

Chemical Speciation and Carbon Isotope Systematics During Kerogen Maturation: An Experimental Study*

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Abstract

Carbon isotope measurements of alkanes have been used as an effective tool to constrain the origin of hydrocarbons. The pattern of carbon isotope compositions of ethane and propane, along with isotope value of methane, are important indicators of thermal maturity of source-rock kerogen. Recent laboratory experiments, however, suggested that pressure and the presence of water could be crucial factors affecting hydrocarbon formation and then carbon isotope fractionations. To assess reaction pathways and controlling factors of carbon isotope compositions of hydrocarbons, a series of hydrous pyrolysis experiments are performed for systematic identification of all organic compounds and corresponding carbon isotope measurement. Experiments are performed at 350°C and 300 bars of total pressure. Kerogen was isolated from Green River shale by a series of acid treatment. In each experiment, the reactor contains 1.5 grams of kerogen and 30 grams of deionized water. After 24 hours of reaction in the first experiment, gaseous products are removed under cryogenic conditions for chemical and carbon isotope analyses. The bitumen product is retrieved and separated into saturated hydrocarbons, aromatics, resins, and asphaltenes (SARA) by HPLC for subsequent analyses. The gaseous compounds from the experiment consisted of CO₂, methane, ethane, propane, *i*-butane, and *n*-butane. Comparison of mass 44 peak of each compound in IRMS analysis indicates that the abundances of *n*-alkanes decreases with carbon number, with CO₂ being more abundant than all alkanes. The $\delta^{13}\text{C}$ values of alkanes are -46.69‰ (C₁), -38.51‰ (C₂), -35.33‰ (C₃), -30.43‰ (*n*-C₄), and -33.91‰ (*i*-C₄), with CO₂ having the highest value of -26.20‰ . For bitumen, gravimetric analysis has shown that weight percentages of saturated, aromatics, resins, and asphaltenes are 1.1, 3.4, 29.5, and 66.0, respectively. High resolution GC/MS and carbon isotope analyses are in progress to identify detailed chemical compositions within each group, and to measure their carbon isotope values as well. The second experiment with longer reaction time and others under different temperature and pressure conditions are also underway to observe changes, if any, in abundance and carbon isotope values of all organic compounds. That would help us get a better understanding of evolution of chemical compositions and carbon isotope systematics during kerogen maturation processes, facilitating reservoir characterization, and effective exploration.

Selected References

Dua, J., J. Zhijun, X. Hongsen, B. Liping, and L. Wei, 2003, Stable carbon isotope compositions of gaseous hydrocarbons produced from high pressure and high temperature pyrolysis of lignite: *Organic Geochemistry*, v. 34/1, p. 97-104.

Fu, Q., B.S. Lollar, J. Horita, G. Lacrampe-Couloume, and W.E. Seyfried, 2007, Abiotic formation of hydrocarbons under hydrothermal conditions; constraints from chemical and isotope data: *Geochimica et Cosmochimica Acta*, v. 71/8, p. 1982-1998.

Lollar, B.S., T.D. Westgate, J.A. Ward, G.F. Slater, and G. Lacrampe-Couloume, 2002, Abiogenic formation of alkanes in the Earth's crust as a minor source for global hydrocarbon reservoirs: *Nature London*, v. 416/6880, p. 522-524.

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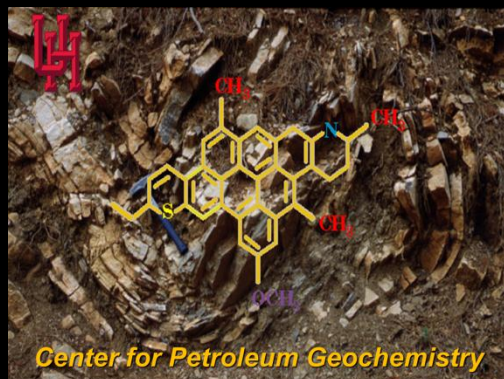
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Motivations

- C isotope measurement – effective tool to constrain the origin of hydrocarbons, and important indicators of thermal maturity of source-rock kerogen as well.
- Recent experiments suggested pressure and the presence of water could be crucial factors affecting hydrocarbon formation and then carbon isotope fractionations.
- Lack of systematic stable isotope measurement for experimental studies at a variety of physical and chemical conditions during kerogen maturation processes.

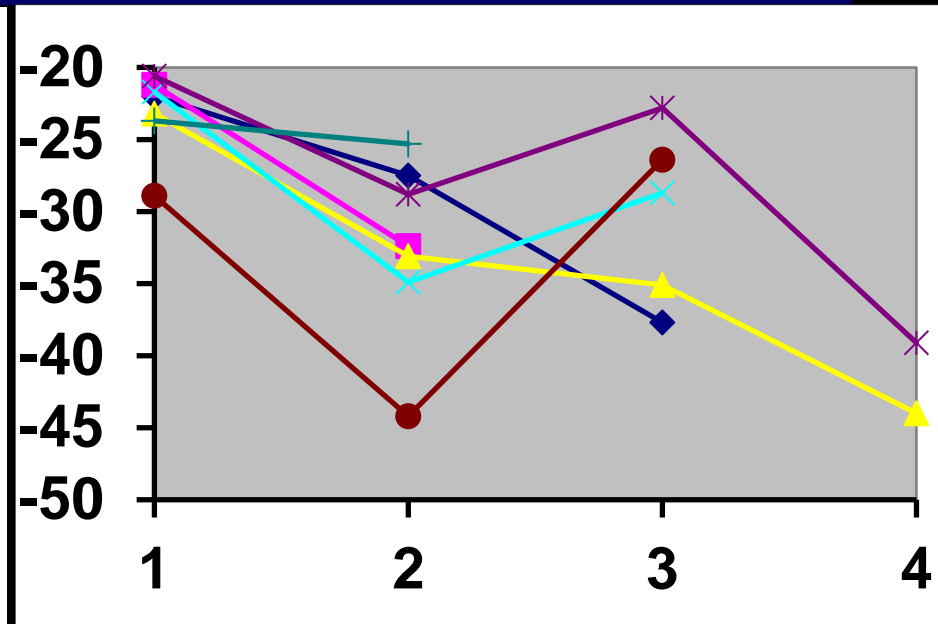
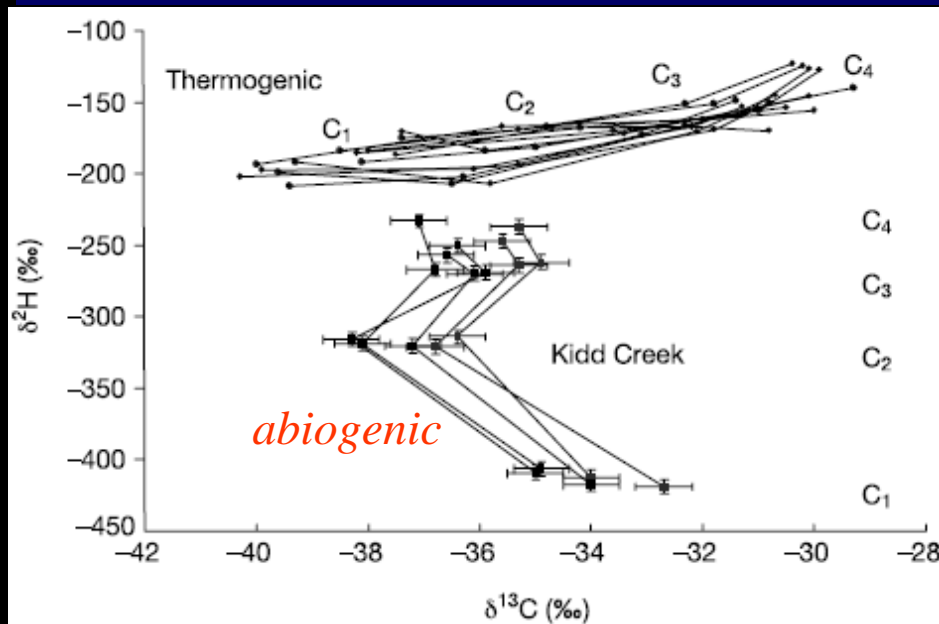
Previous studies – C isotope trend

