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Speciation of uranium and organic compounds on solid matrix studied by supercritical fluid extraction

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

SPECIATION OF URANIUM AND ORGANIC COMPOUNDS ON
SOLID MATRIX STUDIED BY
SUPERCRITICAL FLUID EXTRACTION

A thesis submitted in partial satisfaction of the
requirements for the degree of

MASTER OF SCIENCE
IN
CHEMISTRY

by

Li Chen

1996

To: Dean Arthur W. Herriott
College of Arts and Sciences

This thesis, written by Li Chen, and entitled Speciation of Uranium and Organic Compounds On Solid Matrices Studied by Supercritical Fluid Extraction, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this thesis and recommend that it be approved.

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Date of Defense: May 10, 1996

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Dean Arthur W. Herriott
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Florida International University, 1996

To: Stuart, Peter and Rose

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ABSTRACT OF THE THESIS

SPECIATION OF URANIUM AND ORGANIC COMPOUNDS ON SOLID MATRIX STUDIED BY SUPERCRITICAL FLUID EXTRACTION

by

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Florida International University, 1996

Miami, Florida

Professor Kenneth G. Furton, Major Professor

Professor Rudolf Jaffé, Co - Major Professor

The liquid extraction and spectrophotometric quantitation of uranium from different solid matrices is compared to supercritical fluid extraction (SFE) using various combinations of 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octadione (FOD), tri-n-butylphosphate (TBP), ethanol, and carbon dioxide measuring the UV absorption of the uranium•FOD complex. The matrix is shown to have a tremendous effect on the extractability of uranium from different solid matrices. Compared to liquid extraction, the SFE method yields higher recoveries, is significantly faster, is of equal or greater precision, and greatly reduces the amount of organic solvents used. In the second part of this work, the speciation of hydrophobic organic compounds (HOCs) in ancient sediments is studied by stepwise high temperature SFE and comparisons made to thermodesorption and soxhlet extraction. High

temperature SFE recovers significantly more HOCs compared to soxhlet extraction. For low molecular weight compound thermodesorption is the dominant mechanism whereas for high molecular weight compounds the mechanism is a combined effect of thermodesorption and solubility in the supercritical fluid.

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SECTION A

INTRODUCTION

1.1. Supercritical fluid and its unique properties

A supercritical fluid is a liquid or gas heated above its critical temperature (T_c) and simultaneously compressed, exceeding its critical pressure (P_c). The supercritical fluid region in the schematic phase diagram of CO_2 , shown in Figure 1, represents an extension of the gas and liquid phase regions in which there is no longer distinction between the gas and the liquid and the physicochemical properties of the fluid are continuously variable between those of gas and liquid by changing the temperature and pressure above the critical point.

Table 1 illustrates the properties of supercritical fluid vs. those of gas and liquid.

In general, while the density and viscosity of supercritical fluid, along with the diffusion coefficient of the solute (the analyte) in supercritical fluid are variable between those of gas and liquid, the density is closer to that of liquid, and the viscosity as well as the diffusion coefficient of the analytes is closer to that of gas. In addition, the surface tension of supercritical fluid is zero. Those properties make supercritical fluid a fluid with high solvating power (due to liquid-like density), efficient penetration ability (due to gas-like viscosity and zero surface tension) and give analytes in supercritical fluid rapid transportation ability (due to gas-like diffusion coefficient of solute in supercritical fluid).

Table 2 lists the critical parameters of possible supercritical fluids. Among those

Figure 1. The typical phase diagram for CO₂.

	Gas	Supercritical fluid	Liquid
Density (g/cm ³)	10 ⁻³	0.1 - 1	1
Diff. Coeff. (cm ² /s)	10 ⁻¹	10 ⁻³ - 10 ⁻⁴	< 10 ⁻³
Viscosity (g/cm·s)	10 ⁻⁴	10 ⁻³ - 10 ⁻⁴	10 ⁻²

Table 1. Properties of supercritical fluid vs. those of gas and liquid (taken from McNally and Bright, 1992)

Formula	Name	Pc (psi)	Tc (°C)
CO ₂	Carbon Dioxide	1070.4	31.1
C ₂ H ₄	Ethylene	731.0	9.4
C ₅ H ₁₂	n-Pentane	488.8	196.7
N ₂ O	Nitrous Oxide	1050.1	36.6
C ₃ H ₆	Propylene	677.2	91.9
C ₄ H ₁₀ O	Diethyl Ether	527.9	193.7
H ₂ O	Water	3208.2	374.3
NH ₃	Ammonia	1651.9	132.5
Xe	Xenon	857.5	16.6
CCl ₂ F ₂	Dichlorodifluoromethane	597.6	112.0
CHF ₃	Trifluoromethane	688.6	25.6

Table 2. Critical parameters of possible supercritical fluids

supercritical fluids listed, carbon dioxide has been so far the most commonly used one, because of its moderate critical constants, inertness, non-toxicity, non-flammability and availability in purified form. However, because it is non-polar, supercritical CO₂ has a limited affinity with polar analytes, especially with ion species. It is common now to add small amount of polar modifier to supercritical CO₂ for polar analytes and, recently, to convert the charged species into chelates by using a chelation agent in supercritical CO₂.

1.2. Supercritical fluid extraction vs. liquid solvent extraction

The main task of extraction is to separate analytes from a matrix by investing the minimum amount of effort and time necessary to provide quantitation with acceptably high degrees of accuracy and precision (Miles et al., 1992). Over the decades, for analytes in solid matrix the extraction was achieved mainly by liquid solvent extraction, such as Soxhlet extraction and stirring extraction, as well as sonication. Unfortunately, the conventional liquid solvent extractions often fail to meet the goals of extraction described before. They often require several hours, even days, to perform, and may result in a dilute extract, which must be concentrated when trace analysis is desired. They may also generate large amounts of hazardous waste solvent and may not result in quantitative recovery of target analytes. The limitations of conventional methods support the development of alternative sample extraction methods (Hawthorne, 1990)

The continuously variable physicochemical properties (density, diffusivity, viscosity, etc) of supercritical fluid described before make it an excellent candidate for extraction and recovery of analytes from solid matrix - supercritical fluid extraction (SFE). Because of its unique properties, carbon dioxide has been the most commonly used supercritical fluid in SFE.

SFE is much more efficient than conventional solvent extraction (usually 10 - 60 mins), because of the ability of supercritical fluid to rapidly penetrate into matrix and the ability of analytes to rapidly transport out of matrix. Supercritical CO₂ is a non-toxic gas at ambient conditions. Therefore, much less hazardous waste solvent is generated and the concentration steps are much simpler. Most importantly, SFE usually has higher recovery

of the analytes of interest than conventional solvent extraction.

The recovery of the analytes from solid matrices depends on solubility and diffusion coefficient of the analytes in a solvent or fluid, and particularly, the affinity of the analytes for the matrices, and the speciation of analytes in the solid matrix (the way the analytes associate with the solid matrix) (Furton and Rein, 1992; Furton and Lin, 1993; Knipe et al., 1992; Hawthorne et al., 1993). Although the solubility of the analytes in supercritical fluid is smaller than that in proper solvent, the diffusion coefficient of the analytes is much greater. Because of the variable physicochemical properties of supercritical fluid under different temperature and pressure, and because of the controllable SFE variables, such as temperature, pressure, fluid modifiers and fluid flow rate etc, the overall recovery of SFE can be optimized.

1.3. Extraction of uranyl ion by liquid extraction and supercritical fluid extraction

With the development and application of nuclear power, uranium has become an extremely important energy source. The mining and processing of uranium ores have perceptible effects on the environment (Edwards et al., 1992). Sensitive and accurate methods for uranium nuclear waste analysis, purification and management are therefore required.

The solvent extraction of uranium has been studied by a great number of investigators. Organophosphorus compounds have attracted considerable interest as solvent extracting agents for uranyl ions, U(VI), as well as a large variety of other metal ions. Amongst these, neutral ligands, including the phosphoryl group $P=O$, are of special importance (Rodehuser et al., 1992). Tri-n-butyl phosphate (TBP) is one of the first and most widely used solvent extractants. TBP dissolved in the hydrocarbon diluent (typically 70%) is widely used to extract U(VI) from nitric acidic solutions in counter-current solvent extraction processes (Enokida et al., 1992). Alternatively, uranium had been extracted from nitrate solutions, using TBP adsorbed onto insoluble polymers (Britz et al., 1990). Over the years, a variety of synergistic uranium extractions have been reported, including mixtures of TBP and chelating extractants (often β -diketones). It has also been shown that uranium can be effectively extracted from acidic media using emulsion liquid membranes containing β -diketones and TBP (Akiba et al., 1988). However, these liquid extraction methods are either time consuming or complicated. Relatively large amounts of organic solvent waste are also generated.

Supercritical carbon dioxide extraction has several advantages over conventional

liquid extraction, as mentioned before. However, direct extraction of uranyl ions by supercritical CO₂ is highly inefficient because of the weak solute-fluid interactions (Laintz et al., 1992). Recently, Lin et al. have reported the use of fluorinated β -diketones, 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octadione (FOD) (Lin et al., 1993) as chelating agents, dissolved in supercritical CO₂ for the recovery of lanthanides and actinides (including uranyl ions) from solid materials followed by quantitation by neutron activation analysis (NAA). This method has shown all advantages of SFE over liquid extraction. However, the sample matrix used was filter paper, which is markedly different from real environmental matrix. In addition, neutron activation analysis (NAA) requires very expensive instrument and is not a readily available technique.

OBJECTIVES

The objectives of this work were:

1. To develop a rapid sensitive spectroscopic method utilizing the inexpensive and readily available UV-Vis absorption spectrometer for detecting a wide range of uranium concentrations without the need for post-extraction complex formation.
2. To evaluate the effects of the solid matrices, one of them mimicking real environmental matrix, on achievable uranium recoveries by liquid extraction.
3. To compare liquid and supercritical fluid extraction methods in terms of recovery, precision, ease of use and time of analysis.

EXPERIMENTAL

3.1. Reagents

All chemicals used were purchased in the highest purity available and used without further purification. Absolute ethyl alcohol (ethanol) was purchased from Florida Distillers (Lake Alfred, FL). Tributylphosphate (TBP) and acetic acid were purchased from Fisher Scientific (Orlando, FL). Kaolin [$\text{Al}_2\text{SiO}_5(\text{OH})_4$] (china clay), 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octadione (FOD), chrome azurol S (CAS) benzyldimethyldodecylammonium bromide (sterinol ST) and sodium acetate were obtained from Aldrich (Milwaukee, WI) (see Figure 2 for structures of organics used). Uranyl nitrate hexahydrate (>99%) [$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] was obtained from Baker (Phillipsburg, NJ). 50% polypropylene/50% polyester and 100% cotton balls were obtained from Sentinel (Mentor, OH). DMCS treated glass wool was obtained from Altech (Deerfield, IL). SFC/SFE grade carbon dioxide (Air Products, Allentown, PA) was used for all supercritical fluid extractions.

Tributylphosphate (TBP)

2,2-Dimethyl-6,6,7,7,8,8,8-Heptafluoro-3,5-Octadione (FOD)

Chrome Azurol S (CAS)

Benzyldimethyldodecylammonium Bromide (sterinol ST)

Figure 2. The structures of organics used

3.2. Apparatus

3.2.1. Solvent extraction - stirring

The solvent extraction used for this project was stirring extraction. Corning stirring plates were used for all solvent extractions. The extracts, when necessary, were centrifuged with an Adams compact II centrifuge (Becton Dickinson, Sparks, MD). All volumes needed were measured by enpendorf 1-100, 100-1000 ul pipette (Brinkmann Instruments Inc, Westbury, NY).

3.2.2. Supercritical fluid extraction

A microprocessor-controlled 260D syringe pump and SFX 2-10 extractor (max. temperature limit at 150°C) with a 2.5 ml extraction vessel (ISCO, Lincoln, NE) were used for all of the supercritical fluid extractions. A 15 cm x 50 µm i.d., 375 µm o.d. fused-silica capillary linear restrictor (Polymicro Technologies, Phoenix, AZ) covered by stainless steel tubing (8 cm x 500 µm i.d., 1.5 mm o.d.) was inserted through a 1.5 mm diameter hole drilled through the aluminum heating block. The heating block was heated to 250°C with a silicon extruded heating tape controlled with a stepless temperature controller (Thermolyne, Dubuque, IA). The schematic diagram of SFE system for uranium is shown in Figure 3. Analytes were collected in 2 ml of ethanol in a 5 ml volumetric flask. Absorbances of standards and extracts were measured in 1.00 cm Supracil quartz cuvettes (Fisher Scientific, Orlando, FL) using a Shimadzu UV-2101 PC UV-visible scanning spectrophotometer (Columbia, MD).

