Study of the early stage immature oil produced from the Israeli oil shale, Ghareb and Mishash formations

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Introduction

Recent attempts to develop oil production from the Senonian oil shale deposits of Israel sparked an interest in studying the properties of the oils produced from this type of source rock. The oil shale of the upper Cretaceous Ghareb and Mishash formations are organic-rich chalks with up to 20% of kerogen by volume. The kerogen has high percent of sulfur which classifies it as Type II-S (Orr, 1986). During thermal maturation of a type II-S kerogen, the oil initially released is sulfur-rich due to preferential breaking of weak sulfur-sulfur, or sulfur-carbon bonds. This leads to high concentration of asphaltenes, resins and aromatics that all together make the initial oil dense, viscous and rich in sulfur (Orr, 1986). An additional outcome of breaking weak sulfur bonds is the release of thermally unstable alkyl thiophenes; these compounds might play an important role in determining the viscosity of the early produced oils as they can act as solvents for other compounds in the oil, thus lowering the bulk viscosity of those oils.

Methods

Oil shale samples from the Aderet borehole in the Shfela basin were subjected to semi-open anhydrous pyrolysis at two heating rates: 2 °C/day and 120 °C/day. Oils were collected at designated temperatures and analyzed. API gravity and viscosity of the produced oils were determined by pycnometer and viscometer measurements at 40°C (Zeitfuchs, Cannon instrument). N-alkanes, alkyl thiophenes ($C_n > 10$) and benzothiophenes concentrations were determined by GC-MS (7890A and 5975B, Agilent Technologies). Total sulfur content was determined by LECO carbon - sulfur analyzer (LECO SC632 elemental analyzer). Thermal maturation of oils was estimated from the heating time-temperature program by using the EASY % R_O model (Sweeney and Burnham, 1990) and is represented as vitrinite reflectance equivalent (%R_O equiv.).

Preliminary Results

Produced oils are found to contain high sulfur content (1.6-19.2%) which decreased in their concentration upon maturation of the rock (Fig. 1). The total decrease of sulfur content seems to be continuous and cannot be explained by the formation and decomposition of the analyzed thiophenes and benzothiophenes alone (Fig. 1), suggesting an additional, more abundant sulfur species that controls the observed decrease. The viscosity of oils varies irregularly with respect to thermal maturation and seems to be unrelated to the alkyl thiophene content of the oil (Fig.2). API gravity increases with respect to N-Alkanes content (Fig. 3). Variation of API gravity with respect to kinematic viscosity and thermal maturation shows a similar trend to the one observed by Baskin and Peters (1992) for California oils but on a different magnitude (Fig.4). Correlation to other type II-S oils from Israel show similar trends viscosity, density and sulfur content (Fig. 4 and 5).

Preliminary conclusions

- Pyrolysis oils of the Ghareb and Mishash formations are type IIS oils with an exceptionally high sulfur percent.
- Pyrolysis oils have much lower viscosity than naturally occurring type IIS oils, probably due to low asphaltenes content.
- Variation of sulfur content seems to be independent of alkyl-thiophene ($C_n > 10$) and benzothiophene concentration.
- Heletz-Kokhav oils have probably originated from type IIS kerogen, this finding supports Bein and Sofer (1987) proposal of Barnea formation as the source rock for these oils.