- Thermogenic: Kinetic Isotope Effect (KIE)

^{12}C - ^{12}C bond is easier to break than a ^{12}C - ^{13}C bond



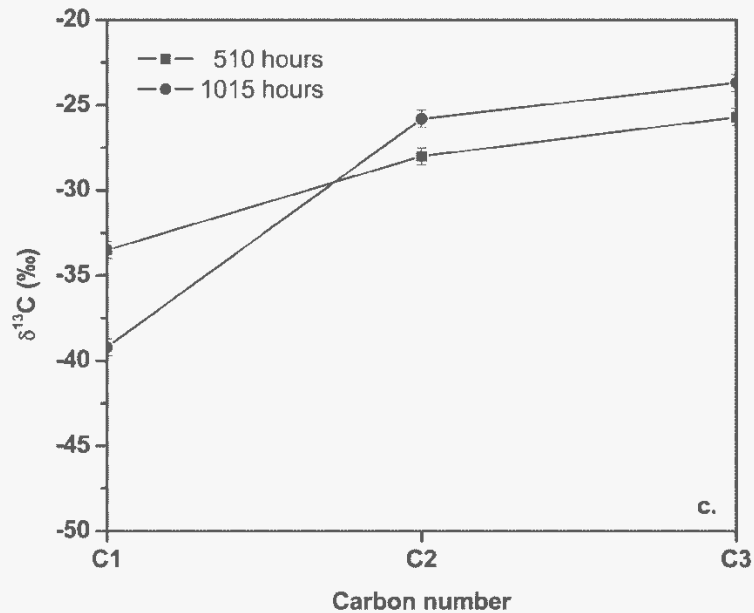
Isotopically lighter products



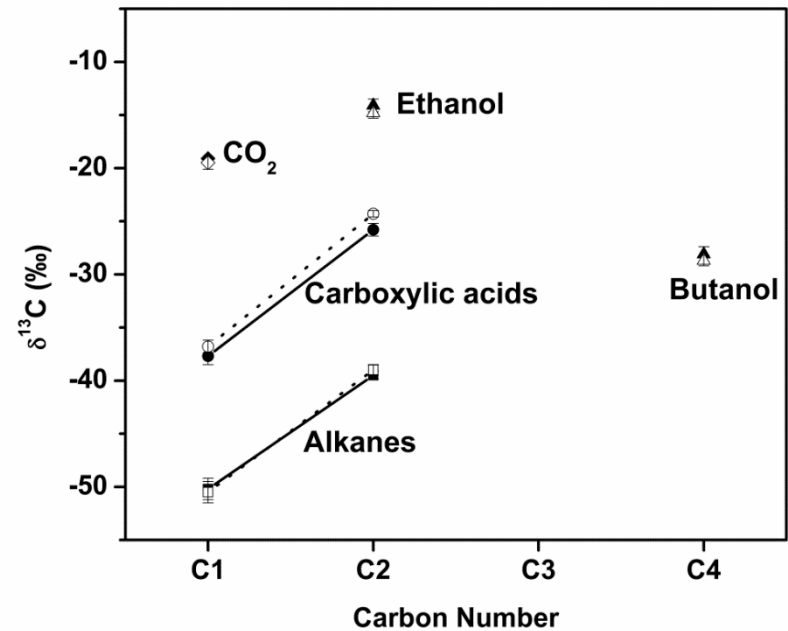
(Sherwood Lollar et al., 2002)

- Hydrous pyrolysis of lignite showed depletion of ^{13}C with carbon number: 600-700 °C and 10-30 Kbars (Du et al., 2003):
Pressure is an important controlling factor.

- Hydrothermal abiogenic experiments: Fischer-Tropsch Synthesis - polymerization



400°C, 500 Bars
(Fu et al., 2007)



750°C, 5.5 KBars
(Fu et al., 2014, in review)

Depolymerization by the presence of H₂O

- Hypothesis: the reaction pathway, which is controlled by physical and chemical conditions (T, P, redox, minerals, etc.), is the crucial factor determining carbon isotope patterns.

Working strategies:

hydrous pyrolysis experiments

+

full suite of chemical composition analysis (GC, GC-MS)

+

C isotope measurement
(GC-EA-IRMS)

(Center for Petroleum Geochemistry, UH)



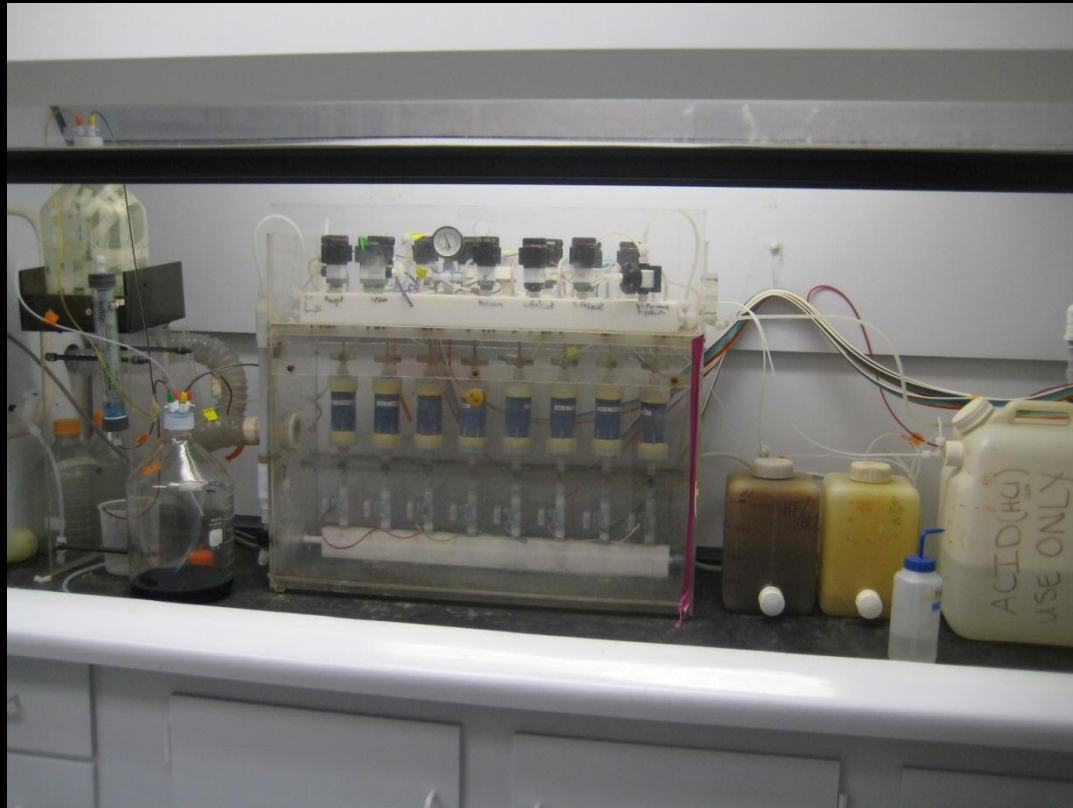
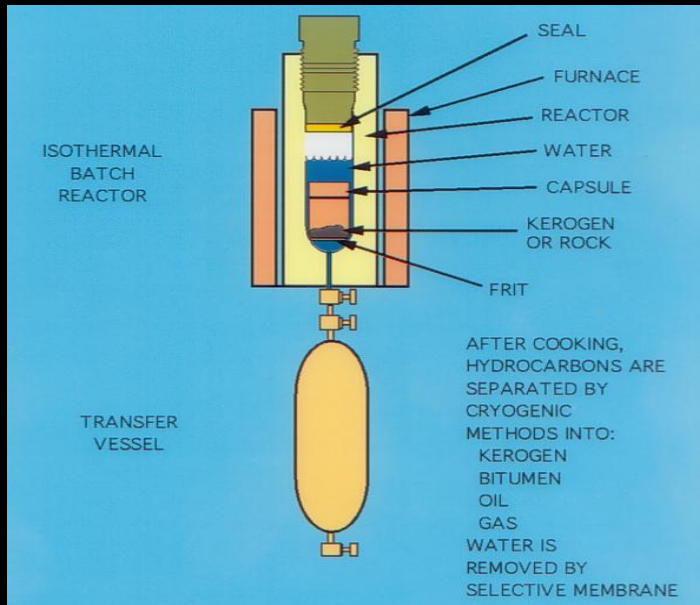
Hydrous Pyrolysis Experiments