Figure 3. The schematic diagram of SFE system

3.3. Procedures of stirring extraction

The samples for stirring extraction were prepared by spiking certain amount of uranyl nitrate hexahydrate $[\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ solution, dissolved in ethanol, onto 3 different solid matrices: DMCS treated glass wool, polypropylene/polyester and cotton, and by pre-coating $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution onto Kaolin (Kaolin packing) (mimicking real environmental matrix). A 660 ppm $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ stock solution was prepared by dissolving 0.07 g uranyl nitrate hexahydrate in 50 ml of ethanol, and 100 μl of this stock solution was then spiked onto 0.1 g samples of matrix: glass wool, polypropylene/polyester and cotton. The matrices were allowed to dry at room temperature. A standard Kaolin packing containing 54 ppm U(VI) was prepared by adding 21.1003 g of Kaolin to a methanolic solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, containing 0.0024 g of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in a glass jar. The methanol was allowed to evaporate at room temperature and the packing was then transferred to another container. The glass jar was extracted and no U(VI) was detected, indicating quantitative transfer of the U(VI) to the Kaolin.

0.1 g glass wool, polypropylene/polyester and cotton samples, pre-spiked with $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ standard solution, were extracted by 5 different solvents described below:

(1) 5 ml of absolute ethanol

(2) 5 ml of absolute ethanol buffered to pH 5.5 with 0.662 ml of pH 3.2 acetic acid-sodium acetate buffer

(3) 5 ml of absolute ethanol and 2.5 ml of TBP buffered to pH 5 with 0.662 ml of pH 3.2 acetic acid-sodium acetate buffer

(4) 4.886 ml of absolute ethanol, along with 0.114 ml of FOD (0.1 M)

(5) 4.752 ml of absolute ethanol, along with 0.114 ml of FOD (0.1M) and 0.134 ml of TBP (0.1 M)

2 g of the Kaolin packing was extracted in the same manner as described above, but with 1.5 times of total solvent amount. The pre-spiked matrices and Kaolin packing were placed in beakers covered by watch glasses to prevent evaporation and stirred for 45 mins at room temperature. The extracts for Kaolin packing were then transferred to centrifuge tubes and centrifuged for 10 mins. Half of the total volume (2.5 ml) of the extracts for glass wool, polyethylene/polyester and cotton extraction and 2.5 ml of the extracts for Kaolin extraction were then individually pipetted into 5.0 ml volumetric flasks and diluted with neat ethanol for the extracts, which included FOD (extractions 4 and 5), or visualized with CAS/ST complexation (extraction 1,2 and 3) as described below.

Trace quantities of U(VI) or U(VI) complex were not sensitive enough for direct determination by UV-Vis spectrophotometer, except for the presence of FOD. The extracts from extraction 1, 2 and 3 were analyzed by UV-Vis using a post-extraction visualization. The post-extraction visualization was accomplished with a complex (with pH 5) formed in the presence of U(VI), 0.525 ml of 1.52×10^{-3} CAS, 0.394 ml of 3.2×10^{-2} M ST, 1.25 ml of TBP, 2.5 ml of ethanol and 0.331 ml of pH 3.2 acetic acid-sodium acetate buffer. Therefore, CAS and ST (for extracts 1, 2 and 3), TBP (for extracts 1 and 2), as well as buffer (for extract 1) were added. 100 μ l of U(VI) stock solution was added

into each solvent (without matrices), with the same combination and amount as what described before, as a standard solution. The standard solution was simultaneously extracted in the same manner of U(VI)-matrix-solvent extraction. The recoveries of U(VI) from different matrices were obtained from comparing the UV absorbance of U(VI) complex from standard solution and extracts.

3.4. Procedures of SFE

The sample used for SFE was pre-coated Kaolin only. The standard Kaolin packing containing 65 ppm U(VI) was prepared by adding 21.8290 g of Kaolin to a methanolic solution of $\text{UO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, containing 0.0030 g of $\text{UO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in a glass jar. The post-treatments of Kaolin packing as described in section 3.3 were also performed. 0.7 g of the Kaolin packing was extracted in a 2.5 ml extraction vessel in the static mode for 20 mins at 70°C and 5000 psi followed by 10 min dynamic extraction with pure supercritical CO_2 at a flow rate of 1.0 ml/min using a 15 cm x 50 μm i.d. linear restrictor. The following modifiers were spiked into the 2.5 ml extraction vessel for the static extraction step:

- (1) 5.6 % v/v absolute ethanol- CO_2 (140 μl ethanol/2.5 ml cell)
- (2) 5.6 % v/v absolute ethanol and 0.1 M TBP - CO_2 (140 μl of TBP+ethanol solution prepared by pipetting 2.380 ml of TBP diluted to 5 ml with ethanol/2.5 ml cell)
- (3) 0.1 M FOD - CO_2 (57 μl FOD/2.5 ml cell)
- (4) 0.1 M of TBP and 0.1 M of FOD - CO_2 (124 μl of FOD+TBP solution prepared by combining 2.036 ml FOD and 2.38 ml TBP/2.5 ml cell)
- (5) 5.6 % v/v absolute ethanol and 0.1 M FOD - CO_2 (140 μl of FOD+ethanol solution prepared by pipeting 2.036 ml FOD diluted to 5 ml with ethanol/2.5 ml cell)
- (6) 5.6 % absolute ethanol and 0.1 M FOD and 0.1 M TBP - CO_2 (140 μl of FOD+TBP+ethanol solution prepared by pipetting 2.036 ml FOD and 2.380 ml TBP diluted to 5 ml with ethanol/2.5 ml cell)

The extracts were diluted to 5 ml with visualizing agents in the same manner as described in section 3.3 (for extracts 1 and 2) and ethanol (for extracts 3, 4, 5 and 6) before quantitation.

Two calibration curves, achieved from measuring the UV absorption of (i) 5 standard solutions varying from 2 to 14 ppm of U(VI) ion in the presence of visualizing reagents and (ii) 15 standard solutions varying from 40 ppb to 85 ppm of U(VI) in the presence of 0.1 M FOD, were used for recovery calculations of extraction (1)-(2) and (3)-(6) respectively (see section 4.1. for detailed information about calibration curves).

5 standard solutions varying from 2 to 14 ppm were prepared by diluting a 1034 ppm $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ stock solution, prepared by dissolving 0.1090 g $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 50 ml. volumetric flask with ethanol, with ethanol in the presence of visualizing reagents in the same manner as described in section 3.3. 15 standard solutions varying from 40 ppb to 85 ppm were prepared by diluting a 1147 ppm $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ stock solution, prepared by dissolving 0.0605 g $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 25 ml volumetric flask with ethanol, with ethanol in the presence of 0.1 M FOD.

RESULTS AND DISCUSSION

4.1. A direct and sensitive UV-Vis absorption spectroscopic method for determination of uranium

Uranium [U(VI)] extracted with FOD was directly measured by UV-Vis spectrophotometer. The U(VI)-FOD complex showed a maximum absorbance at 361 nm. Absorbance spectra for the U(VI)-FOD complex at 5 different concentrations are shown in Figure 4. UV absorption spectra were measured for 15 standard solutions varying from 40 ppb to 85 ppm of U(VI) in the presence of the 0.10 M FOD in ethanol. Absorbances were measured at the $\lambda_{\max}$ of 361 nm and slight variations in baseline were corrected by subtracting the absorbances observed at 426 nm. Linear least squares regression of the data for the U(VI)-FOD complex yielded the following: absorbance at 361-426 nm = $0.022[U_{\text{ppm}}] + 0.009$ (S.D. of the slope = 0.001; S.D. of the intercept = 0.003; $r^2 = 0.999$) (Figure 5). Absorbance spectra measured from 2 ppm to 50 ppm of U(VI) in the presence of 0.1 M FOD and 0.1 M TBP in ethanol were compared to that in the presence of 0.1 M FOD only. Both calibration curves are identical, therefore, the calibration curve from U(VI)-FOD is allowed to be used for all extractions, which included FOD. Beer's law is obeyed over three orders of magnitude from below 100 ppb to nearly 100 ppm of U(VI)-FOD. The molar absorptivity of the U-FOD complex at $\lambda_{\max} = 361$ nm is $5.2 \times 10^3 \text{ l mol}^{-1}\text{cm}^{-1}$. Uranium

[U(VI)] extracted without FOD was converted to a colored complex in a manner similar to that proposed by Kwapulinska and Janoszka using aqueous solutions of Chrome

Figure 4. The absorbance spectra for the U(VI)-FOD complex at 5 different concentrations

Figure 5. Calibration curves of U(VI)+FOD and U(VI)+TBP+CAS+ST

Azurol S (CAS) and benzyldimethyldodecylammonium bromide (ST) (1990). The present method used ethanol as the solvent and included TBP yielding spectra with absorbance maxim at 597 nm. 5 standard solutions varying from 2 to 14 ppm of U(VI) ion were prepared in the presence of 1.52×10^{-3} M CAS, 3.2×10^{-2} ST and 0.92 M TBP in ethanol-water (75:25, v/v) buffered to pH 5 with pH 3.2 acetic acid-sodium acetate buffer. Absorbances were measured at the $\lambda_{\max}$ of 597 nm and slight variations in baseline were corrected by subtracting the absorbances observed at 800 nm. Linear least squares regression analysis of the data for the dye complex method yielded the following: absorbance at 597-800nm = $0.115[U_{\text{ppm}}] - 0.074$ (S.D. of the slope = 0.004; S.D. of the intercept = 0.039; $r^2 = 0.991$) (Figure 5). Beer's law is obeyed over less than an order of magnitude which yielded a significant negative intercept when attempting to apply a linear relationship. The molar absorptivity of the U(VI)·TBP·CAS·ST complex at $\lambda_{\max}=597$ nm is $2.8 \times 10^4 \text{ l mol}^{-1}\text{cm}^{-1}$.

Compare to U(VI)·TBP·CAS·ST method, U(VI)·FOD method does not require any post extraction reagents for UV detection and it is more sensitive with 2 orders of magnitude.

4.2 The effects of the solid matrices on achievable uranium recoveries by liquid extraction

Average % recoveries for triplicate extractions of the U(VI) ion from the different matrices studies using various ethanol solvents are summarized in Table 3 (Details of 5 different modifiers used are given in the experimental part). It is obvious that the matrix has a considerable role in the amount of uranium which can be recovered using a particular solvent. For example, uranium was quantitatively recovered for polypropylene/polyester fibers using ethanol alone; whereas, acidified ethanol was required to quantitatively recover the same uranium concentration from glass wool as seen in Figure 6. For the cotton matrix, 0.1 M FOD in ethanol was required to quantitatively recover the uranium; whereas, the maximum recovery from Kaolin packing was only 80%. Without the chelating agent, FOD, no uranium was recovered from the Kaolin. The matrix effect on the recovery of uranium is probably caused by a different affinity of uranium for different matrices and/or different surface area of these matrices for uranium.

It is apparent that the interactions among these matrices with U(VI) ion are Kaolin > cotton > glass wool > polypropylene/polyester.

Solvent	Polypropylene /polyester	Glasswool	Cotton	Kaolin
100% ethanol	95.2 (5.4)	62.7 (10.0)	76.8 (1.5)	0
Ethanol+buffer (pH 5.5)	95.5 (6.4)	99.1 (0.5)	56.7 (3.7)	0
Ethanol+buffer +TBP (pH5)	89.3 (8.0)	94.1 (3.4)	46.2 (4.1)	0
Ethanol+FOD	106.8 (5.9)	97.9 (1.7)	103.3 (2.3)	80.3 (0.1)
Ethanol+FOD +TBP	102.5 (1.2)	101.1 (5.5)	97.4 (4.5)	81.3 (2.9)

Table 3. % Recovery of U(VI) ions (S.D.) from different matrices using different liquid solvents by stirring extraction

Figure 6. Recovery of U(VI) ions from different matrices using different ethanol solutions

4.3. SFE with chelating agent, a better and more efficient method for extraction of uranyl ions than liquid extraction

Average % recoveries for triplicate extractions of the U(VI) ion from Kaolin using different supercritical fluid CO₂ modifiers is summarized in Table 4 (Details of the 6 different modifiers used are given in the experimental section).

SFE was attempted in the hopes of increasing recoveries, as well as reducing the analysis time and minimizing the amount of solvent needed. Interestingly, whereas ethanol and TBP modifiers resulted in negligible recoveries of U(VI), they appear to have synergistic effects on the recovery of U(VI) when used in combination with FOD. FOD as a modifier alone yielded an average recovery of 46.6%, which increased to 75.7% when combined with TBP. Surprisingly, the recoveries of U(VI) were even higher for FOD combined with ethanol (82.2%), as seen in Figure 7. As described before, recovery of analytes relies mostly on solubility, the diffusion coefficient of the analytes in a solvent or fluid, and extractability of the target analytes in supercritical fluid. While high solubility of the analytes in supercritical fluid is a fundamental factor to achieve high recovery, the diffusivity of the analytes, and the ability of the supercritical fluid to overcome matrix-analyte interactions, as well as the extractability of analytes in the fluid are other critical factors. The U-FOD complex, the analyte of interest, is presumably more soluble in supercritical ethanol-CO₂ than in pure supercritical CO₂ or probably has higher diffusion coefficient in and stronger affinity with supercritical ethanol-CO₂. The highest average recoveries (93.1%) were observed when all three modifiers were used together, 0.1 M FOD + 0.1 M TBP in ethanol-CO₂ (5.6%,v/v).

