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Parameteric Controls on the Composition of Oil Generated by *In Situ* Pyrolysis of Oil Shale

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ABSTRACT: This paper describes closed-system experiments that examine the effects of two potentially important parameters during *in situ* pyrolysis of oil shale; hydrostatic pressure and effective stress. The starting material for all experiments was prepared from a large block of oil shale taken from the Mahogany Zone of the Green River Formation, Utah.

Effective stress on a rock is exerted by overburden and supported via the granular matrix of the rock. To generate effective stress in our experiments, a spring-loaded frame was constructed that applied stress to a 1-inch diameter sample. By using different sets of springs, the samples were loaded with up to 1000 psi. Samples were encased in Berea sandstone cylinders, jacketed in steel, and clamped to limit lateral strain. This uniaxial loading was similar to what the oil shale experiences *in situ*. Special alloy springs ensured that the load did not diminish as the springs were heated along with the sample. The entire device was placed in a Parr bomb for heating. The oil shale cores initially expanded, then shortened by the end of an experiment. The maximum expansion was recorded by a piece of gold foil wrapped on one of the load frame support posts.

Three experiments provide an example of how pyrolysis at progressively higher effective stresses yields hydrocarbon liquids with a lower average molecular weight and a higher API gravity. The 1000-psi effective-stress experiment yields the highest concentrations of chains shorter than nC_7, the 0-psi experiment yields the lowest concentrations, and the 400-psi experiment yields intermediate concentrations. Above $nC_{7,}$ the relationships are reversed.

The systematic relationships demonstrated for the straight-chain alkanes are also found in the aromatic compounds, cyclic alkanes, and branched-chain alkanes. Our experiments also demonstrate that various parameters interact in unexpected ways. For example, variations in hydrostatic pressure have a small influence on the liquid composition; however, when changes in hydrostatic pressure interact with effective stress, the observed variations are more significant.

1. INTRODUCTION

The composition of shale oil generated by *in situ* conversion is, in part, governed by intensive parameters such as pressure, temperature, and stress state. Knowledge of how variations in these parameters relate to compositional aspects of the shale oil provides an opportunity to optimize a conversion strategy to generate an improved hydrocarbon product. In this paper we examine how effective stress and hydrostatic pressure influence the molecular composition of shale oils generated in laboratory experiments that simulate *in situ* pyrolysis.

ExxonMobil's *Electrofrac* process provides an example of an *in situ* conversion technology that could be optimized using our experimental results (Fig. 1). To provide a context for the experimental parameters, we briefly describe this conversion process but stress that the results generalize to any *in situ* conversion technique that relies upon heating to convert kerogen (e.g, radial well-bore heaters). *Electrofrac* heats oil shale *in situ* by hydraulically fracturing the oil shale and filling the fracture with an electrically conductive material forming a heating element [1]. Electrical current flowing through these heating elements is used to generate large planar heating surfaces. The heating conditions can be controlled by varying the energy supplied to the fractures. The shale oil and gas are then produced conventionally.

A variety of intensive parameters (those that are independent of the mass of the system) govern the *in situ* pyrolysis [2,3]. These include hydrostatic pressure, stress state, maximum temperature, heating rate, heating duration, and source composition. Using a variety of techniques, all of these parameters can be controlled or at least influenced during pyrolysis.

We conducted a series of experiments that focused on two of these parameters, the stress state and hydrostatic pressure.

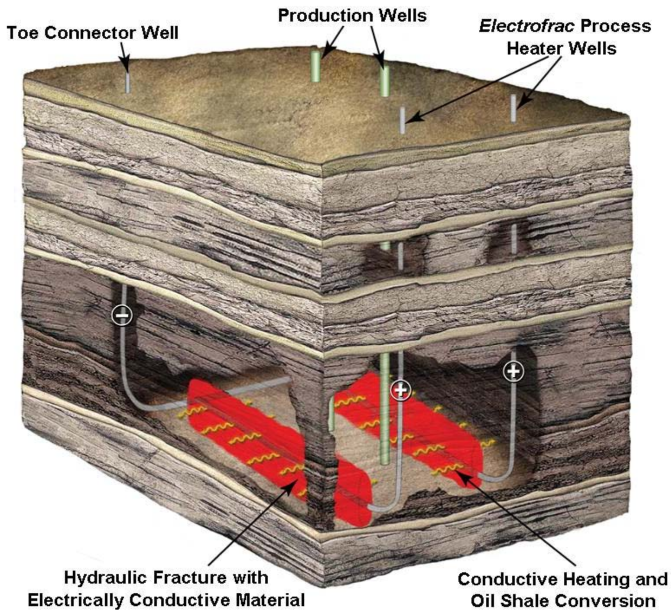

Figure 1. Schematic of the *Electrofrac* Process.

