#### Application of Oil Gravity and Sulfur Content Relationships to Oil Typing and Source Rock Kinetics\*

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#### **Abstract**

API gravity and sulfur (S) content of crude oil are a function of the organic composition and thermal maturity of the source rock as well as oil alteration effects such as biodegradation, water washing, and thermal cracking. Orr (1986, 2001) has shown that the API gravity versus S content relationship is a function of the S content of the source kerogen, and he defined linear boundaries that differentiate oils derived from high sulfur kerogen (Type II-S), medium sulfur kerogen, or low sulfur kerogen. This study builds on Orr's work to develop a method to utilize gravity versus S relationships in chemometric oil typing studies and in basin modeling studies where source-rock organic S content and oil generation kinetics are unknown.

Assuming an x axis intercept of zero % S at 40 degrees API, a slope value for an oil can be calculated: wt% S/(API gravity - 40). Oils with the same slope are derived from source kerogen with the same S content. For example, an oil with a slope of -0.125 (or greater) is derived from Type II-S kerogen, similar to Orr's line that separates the Type II-S and Type II zones. Oil families with known kerogen-sulfur content can be used as calibration for oils of unknown source to determine the appropriate kinetic parameters to use in basin modeling. Examples will be presented illustrating the application of this method to oil typing chemometrics and basin modeling and the limitations of this approach due to oil alteration effects.

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# Application of oil gravity and sulfur content relationships to oil typing and source rock kinetics

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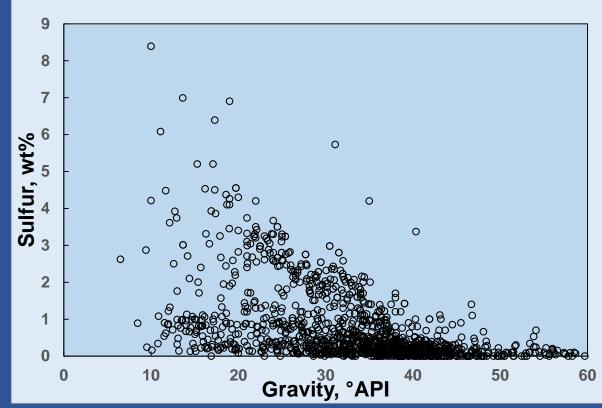
## Summary

- Slope S/Gravity 40 is a quantitative genetic parameter
  - Assumption of 40°API gravity intercept
  - Not recommended for oils greater than 35°API gravity
  - Not recommended for oils with secondary alteration
- Applications for:
  - Genetic characterization of source rock depositional environment
  - Oil-oil correlation with chemometrics
  - Basin modeling / kinetics of oil generation



### Introduction

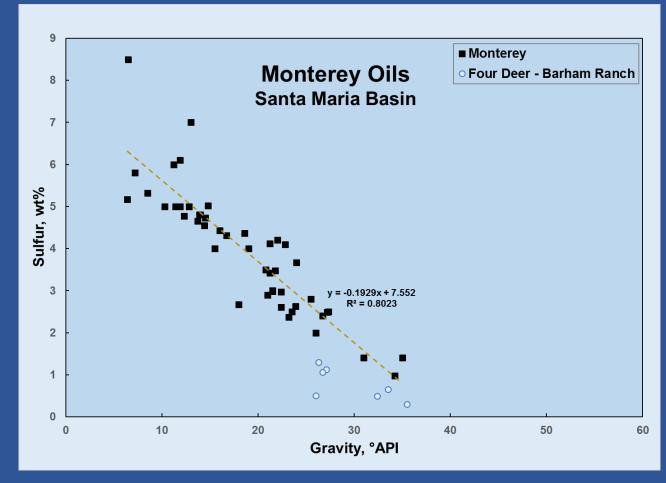
- Oil Gravity Specific gravity Density
  - Degrees API = [141.5/specific gravity] 131.5
- Sulfur content (wt%)
  - Organic sulfur
- Typically are plotted together





## Introduction - previous studies

- Long recognized that Sulfur vs Gravity plots of oils often form a linear trend representing an interdependent genetic relationship
  - Hunt (1953)
  - McIver (1962)
  - Evans et al. (1971)
  - Gransch and Postuma (1974)
  - Milner et al. (1977)
  - Orr (1978)
  - Tissot and Welte (1978)
  - Orr (1986)
  - Baskin and Peters (1992)
  - Baskin and Jones (1993)
  - Orr (2001)





### Introduction – previous studies

- Orr (1986) defined Type II-S kerogen
  - Orr, W.L., 1986, Kerogen/asphaltene/sulfur relationships in sulfur-rich Monterey oils: Organic Geochemistry, v. 10, p. 499-516.
- Orr (2001) defined Type II-S lines on Sulfur vs Gravity plot
  - Orr, W.L., 2001, Evaluating kerogen sulfur content from crude oil properties: Cooperative Monterey Organic Geochemistry Study, in C.M. Isaacs, and J. Rullkötter, eds., The Monterey Formation: From rocks to molecules: New York, Columbia University Press, p. 348- 367.



## Orr (2001)

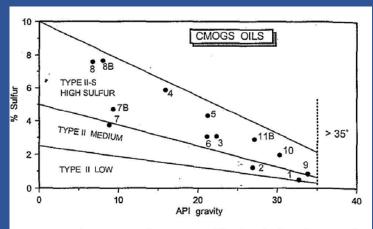


Figure 19.6 Source-kerogen-sulfur-level classification by % S versus API gravity relationships showing CMOGS oils.