References

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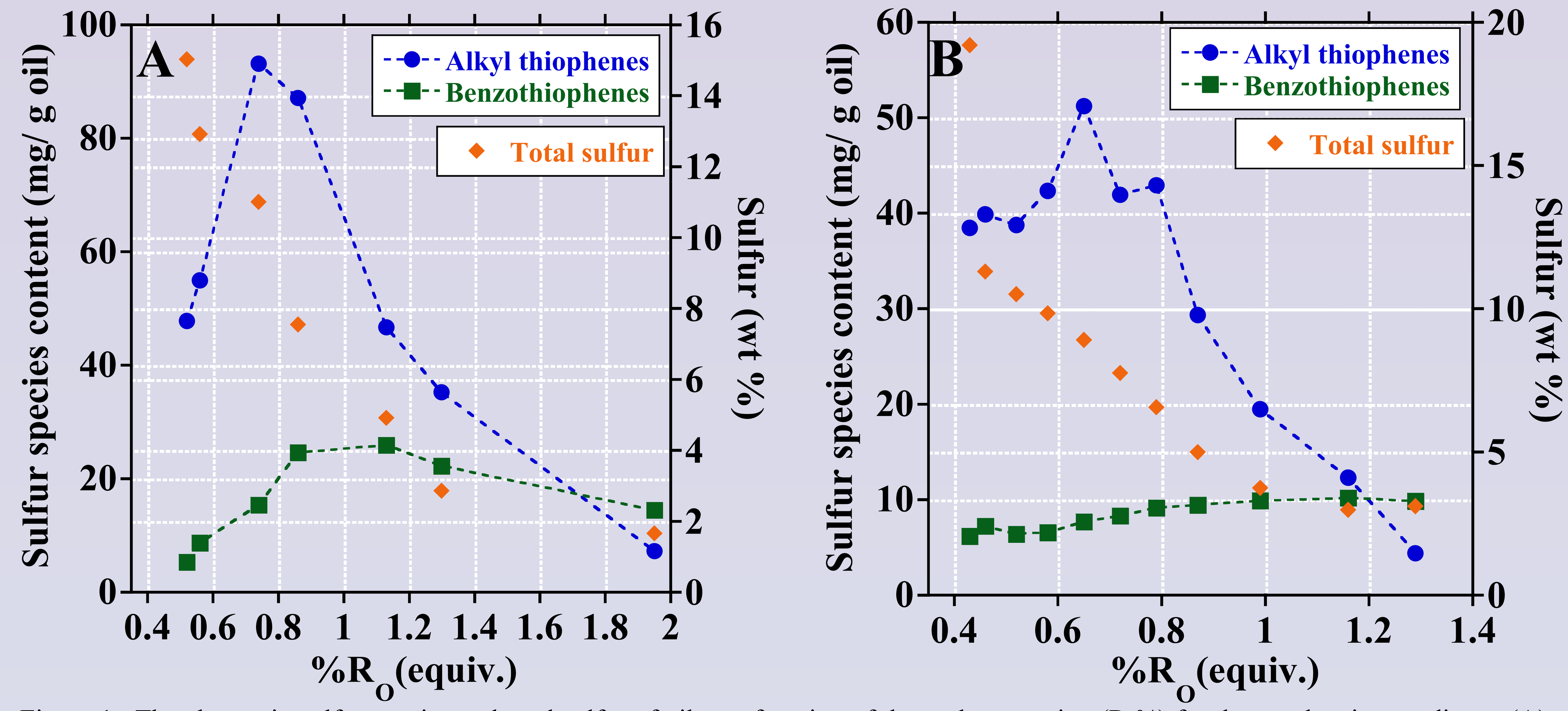

Figure 1 –The change in sulfur species and total sulfur of oil as a function of thermal maturation (R_o%) for the two heating gradients: (A)- 2°C/day, (B)- 120°C/day. The rhombs represent total sulfur of oil (wt.%). The dashed lines represent the sulfur specie content (mg/ g oil) .