2. EXPERIMENTAL PROTOCOL

A primary objective of the experimental program was to identify the effects of hydrostatic pressure and effective stress on the compositions of oils produced during heating of oil shale. In describing the experimental setup we begin with those aspects of the experiments that were held constant. All experiments were conducted in a 465 ml Hastelloy Parr bomb heated externally by a custom furnace regulated by thermocouple feedback. The experiments were closed-system and run for 24 hours. The bomb assembly was placed in a furnace and brought to 393ºC over 1.5–2 hours. After 24 hours at temperature, the furnace was turned off, the bomb was removed, and allowed to cool passively. The gas pressure was then bled off gradually, the bomb opened, and the liquid and solid products collected. Monitoring instruments included: two thermocouples on the exterior bomb wall, another near the sample in the bomb's interior, and an internal pressure transducer (data points every 10 seconds). All monitoring instruments measured heat-up, run, and cool-down periods.

All experiments used the same oil shale, collected in Hell's Hole Canyon, Utah, as the starting material (Fig. 2). This sample (HHC-2) is typical of relatively-rich oil shale from the Mahogany Zone of the Green River Formation [4]. It was cut parallel to layering to yield a block suitable for drilling cores from the same stratigraphic interval. This was done to assure homogeneity of the starting material.

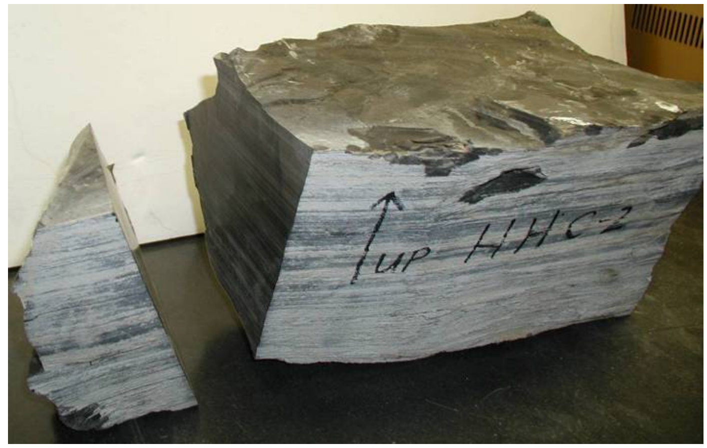

Figure 2. Block used as starting material for all experiments. It is approximately six inches in height and was trimmed along cardinal directions, relative to the cut shown, to generate a slab whose upper and lower faces correspond to bedding surfaces.

Argon (Ar) was used to supply a hydrostatic pressure. The bomb was sealed, flushed and pressurized with Ar. Initial Ar-pressures used were 50, 200, and 500 psi. The hydrostatic pressures at temperature were more than double the initial pressures because of expansion of the Ar and generation of gas from the oil shale kerogen.

To examine the role of effective stress on the pyrolysis products, we used a mini-loadframe that was inserted into the bomb (Fig. 3). Effective stress, in this context, refers to the portion of the lithostatic load that is directly supported by the solid framework of the rock. The confining assembly consists of a sleeve and two endcaps made of Berea sandstone (fired at 500ºC for two hours), that is re-enforced, and prevented from expanding laterally, by a slotted metal sleeve and two hose clamps (Fig 3a and 3b). The sample was placed in the loadframe with Berea endcaps inserted between the loadframe and each end of the sample. An effective stress of either 400 or 1000 psi was exerted on the sample using one of two sets of three springs compressed a fixed amount by appropriately torquing nuts on threaded rods connecting the top and base plates of the loadframe. The springs are made of a high-temperature alloy that allows the spring to retain a fixed spring constant at the temperatures of these experiments. Gold foil wrapped around the threaded rod below the middle plate of the loadframe provided an indicator of the expansion of the oil shale during conversion. In all experiments the gold foil is slightly crushed indicating expansion against the spring force.

(a) (b) (c)

Figure 3. (a) Oil Shale plug with Berea sandstone sleeve and end-caps. (b) Oil shale plug in Berea sandstone sleeve and supported by metal sleeve. (c) Sample assembly placed in load frame and compressed.

3. EXPERIMENTAL RESULTS

Oils were analyzed by a variety of techniques. Here we focus on: whole oil gas chromatography results (nC_5 – nC_{40}) and detailed gas chromatography (nC_4 – nC_{19}). These techniques provide some overlap and demonstrate internal consistency of our results.

The following general relationships were documented for the effect of effective stress and hydrostatic pressure on shale oil composition.

Increasing effective stress causes:

1. a decrease in *n*-alkanes heavier than ~ nC_7 to nC_8
2. an increase in aromatic ring concentrations
3. an increase in saturated ring concentrations
4. a decrease in isoprenoid concentrations

Increasing hydrostatic pressure causes:

1. essentially no compositional effect in the absence of effective stress
2. reduces the effective stress effect

The decrease in longer *n*-alkanes with increasing effective stress is readily seen in simplified whole oil chromatograms (Fig. 4). By comparing experiments conducted at the same temperature (393ºC), durations (24 hours), hydrostatic pressure (initial Ar pressure = 500 psi), and with the same starting material, the effect of changing the effective stress can be isolated. Among these three experiments, the 0 psi effective-stress result has the highest proportion of long chain alkanes and the proportion decreases as the effective stress increases to 400 psi and 1000 psi.