Modifier	Kaolin
100% Ethanol	0
Ethanol + Buffer + TBP (pH 5)	2.20 (0.4)
FOD	46.6 (2.3)
FOD + TBP	75.7 (3.4)
Ethanol + FOD	82.2 (3.5)
Ethanol + FOD + TBP	93.1 (1.3)

Table 4. % Recovery of U(VI) ions (S.D.) with Kaolin using different modifiers by SFE

Figure 7. Recovery of U(VI) ions from Kaolin using different supercritical CO_2 modifiers

Compared to liquid extraction, the SFE method described here yields higher recoveries in less than half the time with equal or greater precision and a significant reduction in the amount of organic solvents used.

CONCLUSION

Determination of U(VI) ions using chelation agent FOD makes direct UV monitoring and, therefore, in situ quantitation, of the amount of uranium extracted feasible with commercially available high-pressure UV view cells. The type of solid matrix is shown to dictate the achievable uranium recoveries. The extraction of U(VI) by supercritical CO₂, modified by FOD, TBP and ethanol, is better than that by liquid extraction. This rapid and efficient chelation-supercritical fluid extraction approach may have significant application for analysis and treatment for real uranium-contaminated environmental samples.

SECTION B

INTRODUCTION

6.1. Speciation of lipids in geological solids

Lipids in environmental samples are organism-produced substances such as fats from animals, waxes from higher plants and planktonic organic matter. They are commonly found in recent and ancient sediments and are important contributors to the formation of petroleum and natural gas. Many studies on the evolution of lipids from the time of deposition to the formation of petroleum have been reported, and the evolution of lipids has been found to be useful as a molecular indicator for petroleum exploration purposes (Tissot and Welte, 1984). Therefore, studies concerning the speciation of lipids in sediments are of great interest in organic geochemistry.

Speciation of lipids is the way these compounds associate with the sediment matrix on a molecular level. A thorough understanding of the speciation of lipids in sediments can greatly help environmental chemists to accurately evaluate the fate of organic pollutants in the environment and aid organic geochemists in petroleum exploration.

It is believed that lipids are primarily associated with the bulk organic matter (OM) in sediments. Therefore, it is likely that the speciation of lipids is strongly dependent on the geochemical transformation of OM in sediments. During the burial of recent sediments, there are four zones of geochemical transformation of OM: diagenesis, catagenesis, metagenesis and metamorphism (Tissot and Welte, 1984). During diagenesis,

OM undergoes a variety of chemical and physical changes induced by microbial activity (biochemical degradation), followed by polycondensation and insolubilization under mild increase of temperature and pressure. The whole diagenetic process leads OM in sediments from biogenic polymers (biopolymers) to geopolymers, new polycondensed structures precursing kerogen, through fractionation, partial destruction and rearrangement of the building blocks of these macromolecules (Tissot and Welte, 1984). In catagenesis, kerogen produced at the end stage of diagenesis is influenced by a considerable increase in temperature and pressure. Thermal decomposition, such as massive bond cleavage of kerogen, results in the generation of hydrocarbons in the form of petroleum and natural gas. Metagenesis and metamorphism are the last two stages of the evolution of OM. In those two stages, the temperature and pressure reach very high values, and the residual kerogen is converted to graphic carbon releasing methane (Tissot and Welte, 1984).

It is widely accepted that lipids are associated with OM in sediments through partitioning, adsorption and binding processes. The lipids are therefore classified into 'free' and 'bound' categories. However, recent studies have suggested other types of speciation, such as 'trapping', which is neither 'free' nor 'bound' but 'encapsulating' or 'including' of lipids into the porous micro environment of OM (Jaffé and Gardinali, 1990). Jaffé and coworkers have indicated that the partitioning and binding processes may be the initial pathways for lipids to become associated with OM. During the deposition of OM with which lipids interact, due to macromolecule changes of the OM in sediments (during diagenesis and catagenesis), some lipids originally partitioned on or bound to OM may

become 'trapped' in internal voids of polymeric structures of OM in sediments (see Figure 8 and 9), and as such preserved from further degradation.

"Biological markers (biomarkers) are those lipids detected in the geosphere, whose basic skeleton suggests an unambiguous link with a known contemporary natural product" (Mackenzie, 1984). Over the years, biomarkers have been used for a great variety of speciation studies by geochemists. The four zones of geochemical transformation mentioned before have certainly influenced lipid biomarkers deposited in sediments. During the stage of diagenesis and catagenesis, the basic carbon skeletons of biomarkers have managed to survive with only minor alterations. The major chemical transitions of biomarkers are defunctionalization, reduction, structural rearrangements (isomerization), and aromatization. These molecular changes have been successfully applied in the assessment of diagenetic changes and thermal maturation of biomarkers and OM in general. The capability of survival of the carbon skeleton and the molecular changes in the molecular structure (e.g. isomerization) make biomarkers important tools for geochemical studies. Since 'trapped' biomarkers may be sterically hindered from isomerizing (Jaffé and Gardinali, 1990), and therefore may present a different molecular distribution compared to the 'free' biomarkers, they can be used in the assessment of speciation of organic molecules in geological samples.

Figure 8. Hypothetical structure of sedimentary organic matter with 'trapped' lipids [$17\alpha(H)$, $21\beta(H)$ -hopane]

Figure 9. Hypothetical speciation of lipids in sediments

6.2. SFE of geological samples

Identification and qualification of lipids in geological solids are usually accomplished by solvent extraction such as Soxhlet extraction or thermodesorption followed by GC-FID or GC-MS analysis. However, it is believed that while Soxhlet extraction can only recover 'free' fraction of lipids from sediments and has all drawbacks of solvent extraction mentioned in section 1.2., thermodesorption apparently discriminates against higher molecular weight compounds (Monin et al., 1987; Hopfgartner et al., 1990; Greibrokk et al., 1992). A few attempts have been made for the recovery of 'bound' and 'trapped' fractions of lipids from sediments, such as saponification and other chemical degradation processes (Albaiges et al., 1984; Lajat et al., 1990). However there are still common disadvantages of such extraction methods, especially, the harsh chemical conditions are involved.

Due to the unique physicochemical characteristics of supercritical fluids mentioned in section 1.1., SFE has been increasingly accepted as an alternative to the use of Soxhlet extraction and thermodesorption for extracting lipids from geological sediments (Monin et al., 1988; Kramer and Levy, 1989; Hopfgartner et al., 1990; Greibrokk et al., 1992; Ashraf-Khorassani et al., 1992; Furton et al., 1994 and others).

Early SFEs of sediments were performed by using toluene and pentane as supercritical fluids (Whitehead et al., 1975; Barlte et al. 1979; Smith et al., 1983). However, supercritical CO₂ soon became the most widely used supercritical fluid because of the advantages mentioned in section 1.1.. Pure supercritical CO₂ at 'normal' extraction conditions, e.g. 5000 psi and 50°C-80 °C, was used to extract biomarkers from sediments

and the results obtained for hopanes and steranes were in good agreement with those of solvent extraction, but with 45 mins of SFE vs. several hours of liquid extraction (Hopfgartner et al., 1990). Alternatively, small amounts of 2-propanol mixed with CO₂ as a modified supercritical CO₂ were used to extract petroleum source rocks to increase extraction yields (Greibrokk et al., 1992). However, because of the complex nature of the speciation of lipids with OM in sediments, 'normal' supercritical CO₂ extraction conditions apparently have insufficient ability to extract those lipids having stronger interaction with OM in sediments, such as those derived from 'binding' to and 'trapping' within the matrix. The recovery of lipids under 'normal' supercritical CO₂ extraction condition is, therefore, only similar to that from solvent extraction. Modified supercritical CO₂ extractions have yielded higher recoveries, possibly due to higher affinity of modified fluid for the matrix associated lipids or the removal/rearrangement of more polar structures within the matrix or pore environments. However, it is still unlikely that the modified CO₂ can efficiently approach those lipids 'trapped' in the internal voids of polymeric structures of OM in sediments.

Recently, Furton et al. (1994) and Jaffé et al. (1996) have reported the use of high temperature SFE (HT-SFE) for recovery of hydrophobic organic compounds in geological samples. They have found that HT-SFE (350°C) showed much higher recoveries, up to 200 %, when compared with Soxhlet extractions (24 hr.) using methylene chloride (Furton et al., 1994). These authors have suggested that higher extraction temperatures, which are impossible to achieve for standard solvent extraction, are likely to facilitate release of those lipids with stronger interaction with matrix (such as 'trapped' lipids), due to

thermally induced structural rearrangement of macromolecular OM of sediments, and increased desorption kinetics (Furton et al., 1994). In addition, the supercritical fluid has better access to the 'trapped' lipids, compared to solvents, because of its ability to penetrate into the opening porous matrix (due to thermally induced structural rearrangement of macromolecular OM of sediments). With the help of high diffusion coefficient of lipids in supercritical fluid, 'trapped' lipids can be released efficiently during high temperature experiments, possibly aided by thermal desorption, . During these earlier studies, however, only pyrolysis derived hydrocarbons such as alkanes, naphthalenes and phenanthrenes were studied. A more detailed study of biomarkers, and changes in their fingerprint/molecular distribution with increasing extraction temperature is needed to better understand the application of stepwise HT-SFE as a technique for speciation studies.

OBJECTIVES

There were two major objectives for this work:

1. To better understand the speciation of lipids in geological samples by means of evaluating the molecular maturity parameters of pentacyclic triterpenoids (hopanes), and aromatic steranes recovered from stepwise HT-SFE.
2. To evaluate the effect of stepwise HT-SFE on the relative recovery of n-alkanes, polyaromatic hydrocarbons (naphthalene, methylated naphthalenes, phenanthrene, methylated phenanthrenes, anthracene and methylated anthracenes) and biomarkers from sediments by comparison with the recovery of those compounds from Soxhlet extraction and thermodesorption.

EXPERIMENTAL

8.1. Materials

Two shale samples were analyzed: Posidonia shale [Germany; OM type I, Vitrinite reflectance: 0.36 % Ro, TOC: 10.27 (% wt.)] and Kupferschiefer shale [Germany; OM type II, Vitrinite reflectance: 0.43 % Ro, TOC: 3.09 (% wt.)]. Both samples were kindly supplied by Dr. Christian Eckardt from Bristol University, UK.

SFC/SFE grade carbon dioxide was purchased from Air Products and Chemicals (Allentown, PA) and used for all SFE experiments. UHP/zero grade nitrogen gas used for concentrating the extracts and for the thermodesorption experiment was also obtained from Air Products and Chemicals. All solvents used were optima grade and were purchased from Fisher Scientific (Orlando, FL).

8.2. Instrumentation and extraction

8.2.1. Supercritical fluid extraction

The same microprocessor-controlled syringe pump as described in section 3.2.2. was used for all supercritical fluid extractions. However, the SFX-240 extractor was replaced by a Varian 3700 GC oven (max. temperature limit at 400°C), in order to obtain higher temperatures. A 15 cm x 1 cm i.d. (1/2 in. o.d.) custom-built high pressure stainless steel column (Keystone Scientific, Inc., Bellefonte, PA) was used as the extraction cell. Two 2 μ m-sieving pore stainless steel frits (Keystone Scientific) were placed at two ends of the stainless steel column described above to prevent small samples from being flushed out. A 1 m coil of 1.6 mm o.d. (1/16 inch x 0.76 mm i.d. stainless steel tubing) (Upchurch Scientific, Inc., Oak Harbor, WA) was placed in the GC oven prior to the extraction cell as pre-equilibrium zone to pre-heat the CO₂. A needle valve (Scientific System, Inc., State College, PA), heated to 250°C with the same heating tape described in section 3.2.2. to prevent it from plugging, was used to control the flow. A glass vial containing about 5 ml methylene chloride with constant adding up to maintain the solvent volume was used for fluid decompression and analytes collection through a 9 cm x 50 μ m i.d. fused silica capillary linear restrictor (Furton et al., 1994).

The schematic diagram of the SFE system is shown in Figure 10. 3 g sample of Posidonia or Kupferschiefer shale was placed in the extraction cell and extracted by supercritical CO₂ at 5000 psi and at a consecutive stepwise temperature profile described below. The extraction temperature was controlled so that the sample was extracted at 50°C, 150°C, 250°C and 350°C, each for 30 mins followed by a lower temperature step at

Figure 10. The schematic diagram of HT-SFE system

50°C after each extraction temperature (also see Furton et al., 1994). The extraction time for each step, including the time needed for heating up and cooling down to 50°C was 60 mins. Therefore, the total extraction time for each sample, with 4 consecutive steps, was 4 hours. The stepwise temperature profile for SFE is shown in Figure 11. The flow rate used was 2.0 ml/min.