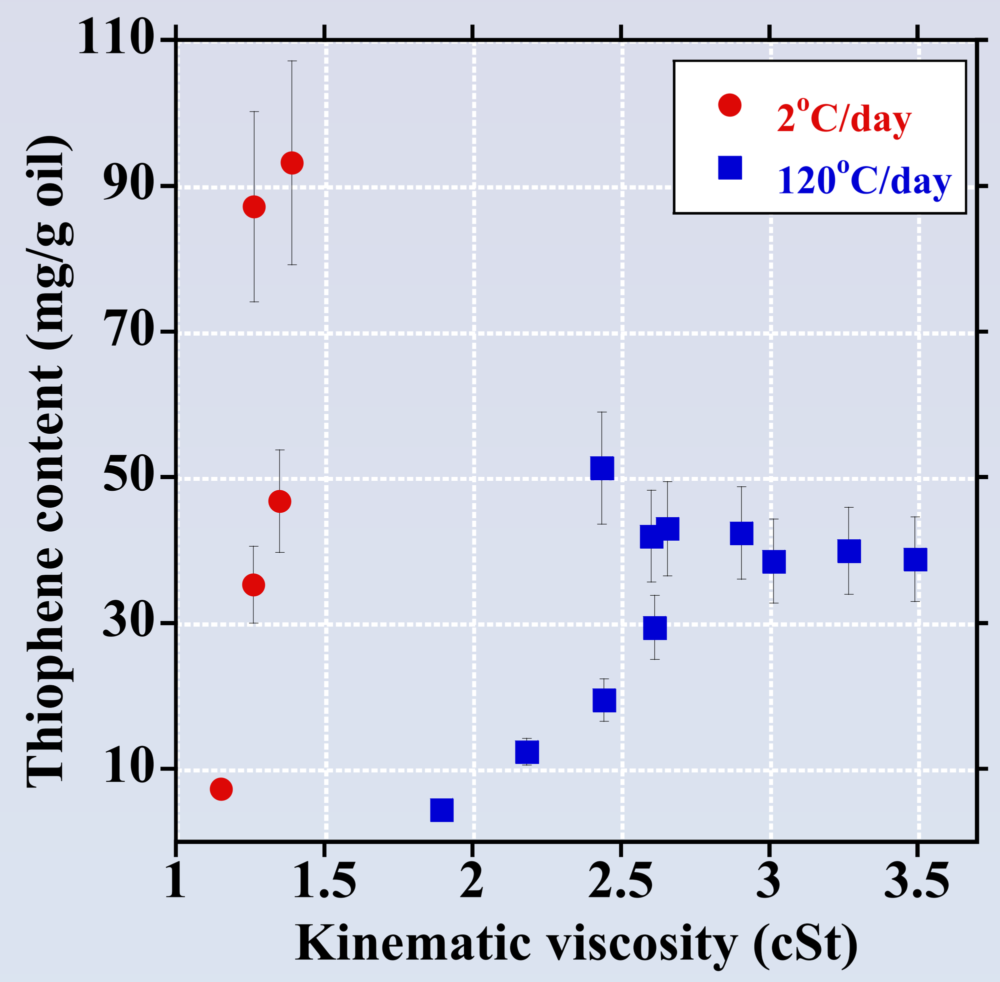

Figure 2 – The relation of thiophene content (mg/g oil) to kinematic viscosity (cSt). Error bars are smaller than the symbols.