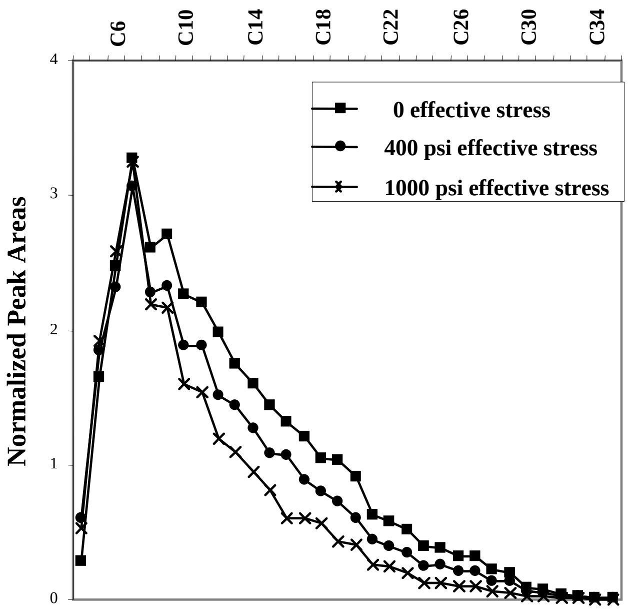

Figure 4. Simplified whole oil chromatograms showing the effect of changing effective stress on the proportions of straight-chain alkanes.

The simplified whole-oil chromatograms provide a way to visualize some results. However, as the number of molecules to be considered increases, contrasting raw or modified chromatograms is less illustrative. To simplify the data presentation we have adopted the use of normalized chromatograms (Fig. 5).

Normalized chromatograms are generated by first normalizing the integrated areas of all identified peaks for each sample to 100%. The compounds in each normalized analysis are then re-normalized by dividing by the same compound in a reference analysis. This yields a smoothed plot showing the ratios of the two analyses. Two experiments that yield identical results have a ratio of unity for all compounds. Therefore systematic deviations from unity can be viewed as relative enrichments or depletions of the numerator experiment(s) relative to the denominator experiment.