T 350 °C

P 300 bars

Duration 24, 48, 72 hrs

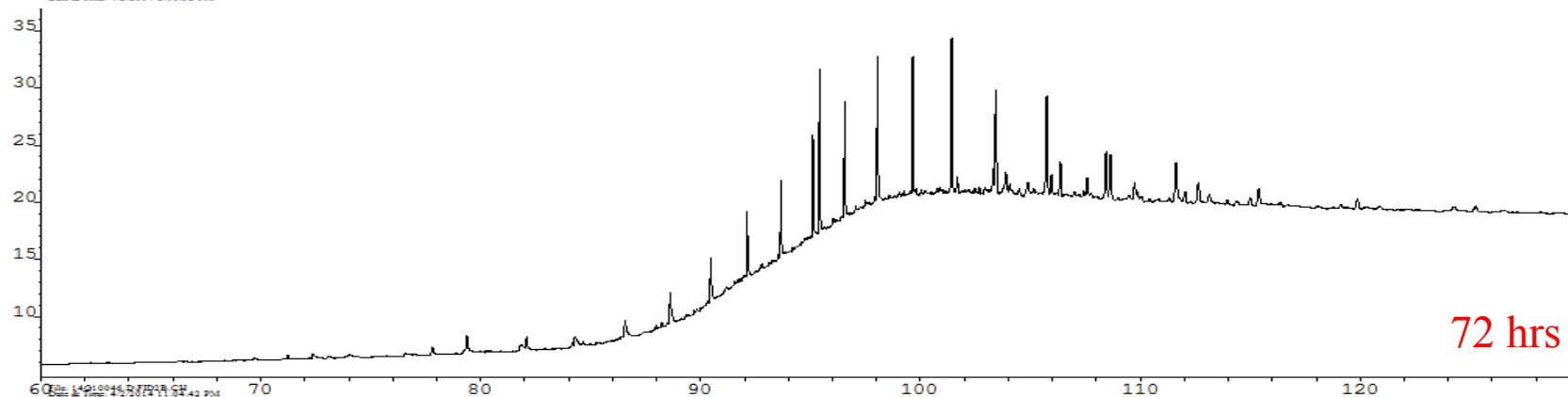
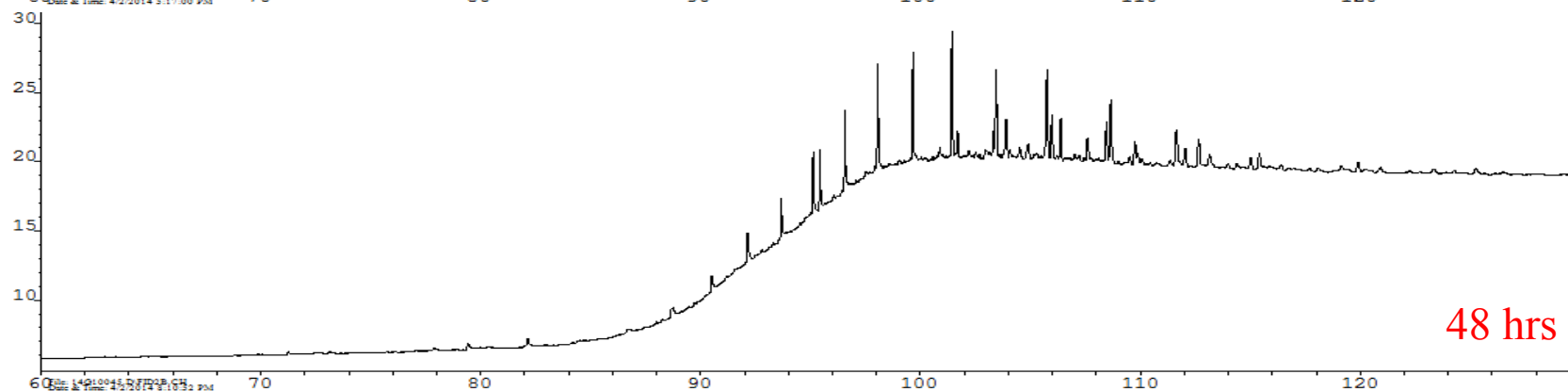
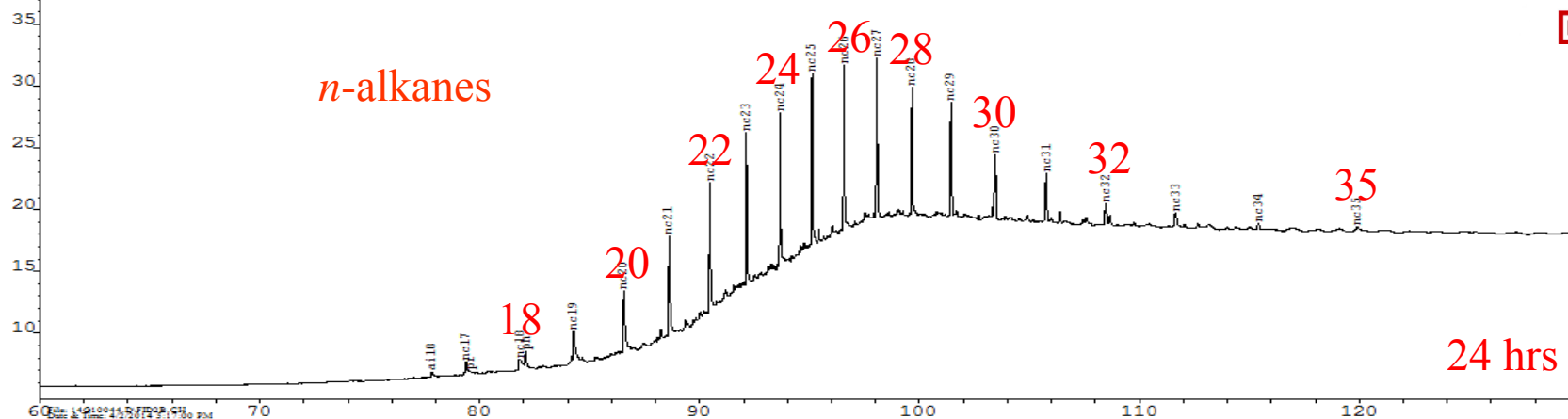
Starting Material Green river shale kerogen (1.5g)
DI H₂O (30g)