Four fractions of extracts at every extraction temperature were individually collected. A 1899 ppm squalane standard solution was prepared by weighing 0.0959 g of squalane (99%) in a 50 ml volumetric flask, mixing and diluting to volume with methylene chloride. 10 µl and 5 µl of this standard solution was added to Posidonia shale extracts at 50°C, 350°C and 150°C, 250°C respectively as internal standard before concentrating. 5 µl of another squalane internal standard solution with concentration of 1860 ppm was used for all Kupferschiefer shale extracts. Extracts were then concentrated by gentle nitrogen gas blow down prior to analysis.

8.2.2. Thermodesorption

Thermodesorption was performed for Posidonia shale only. 3 g of sample was extracted using the identical apparatus and temperature profile as used for SFE, except that the CO₂ was replaced by N₂ gas (ca. 50 psi) with a flow of 900 ml/min in order to contain a similar volume of gas N₂ to the liquid CO₂ with a flow of 2 ml/min. The pre-equilibrium coil of stainless steel tube was replaced by the same tube but with only 30 cm of length. A 530 µm i.d. uncoated fused silica capillary restrictor (Alltech Associates, Inc., Deerfield, IL) with a length of 9 cm was used as the outlet restrictor. Four fraction of extracts were collected and concentrated in the same manner as used for the extracts

Figure 11. The stepwise temperature profile for HT-SFE

from SFE. 5 μ l of 1899 ppm squalane standard solution was added to the extracts prior to concentrating as internal standard for quantitation.

8.2.3. Soxhlet extraction

All Soxhlet extractions were performed with approximate 150 ml of methylene chloride for 48 h at ca. 50°C. 10 g samples of Posidonia and Kupferschiefer shale were used. After 48 hours of extraction, 10 μ l of 1860 ppm squalane internal standard solution was added to each extract. Extracts were then concentrated with a rotary evaporator and further concentrated by N₂ gas blow down. Prior to analysis, the aliphatic and aromatic hydrocarbons in the total extracts were separated by adsorption chromatography on 21 g of 5 % activated silica column. Fractions 1 (aliphatics with the squalane internal standard), 2 and 3 (aromatics) were eluted with 60 ml hexane, 45 ml hexane/15 ml toluene and 30 ml hexane/30 ml toluene respectively and collected together. The total of 180 ml of solvents was used to ensure the analytes of interest (aliphatics, aromatics as well as internal standard) to be completely eluted out. The total extract was then concentrated by rotary evaporator and gentle N₂ gas blow down.

8.3. Identification and quantification

In addition to the biomarkers, mainly the hopanes and aromatic steranes, aliphatic hydrocarbons, such as n-alkanes, and acyclic isoprenoids, such as pristane and phytane; aromatic hydrocarbons, such as naphthalene and alkylnaphthalenes, phenanthrene and alkylphenanthrenes, anthracene and alkylanthracenes, were the target analytes for the project. All extracts were identified and quantified on an HP 5890 Series II GC (Hewlett-Packard, Palo Alto, CA) equipped with a 30m DB-5MS column (J&W Scientific, Folsom, CA) and with an HP 5971 mass selective detector (MS) (Hewlett-Packard). The temperature programming of the GC for aliphatic and aromatic hydrocarbons was 1.0 min at 40°C followed by a temperature increase rate of 6.0°C/min to 300°C and held isothermally for 20 mins. For biomarkers, the GC temperature was controlled at the same initial temperature and the same rate of increase as described above but with a constant temperature at 300°C for 30 mins. The aliphatic and aromatic hydrocarbons were analyzed by Total Ion Chromatography (TIC) and all biomarkers were analyzed by Selected Ion Monitoring (SIM). All GC/MS runs were performed in the electron impact (EI) mode at an ionization energy of approximately 70 e.v..

RESULTS AND DISCUSSION

9.1. Speciation of lipids in geological samples

Hopanes and aromatic steranes (mono and tri) detected in ancient sediments are believed to be derived from the diagenesis of natural product 'rigidifiers' of cell wall members (e.g. bacterio-hopanotetrol) and sterols (e.g. cholesterol) in organisms (Mackenzie 1984). As described in section 6.1., during diagenesis and catagenesis, these biomarkers undergo chemical transitions of defunctionalization, isomerization and aromatization. This process is initially induced by microorganisms and followed by temperature effects. The chemical transitions from the precursor molecules to thermally matured biomarkers (e.g. hopanes and aromatic steranes) are shown in Figures 12 and 13. Those thermal maturation processes of biomarkers are useful parameters in geochemical exploration.

As shown in Figure 12, polyhydroxybacteriohopane, one of the precursors of hopanes, is converted to the least stable configuration of hopanes I [$17\beta(\text{H})$, $21\beta(\text{H})$] by mainly microbial activity during early diagenesis. The least thermodynamically stable hopanes [$17\beta(\text{H})$, $21\beta(\text{H})$] are then isomerized to II [$17\beta(\text{H})$, $21\alpha(\text{H})$] (moretanes) and III [$17\alpha(\text{H})$, $21\beta(\text{H})$] (hopanes), the most stable configuration during maturation. If R in Figure 1b is equal or greater than $-\text{CH}_3$ ($\geq \text{C}_{31}$), there is a chiral center at C-22. During maturation, the biogenic 22R configuration (immature stage) is converted to a 3:2 mixture of 22S and 22R components. At this stage, thermodynamic equilibrium is reached and the isomerization process ends.

Figure 12. Polyhydroxybacteriohopanes are the presumed presursors of the ubiquitous extended hopanes found in recent and ancient sediments and in petroleum. Stereoisomers represented by the hopane structures I-III are present during early diagenesis. Stability increases in the order I [$17\beta(\text{H})$, $21\beta(\text{H})$] < II [$17\beta(\text{H})$, $21\alpha(\text{H})$] < III [$17\alpha(\text{H})$, $21\beta(\text{H})$]. The major biological input is I, but geological isomerization of the alkanes means that this converted by isomerization at C-17 to mainly III with increasing maturity. Ib, IIb and IIIb have a chiral center at C-22 ($\text{R} \geq \text{CH}_3$). In immature sediments only the 22R configuration derived from the natural product precursors. Isomerization converts this to a 3:2 mixture of 22S and 22R components (Taken from Mackenzie 1984 in *Advanced in Petroleum Geochemistry*, Volume I, pg. 128 and pg. 131; J. Brooks and D. Welte. 1984)

Figure 13. Simplified reaction scheme to show the conversion of a sterol, I, to various aromatic hydrocarbons. An arrow labeled M implies that reaction occurs in more than one step. One labeled R implies aromatization of the A ring, but with retention of the C-19 methyl group which is rearranged from C-10 to either C-1, C-4 or other positions. One labeled L implies aromatization of the B ring with the loss of the C-19 methyl group. The monoaromatic hydrocarbons II, V and VI appear during early diagenesis, but are both further aromatized to triaromatic steranes (IV, VII and VIII). The C-19 methyl group is chiefly lost when the order in which the aromatization of the rings occurs is C-B-A, but is retained if the order is A-B-C. The structure of III is not proven and is proposed on the basis of the GC-MS results. The conversion of II and III is the basis of the GC-MS results (Taken from Mackenzie 1984 in *Advanced in Petroleum Geochemistry*, Volume I, pg. 128 and pg. 131; J.Brooks and D.Welte. 1984)

For the steroidal compounds, the maturation processes are more complex. Dehydration and reduction of double bonds, structural rearrangements, configurational isomerization and aromatization are involved. The transition of a sterol (I) to various aromatic steranes shown in Figure 13 is a simplified proposed pathway of aromatization of steranes. During thermal maturation, monoaromatic steranes are converted to triaromatic steranes.

Molecular thermal maturity parameters, such as: the ratio of 22S to the sum of 22S and 22R [$22S/(22S+22R)$] and the ratio of $\beta\alpha$ -Moretanes to $\alpha\beta$ -hopanes [$\beta\alpha$ -Moretanes/ $\alpha\beta$ -hopanes] for hopanes and the ratio of triaromatic steranes to the sum of triaromatic and monoaromatic steranes [$TA/(TA+MA)$] are often used by organic geochemists for thermal maturity evaluation of the sediment, petroleum and rock samples. From the maturity conversion described before, it is obvious that with the increase of thermal maturity, the ratio of [$22S/(22S+22R)$], and [$TA/(TA+MA)$] increases and that of [$\beta\alpha$ -Moretanes/ $\alpha\beta$ -hopanes] decreases.

Inversion of such molecular maturity parameters trends has rarely been observed in the natural environment. Jaffé and Gardinali (1990) observed a relative increase in the abundance of the thermodynamically less stable (17β , 21β) isomers of the hopanoic acids in highly mature rock samples. Similarly, Kawamura et al. (1986) observed an increase in abundance of less mature long chain acids in the tightly bound fraction of shale samples. Both studies suggest that molecular speciation plays an important role in these 'apparent' maturity inversions. The explanation of this phenomenon is that immature biomarkers, encapsulated into the organic matrix at early stages of diagenesis, become 'trapped' in, or

chemically bound (e.g. via sulfur bounds; Richnow et al., 1992) to the organic matrix of the sediments. At high temperature regimes, these components, which are protected from maturation processes by steric effects of the matrix, become released causing the 'apparent' maturity inversion. Based on the hypothesis described above, biomarker maturity parameters can be used to study speciation of organic compounds in sediments and rock samples. This would be particularly useful if it is assumed that 'trapped' components are released during stepwise HT-SFE experiments. Data in support of this assumption has been produced by former research activities in our laboratories by studying the pyrolysis derived hydrocarbons such as alkanes, naphthalenes and phenanthrenes (Huang, 1994; Gong, 1995; Furton et al., 1994). Based on these results, a decrease in the thermal maturity parameters $[22S/(22S+22R)]$ and $[TA/(TA+MA)]$, and an increase in $[\beta\alpha\text{-Moretanes}/\alpha\beta\text{-hopane}]$ of biomarkers would be expected with increasing extraction temperature, if release of 'trapped' hydrocarbons actually occurs under these conditions.

Hopanes and aromatic steranes extracted from Posidonia and Kupferschiefer shale by stepwise HT-SFE were used for molecular maturity and speciation study in this project. The ion 191, 253 and 231 (mass chromatograms) of hopanes, mono and triaromatic steranes from HT-SFE of Posidonia shale at 50°C fraction are shown in Figures 14, 15 and 16. The peaks identified are listed in Tables 5, 6 and 7. Average recoveries of hopanes, mono and triaromatic steranes from triplicate and single stepwise HT-SFE of Posidonia and Kupferschiefer shale at each fraction (50°C, 150°C, 250°C and 350°C) are summarized in Tables 8, 9, 10, 11, 12, and 13. It is apparent that the amount of biomarkers released at each temperature is different, indicating possible differences in the speciation of these

Figure 14. $m/z = 191$ Mass chromatogram of hopanes from stepwise HT-SFE of Posidonia shale at 50°C

Figure 15. $m/z = 253$ Mass chromatogram of monoaromatic steranes from stepwise HT-SFE of Posidonia shale at 50°C

Figure 16. $m/z = 231$ Mass chromatogram of triaromatic steranes from stepwise HT-SFE of Posidonia shale at 50°C

Peak number	Formula	Name
1	C ₂₉ H ₅₀	17 α (H),21 β (H)-30-norhopane
2	C ₂₉ H ₅₀	17 β (H),21 α (H)-30-norhopane (normoretane)
3	C ₃₀ H ₅₂	17 α (H),21 β (H)-hopane
4	C ₃₀ H ₅₂	17 β (H),21 α (H)-hopane (moretane)
5	C ₃₁ H ₅₄	17 α (H),21 β (H)-29-homohopane (22S)
6	C ₃₁ H ₅₄	17 α (H),21 β (H)-29-homohopane (22R)
7	C ₃₂ H ₅₆	17 α (H),21 β (H)-29-bishopane (22S)
8	C ₃₂ H ₅₆	17 α (H),21 β (H)-29-bishopane (22R)
9	C ₃₃ H ₅₈	17 α (H),21 β (H)-29-trishopane (22S)
10	C ₃₃ H ₅₈	17 α (H),21 β (H)-29-trishopane (22R)
11	C ₃₄ H ₆₀	17 α (H),21 β (H)-29-tetrakishopane (22S)
12	C ₃₄ H ₆₀	17 α (H),21 β (H)-29-tetrakishopane (22R)
13	C ₃₅ H ₆₂	17 α (H),21 β (H)-29-pentakishopane (22S)
14	C ₃₅ H ₆₂	17 α (H),21 β (H)-29-pentakishopane (22R)

Table 5. The peaks identified for m/z = 191 (hopanes) mass chromatogram from stepwise HT-SFE of Posidonia shale at 50°C (The name of peaks: The Biomarker Guide, Peters and Molddowan, 1993. pg.: 77)

Peak number	Formula	Name
15	C ₂₇ H ₄₂	5β(H) cholestane (20S)
16	C ₂₇ H ₄₂	5β(H) cholestane (20R)
17	C ₂₇ H ₄₂	5α(H) cholestane (20S)
	C ₂₈ H ₄₄	5β(H) ergostane (20S)
18	C ₂₇ H ₄₂	5α(H) cholestane (20R)
	C ₂₈ H ₄₄	5α(H) ergostane (20S)
	C ₂₈ H ₄₄	5β(H) ergostane (20R)
	C ₂₉ H ₄₆	5β(H) stigmastane (20S)
19	C ₂₉ H ₄₆	5α(H) stigmastane (20S)
20	C ₂₈ H ₄₄	5α(H) ergostane (20R)
	C ₂₉ H ₄₆	5β(H) stigmastane (20R)
21	C ₂₉ H ₄₆	5α(H) stigmastane (20R)