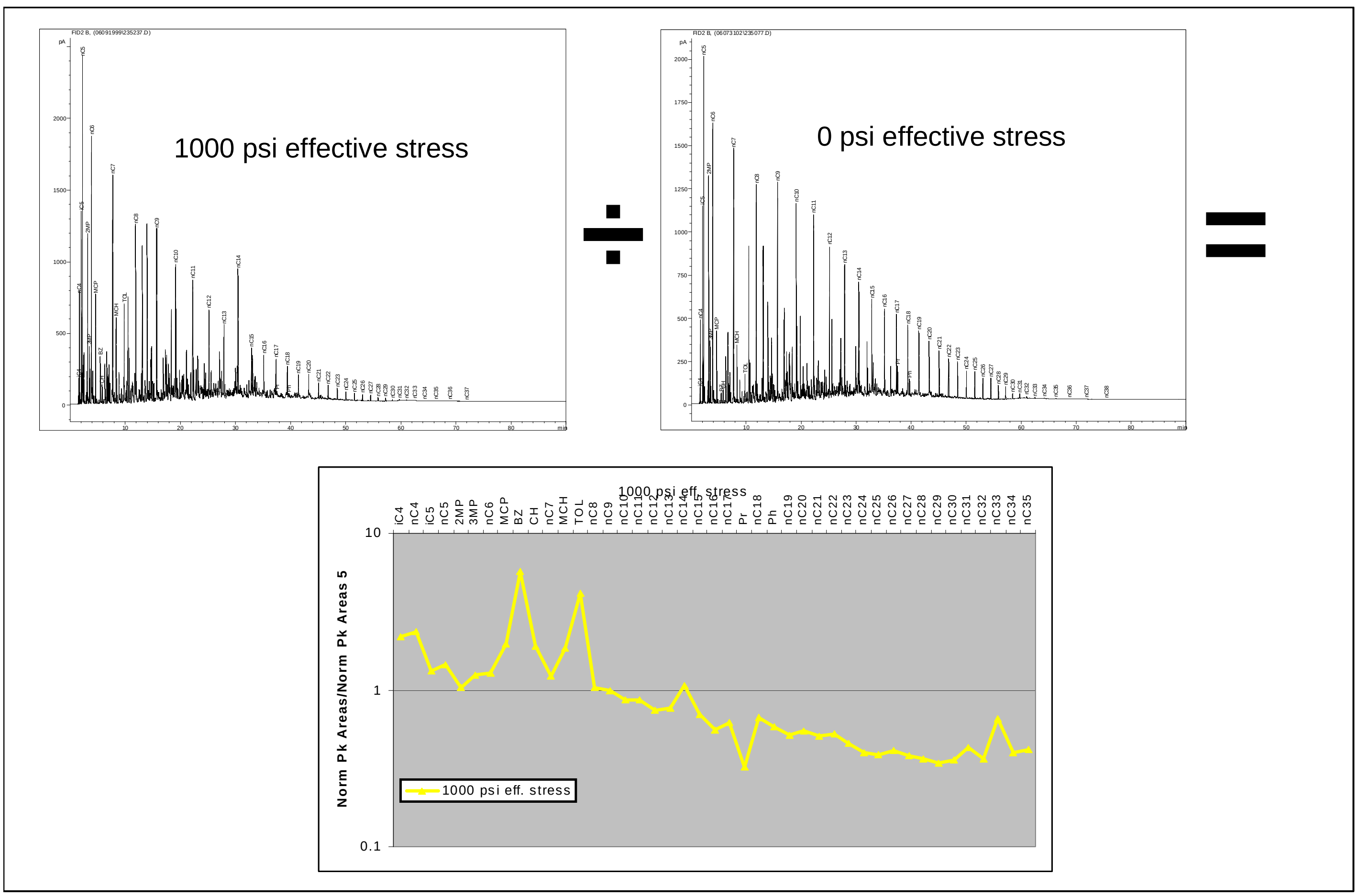

Figure 5.Whole oil chromatograms (x-axis = time, y-axis = counts) for 0 psi and 1000 psi experiments (see Fig. 4). Also shown is the normalized chromatogram(x-axis = molecules arranged in order of increasing boiling point, y-axis = normalized counts on a log scale) generated by dividing the 1000 psi result with the 0 psi result (see text for explanantion).

The choice of the normalizing analysis allows deviations to be interpreted in terms of a desired analytical or experimental parameter. For example, Figure 5 shows the ratios for the 0 psi and 1000 psi experiments depicted in Figure 4. The plot provides quick visual confirmation that the 1000 psi experiment is relatively depleted in larger molecules (plot falls below one). The normalized chromatograms allow compounds present in low concentrations to be compared alongside those present in much greater proportions. Unfortunately compounds close to the detection limits, and therefore not well quantified, can generate anomalous spikes. These should be ignored in interpreting the results.

The results presented in Figure 4 can be usefully revisited using normalized chromatograms (Fig. 6). In this presentation it is clear that not only does the 1000 psi effective stress have the lowest proportion of heavy molecules it also has a higher proportion of smaller molecules (although similar to that of the 400 psi effective stress experiment).

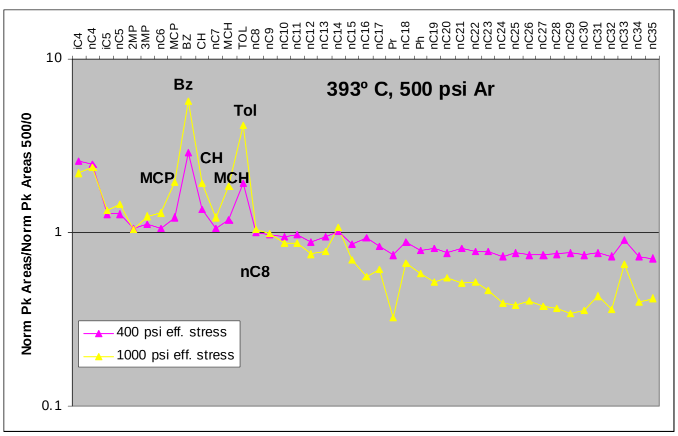

Figure 6. Normalized whole oil chromatograms showing the effect of changing effective stress on the proportions of straight-chain alkanes. X-axis = molecules arranged in order of increasing boiling point, Y-axis = normalized counts on a log scale.

That higher effective stress leads to more aromatic ring compounds can be seen by examining the detailed chromatograms of the same experiments seen in Figure 6 (Fig. 7). The 1000 psi effective stress experiment has the highest concentrations of both single ring (benzene, toluene, xylene) and double ring aromatics (naphthalene). Similar trends are seen for the 400 psi experiment, although certain variably-methylated naphthalenes are not substantially different from the 0 psi experiment.

As with the aromatic rings, the proportion of saturated rings increases with increasing effective stress. This is shown in Figure 8 which depicts the same analyses in Figure 7 with the aromatic rings highlighted. Both the cyclopentane-based and cyclohexane-based molecules are present in the highest proportions in the 1000 psi experiments. As with the aromatic rings, most saturated rings show an increase in proportion going from 0 to 400 to 1000 psi effective stress.