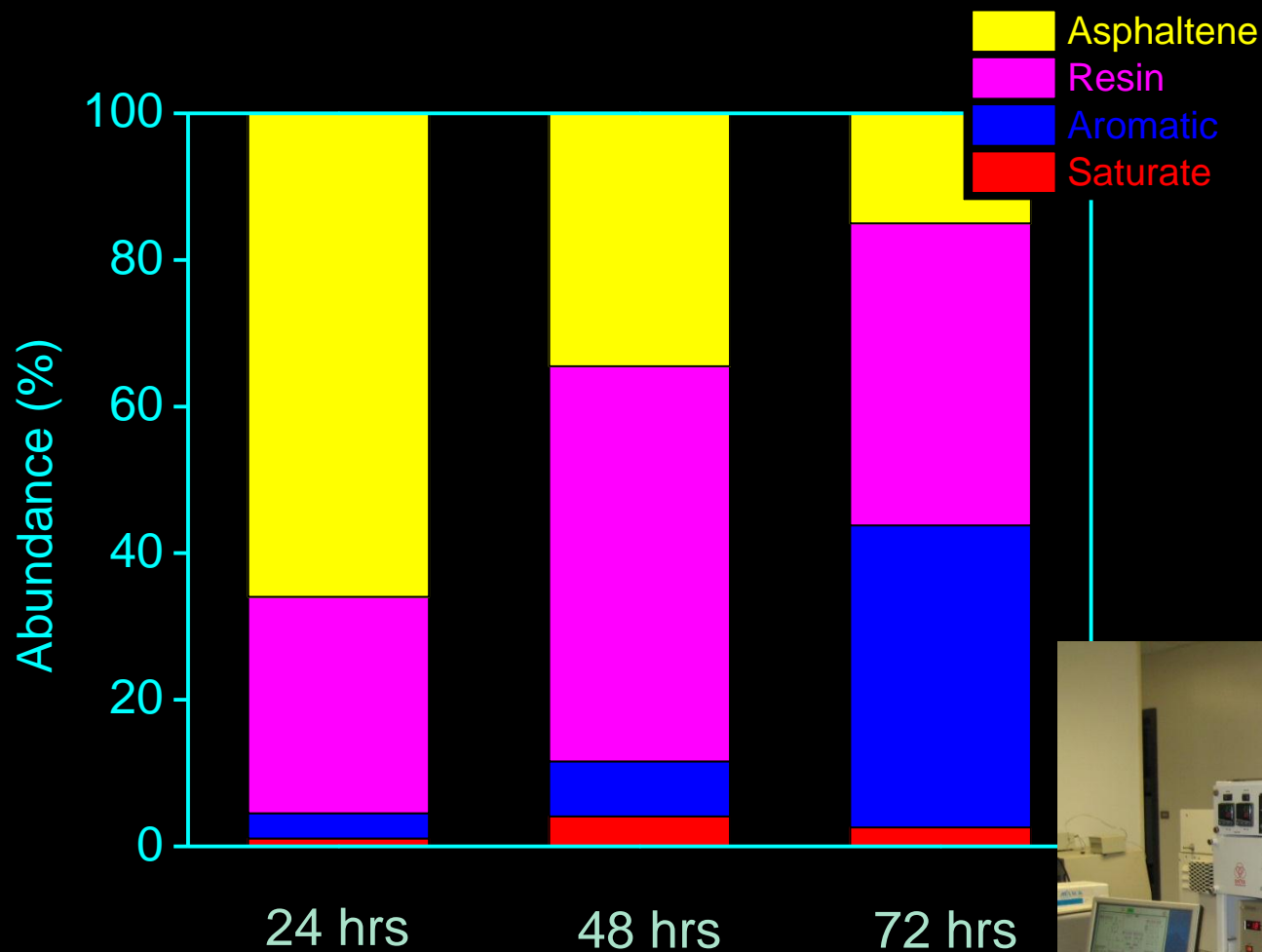
Bitumen extract – Gas Chromatography (GC)