Table 6. The peaks identified for $m/a = 253$ (monoaromatic steranes) mass chromatogram from stepwise HT-SFE of Posidonia shale at 50°C (The name of peaks: The biomarker Guide, Peters and Molddowan, 1993. pg.: 79)

Peak number	Formula	Name
22	C ₂₆ H ₃₂	Cholestane (20S)
23	C ₂₆ H ₃₂	Cholestane (20R)
	C ₂₇ H ₃₄	Ergostane (20S)
24	C ₂₈ H ₃₆	Stigmastane (20S)
25	C ₂₇ H ₃₄	Ergostane (20R)
26	C ₂₈ H ₃₆	Stigmastane (20R)

Table 7. The peaks identified for $m/z = 231$ (triaromatic steranes) mass chromatogram from stepwise HT-SFE of Posidonia shale at 50°C (The name of peaks: The biomarker Guide, Peters and Molddowan, 1993. pg.: 81)

Comp	50°C (ppm)(S.D.)	150°C (ppm)(S.D.)	250°C (ppm)(S.D.)	350°C (ppm)(S.D.)
C ₂₉ αβ	0.522(0.01)	0.827(0.4)	0.183(0.07)	0.110(0.03)
C ₂₉ βα	0.126(0.008)	0.171(0.03)	0.025(0.008)	0.029(0.01)
C ₃₀ αβ	0.967(0.06)	1.34(0.6)	0.118(0.05)	0.031(0.01)
C ₃₀ βα	0.214(0.01)	0.280(0.07)	0.020(0.008)	0.017(0.008)
C ₃₁ αβ(S)	0.377(0.03)	0.444(0.09)	0.054(0.02)	0.009(0.004)
C ₃₁ αβ(R)	0.276(0.02)	0.327(0.06)	0.040(0.01)	0.018(0.008)
C ₃₂ αβ(S)	0.212(0.02)	0.259(0.08)	0.025(0.01)	0.003(0.0007)
C ₃₂ αβ(R)	0.202(0.02)	0.249(0.09)	0.028(0.01)	0.013(0.005)
C ₃₃ αβ(S)	0.337(0.05)	0.376(0.08)	0.030(0.01)	N.D.
C ₃₃ αβ(R)	0.327(0.05)	0.347(0.07)	0.037(0.01)	N.D.
C ₃₄ αβ(S)	0.232(0.04)	0.210(0.03)	0.016(0.007)	N.D.
C ₃₄ αβ(R)	0.204(0.02)	0.198(0.03)	0.022(0.008)	N.D.
C ₃₅ αβ(S)	0.170(0.04)	0.162(0.03)	0.014(0.007)	N.D.
C ₃₅ αβ(R)	0.238(0.05)	0.203(0.03)	0.017(0.007)	N.D.

Table 8. Recoveries of Hopanes (S.D.) from triplicate stepwise HT-SFE of Posidonia shale

Comp	50°C (ppm)(S.D.)	150°C (ppm)(S.D.)	250°C (ppm)(S.D.)	350°C (ppm)(S.D.)
5β(H)C ₂₇ (20S)	0388(0.04)	0.444(0.03)	0.020(0.008)	N.D.
5β(H)C ₂₇ (20R)	0.485(0.03)	0.541(0.06)	0.027(0.01)	N.D.
*	1.38(0.11)	1.76(0.22)	0.083(0.04)	N.D.
**	2.68(0.24)	3.37(0.37)	0.144(0.007)	N.D.
5α(H)C ₂₉ (20S)	0.818(0.06)	1.13(0.01)	0.046(0.02)	N.D.
***	1.25(0.06)	1.52(0.05)	0.056(0.03)	N.D.
5α(H)C ₂₉ (20R)	0.502(0.005)	0.618(0.09)	0.023(0.01)	N.D.

*: 5α(H)C₂₇(20S) + 5β(H)C₂₈(20S)

**: 5α(H)C₂₇(20R) + 5α(H)C₂₈(20S) + 5β(H)C₂₈(20R) + 5β(H)C₂₉(20S)

***: 5α(H)C₂₈(20R) + 5β(H)C₂₉(20R)

Table 9. Recoveries of monoaromatic steranes (S.D.) from triplicate stepwise HT-SFE of Posidonia shale

Comp	50°C (ppm)(S.D.)	150°C (ppm)(S.D.)	250°C (ppm)(S.D.)	350°C (ppm)(S.D.)
C ₂₆ (20S)	1.05(0.09)	1.07(0.11)	0.088(0.007)	0.005(0.003)
*	2.37(0.36)	2.18(0.31)	0.149(0.03)	0.010(0.005)
C ₂₈ (20S)	1.39(0.32)	1.38(0.21)	0.080(0.01)	0.007(0.002)
C ₂₇ (20R)	1.32(0.43)	1.16(0.16)	0.078(0.01)	0.005(0.003)
C ₂₈ (20R)	2.12(0.45)	1.38(0.24)	0.083(0.02)	0.008(0.002)

* C₂₆(20R) + C₂₇(20S)

Table 10. Recoveries of triaromatic steranes (S.D.) from triplicate stepwise HT-SFE of Posidonia shale

Comp	50°(C)(ppm)	150°(C)(ppm)	250°(C)(ppm)	350°(C)(ppm)
C ₃₀ αβ	0.065	0.065	0.046	0.132
C ₃₀ βα	0.052	0.048	0.030	0.182
C ₃₁ αβ(S)	0.022	0.023	0.016	0.010
C ₃₁ αβ(R)	0.107	0.109	0.076	0.139
C ₃₂ αβ(S)	0.005	0.006	0.004	0.004
C ₃₂ αβ(R)	0.032	0.032	0.023	0.056

Table 11. Recoveries of Hopanes from single stepwise HT-SFE of Kupferschiefer shale

Comp	50°(C)(ppm)	150°(C)(ppm)	250°(C)(ppm)	350°(C)(ppm)
5β(H)C ₂₇ (20S)	0.115	0.085	0.023	0.005
5β(H)C ₂₇ (20R)	0.138	0.102	0.032	0.012
*	0.390	0.314	0.101	0.027
**	1.04	0.824	0.236	0.086
5α(H)C ₂₉ (20S)	0.419	0.362	0.106	0.042
***	0.612	0.473	0.123	0.052
5α(H)C ₂₉ (20R)	0.304	0.243	0.065	0.034

*: 5α(H)C₂₇(20S) + 5β(H)C₂₈(20S)

**: 5α(H)C₂₇(20R) + 5α(H)C₂₈(20S) + 5β(H)C₂₉(20S) + 5α(H)C₂₉(20R)

***: 5α(H)C₂₈(20R) + 5β(H)C₂₉(20R)

Table 12. Recoveries of monoaromatic steranes from single stepwise HT-SFE of Kupferschiefer shale

Comp	50°(C)(ppm)	150°(C)(ppm)	250°(C)(ppm)	350°(C)(ppm)
C ₂₆ (20S)	0.025	0.026	0.022	0.064
*	0.055	0.057	0.045	0.110
C ₂₈ (20S)	0.077	0.085	0.062	0.147
C ₂₇ (20R)	0.028	0.031	0.026	0.071
C ₂₈ (20R)	0.068	0.066	0.055	0.152

* C₂₆(20R) + C₂₇(20S)

Table 13. Recoveries of triaromatic steranes from single stepwise HT-SFE of Kupferschiefer shale

biomarkers. The majority of the hopanes in Posidonia shale were released at 50°C and 150°C (see Table 8). They likely belong to 'free' and/or 'weakly binding' categories, which are not strongly associated with OM in sediments and, are, therefore, the easiest to be released. Small amount of hopanes extracted at 250°C were probably 'strongly associated' species, which need higher thermal energy for their release. About 3 % of hopanes were released at 350°C with a significantly different molecular distribution. The comparison of ion 191 mass chromatogram of hopanes from stepwise HT-SFE of Posidonia shale at 50°C and 350°C is shown in Figure 17. It is apparent that hopanes with immature configurations are released at 350°C, suggesting a different speciation of these compounds from 'free' and 'strongly associated' species. Such changes of maturity parameter vs. temperature can provide insight to this different speciation. Tables 14 and 15 are summarized results of maturity parameter for hopanes at each temperature fraction from triplicate stepwise HT-SFE of Posidonia shale (the ratio of peak area were used for all maturity parameter calculation). A decrease of ratio $[22S/(22S+22R)]$ and increase of ratio $[\beta\alpha\text{-Moretanes}/\alpha\beta\text{-hopanes}]$ at extraction temperature of 350°C, indicated that significant amount of immature configurations does exist in the 'trapped' or 'strongly associated' fraction. Such a maturity inversion (see Figures 18 and 19) agrees with the results observed by Jaffé and coworkers (1990) in ancient rock samples and, who suggested this to be caused by steric hindrance of isomerization of immature compounds 'trapped' within internal voids of macromolecular OM. Release of those 'trapped' compounds occurs during rearrangement of the macromolecular matrix under high temperature conditions. Interestingly, about 40% of hopanes in Kupferschiefer shale

Figure 17. Mass chromatograms of hopanes ($m/z = 191$) from stepwise HT-SFE of Posidonia shale at 50°C and 350°C

Comp	50°C(S.D.)	150°C(S.D.)	250°C(S.D.)	350°C(S.D.)
C ₃₁	0.578(0.002)	0.576(0.005)	0.576(0.002)	0.325(0.01)
C ₃₂	0.512(0.01)	0.513(0.01)	0.475(0.004)	0.217(0.03)
C ₃₃	0.507(0.009)	0.519(0.002)	0.448(0.01)	N.D.
C ₃₄	0.531(0.02)	0.514(0.001)	0.429(0.01)	N.D.
C ₃₅	0.416(0.003)	0.444(0.001)	0.446(0.02)	N.D.

Table 14. Maturity parameter of [22S/(22S + 22R)] (S.D.) for Posidonia shale from triplicate stepwise HT-SFE

Comp	50°C(S.D.)	150°C(S.D.)	250°C(S.D.)	350°C(S.D.)
C ₂₉	0.241(0.02)	0.203(0.01)	0.140(0.01)	0.260(0.02)
C ₃₀	0.221(0.003)	0.199(0.02)	0.168(0.003)	0.556(0.06)

Table 15. Maturity parameter of [$\beta\alpha$ -Moretane/ $\alpha\beta$ -Hopane] (S.D.)for Posidonia shale from triplicate stepwise HT-SFE

Figure 18. Maturity parameter of $[22S/(22S+22R)]$ vs. temperature of Posidonia shale

Figure 19. Maturity parameter of $[\beta\alpha\text{-Moretane}/\alpha\beta\text{-Hopane}]$ vs. temperature of Posidonia shale

were released at 350°C, much more than those in Posidonia shale (see Table 11). Correspondingly, the inversions of molecular maturity parameters of $[22S/(22S+22R)]$ and $[\beta\alpha\text{-Moretane}/\alpha\beta\text{-Hopane}]$ for Kupferschiefer shale were more significant than for Posidonia shale. (See Tables 16, 17 and Figures 20 and 21). Apparently more hopanes are 'trapped' in Kupferschiefer shale.

