocarbon (PAHs) structural motifs: a mixture of single-core "island", and multicore "archipelago" structures. The mass fraction of each motif is sample-dependent. Thus, knowledge of a potential structural dependence on the production of water-soluble species from asphaltenes is key to understanding the contribution of photochemically generated dissolved organic matter from fossil fuels (potential environmental impact).

Detailed molecular analysis of asphaltenes and weathered fossil fuels demands high-field Fourier transform ion cyclotron resonance mass spectrometry, chemical separations, and advanced precursor ion isolation coupled to gas-phase fragmentation, due to extreme structural and compositional complexity (Figure 1, top right).

FT-ICR MS, SWIFT, IRMPD, Selective Ionization, Extrography

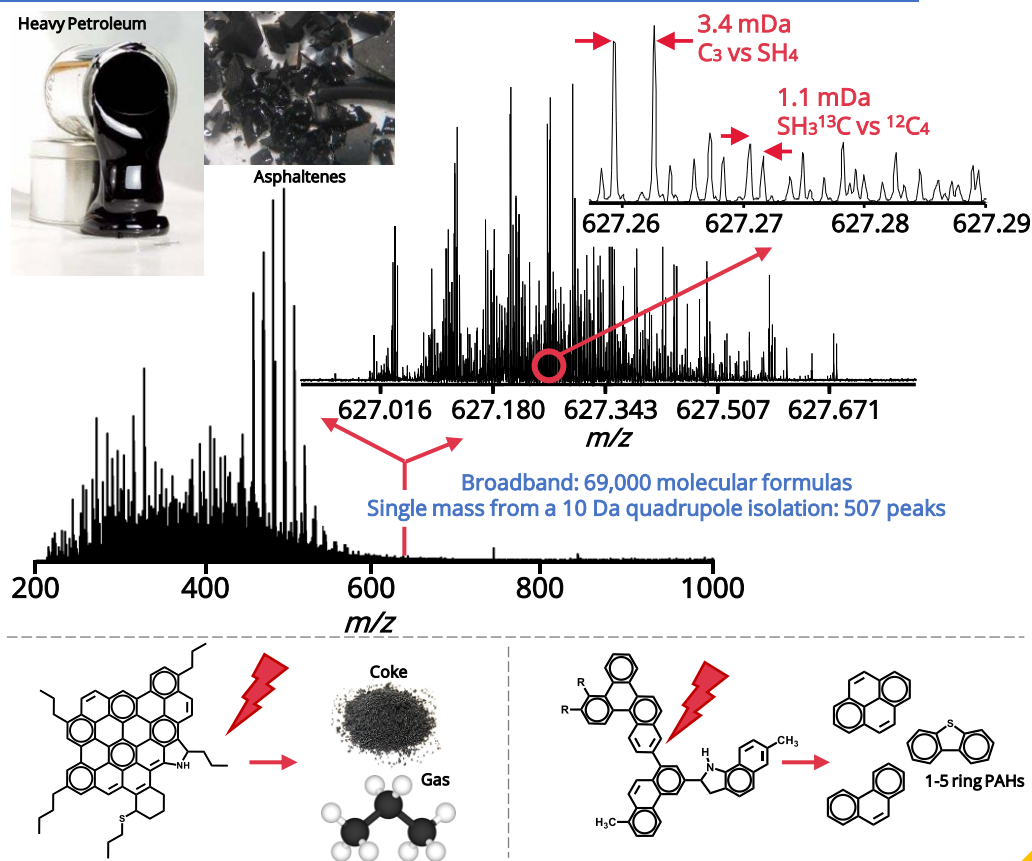


FIGURE 1. Upper panel: (+) APPI 21 Tesla FT-ICR mass spectrum for Arabian heavy asphaltenes. Lower panel: Petroleum structural motifs and their products from cracking processes.