Sample Ker-1



S.A.R.A. separation

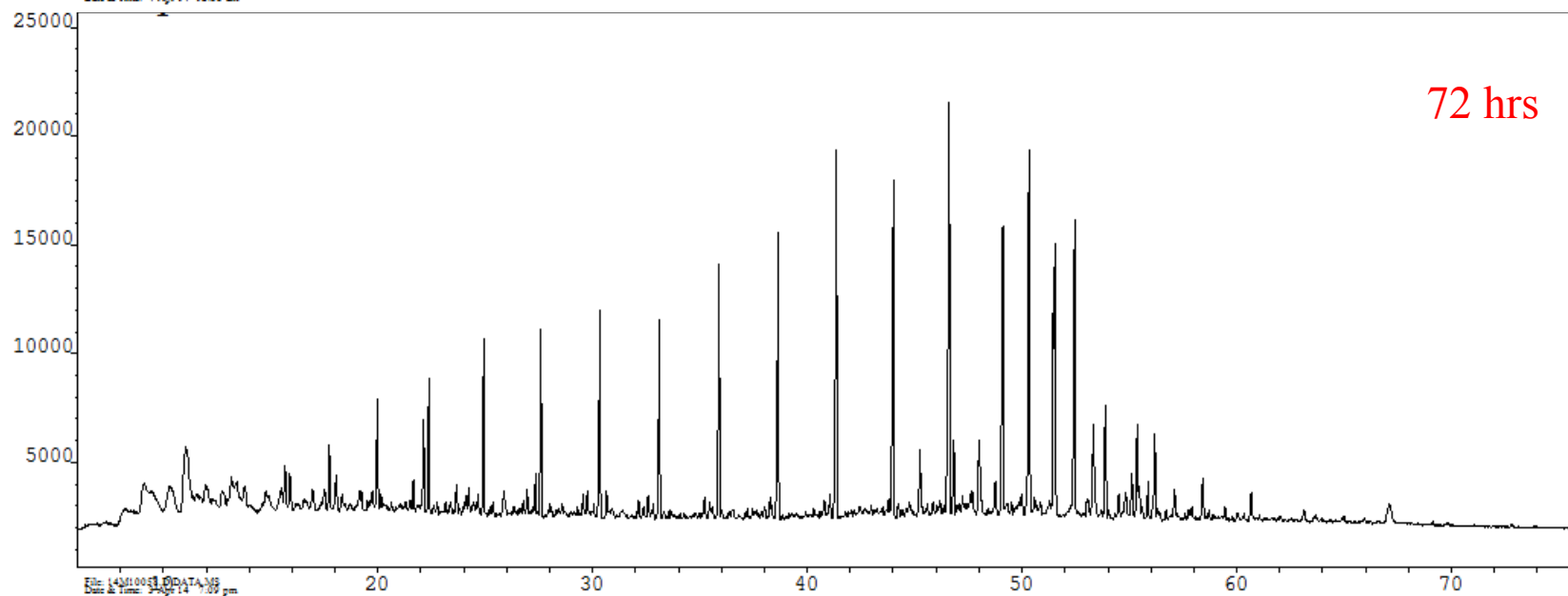
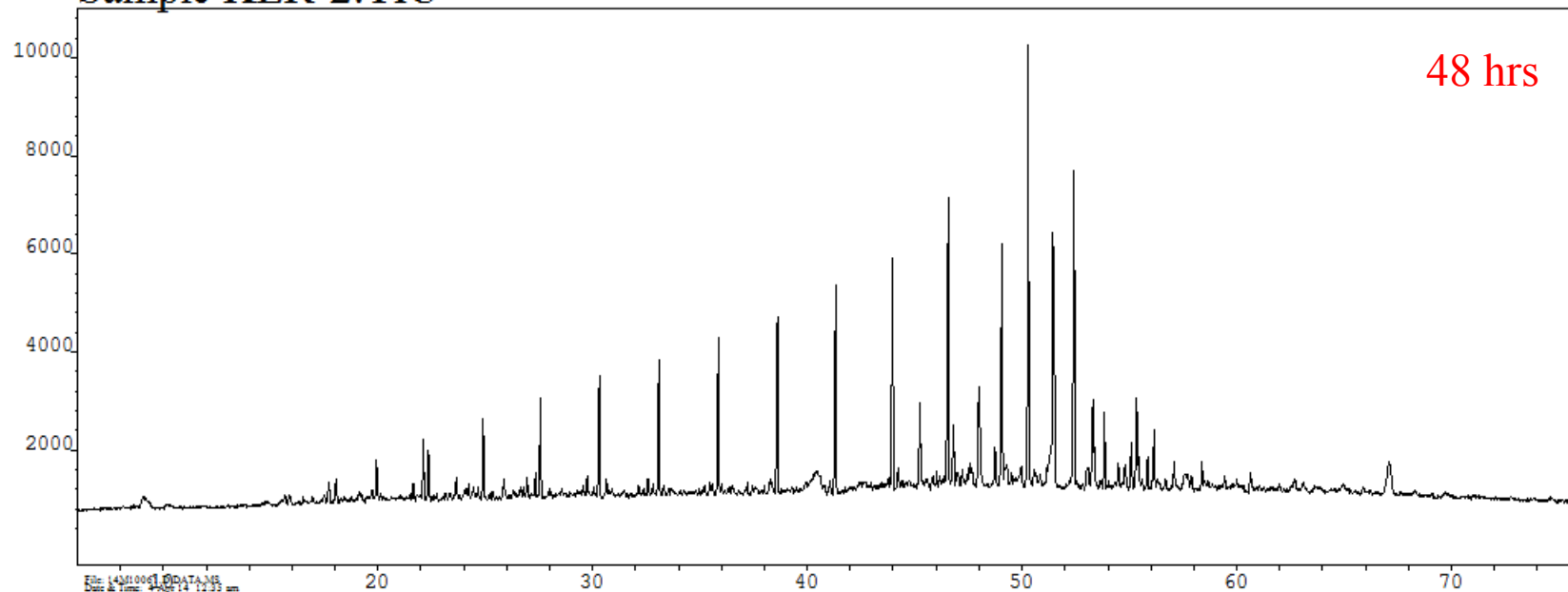


HPLC

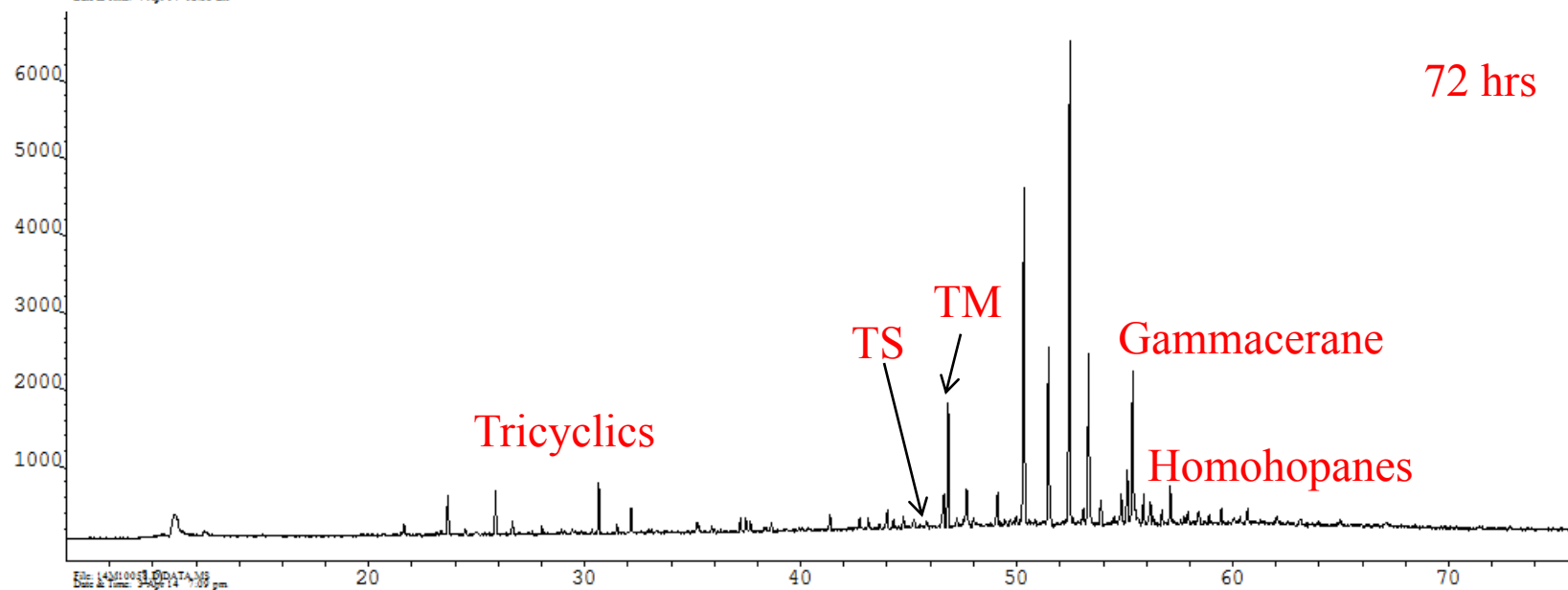
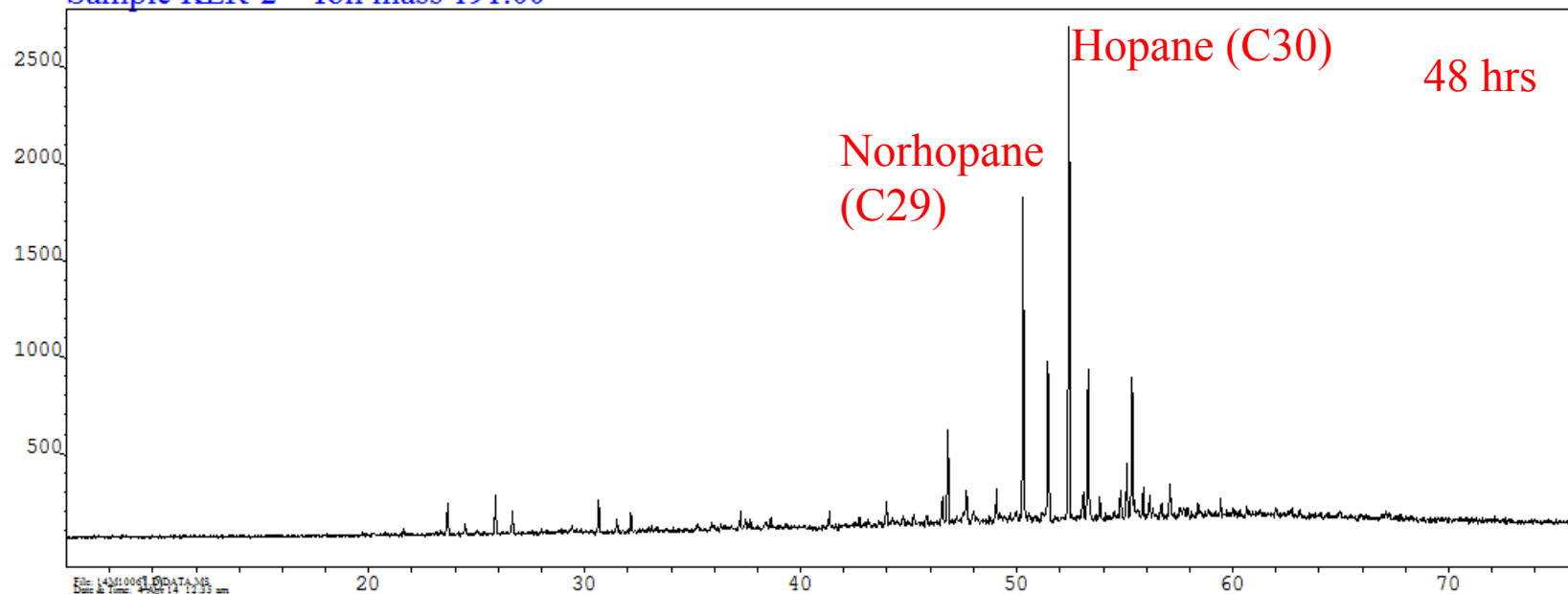