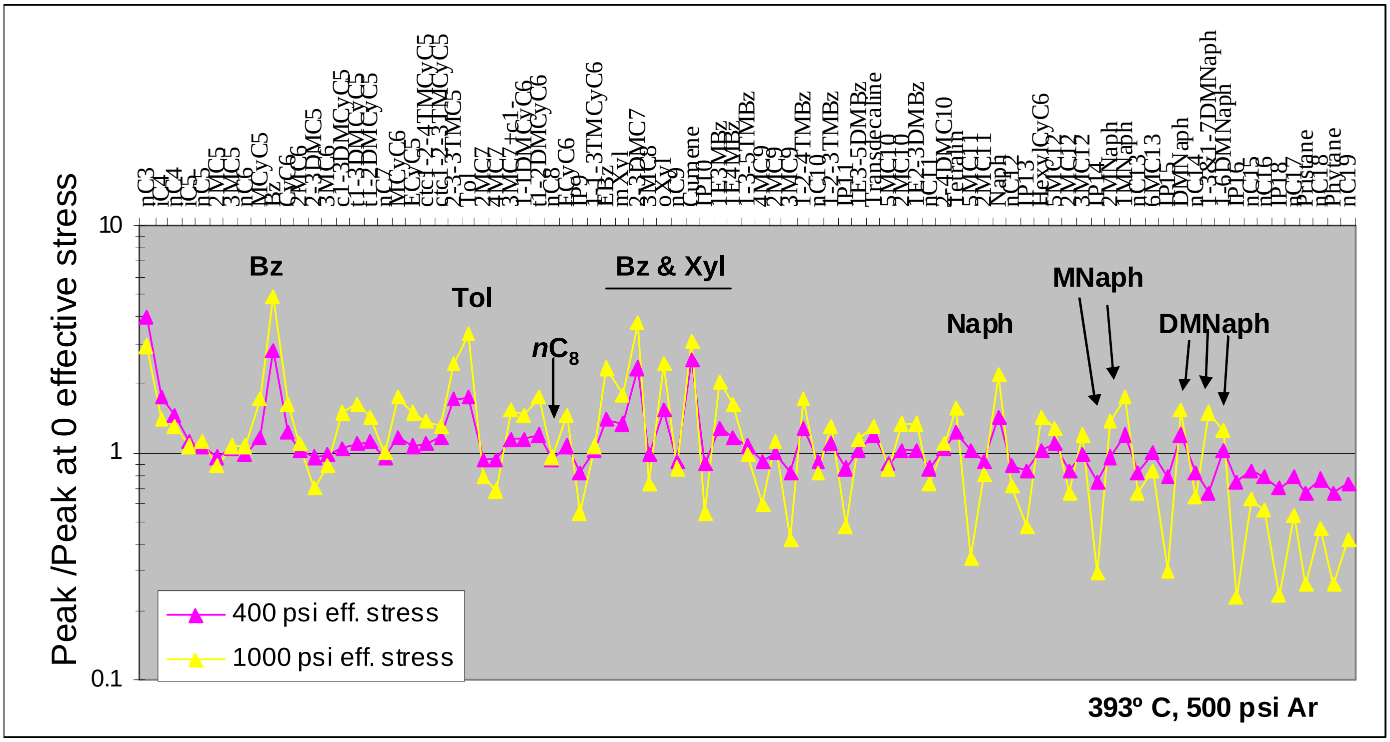

Figure 7. Detailed chromatogram highlighting relative enrichments in aromatic ring compounds with increasing effective stress. Highlighted compound abbreviations are Bz = benzene, Tol = Toluene, Xyl = xylene, Naph = naphthalene. X-axis = molecules arranged in order of increasing boiling point, y-axis = normalized counts on a log scale.