Similar to the hopanes, for Posidonia shale, most mono and triaromatic steranes were released at 50°C and 150°C. Very small amount of mono and triaromatic steranes were extracted at 250°C. For extracts at 350°C, only trace amounts of triaromatic steranes were found. Monoaromatic steranes were not detected at 350°C (Table 9 and 10). Table 18 illustrated the maturity parameter of $[TA/(TA+MA)]$ at each temperature fraction from triplicate stepwise HT-SFE of Posidonia shale. Interestingly, the ratio of $[TA/(TA+MA)]$ follows an increasing thermal maturity trend (opposed to the hopanes), which is that the ratio increases with increase of temperature (Table 18 and Figure 22). There are two possible reasons. One is possibly that the steric hindrance has no effect on aromatization process due to the planar molecular shape of the aromatic hydrocarbons. Therefore, 'trapped' monoaromatic steranes can still be converted to triaromatic steranes by temperature effects. The other is likely that triaromatic steranes have stronger interaction with the matrix than monoaromatic steranes (as shown by the behavior of the phenanthrenes, see below). The later are less aromatic, and less planar and should, therefore, have a weaker interaction with the organic matrix and can, therefore, be extracted at lower temperatures (i.e. lower energies). Tables 12 and 13 show the amount of mono and triaromatic steranes recovered from Kupferschiefer shale by stepwise

Comp	50°C	150°C	250°C	350°C
C ₃₁	0.174	0.177	0.179	0.064
C ₃₂	0.148	0.148	0.153	0.007

Table 16. Maturity parameter of [22S/(22S+22R)] for Kupferschiefer shale from single stepwise HT-SFE

Comp	50°C	150°C	250°C	350°C
C ₃₀	0.802	0.734	0.669	1.379

Table 17. Maturity parameter of [$\beta\alpha$ -Moretane/ $\alpha\beta$ -Hopane] for Kupferschiefer shale from single stepwise HT-SFE

50°C(S.D.)	150°C(S.D.)	250°C(S.D.)	350°C(S.D.)
0.516(8.2)	0.414(8.5)	0.548(14.4)	1

Table 18. Maturity parameter of [TA/(TA+MA)] for Posidonia shale from triplicate stepwise HT-SFE

50°C(S.D.)	150°C(S.D.)	250°C(S.D.)	350°C(S.D.)
0.077	0.099	0.235	0.679

Table 19. Maturity parameter of [TA/(TA+MA)] for Kupferschiefer shale from single stepwise HT-SFE

Figure 20. Maturity parameter of $[22S/(22S+22R)]$ vs. temperature of Kupferschiefer shale

Figure 21. Maturity parameter of $[\beta\alpha\text{-Moretane}/\alpha\beta\text{-Hopane}]$ vs. temperature of Kupferschiefer shale

Figure 22. Maturity parameter of $[TA/(MA+TA)]$ vs. temperature of Posidonia shale

Figure 23. Maturity parameter of $[TA/(MA+TA)]$ vs. temperature of Kupferschiefer shale

HT-SFE. In agreement with the Posidonia shale experiment, it is apparent that a tremendous amount of aromatic steranes in Kupferschiefer shale was 'trapped' within the internal voids of macromolecular OM. However, the aromatic steranes are not sterically hindered from aromatization reactions when in the 'trapped' form. Therefore, the increment in the $[TA/(TA+MA)]$ was observed (Table 19 and Figure 23).

It can be concluded that molecular maturity parameters of biomarkers can be a useful geochemical tool for speciation studies with stepwise HT-SFE as a technique. The thermal maturity inversion of the hopanes clearly shows the release of 'trapped' hydrocarbons at elevated SFE extraction temperature.

9.2. Stepwise HT-SFE, thermodesorption and Soxhlet extraction on recovery of hydrocarbons and biomarkers

Aliphatic and aromatic hydrocarbons detected in ancient sediments are believed to be derived from the thermal degradation of kerogen. As described in section 6.1., Kerogen, which is the product of diagenesis, undergoes thermal decomposition (massive bond cleavage) due to temperature effects during catagenesis.

Aliphatic hydrocarbons, such as n-alkanes, as well as branched alkanes (pristane and phytane), and aromatic hydrocarbons, such as naphthalene, alkyl-naphthalenes, anthracene, alkyl-anthracenes, phenanthrene, alkyl-phenanthrenes in Posidonia shale and biomarkers, such as hopanes, monoaromatic steranes and triaromatic steranes in both Posidonia and Kupferschiefer shales were target analytes. The ion 57 mass chromatogram of aliphatic hydrocarbons and the ions 128, 142, 156 and 170 of naphthalene, methyl-naphthalenes, dimethyl-naphthalenes and trimethyl-naphthalenes, as well as the ions 178, 192 and 206 mass chromatograms of phenanthrene, methyl-phenanthrenes and dimethyl-phenanthrenes (as well as the corresponding anthracenes) from stepwise HT-SFE of Posidonia shale at 50°C fraction (and 350°C fraction for phenanthrenes only) are shown in Figures 24, 25, 26 and 27. The peaks identified are listed in Tables 20, 21 and 22. The mass chromatograms and the peaks identified of biomarkers are shown in section 9.1..

Average results of the recovery of aliphatic and aromatic hydrocarbons from each fraction of triplicate stepwise HT-SFE of Posidonia shale are summarized in Tables 23, 24 and 25. Average results of the recovery of biomarkers are shown in section 9.1.. For aliphatic and aromatic hydrocarbons, it is apparent that recovery from stepwise HT-SFE is

Figure 24. $m/z=57$ Mass chromatogram of aliphatic hydrocarbons from stepwise HT-SFE of Posidonia shale at 50°C

Figure 25. $m/z=128, 142, 156$ and 170 Mass chromatograms of naphthalene, methyl-naphthalenes, dimethyl-naphthalenes and trimethyl-naphthalenes (aromatic hydrocarbons) from stepwise HT-SFE of Posidonia shale at 50°C

Figure 26. $m/z=178$, 192 and 206 Mass chromatograms of phenanthrene, methyl-phenanthrenes and dimethyl-phenanthrenes (aromatic hydrocarbons) from stepwise HT-SFE of Posidonia shale at 50°C

Figure 27. $m/z=178$, 192 and 206 Mass chromatograms of phenanthrene, anthracene, methyl-phenanthrenes, methyl-anthracenes, dimethyl-phenanthrenes and dimethyl-anthracenes (aromatic hydrocarbons) from stepwise HT-SFE of Posidonia shale at 350°C

Peak number	Formula	Name
27	C ₁₀ H ₂₂	Decane
28	C ₁₁ H ₂₄	Undecane
29	C ₁₂ H ₂₆	Dodecane
30	C ₁₃ H ₂₈	Tridecane
31	C ₁₄ H ₃₀	Tetradecane
32	C ₁₅ H ₃₂	Pentadecane
33	C ₁₆ H ₃₄	Hexadecane
34	C ₁₇ H ₃₆ +C ₁₉ H ₄₀ (Pri)	Heptadecane+Pristane
35	C ₁₈ H ₃₈	Octadecane
36	C ₂₀ H ₄₂ (Phy)	Phytane
37	C ₁₉ H ₄₀	Nonadecane
38	C ₂₀ H ₄₂	Eicosane
39	C ₂₁ H ₄₄	Heneicosane
40	C ₂₂ H ₄₆	Docosane
41	C ₂₃ H ₄₈	Tricosane
42	C ₂₄ H ₅₀	Tetracosane
43	C ₂₅ H ₅₂	Pentacosane
44	C ₂₆ H ₅₄	Hexacosane
45	C ₂₇ H ₅₆	Heptacosane
46	C ₂₈ H ₅₈	Octacosane
47	C ₂₉ H ₆₀	Nonacosane
48	C ₃₀ H ₆₂	Triacontane
49	C ₃₁ H ₆₄	Hentriacontane
50	C ₃₂ H ₆₆	Dotriacontane
51	C ₃₃ H ₆₈	Tritriacontane

Table 20. The peaks identified for $m/z = 57$ (aliphatic hydrocarbons) mass chromatogram from stepwise HT-SFE of Posidonia shale at 50°C

Peak number	Formula	Name
52	C ₁₀ H ₈	Naphthalene
53	C ₁₁ H ₁₀	C-1 methyl-naphthalene
54	C ₁₁ H ₁₀	C-2 methyl-naphthalene
55	C ₁₂ H ₁₂	1-ethyl+2-ethyl-naphthalene
56	C ₁₂ H ₁₂	2,6+2,7 dimethyl- naphthalene
57	C ₁₂ H ₁₂	1,3+1,7 dimethyl- naphthalene
58	C ₁₂ H ₁₂	1,6 dimethyl- naphthalene
59	C ₁₂ H ₁₂	1,4+1,3+1,5 dimethyl- naphthalene
60	C ₁₂ H ₁₂	1,8 dimethyl- naphthalene
61	C ₁₃ H ₁₄	1,3,7 trimethyl-naphthalene
62	C ₁₃ H ₁₄	1,3,6 trimethyl-naphthalene
63	C ₁₃ H ₁₄	1,4,6+1,3,5 trimethyl-naphthalene
64	C ₁₃ H ₁₄	2,3,6 trimethyl-naphthalene
65	C ₁₃ H ₁₄	1,2,7+1,6,7+1,2,6 trimethyl-naphthalene
66	C ₁₃ H ₁₄	1,2,5 trimethyl-naphthalene

Table 21. The peaks identified for m/z = 128, 142, 156 and 170 (aromatic hydrocarbons) mass chromatogram from stepwise HT-SFE of Posidonia shale at 50°C

Peak number	Formula	Name
67	C ₁₄ H ₁₀	Phenanthrene
68	C ₁₄ H ₁₀	Anthracene
69	C ₁₅ H ₁₂	3 methyl-phenanthrene
70	C ₁₅ H ₁₂	2 methyl-phenanthrene
71	C ₁₅ H ₁₂	2 methyl-anthracene
72	C ₁₅ H ₁₂	9 methyl-phenanthrene
73	C ₁₅ H ₁₂	1 methyl-phenanthrene
74	C ₁₅ H ₁₂	1 methyl-phenanthrene+1 methyl-anthracene
75	C ₁₅ H ₁₂	9 methyl-anthracene

Table 22. The peaks identified for m/z = 178, 192, and 206 (aromatic hydrocarbons) mass chromatogram from stepwise HT-SFE of Posidonia shale at 50°C and 350°C

Comp	50°C (ppm)(S.D.)	150°C (ppm)(S.D.)	250°C (ppm)(S.D.)	350°C (ppm)(S.D.)
C ₁₀	14.1(0.9)	1.71(0.3)	0.515(0.1)	0.788(0.2)
C ₁₁	15.0(1.2)	1.78(0.3)	0.536(0.1)	1.15(0.3)
C ₁₂	12.0(2.6)	2.07(0.4)	0.523(0.2)	1.10(0.2)
C ₁₃	12.9(0.7)	2.17(0.3)	0.648(0.2)	1.31(0.3)
C ₁₄	13.0(0.2)	2.50(0.4)	0.731(0.3)	1.02(0.3)
C ₁₅	13.1(0.7)	2.60(0.3)	0.579(0.1)	0.950(0.3)
C ₁₆	11.9(1.3)	2.40(0.4)	0.541(0.1)	0.722(0.2)
C ₁₇ +Pri	37.9(3.3)	10.0(0.8)	1.89(0.4)	0.930(0.1)
C ₁₈	9.09(1.3)	2.03(0.2)	0.476(0.1)	0.488(0.2)
Phy	13.0(1.5)	4.04(0.4)	0.808(0.2)	N.D.
C ₁₉	7.50(0.9)	1.83(0.3)	0.524(0.1)	0.501(0.1)
C ₂₀	6.33(0.2)	1.58(0.3)	0.456(0.04)	0.616(0.2)
C ₂₁	5.42(0.09)	1.44(0.3)	0.434(0.07)	0.535(0.2)
C ₂₂	4.36(0.2)	1.34(0.2)	0.401(0.07)	0.521(0.2)
C ₂₃	4.18(0.2)	1.36(0.2)	0.424(0.09)	0.494(0.1)
C ₂₄	4.20(0.3)	1.58(0.1)	0.519(0.09)	0.447(0.1)
C ₂₅	3.68(0.5)	1.55(0.3)	0.496(0.09)	0.418(0.09)
C ₂₆	3.15(0.4)	1.62(0.4)	0.505(0.1)	0.477(0.1)
C ₂₇	1.99(0.1)	1.05(0.3)	0.351(0.05)	0.339(0.1)
C ₂₈	1.90(0.03)	0.872(0.06)	0.350(0.1)	0.321(0.08)
C ₂₉	1.53(0.2)	0.664(0.05)	0.231(0.04)	0.305(0.06)
C ₃₀	1.53(0.3)	0.754(0.04)	0.223(0.03)	0.267(0.07)
C ₃₁	1.30(0.3)	0.877(0.07)	0.245(0.08)	0.220(0.08)
C ₃₂	0.965(0.2)	0.713(0.04)	0.187(0.06)	0.187(0.06)
C ₃₃	0.876(0.2)	0.694(0.1)	0.165(0.04)	N.D.