Saturated Biomarkers (GC-MS)

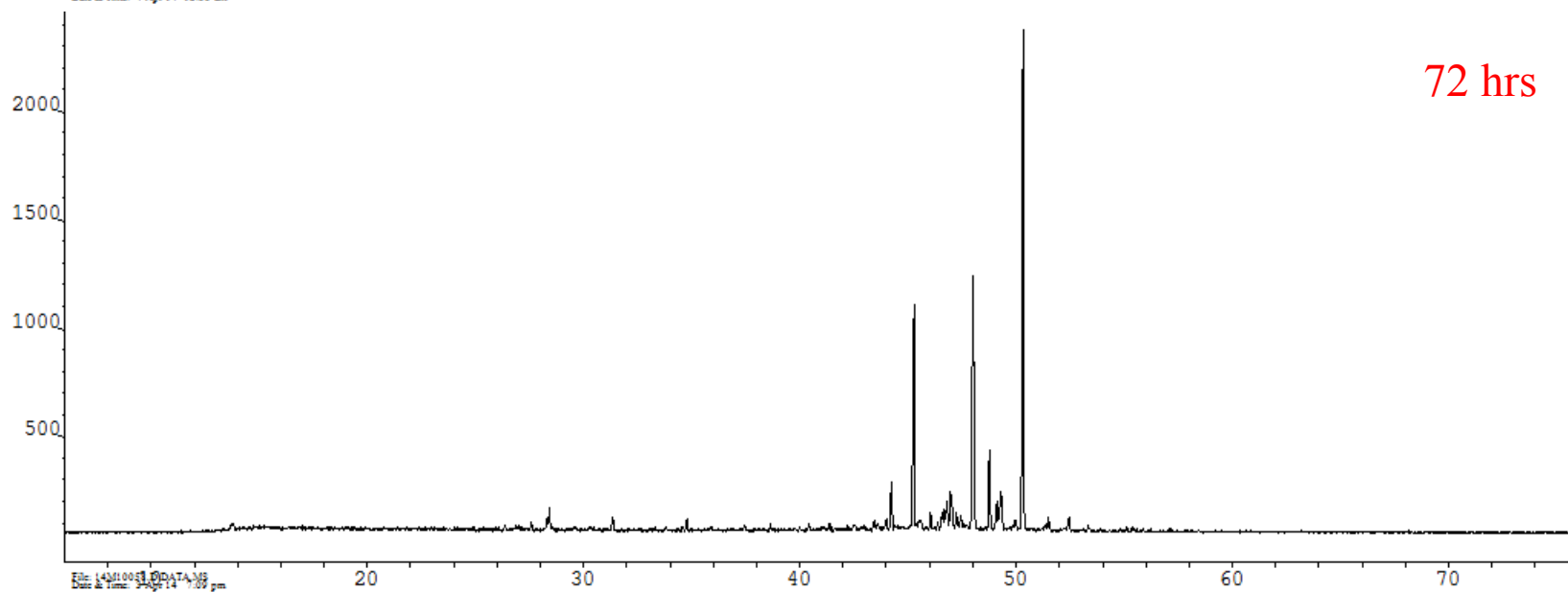
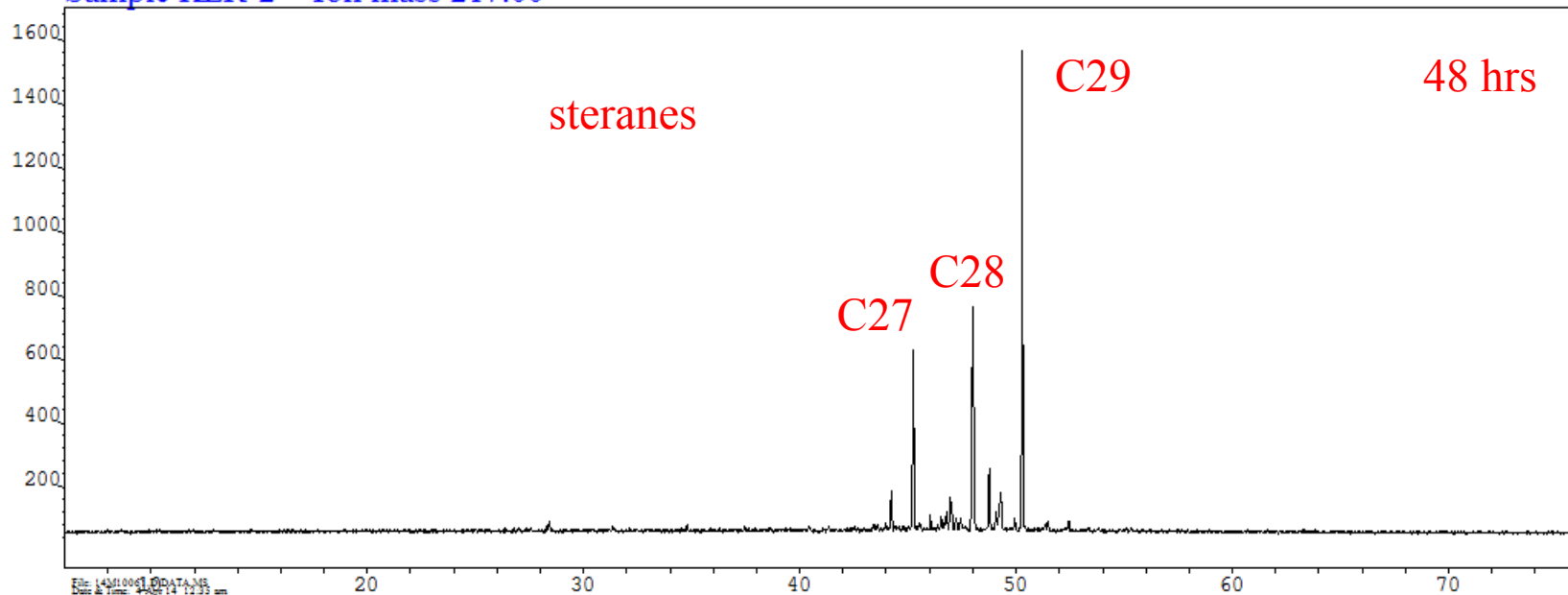
Sample KER-2:TIC