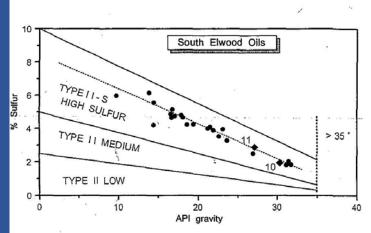
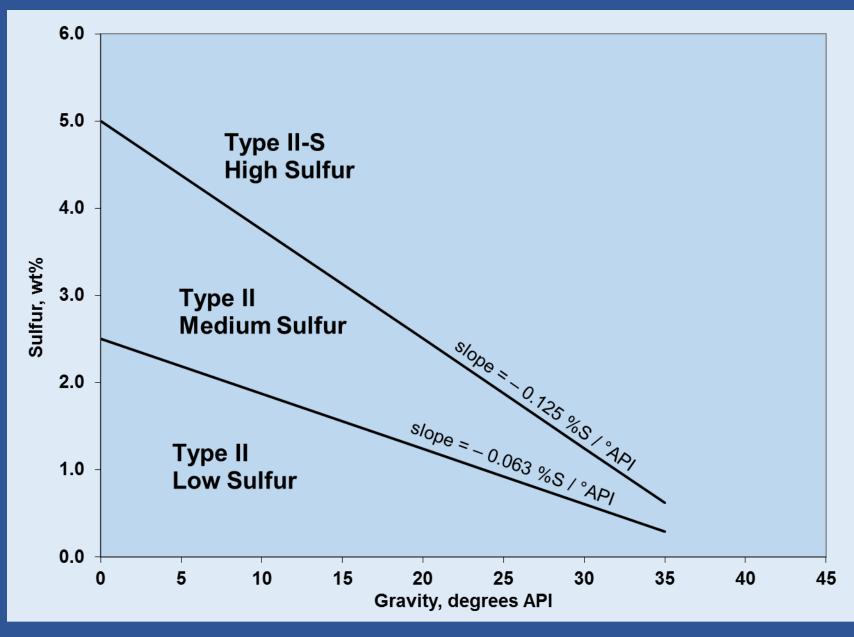


Figure 19.7 Comparison of South Elwood Oils 10 and 11B with previous analyses of South Elwood Monterey oils (Orr 1986, with unpublished additions).





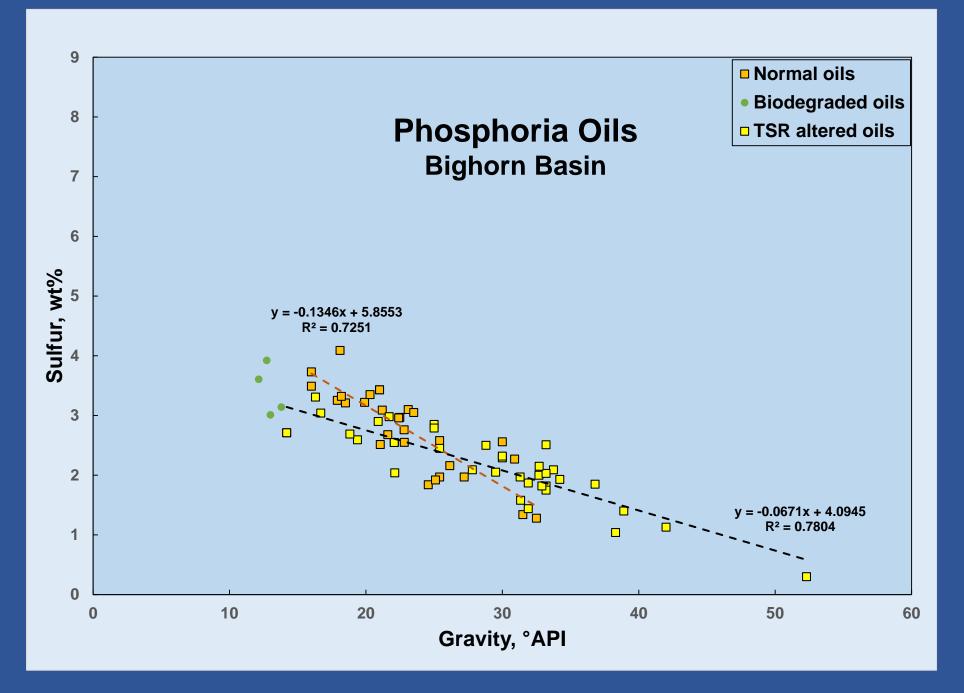
## Introduction – processes

- Primary process
  - Source rock kerogen organic sulfur content (organic S/C)
  - Source rock maturity at oil expulsion
  - Genetic interdependent relationship API Gravity vs. wt% Sulfur
- Secondary effects
  - Biodegradation/water washing
  - Thermochemical sulfate reduction (TSR)
  - Oil cracking



# Primary processes and secondary effects

Lillis and Selby (2013) GCA, v. 118, p. 312-330.





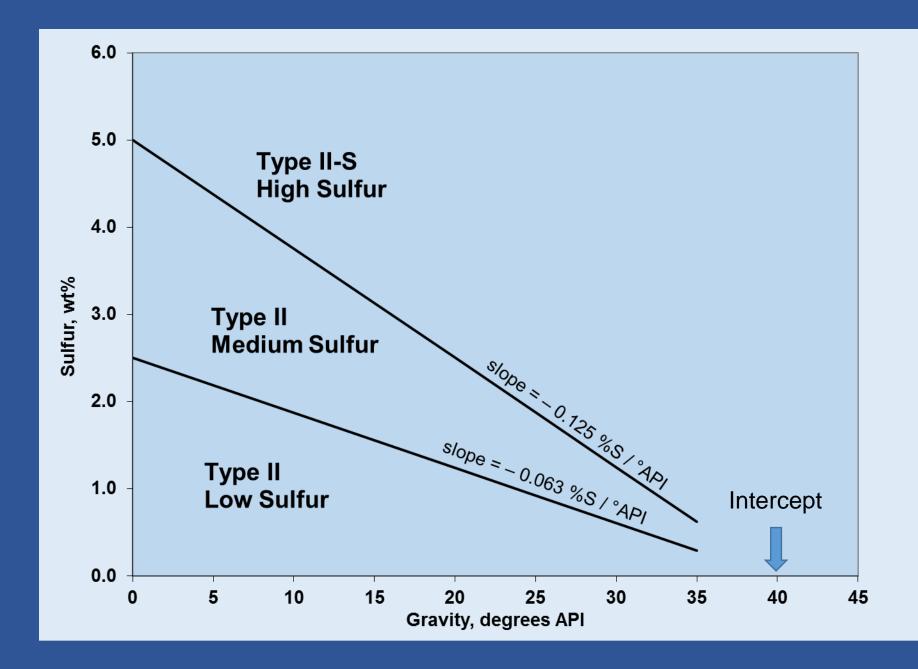
## Approach

- Problem Genetic oil type has distinct slope and intercept of S/API Gravity but cannot be represented as a single value
- Assume an intercept of 40 gravity (°API) at zero % sulfur content
  - Based on Orr (2001)
- Slope (m) = wt% S / (API gravity 40)
- Solution quantitative genetic parameter useful for chemometric analysis