Table 23. Recovery of aliphatic hydrocarbons (S.D.) from triplicate stepwise HT-SFE of Posidonia shale

Comp	50°C (ppm)(S.D.)	150°C (ppm)(S.D.)	250°C (ppm)(S.D.)	350°C (ppm)(S.D.)
Naphthalene	12.8(1.3)	2.26(0.8)	3.99(0.6)	6.78(2.1)
C-1 MN	15.1(1.2)	3.51(0.6)	5.23(1.5)	13.5(3.1)
C-2 MN	13.9(1.1)	4.77(0.7)	4.66(1.3)	8.19(1.7)
Total MN	29.0(1.6)	8.28(1.2)	9.89(2.7)	21.7(4.8)
1-E,2-EN	2.84(0.3)	0.976(0.1)	1.30(0.3)	3.09(0.6)
2,6,2,7-DMN	4.36(0.5)	1.27(0.2)	2.51(0.6)	8.65(1.9)
1,3;1,7-DMN	6.07(0.5)	2.26(0.2)	3.07(0.8)	10.0(1.9)
1,6-DMN	6.5(1.1)	2.70(0.2)	3.32(0.6)	6.43(0.8)
*	4.85(0.4)	1.81(0.3)	2.21(0.4)	5.49(0.9)
1,8-DMN	2.06(0.2)	0.830(0.2)	1.06(0.2)	2.66(0.3)
Total DMN	26.7(2.7)	9.84(0.9)	13.5(2.6)	36.3(6.3)
1,3,7-TMN	2.26(0.4)	1.10(0.1)	1.33(0.3)	6.86(1.4)
1,3,6-TMN	3.42(0.6)	1.64(0.2)	1.59(0.4)	7.11(1.6)
1,4,6,1,3,5-TMN	2.18(0.3)	1.27(0.07)	1.15(0.3)	4.83(0.9)
2,3,6-TMN	1.30(0.1)	0.527(0.07)	0.787(0.2)	5.12(0.8)
**	3.17(0.4)	1.58(0.05)	1.86(0.4)	8.78(1.5)
1,2,5-TMN	1.45(0.1)	0.812(0.1)	0.711(0.1)	1.60(0.1)
Total TMN	13.8(1.9)	6.93(0.4)	7.43(1.7)	34.3(6.1)

*: 1,4+1,3+1,5 DMN

**: 1,2,7+1,6,7+1,2,6TMN

Table 24. Recovery of naphthalene and alkyl-naphthalenes (aromatic hydrocarbons) (S.D.) from triplicate stepwise HT-SFE of Posidonia shale

Comp	50°C (ppm)(S.D.)	150°C (ppm)(S.D.)	250°C (ppm)(S.D.)	350°C (ppm)(S.D.)
Phenanthrene	2.30(0.1)	0.932(0.2)	1.59(0.2)	3.58(0.7)
Anthracene	N.D.	N.D.	N.D.	1.81(0.4)
3-MP	0.709(0.08)	0.394(0.05)	0.509(0.09)	2.29(0.4)
2-MP	0.885(0.2)	0.469(0.05)	0.619(0.1)	2.80(0.5)
2-MA	N.D.	N.D.	N.D.	2.21(0.9)
9-MP	1.07(0.2)	0.635(0.05)	0.672(0.1)	2.71(0.5)
1-MP	1.30(0.2)	0.825(0.07)	1.48(0.1)	N.D.
1-MP+1-MA	N.D.	N.D.	N.D.	5.03(1.4)
9-MA	N.D.	N.D.	N.D.	0.667(0.3)
Total MP	3.97(0.8)	2.32(0.08)	3.28(0.5)	N.D.
Total MP+MA	N.D.	N.D.	N.D.	15.7(2.0)
Total DMP	2.85(0.6)	1.85(0.2)	2.16(0.4)	N.D.
*	N.D.	N.D.	N.D.	21.0(4.6)

*: Total DMP+DMA

Table 25. Recovery of Phenanthrene, anthracene, alkyl-phenanthrenes and alkyl-anthracenes (aromatic hydrocarbons) (S.D.) from triplicate stepwise HT-SFE of Posidonia shale

varied for different types of hydrocarbons and different extraction temperatures. As seen in Figures 28, 29 and 30, most hydrocarbons showed high recoveries at 50°C followed by decreases in recoveries at 150°C and 250°C with an increment at 350°C (especially for most aromatic hydrocarbons). However, whilst aliphatic hydrocarbons showed a minimum at 250°C, the aromatics reached the minimum at 150°C. In addition, the ratio of extracted compounds at 50°C vs 350°C (50/350) was larger than one for the aliphatics, naphthalene, and methyl-naphthalenes, but is much below unity for other aromatics. The ratio of 50/350 also decreased with increasing number of aromatic rings and with increasing degree of alkylation. In addition, anthracene and alkyl-anthracenes were only released at 350°C. As mentioned in section 1.2., the recovery of the analytes from solid matrices depends on solubility and diffusivity of analytes in a solvent or fluid, and particularly, the competition between the affinity of the analytes for the matrix (OM in this study) and for solvent or fluid, and the speciation of analytes. In general, the hydrocarbons obtained in the 50°C fraction of stepwise HT-SFE are presumably those weakly associated with matrix and the main reason for their release is solubility. The density of a supercritical fluid (the solubility of analytes in supercritical fluid) decreases with the increase of the temperature under the same pressure. Therefore, compared to the extractions performed at other temperatures, the solubility of analytes in supercritical CO₂ (at 5000 psi) at 50°C is the highest. A significant increase of recoveries at 350°C has definitely some connection with the thermally energy supply and the advantages of supercritical fluid extraction. As mentioned before, hydrocarbons in geological samples were produced by pyrolysis of kerogen. Therefore, it is understandable that many of them

Figure 28. Aliphatic hydrocarbons recovered (ppm) from HT-SFE of Posidonia shale vs. temperature

Figure 29. Naphthalene and alkyl-naphthalenes recovered (ppm) from HT-SFE of Posidonia shale vs. temperature

Figure 30. Phenanthrene alkyl-phenanthrenes and alkyl-anthracenes recovered (ppm) from HT-SFE of Posidonia shale vs. temperature

are strongly associated with and 'trapped' within internal voids of polymeric structures of OM. With the help of thermally induced rearrangement of the macromolecular OM (presumably occurring at high temperature), and the efficient penetration of supercritical fluid into the open porous and the high diffusion coefficient of analytes in supercritical fluid, those hydrocarbons strongly associated with OM were able to overcome interactions with OM and be released. Those hydrocarbons 'trapped' within polymeric structure of OM were, therefore, (for the same reasons) accessible for the supercritical fluid and extracted. The reason that the ratio of extracted compounds at 50°C vs 350°C was more than one for aliphatics and less than one for aromatics, and the fact that the ratio decreased for aromatics with the increase the number of aromatic rings and degree of alkylation, is most likely due to the strong interactions of those hydrocarbons with the matrix. As mentioned in section 9.1., the more aromatic, the more planar. Therefore, the more surface areas were available for interacting with the matrix and the more difficult to be released. Additionally, as these compounds became alkylated, they become more difficult to recover from the matrix. However, due to the increased desorption kinetics at high temperature and the higher volatility of these aromatics, they were able to be efficiently released. Anthracene and alkyl-anthracenes must either have stronger interactions with OM in sediments than phenanthrenes, or have a different origin, therefore, they were only released at high temperature. Recently Smith et al (1995) have suggested that significant increment of alkyl-aromatics during heating experiments (66hrs) at 350°C -400°C is the result of syntheses of alkyl-aromatics by the reaction of parent aromatic hydrocarbons (naphthalene and phenanthrene) with n-alkanes (Smith et al.,

1995). Investigation on methylation is under way in our research group in order to find out whether or not this is another reason that the ratio of 50/350 decreases with the increase of the number of aromatic ring and the degree of alkylation.

To further evaluate the effect of thermal energy supply on the recovery of hydrocarbons, Posidonia shale was subjected to thermodesorption. Average results of the recovery of aliphatic, aromatic hydrocarbons from each fraction of triplicate thermodesorption of Posidonia shale are summarized in Tables 26, 27 and 28. No biomarkers were recovered from thermodesorption. The recovery of analytes by thermodesorption is mainly due to the volatilizing the analytes on the basis of the thermal energy supply. It is apparent that, whilst there was no recovery of any analytes at extraction temperature of 50°C, C₁₀-C₁₅ of aliphatics and naphthalene showed increased recoveries at 150°C. At extraction temperature of 250°C, all naphthalenes and phenanthrenes, except dimethyl-phenanthrenes, were detected but only aliphatics up to C₂₀ were detected. Dimethyl-phenanthrenes and aliphatics of C₂₁ up to C₂₉ started to be released only at 350°C. No C₃₀ - C₃₃ of aliphatics or any biomarkers were released by thermodesorption. Figures 31, 32 and 33 illustrate aliphatics and aromatics recovered from thermodesorption of Posidonia shale vs. temperature. All these results can be explained by the different boiling point, different molecular weight of these analytes and their interaction with the matrix. The lower the boiling point (the lower the molecular weight), the less the thermal energy needed for the release. For real geological samples, the thermal energy supplied in thermodesorption has to be high enough to overcome the

Comp	50°C (ppm)(S.D.)	150°C (ppm)(S.D.)	250°C (ppm)(S.D.)	350°C (ppm)(S.D.)
C ₁₀	N.D.	8.13(2.8)	3.37(1.3)	0.830(0.1)
C ₁₁	N.D.	9.37(3.0)	1.91(0.6)	1.26(0.03)
C ₁₂	N.D.	6.51(2.7)	8.08(3.8)	1.14(0.1)
C ₁₃	N.D.	3.70(1.9)	9.90(2.5)	1.31(0.5)
C ₁₄	N.D.	1.67(0.9)	9.60(1.4)	1.42(0.4)
C ₁₅	N.D.	0.792(0.4)	9.05(1.4)	2.01(0.8)
C ₁₆	N.D.	N.D.	7.40(1.9)	2.50(0.9)
C ₁₇ +Pri	N.D.	N.D.	8.99(3.9)	3.30(0.8)
C ₁₈	N.D.	N.D.	3.48(1.3)	3.04(0.3)
Phy	N.D.	N.D.	1.54(0.7)	0.766(0.3)
C ₁₉	N.D.	N.D.	2.37(1.2)	2.53(0.7)
C ₂₀	N.D.	N.D.	1.35(0.6)	1.90(0.4)
C ₂₁	N.D.	N.D.	N.D.	1.53(0.3)
C ₂₂	N.D.	N.D.	N.D.	1.20(0.3)
C ₂₃	N.D.	N.D.	N.D.	0.914(0.07)
C ₂₄	N.D.	N.D.	N.D.	0.702(0.2)
C ₂₅	N.D.	N.D.	N.D.	0.821(0.5)
C ₂₆	N.D.	N.D.	N.D.	0.384(0.04)
C ₂₇	N.D.	N.D.	N.D.	0.177(0.02)
C ₂₈	N.D.	N.D.	N.D.	0.115(0.04)
C ₂₉	N.D.	N.D.	N.D.	N.D.
C ₃₀	N.D.	N.D.	N.D.	N.D.
C ₃₁	N.D.	N.D.	N.D.	N.D.
C ₃₂	N.D.	N.D.	N.D.	N.D.
C ₃₃	N.D.	N.D.	N.D.	N.D.

Table 26. Recovery of aliphatic hydrocarbons (S.D.) from triplicate thermodesorption of Posidonia shale

Comp	50°C (ppm)(S.D.)	150°C (ppm)(S.D.)	250°C (ppm)(S.D.)	350°C (ppm)(S.D.)
Naphthalene	N.D.	2.20(0.9)	14.7(7.8)	5.57(1.3)
C-1 MN	N.D.	N.D.	19.0(5.6)	12.1(3.1)
C-2 MN	N.D.	N.D.	15.2(4.1)	7.27(2.1)
Total MN	N.D.	N.D.	34.2(9.7)	19.3(5.2)
1-E,2-EN	N.D.	N.D.	3.40(0.8)	3.07(0.6)
2,6,2,7-DMN	N.D.	N.D.	5.63(1.6)	9.98(1.9)
1,3;1,7-DMN	N.D.	N.D.	6.43(2.0)	11.0(2.2)
1,6-DMN	N.D.	N.D.	6.27(2.0)	8.95(0.8)
*	N.D.	N.D.	4.46(1.3)	6.90(0.9)
1,8-DMN	N.D.	N.D.	2.16(0.6)	3.07(0.3)
Total DMN	N.D.	N.D.	28.4(8.3)	42.9(6.4)
1,3,7-TMN	N.D.	N.D.	1.62(0.6)	6.95(1.0)
1,3,6-TMN	N.D.	N.D.	1.28(0.5)	7.97(0.5)
1,4,6,1,3,5-TMN	N.D.	N.D.	1.03(0.4)	5.40(0.2)
2,3,6-TMN	N.D.	N.D.	0.60(0.2)	5.43(0.5)
**	N.D.	N.D.	1.65(0.7)	11.0(4.5)
1,2,5-TMN	N.D.	N.D.	0.662(0.3)	2.42(0.4)
Total TMN	N.D.	N.D.	6.86(2.7)	39.2(2.4)

*: 1,4+1,3+1,5 DMN

** : 1,2,7+1,6,7+1,2,6 TMN

Table 27. Recovery of naphthalene and alkyl-naphthalenes (aromatic hydrocarbons) (S.D.) from thermodesorption of Posidonia shale

Comp	50°C (ppm)(S.D.)	150°C (ppm)(S.D.)	250°C (ppm)(S.D.)	350°C (ppm)(S.D.)
Phenanthrene	N.D.	N.D.	2.27(0.9)	5.30(0.3)
Anthracene	N.D.	N.D.	N.D.	2.50(0.3)
3-MP	N.D.	N.D.	0.412(0.2)	2.98(0.02)
2-MP	N.D.	N.D.	0.353(0.2)	3.45(0.2)
2-MA	N.D.	N.D.	N.D.	2.49(0.6)
9-MP	N.D.	N.D.	0.449(0.2)	3.67(0.6)
1-MP	N.D.	N.D.	0.580(0.2)	N.D.
1-MP+1-MA	N.D.	N.D.	N.D.	7.02(1.9)
9-MA	N.D.	N.D.	N.D.	0.787(1.4)
Total MP	N.D.	N.D.	1.79(0.8)	N.D.
Total MP+MA	N.D.	N.D.	N.D.	20.4(2.7)
Total DMP	N.D.	N.D.	N.D.	N.D.
*	N.D.	N.D.	N.D.	19.9(0.2)

*: Total DMP+DMA

Table 28. Recovery of phenanthrene, anthracene, alkyl-phenanthrenes and alkyl-anthracenes (aromatic hydrocarbons) (S.D.) from thermodesorption of Posidonia shale

Figure 31. Aliphatic hydrocarbons recovered (ppm) from thermodesorption of Posidonia shale vs. temperature

Figure 32. Naphthalene and alkyl-naphthalenes recovered (ppm) from thermodesorption of Posidonia shale vs. temperature

Figure 33. Phenanthrene alkyl-phenanthrenes and alkyl-anthracenes recovered (ppm) from thermodesorption of Posidonia shale vs. temperature

interactions between analytes and matrices. Similar to SFE, a significant increment of recovery of aromatic hydrocarbons (except naphthalene and methyl-naphthalenes) at high temperature, especially, with the increase of aromatic rings and the degree of alkylation, was observed for thermodesorption. In addition, anthracene and alkyl-anthracenes were only observed at 350°C fraction for thermodesorption as well as for HT-SFE. It was confirmed that thermal energy has more effect on aromatic hydrocarbons due to their interaction with matrices and lower volatility.