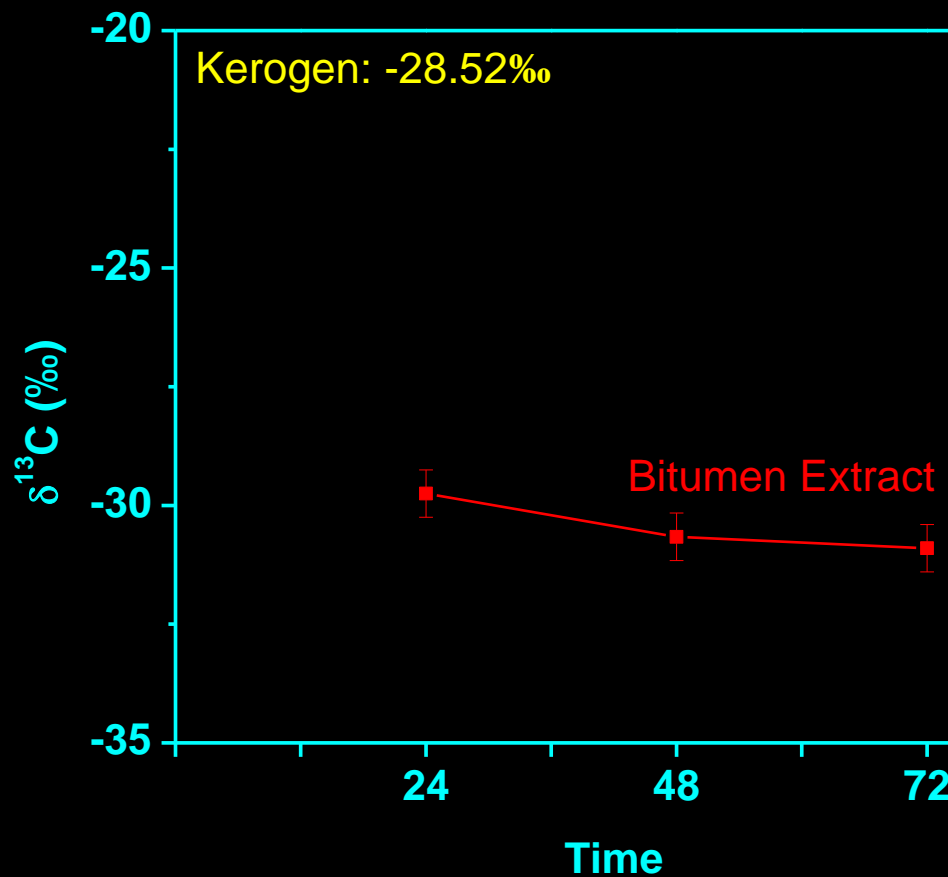


Sample KER-2 Ion mass 191.00



Sample KER-2 Ion mass 217.00

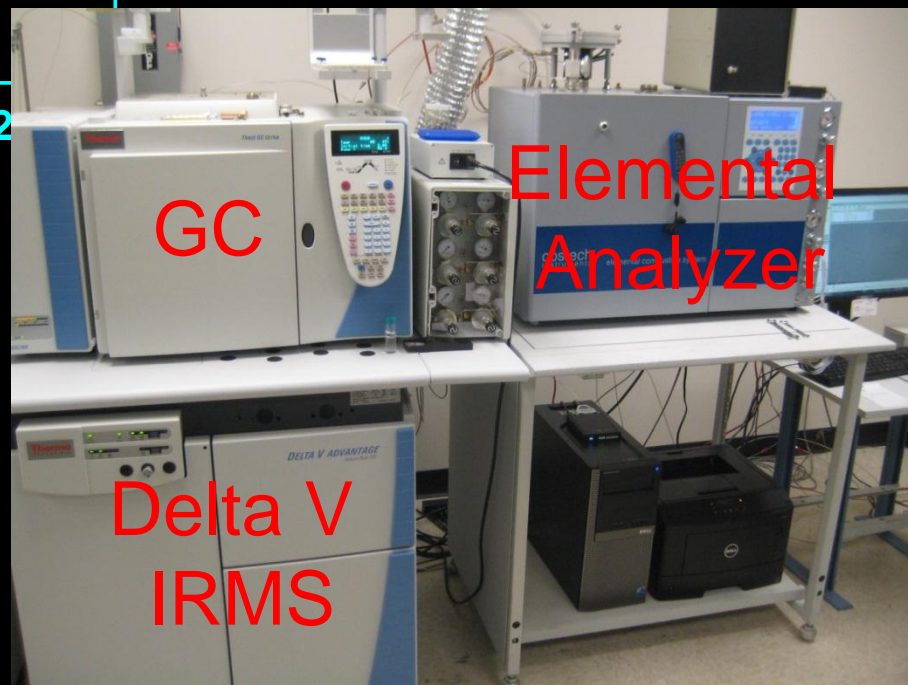


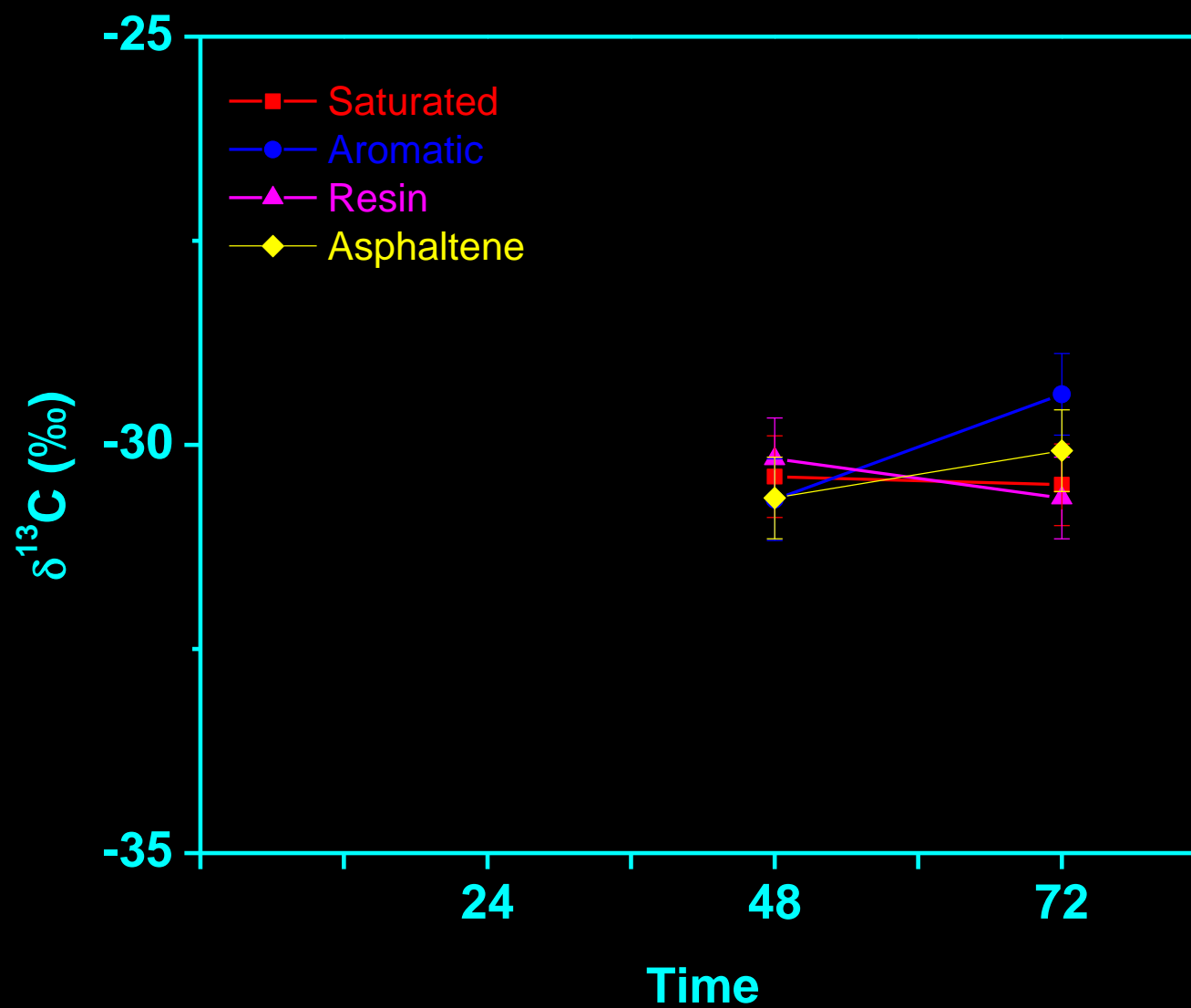


carbon isotope

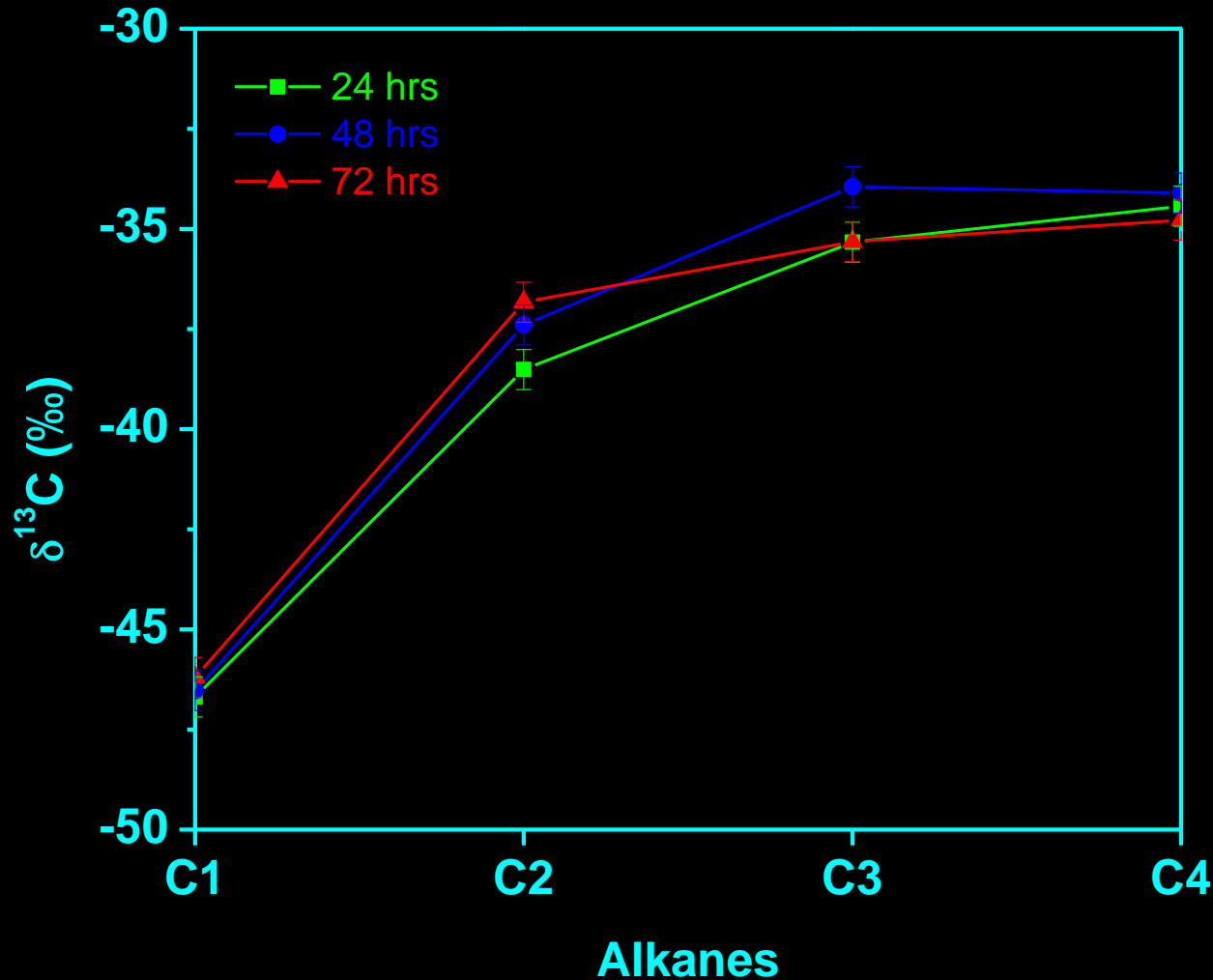
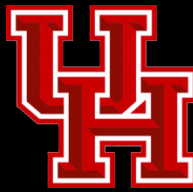
GC-EA-IRMS

- $\delta^{13}\text{C}$ of bitumen becomes lighter with time, and $\sim 2.5\text{‰}$ lighter than original kerogen after 72 hrs





Gas hydrocarbons



- abundances of n-alkanes decreases with carbon number
- CO_2 is more abundant than alkanes, with $\delta^{13}\text{C}$ of -22.4‰

Conclusions

- Chemical compositions: aromatic fractions become abundant with time, with saturated biomarkers showing low maturation after 72 hrs.
- Bitumen extract becomes lighter in ^{13}C with time, which most likely is caused by ^{13}C -depleted resin with higher abundance.
- While $\delta^{13}\text{C}$ values of C1 and C2 alkanes increase with time, it's not true for C3 and C4 after 72 hrs. Overall, $\delta^{13}\text{C}$ of C1 – C4 alkanes follow the “thermogenic” trend at experimental conditions.



Future Work

- Other potential controlling factors: redox, mineral, etc.
- Different kerogen types
- Compound-specific isotope analysis of SARA fractions
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