## Orr (2001)

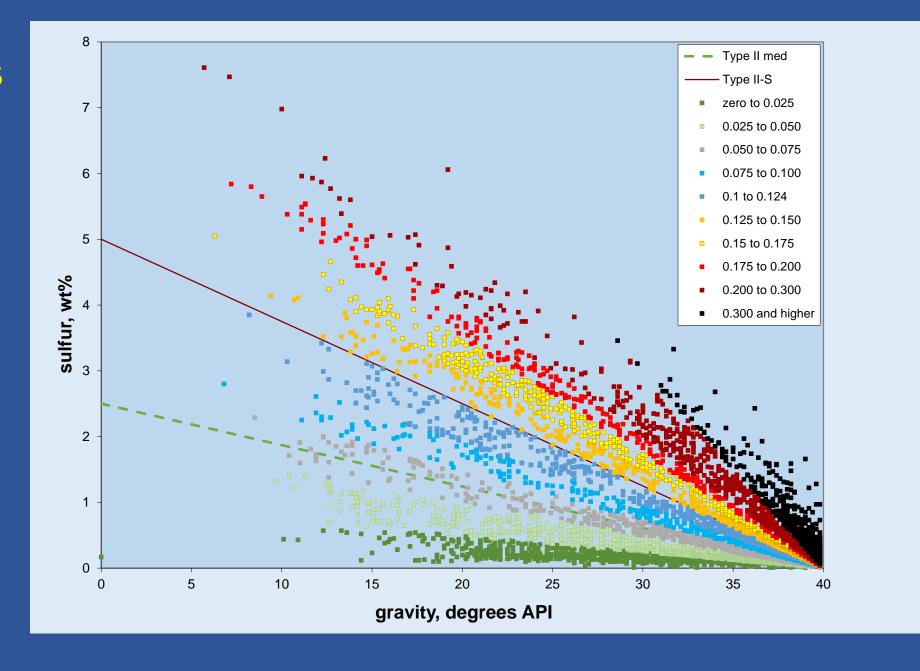
Assume intercept = 40°API





Example: U.S.
Bureau of Mines
Database Slope (m) =
S/(Gravity – 40)

n= 6295



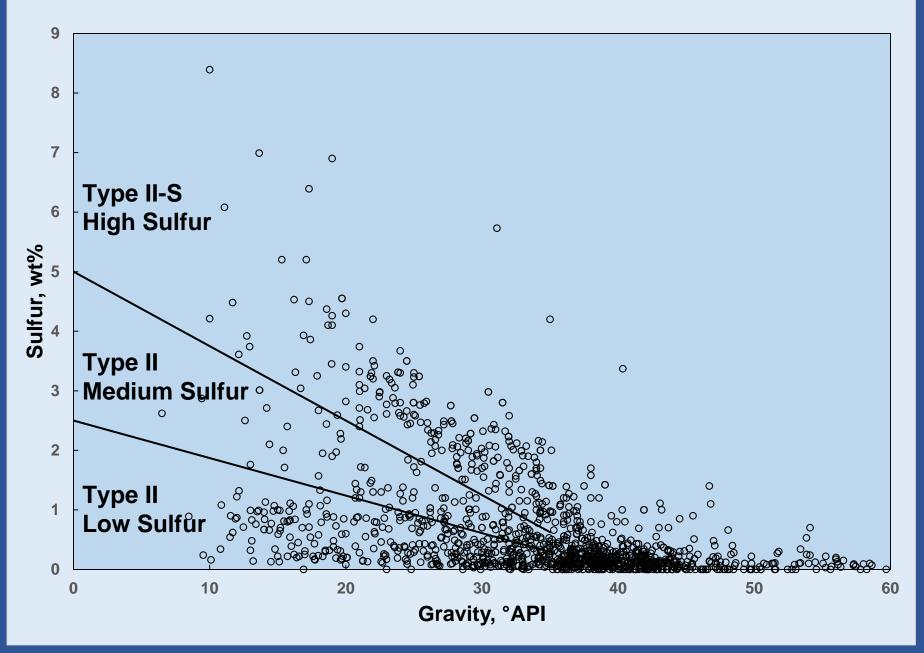


### Limitations

- Assumption of 40 gravity intercept
  - Cannot be used for oils greater than 40°API
- More scatter/error greater than 35° API
- Secondary effects will affect the slope
  - Biodegradation/Water washing
  - Thermochemical sulfate reduction (TSR)
  - Oil cracking
- Oil mixing from multiple sources



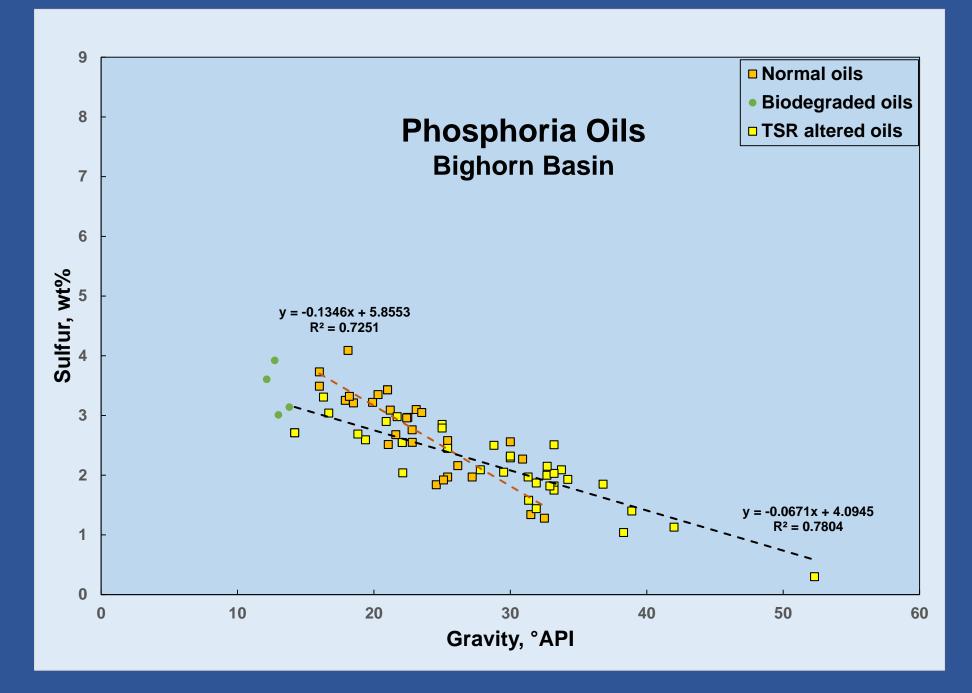
### Limitations not recommended above 35 °API