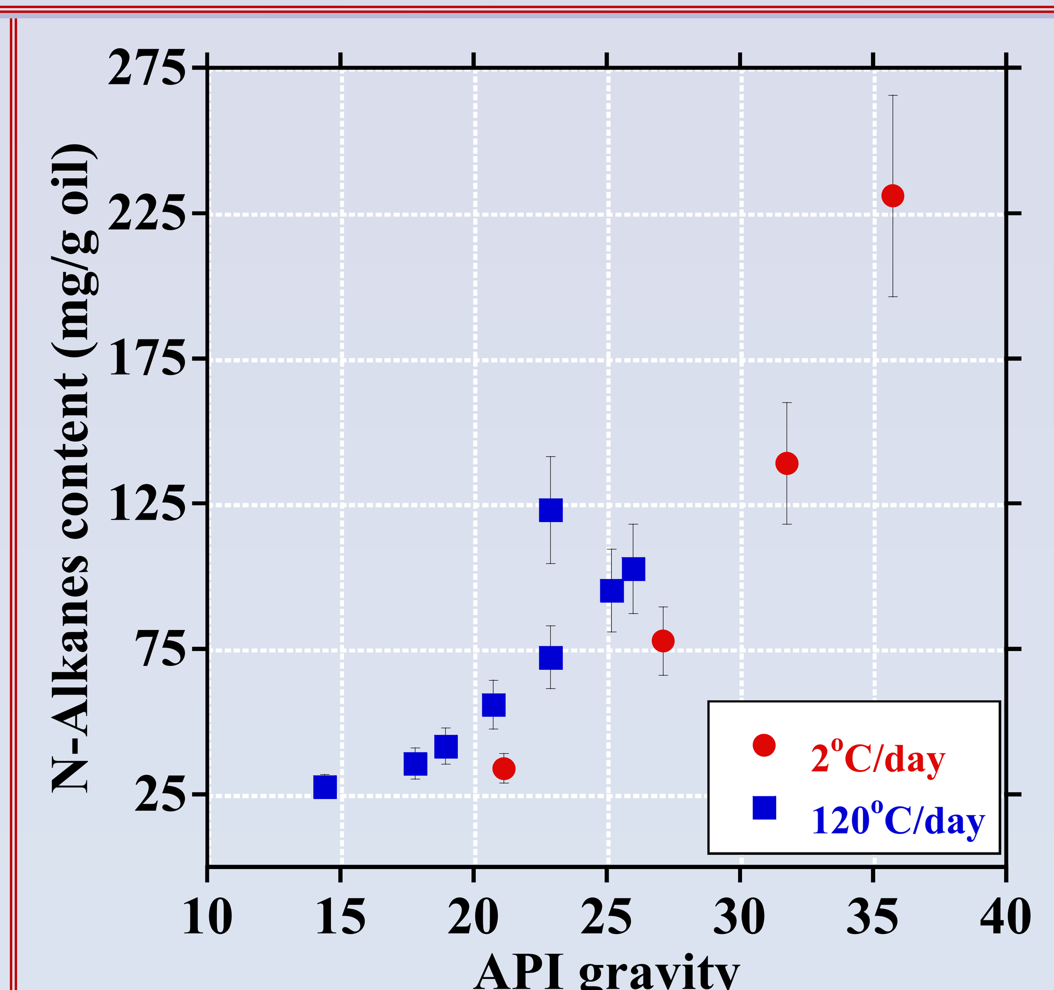

Figure 3 – The relation of N-Alkanes content (mg/g oil) to API gravity (°). Error bars are smaller than the symbols.

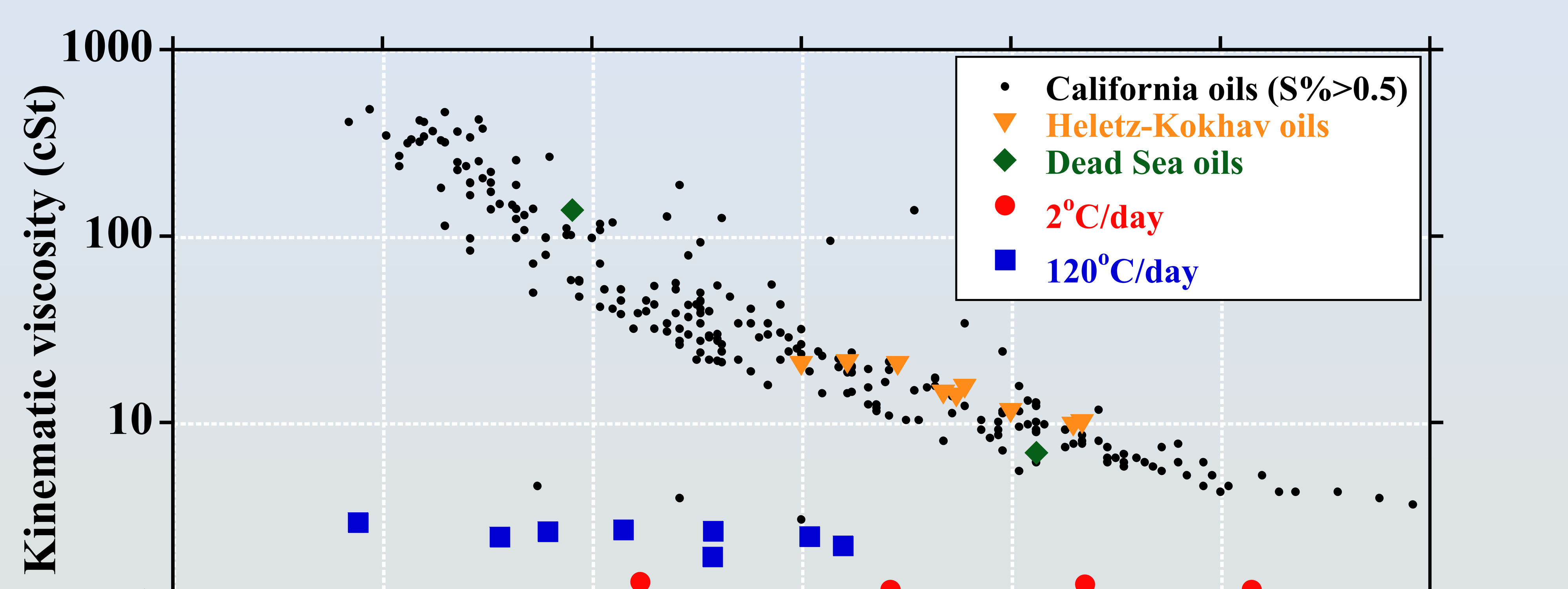

Figure 4 – The relation of kinematic viscosity (cSt) (Logarithmic scale) to API gravity (°) of oils. Black dots represent oils produced in California with sulfur content higher the 0.5%. Orange triangles represent oils produced at Helez and Kokhav fields of the coastal plane in Israel. Green rhombs represent oils produced at the Dead Sea basin. Red dots and blue squares represent the oils produced by pyrolysis.