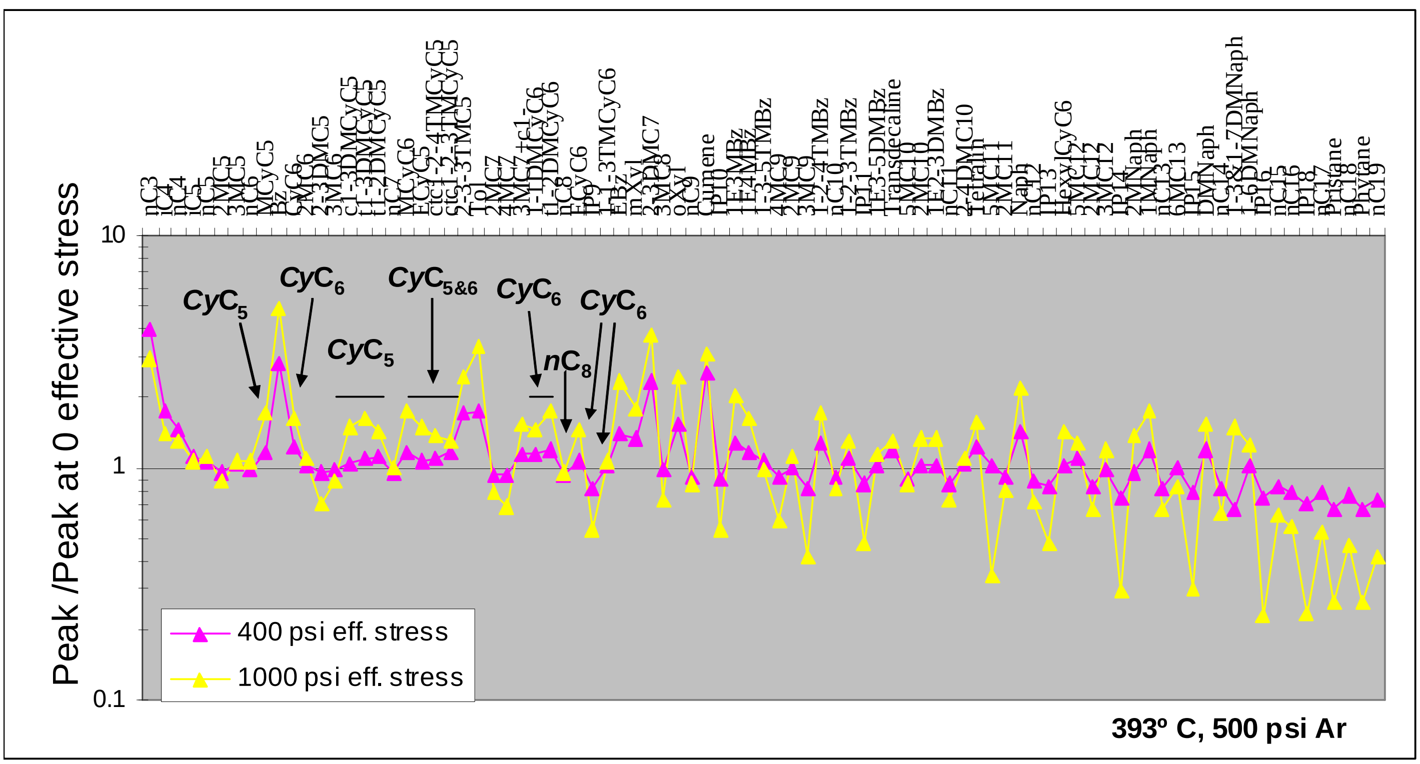

Figure 8. Detailed chromatogram highlighting relative enrichments in saturated ring compounds with increasing effective stress. Highlighted compound abbreviations are *Cy*C_5 = cyclopentane, *Cy*C_6 = cyclohexane. X-axis = molecules arranged in order of increasing boiling point, y-axis = normalized counts on a log scale.

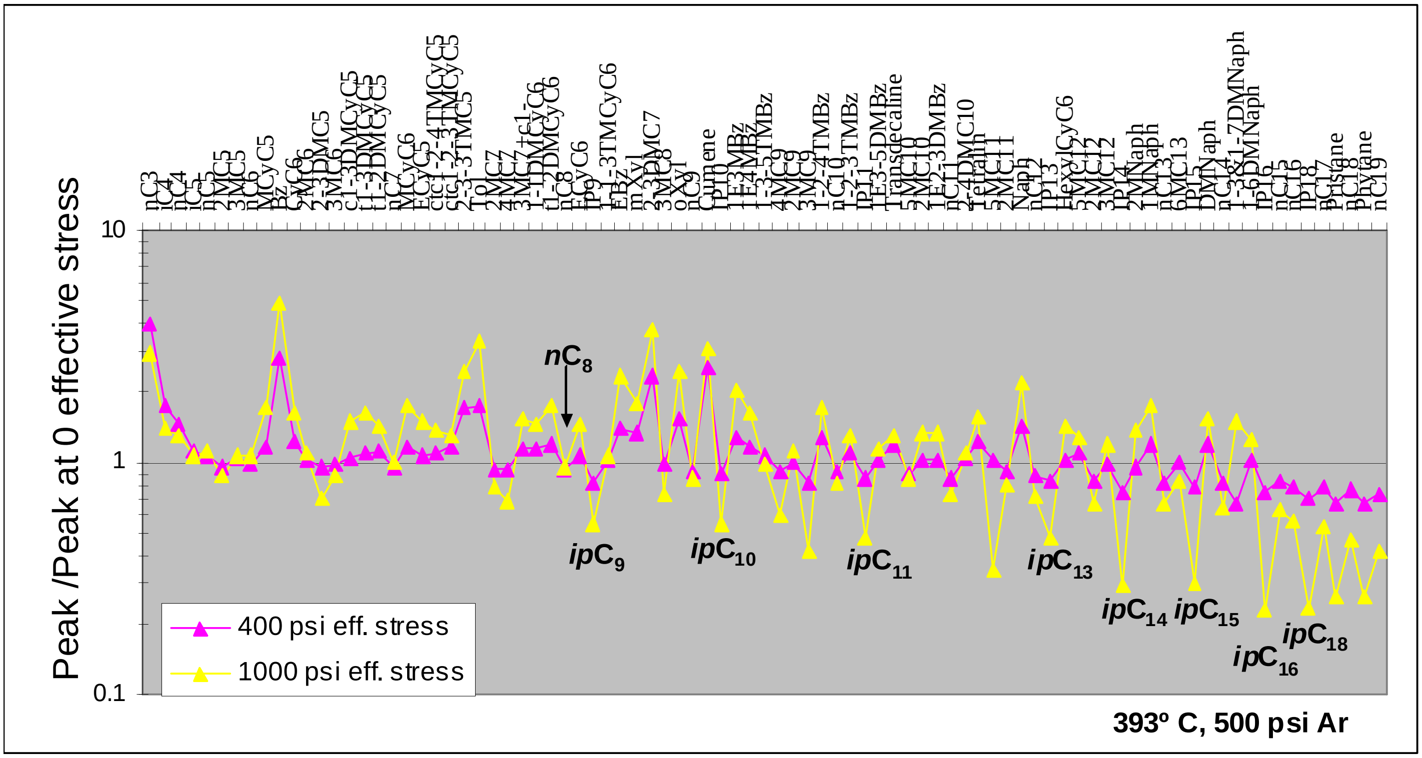

Figure 9. Detailed chromatogram highlighting decimation of isoprenoids relative to adjacent *n*-alkanes with increasing effective stress. Highlighted compound abbreviations are *ip*C_x = an isoprenoid with x carbons (where x ranges from 9 to 20 – including pristane and phytane). X-axis = molecules arranged in order of increasing boiling point, y-axis = normalized counts on a log scale.