## Limitations - secondary effects

Lillis and Selby (2013) GCA, v. 118, p. 312-330.





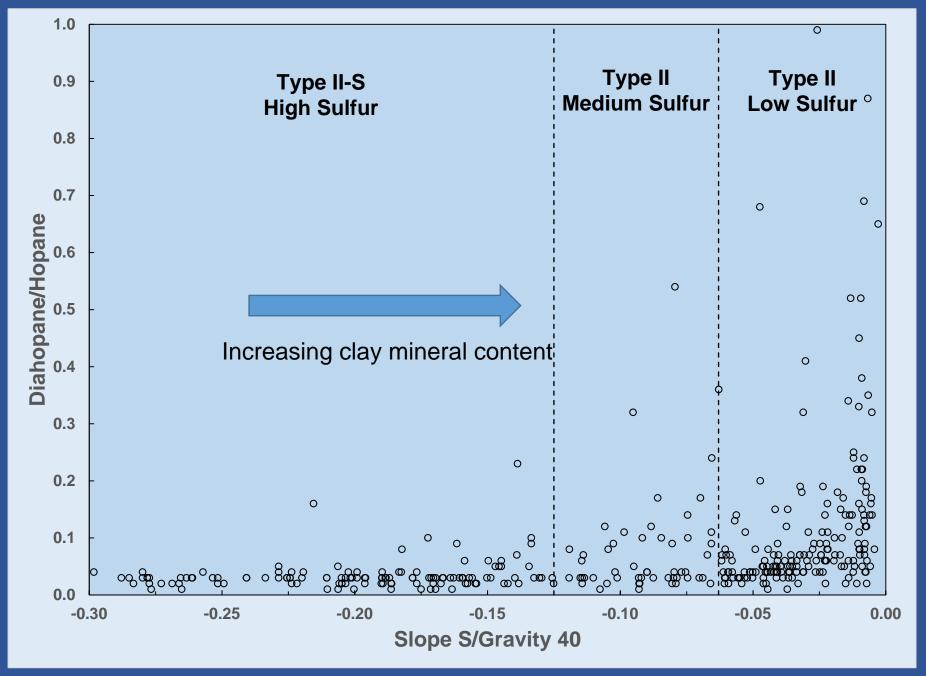
## Applications

- Oil Typing Studies
  - Genetic characterization of source rock depositional environment
  - Chemometric oil-oil correlation
- Basin Modeling Studies
  - Kinetics of oil generation if source is unknown



Diahopane

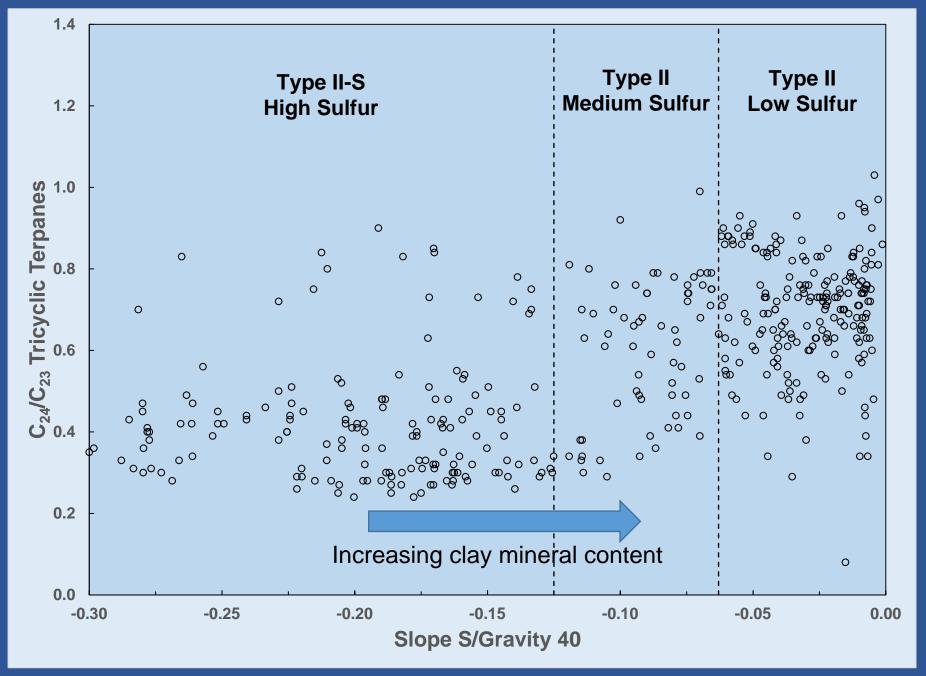
oxic-suboxic or clay mineral rich environment