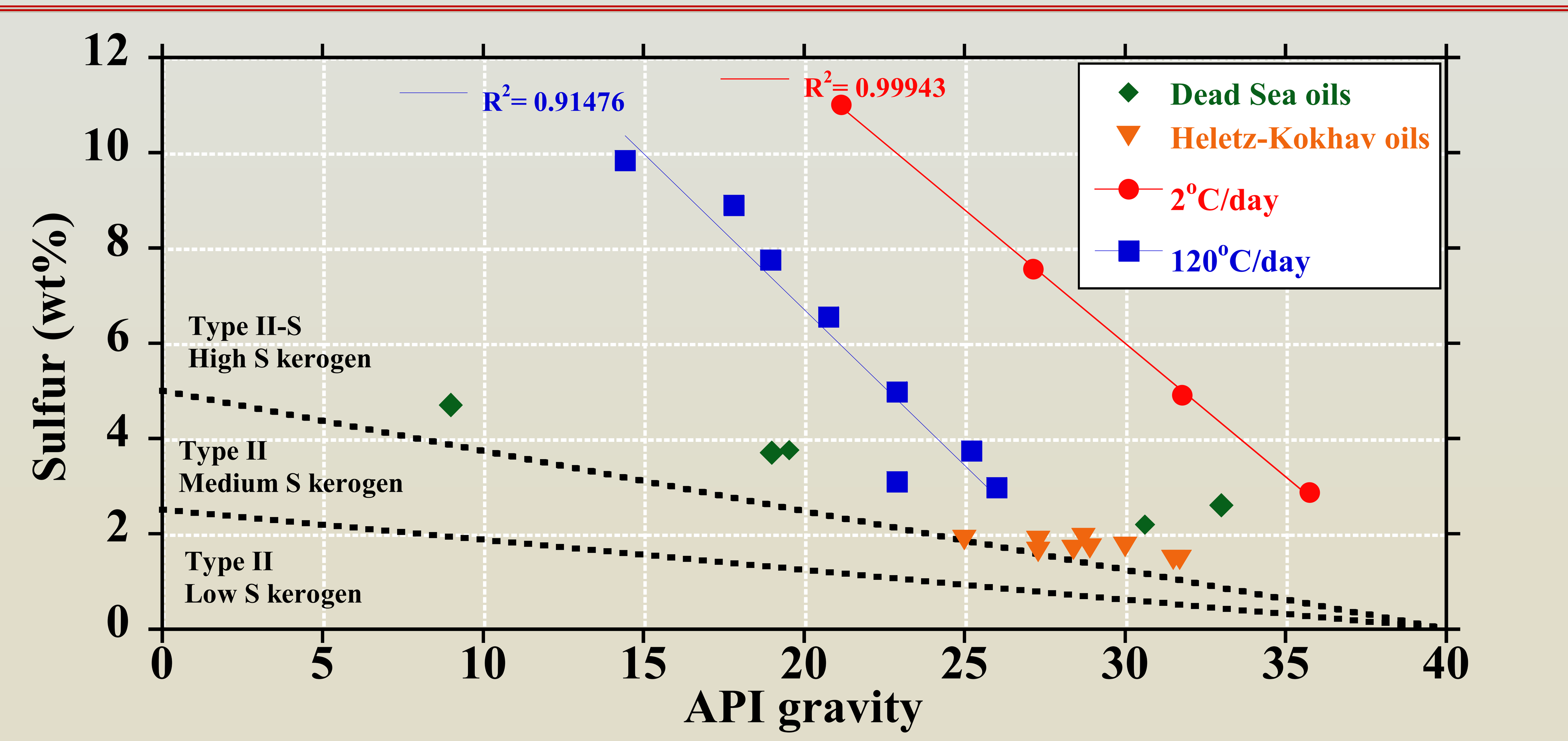

Figure 5- The relation of sulfur (wt%) to API gravity (°) of oils. Boundary lines are from Orr (2001). Orange triangles represent oils produced at Helez and Kokhav fields of the coastal plane in Israel. Green rhombs represent oils produced at the Dead Sea basin. Red dots and blue squares represent the oils produced by pyrolysis.