Increasing effective stress leads to selective decimation of isoprenoids relative to adjacent *n*-alkanes (Fig. 9). Isoprenoids are branched-chain alkanes with a direct biological origin. Because they are of biological origin, their proportion relative to an adjacent *n*-alkane provides a measure of cracking in a hydrocarbon system. This is a consequence of no new isoprenoids being generated by cracking while new *n*-alkane molecules can be generated by cracking of longer chains. The 1000 psi effective stress experiments show the most pronounced decimation of the isoprenoids. The 400 psi effective stress experiments show essentially the same relationships but more subdued.

The compositional response seen in the generated shale oil to changes in the hydrostatic pressure is more complicated than the relationship seen for changes in effective stress. In the absence of effective stress, changes in the hydrostatic pressure have a negligible compositional effect. Comparing two experiments with a pressure difference of more than two times (200 versus 500 psi Ar initial), the shale oil compositions are nearly identical resulting in a normalized plot that falls at or near unity for most molecules (Fig. 10).

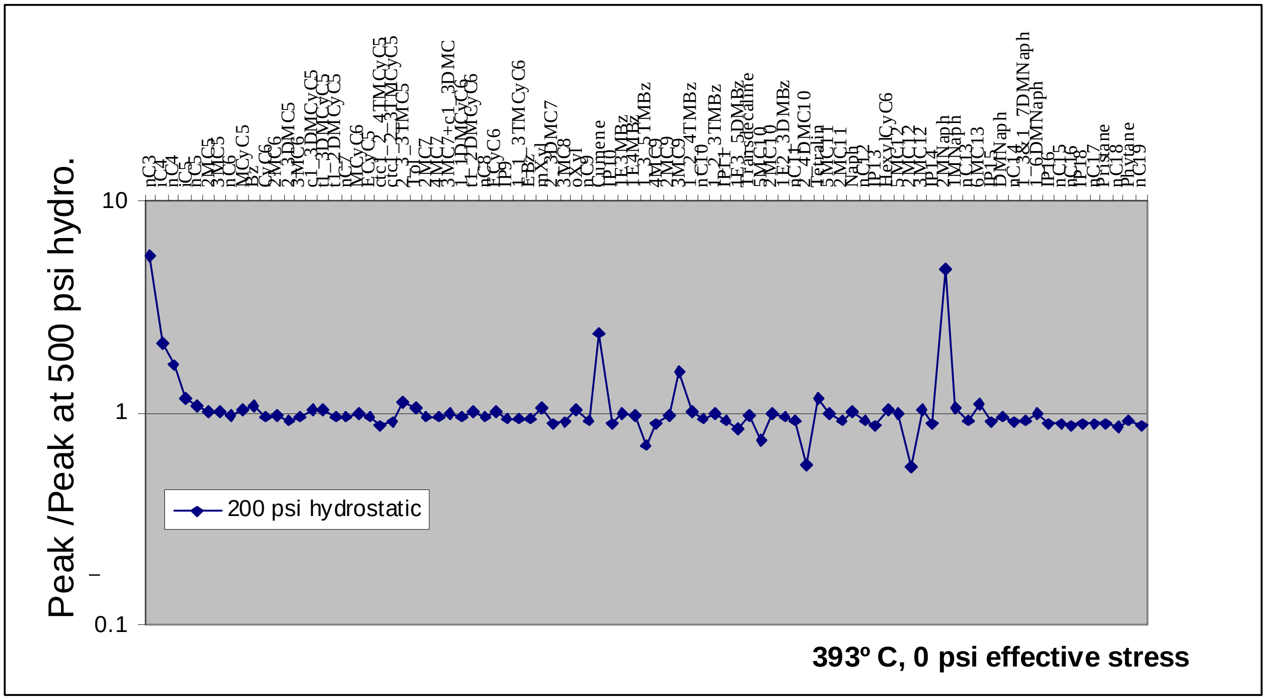

Figure 10. Comparison of two experiments both conducted at 393ºC and 0 psi effective stress with a 200 psi initial Ar pressure experiment normalized to a 500 psi initial Ar experiment. X-axis = molecules arranged in order of increasing boiling point, y-axis = normalized counts on a log scale. (Note that the large deviation from unity in the light hydrocarbon range is caused by volatile loss. Spikes at higher carbon numbers are related to concentrations being near detection limits.)