C<sub>24</sub>/C<sub>23</sub> Tricyclics

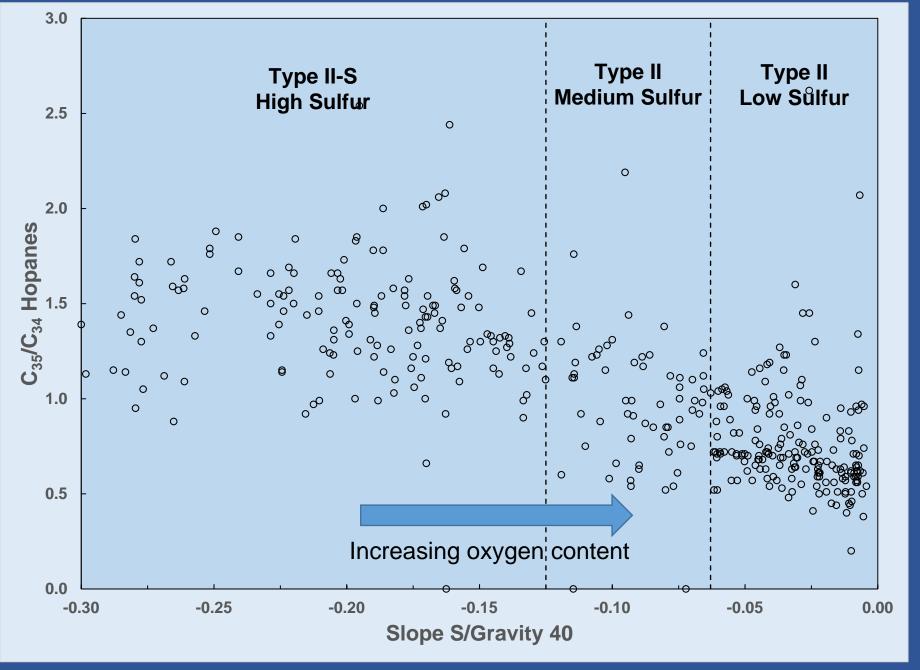
clastic/clay mineral rich environments





C<sub>35</sub>/C<sub>34</sub> homohopane index

anoxia indicator/ marine carbonates





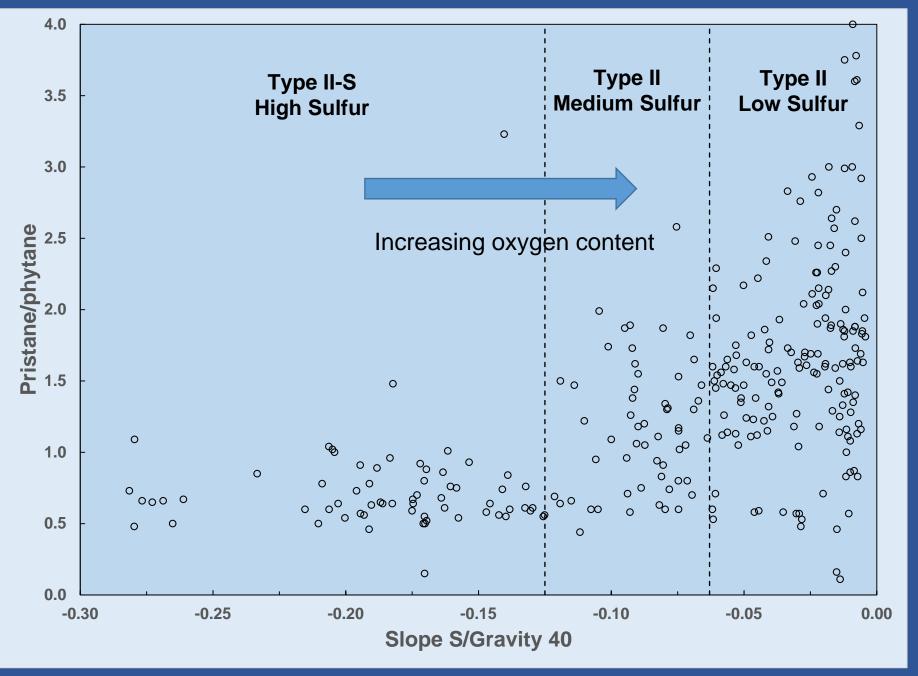
Pristane/phytane (after Hughes et al 1995)

>3 = fluvial-deltaic, periodically oxic/dysoxic

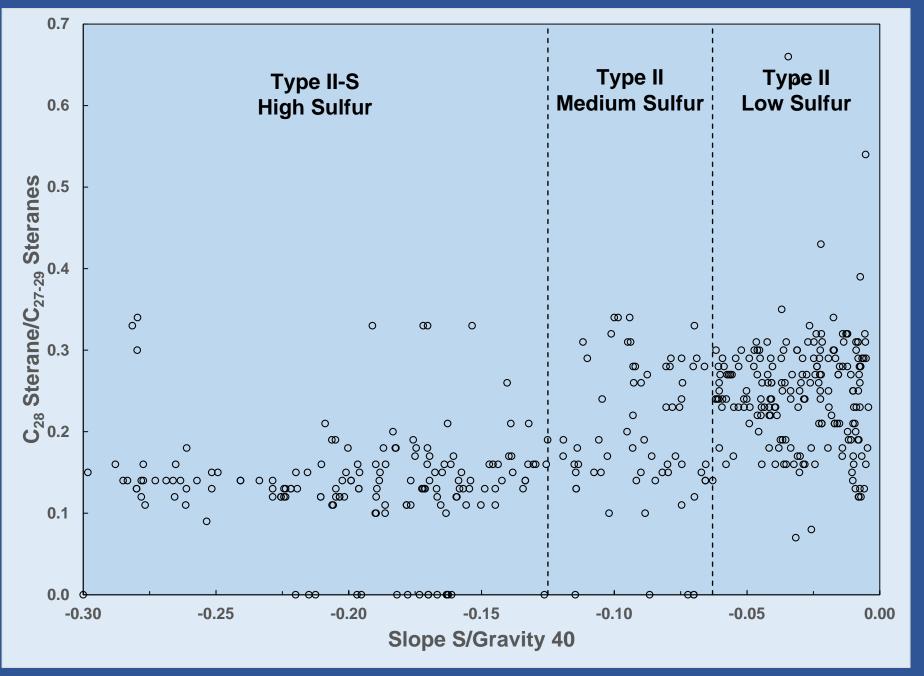
1 to 3 = marine/lacustrine, anoxic nonsulfidic