METHODS

Separation by Molecular Selectivity

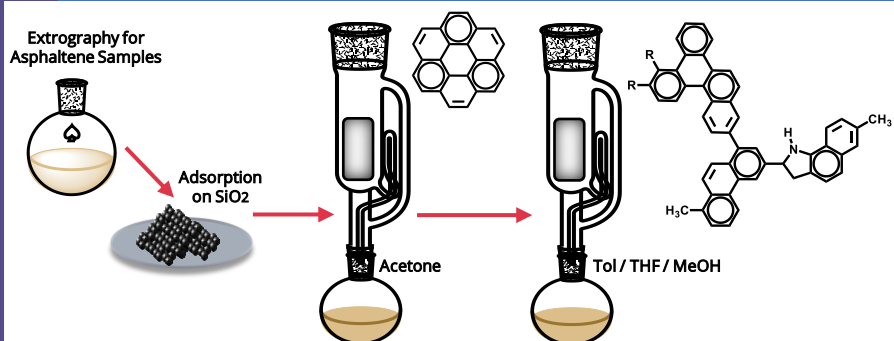
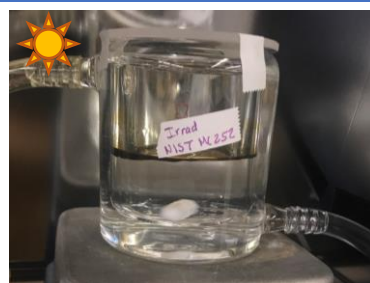


FIGURE 2. Separation of single-core and multicore motifs in petroleum asphaltenes is enabled by extrography. Disruption of dipolar interactions in acetone assists the initial isolation of single-core PAHs, whereas Tol/THF/MeOH favors multicore species.

Simulated Photooxidation



Petroleum film on artificial sea water
1 day of irradiation = 4 days of natural sunlight

FIGURE 3. Laboratory-scale photo-oxidation of petroleum films.

Advanced Structural Characterization

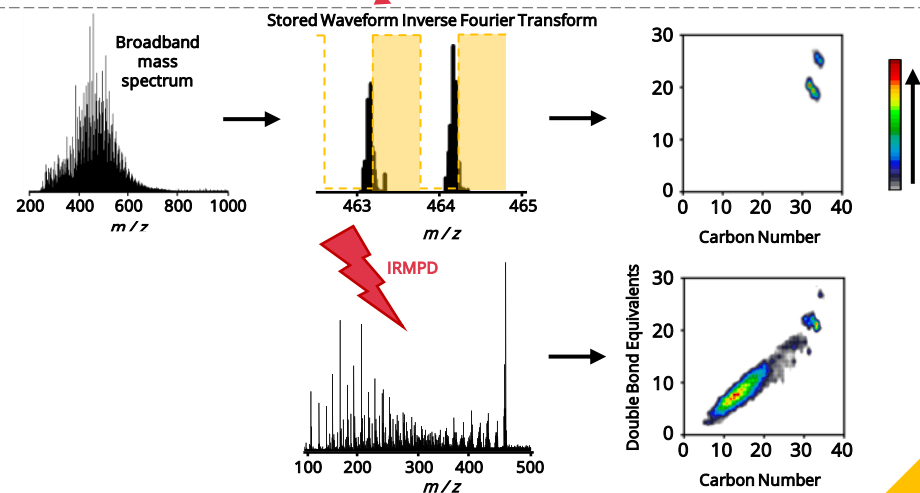
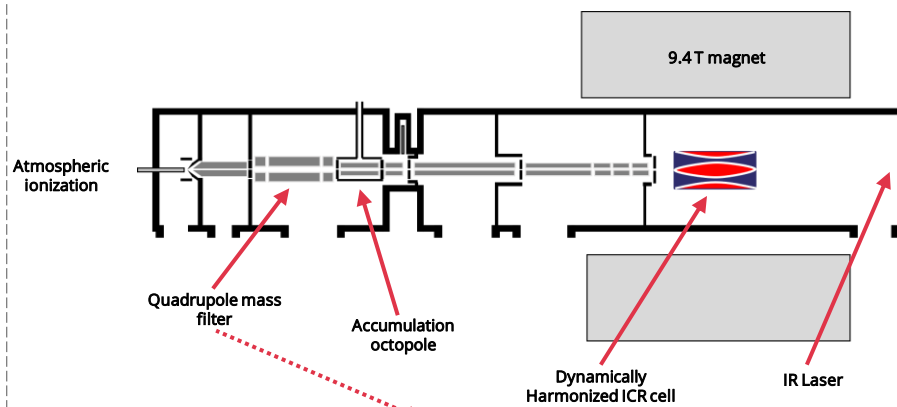


FIGURE 4. Upper panel: 9.4 T FT-ICR mass spectrometer used for complex mixture analysis. Lower panel: characterization of petroleum structural motifs.