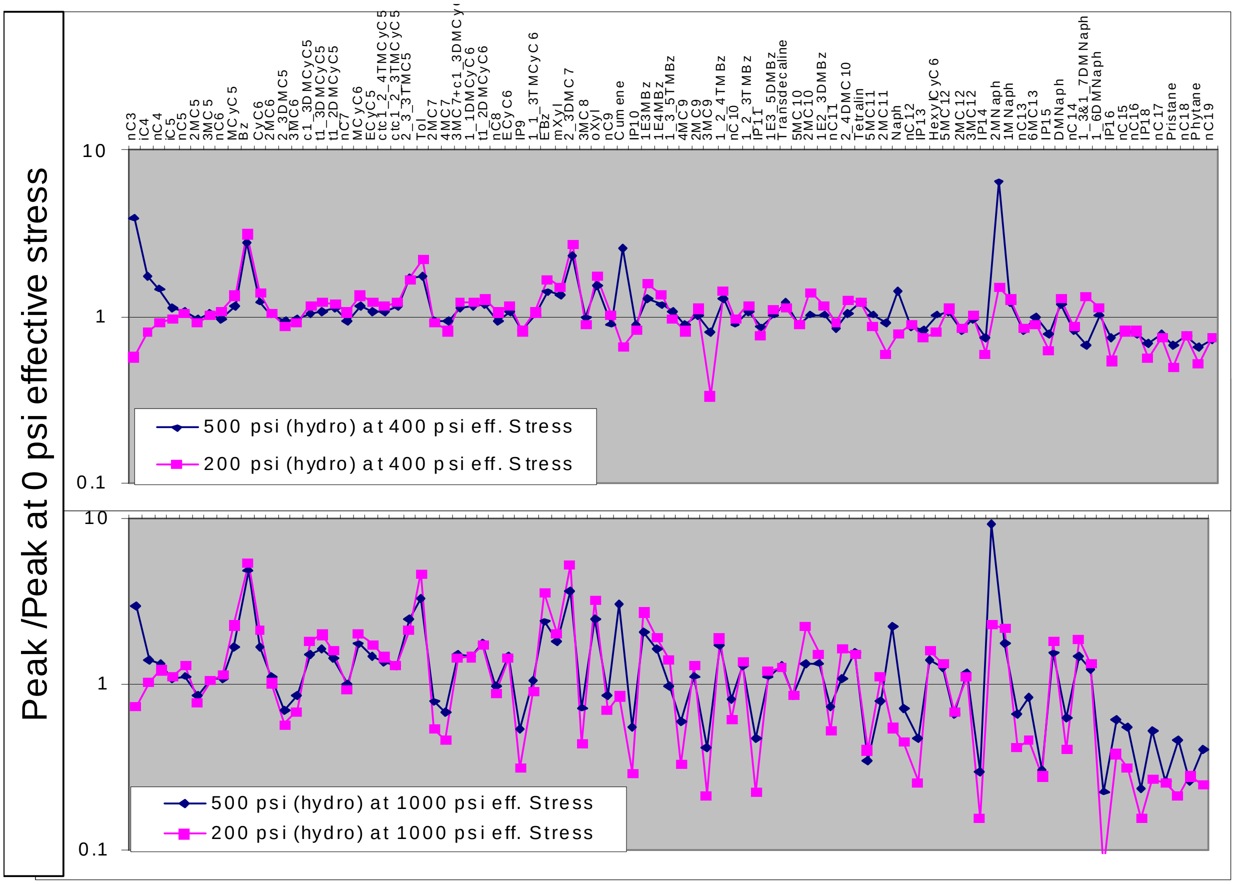

Figure 11. Each plot compares four experiments (all conducted at 393ºC). In both graphs, the plotted data are for experiments conducted at 500 psi (blue diamonds) and 200 psi Ar initial (magenta squares) normalized to experiments conducted at the same Ar pressure but at 0 psi effective stress. In the upper graph the normalized results are from experiments conducted at 400 psi effective stress, while in the lower graph the normalized results are for experiments conducted at 1000 psi effective stress. X-axis = molecules arranged in order of increasing boiling point, y-axis = normalized counts on a log scale.

In the presence of effective stress, an increase in hydrostatic pressure modifies the consequence of that effective-stress. This result is demonstrated by the plots presented in Figure 11 Both show experiments conducted at either 400 psi (upper) or 1000 psi (lower) effective stress. The results are normalized to experiments conducted at 0 psi effective stress but otherwise the same conditions. In each plot the general variation from unity reflects the consequence of effective-stress as described above. The amount of deviation from unity is greater in the lower graph because the experiments were conducted at higher effective stress. The key features of these graphs is that the experiments conducted at higher hydrostatic pressure (500 psi versus 200 psi Ar initial pressure) plot closer to unity for both effective stress conditions. Thus, increasing the hydrostatic pressure, in the presence of an effective stress, reduces the compositional consequence of that effective stress.

4. SUMMARY

Our investigation of the compositional influence of effective stress and hydrostatic pressure demonstrates clearly that modifying these intensive parameters, during *in situ* conversion of oil shale, it is possible to generate an improved hydrocarbon product. Our primary conclusion is that variations in effective stress exert a surprisingly major control on the composition of *in situ* generated shale oil. Therefore knowledge of the stress field in an oil shale is critical for planning an optimized *in situ* conversion technology [5]. In our experiments, systematic changes in effective stress generated systematic changes in the composition of shale oil generated. This demonstrates the robustness of the result. Another important observation is that changes in hydrostatic pressure have a minimal effect in the absence of effective stress, and otherwise act to merely modify the effective-stress effect.

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