<1 = marine/lacustrine, anoxic sulfidic



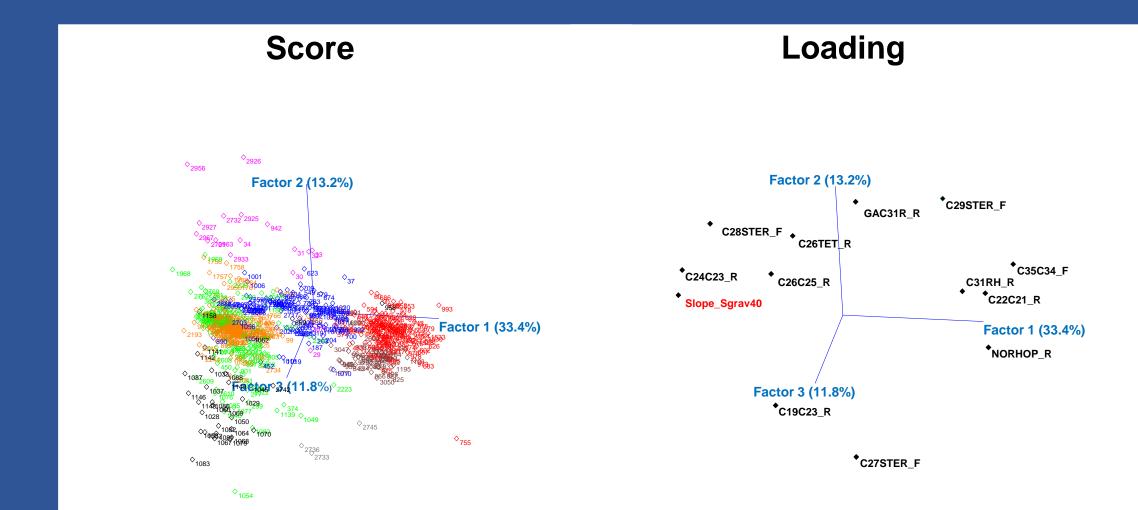


C<sub>28</sub> Steranes





#### Application for oil-oil correlation – chemometric analysis



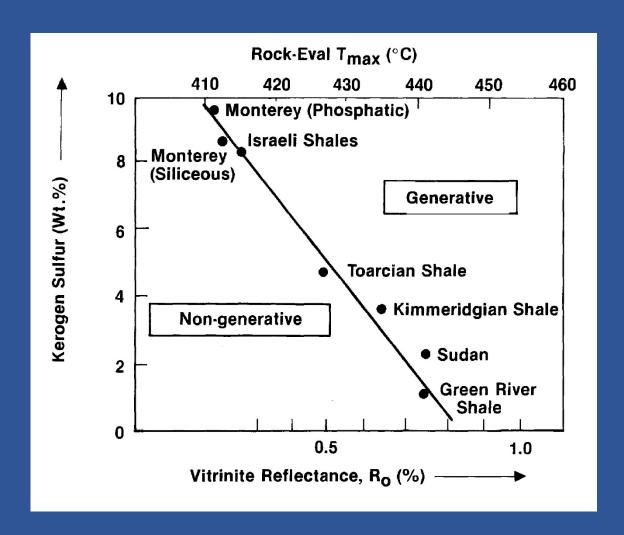


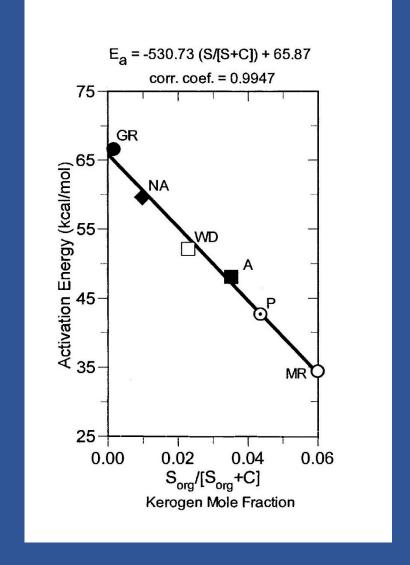
## Applications – kinetics of oil generation

- Kinetics a function of organic sulfur content
  - Wt% organic sulfur in kerogen
  - Organic S/C
  - Type II-S has S/C > 0.04 (Orr, 1986)
- Slope S/Gravity reflects S/C