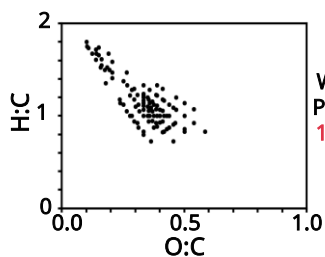
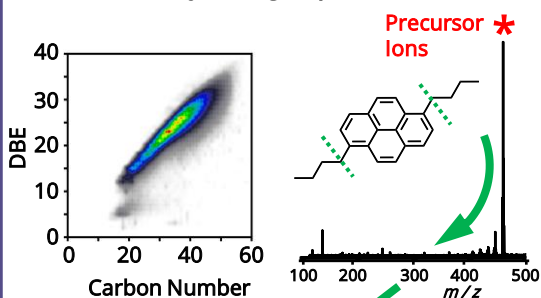
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RESULTS

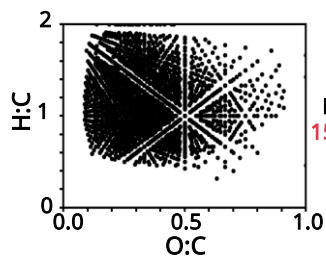
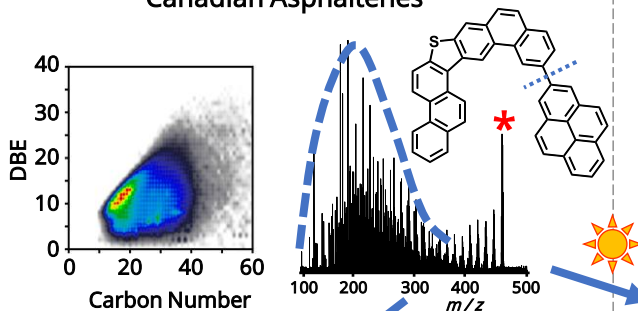
Petroleum Photooxidation is Sample Dependent

Wyoming Asphaltenes



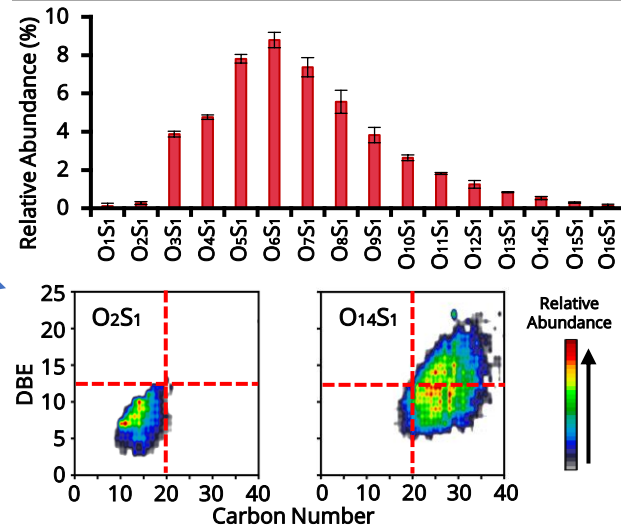
Water-Soluble Photoproducts
105 molecular formulas

Canadian Asphaltenes



Water-Soluble Photoproducts
15,292 molecular formulas

Multicore motifs readily undergo photooxidation and phototransformation to produce abundant water-soluble compounds that reveal an ultra-complex composition.



Photooxidation, fragmentation, and polymerization of multicore motifs

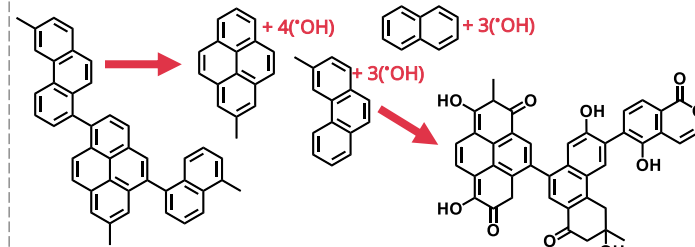


FIGURE 5. Left and middle panels: structural motifs for Wyoming and Canadian asphaltenes, and respective photooxidation behavior. Right panel: Molecular composition for S-containing DOM derived from Canadian asphaltenes and proposed transformation pathways.