#### Correlation between kerogen sulfur content and kinetics of oil generation

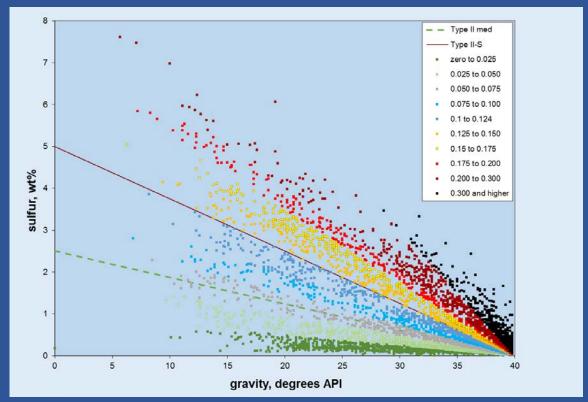




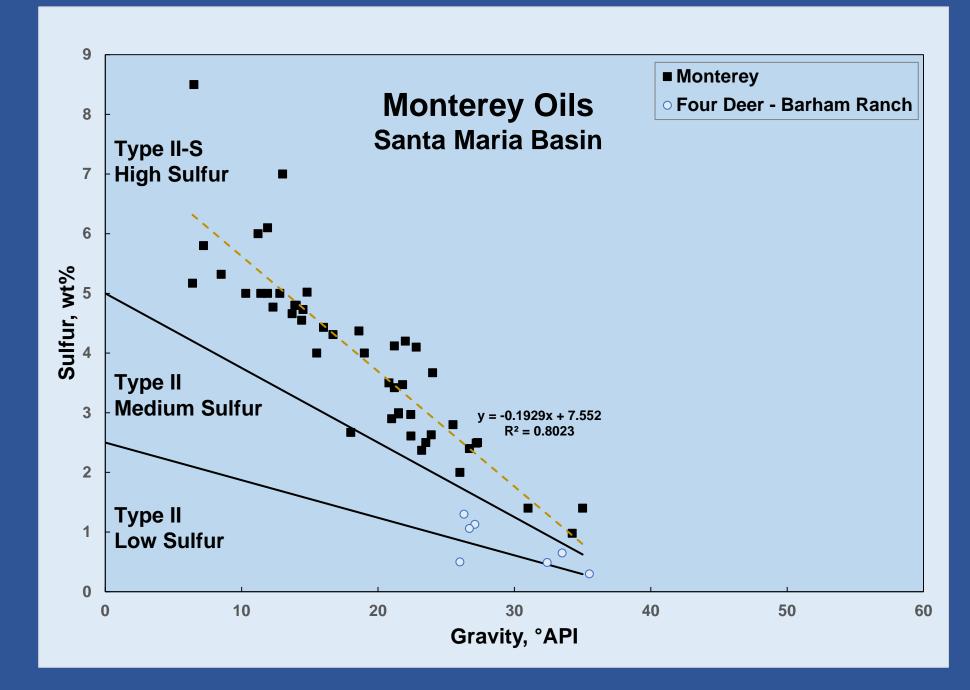


## Applications – kinetics of oil generation

- Use analog source rock oil types with known kinetics
- Assume oil type with similar slope has similar kinetics.

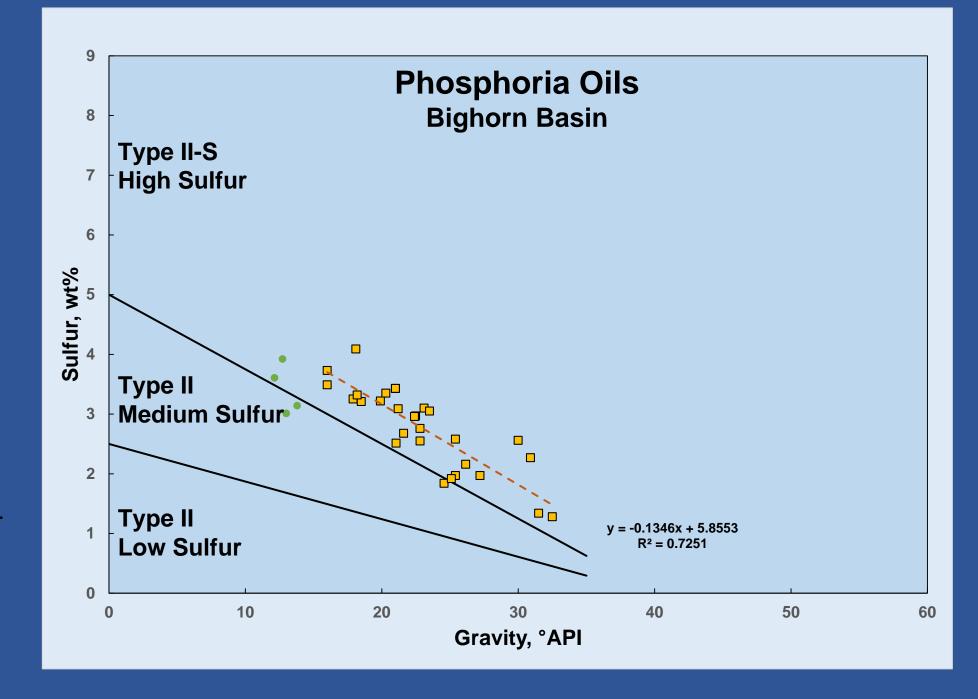




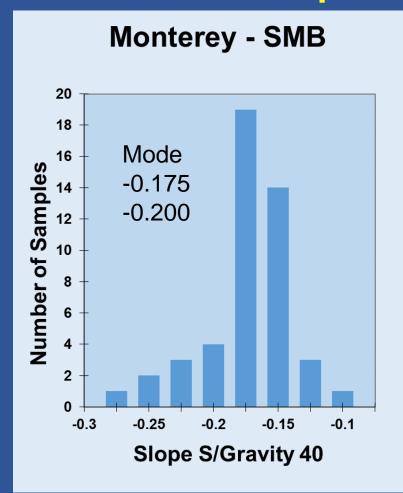


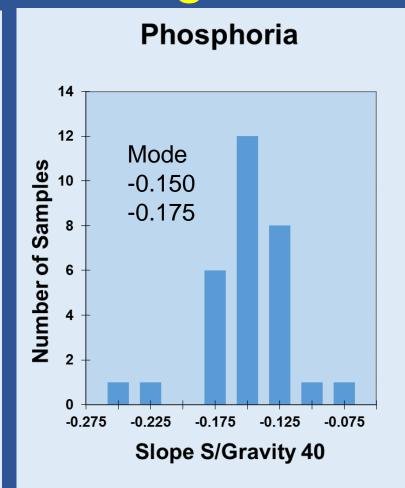


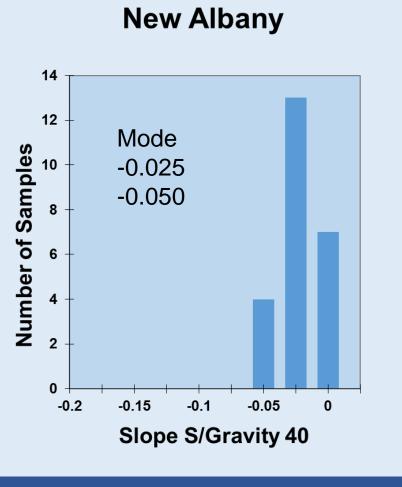
Lillis and Selby (2013) GCA, v. 118, p. 312-330











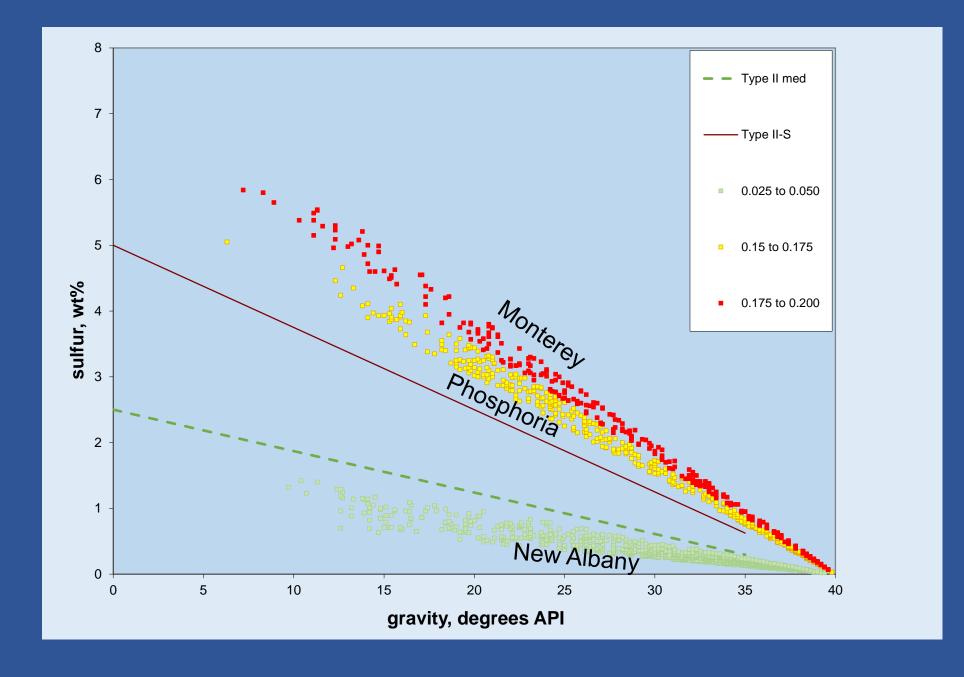
34.3 kcal/mole

42.7 kcal/mole

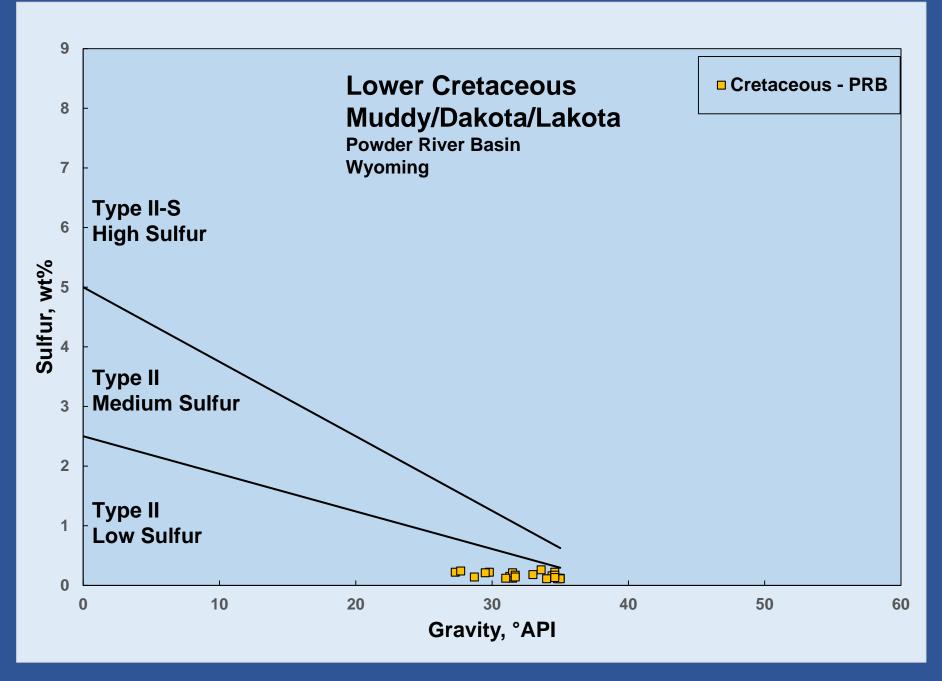
59.6 kcal/mole



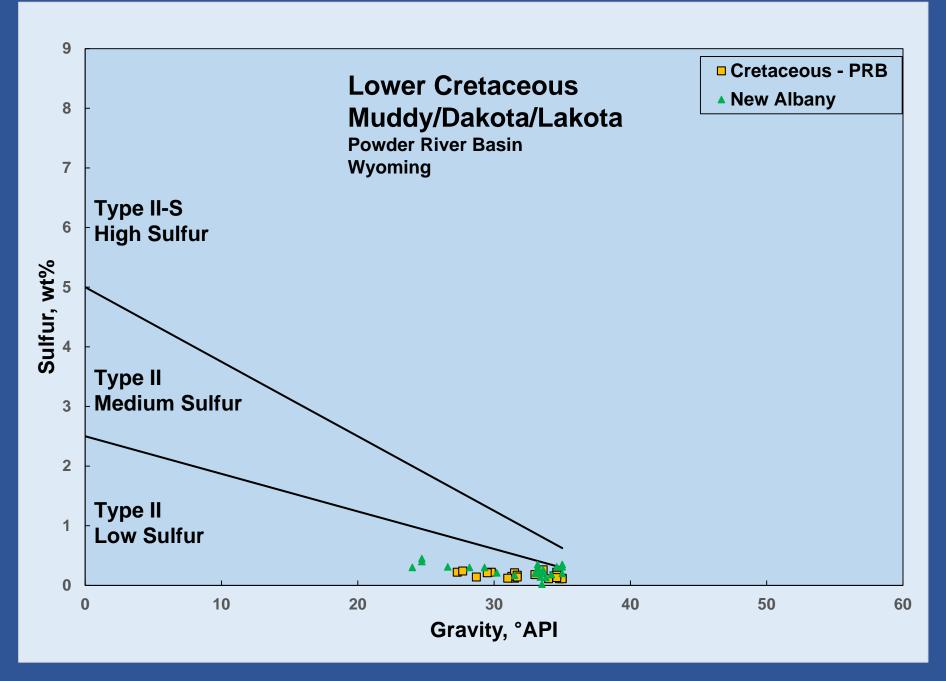
## analogs with known kinetics













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