RESULTS

Petroleum Weathering Involves Polymerization

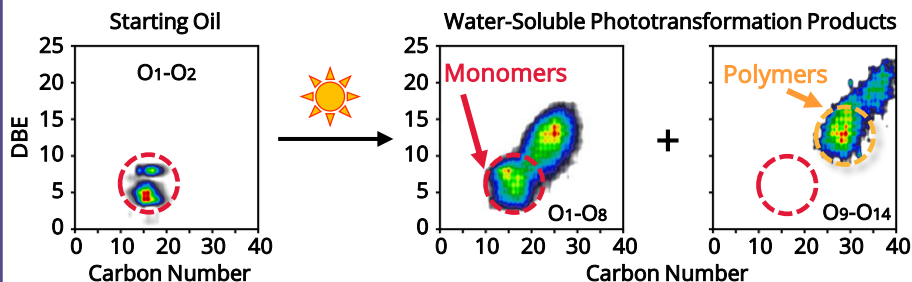


FIGURE 6. Phototransformation of a low-boiling distillate, with a fixed range of carbon number and DBE and only up to two oxygen atoms per molecule, into water-soluble compounds with twice DBE and carbon content and up to fourteen oxygen atoms.

Implications to the Built Environment

Asphalt Binder

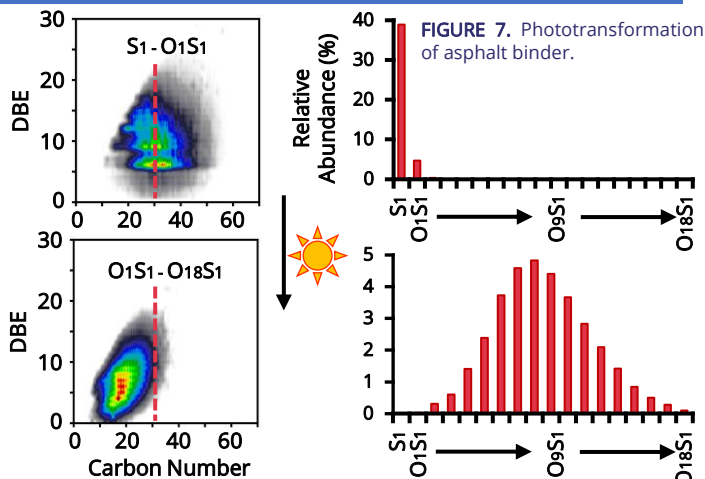
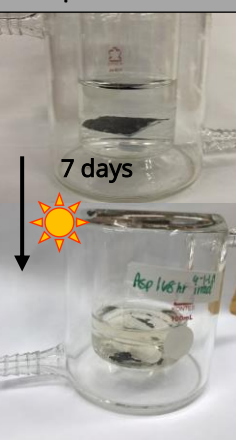


FIGURE 7. Phototransformation of asphalt binder.

CONCLUSION & DISCUSSION

Conclusions

Highly aromatic asphaltenes with dominant island structure resist photofragmentation and yield limited water-soluble species as detected by mass spectrometry. Conversely, asphaltenes with abundant archipelago structural motifs yield abundant water-soluble species with a molecular composition characteristic of petroleum-derived dissolved organic matter. The compositional range of the water-soluble phototransformation products suggests that photofragmentation of archipelago motifs is central in the transformation of asphaltenes into DOM.

Furthermore, the photooxidation of petroleum species with a fixed carbon number range and DBE yields water-soluble compounds with ~2-fold carbon number and DBE increase, which suggests that polymerization reactions are also involved in petroleum phototransformation.

The results highlight that petroleum degradation by sunlight involves three concerted processes: photooxidation, photofragmentation, and polymerization. The importance of each in the long-term fate of weathered petroleum is currently unknown and will require longer time period photomicrocosms and comparison to field samples.

Future Research Directions

- Investigate whether the extensive applications of asphaltene-enriched fossil fuels in the built environment, *e.g.*, pavement and coal tar, have a negative impact on human health and wildlife.
- Collaboration with the White Lab (MIT) to understand cellular toxicity of petroleum phototransformation products.

References

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- Chacón-Patiño M. L., et al. *Environmental Science & Technology* 2020, 54, 16, 9968–9979.
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