Soxhlet extraction is the traditional extraction method for the preparation of geological sample for GC/MS analysis. The Posidonia shale was also subjected to Soxhlet extraction in order to evaluate the effect of stepwise HT-SFE on the recovery of hydrocarbons in real geological samples. Average results of the recovery of aliphatic, aromatic hydrocarbons and biomarkers from single Soxhlet extraction of Posidonia shale are summarized in Tables 29, 30, 31, 32, 33 and 34. The recovery of analytes by Soxhlet extraction is solely due to dissolving the analytes in the solvent used. Since Soxhlet extraction can only be performed at low temperature (the boiling point of the solvent) and the solvent only has access to the analytes adsorbed at the surface of the matrix, the analytes recovered by Soxhlet extraction may primarily be those having weak interactions with matrix.

Compound	(ppm)
C ₁₀	1.66
C ₁₁	4.87
C ₁₂	7.39
C ₁₃	9.60
C ₁₄	10.5
C ₁₅	11.7
C ₁₆	11.2
C ₁₇	13.6
PRI	21.0
C ₁₈	9.75
PHY	13.2
C ₁₉	7.56
C ₂₀	6.40
C ₂₁	5.80
C ₂₂	5.16
C ₂₃	4.85
C ₂₄	5.10
C ₂₅	4.04
C ₂₆	4.30
C ₂₇	2.88
C ₂₈	1.99
C ₂₉	1.56
C ₃₀	1.49
C ₃₁	1.94
C ₃₂	1.24
C ₃₃	1.46

Table 29. Recovery of aliphatic hydrocarbons from single Soxhlet extraction of Posidonia shale

Compound	(ppm)
Naphthalene	10.7
C-1 MN	16.5
C-2 MN	14.8
Total MN	31.3
1-E,2-EN	3.24
2,6,2,7-DMN	5.44
1,3,1,7-DMN	7.92
1,6-DMN	7.13
1,4;1,3;1,5-DMN	5.75
1,8-DMN	2.79
Total DMN	32.3
1,3,7-TMN	3.09
1,3,6-TMN	3.68
1,4,6,1,3,5-TMN	2.94
2,3,6-TMN	1.52
1,2,7;1,6,7;1,2,6-TMN	4.10
1,2,5-TMN	1.62
Total TMN	16.9

Table 30. Recovery of naphthalenes (aromatic hydrocarbons) from single Soxhlet extraction of Posidonia shale

Compound	(ppm)
Phenanthrene	4.61
3-MP	1.55
2-MP	1.48
9-MP	2.39
1-MP	2.29
Total MP	7.72
Total DMP	4.59

Table 31. Recovery of phenanthrenes (aromatic hydrocarbons) from single Soxhlet extraction of Posidonia shale

Compound	(ppm)
C ₂₉ αβ	1.02
C ₂₉ βα	0.237
C ₃₀ αβ	1.74
C ₃₀ βα	0.390
C ₃₁ αβ(S)	0.692
C ₃₁ βα(R)	0.533
C ₃₂ αβ(S)	0.432
C ₃₂ βα(R)	0.401
C ₃₃ αβ(S)	0.641
C ₃₃ βα(R)	0.659
C ₃₄ αβ(S)	0.395
C ₃₄ βα(R)	0.425
C ₃₅ αβ(S)	0.369
C ₃₅ βα(R)	0.341

Table 32. Recovery of hopanes from single Soxhlet extraction of Posidonia shale

Compound	(ppm)
5 β (H)C ₂₇ (20S)	0.799
5 β (H)C ₂₇ (20R)	1.05
5 α (H)C ₂₇ (20S)+5 β (H)C ₂₈ (20S)	2.86
*	5.59
5 α (H)C ₂₉ (20S)	1.90
5 α (H)C ₂₈ (20R)+5 β (H)C ₂₉ (20R)	2.95
5 α (H)C ₂₉ (20R)	0.954

*: 5 α (H)C₂₇(20R)+5 α (H)C₂₈(20S)+ 5 β (H)C₂₈(20R)+5 β (H)C₂₈(20S)

Table 33. Recovery of monoaromatic steranes from single Soxhlet extraction of Posidonia shale

Compound	(ppm)
C ₂₆ (20S)	2.13
C ₂₆ (20R)+C ₂₇ (20S)	5.19
C ₂₈ (20S)	3.56
C ₂₇ (20R)	3.01
C ₂₈ (20R)	4.31

Table 34. Recovery of triaromatic steranes from single Soxhlet extraction of Posidonia shale

9.3. Evaluation of the effect of stepwise HT-SFE on recovery of hydrocarbons vs Soxhlet extraction and thermodesorption

A better insight into the effect of thermal energy supply on HT-SFE can be obtained by comparing the recovery of hydrocarbons from thermodesorption and HT-SFE, due to the fact that the recovery of analytes from thermodesorption is only achieved by thermal energy supply. Among all the analytes targeted in this project, relative low, medium and high molecular weight of aliphatic hydrocarbon (C_{10-12} , C_{20-22} and C_{30-32} respectively), and the aromatic hydrocarbons, as well as the biomarkers described in section 9.2 were used for this study as individual class of analytes. The accumulative recoveries of these compounds by thermodesorption and HT-SFE (in triplicate) and the % relative recovery from thermodesorption to recovery from SFE are shown in Table 35. It is clear that the contribution of temperature (thermodesorption) on the recovery of hydrocarbons in geological samples by HT-SFE is highly dependent on the class, volatility and molecular weight of the analytes. As seen in Table 35, the contribution of the thermal effect on the recovery from HT-SFE for all classes of analytes was zero at 50°C and for the accumulative recovery between 50°C and 150°C was noticeable only for the most volatile compounds such as C_{10-12} and naphthalene. The effect of temperature on the recovery from HT-SFE reached 80% for low molecular weight and high volatile analytes, such as C_{10-12} , naphthalene, alkyl-naphthalenes, phenanthrene, anthracene, alkyl-phenanthrenes and alkyl-anthracenes at accumulative recovery from 50°C - 350°C. For high molecular weight and non-volatile analytes, such as C_{30-33} and all biomarkers, the contribution of temperature was zero even with high temperature applied (350°C). As

seen in Figures 34, 35 and 36, as well as in Table 35, whilst the thermal effect decreased with the increase of molecular weight for aliphatic hydrocarbons, it increased with the increase of aromaticity and degree of alkylation for aromatic hydrocarbons. For example, the % relative recovery of thermodesorption (solely thermal effect) to HT-SFE for the accumulative recovery from 50°C-350°C decreased from 79 to 25 to 0 for C₁₀₋₁₂, C₂₀₋₂₂ and C_{30-C32} respectively (increase of molecular weight). For aromatic hydrocarbons, the comparison of the % relative recovery from 50°C-250°C to 50°C-350°C for naphthalene class (including alkyl-naphthalenes) and phenanthrene class (including alkyl-phenanthrenes) clearly showed that while the average % relative recovery increased from 50°C-250°C to 50°C-350°C was 20 for naphthalene class (2 aromatic rings), that was 56 for phenanthrene class (3 aromatic rings). On the other hand, for the same class with different alkylations, the average % relative recovery increased from 27 to 69 to 71 for phenanthrene, methyl-phenanthrenes and dimethyl-phenanthrenes. For the naphthalene class, the same trend was observed. As discussed in section 9.2, the most likely cause of these results is the different nature of these different classes of analytes (aliphatics or aromatics, the degree of aromaticity and the degree of alkylation) and the different intensity of interactions of these different classes of analytes with OM (the available surface for interaction). For biomarkers, there was no thermal effect on the recovery from HT-SFE due to the fact that no biomarkers were recovered by thermodesorption. Based on the hypothesis of this part of the project, the thermally induced structural rearrangement of macromolecular OM of sediments should still occur during thermodesorption, the reason that no any biomarkers were recovered is, therefore, most

Comp	50°C		50°C+150°C		50°C+150°C+250°C		Total (4 fractions)	
	Thermo.	SFE	Thermo.	SFE	Thermo.	SFE	Thermo.	SFE
C ₁₀ +C ₁₁ +C ₁₂	0(0)	41.1	24.0(51)	46.7	37.4(77)	48.3	40.6(79)	51.3
C ₂₀ +C ₂₁ +C ₂₂	0(0)	16.1	0(0)	20.5	1.35(6)	21.8	5.98(25)	23.5
C ₃₀ +C ₃₁ +C ₃₂	0(0)	3.14	0(0)	5.42	0(0)	6.02	0(0)	6.43
Naphthalene	0(0)	12.8	2.20(15)	15.1	16.9(88)	19.1	22.5(87)	25.9
M-NAs ^(b)	0(0)	29.0	0(0)	37.3	34.2(72)	47.2	53.5(78)	68.9
DM-NAs ^(b)	0(0)	26.7	0(0)	36.5	28.4(57)	50.0	71.3(83)	86.3
TM-NAs ^(b)	0(0)	13.8	0(0)	20.7	6.86(24)	28.1	46.1(74)	62.4
Phenanthrene	0(0)	2.30	0(0)	3.23	2.27(47)	4.82	7.58(74)	10.2 ^(c)
M-PHs ^(b)	0(0)	3.97	0(0)	6.29	1.79(19)	9.57	22.2(88)	25.3 ^(d)
DM-PHs ^(b)	0(0)	2.85	0(0)	4.70	0(0)	6.86	19.9(71)	27.9 ^(e)
Hopanes ^(b)	0(0)	4.40	0(0)	9.80	0(0)	10.4	0(0)	10.6
Monoaromatics ^(b)	0(0)	7.50	0(0)	16.9	0(0)	17.3	0(0)	17.3
Triaromatics ^(b)	0(0)	8.26	0(0)	15.4	0(0)	15.88	0(0)	15.92

(a): n-alkanes

(b): Total

(c): Total of phenanthrene and anthracene at 350°C extraction for Thermodesorption and SFE

(d): Total of methyl phenanthrene and methyl anthracene at 350°C extraction for Thermodesorption and SFE

(e): Total of dimethyl phenanthrene and dimethyl anthracene at 350°C extraction for Thermodesorption and SFE

Table 35. Accumulative recovery of hydrocarbons and biomarkers (ppm) from triplicate thermodesorption and SFE, as well as % relative recovery from thermodesorption to recovery from SFE (in parenthesis)

Figure 34. The % recovery of aliphatic hydrocarbons from thermodesorption to recovery from HT-SFE vs. temperature

Figure 35. The % recovery of naphthalene and alkyl-naphthalenes from thermodesorption to recovery from HT-SFE vs. temperature

Figure 36. The % recovery of phenanthrene, anthracene, alkyl-phenanthrenes and alkyl-anthracenes from thermodesorption to recovery from HT-SFE vs. temperature

likely that these biomarkers are non-volatile compounds.

Table 36 illustrates the accumulative recovery of hydrocarbons and biomarkers from single Soxhlet extraction and triplicate HT-SFE and the % relative recovery from HT-SFE to recovery from Soxhlet extraction. In general, compared to Soxhlet extraction, HT-SFE shows an increment in relative recoveries, ranging from 100 to 600 % for all the analytes, depending on the temperature employed and the analytes. For most of analytes, the % relative recovery of HT-SFE to Soxhlet reached 100 at either 50°C fraction or the combination of 50°C and 150°C fractions (the combination of 50°C to 250°C for phenanthrene and methyl-phenanthrenes). This clearly shows the higher efficiency of HT-SFE vs. Soxhlet (1 - 2 hours of HT-SFE vs 48 hr of Soxhlet extraction). The reason for this observation is the combination of high solubility as well as the diffusion coefficient of the analytes in supercritical fluid and the penetration ability of the supercritical fluid. The successive SFE at high temperature clearly released the analytes with high interactions with the matrix due to the combined effect of the thermal energy supply (the main reason for low molecular weight and volatile compounds) and the advantages of SFE described before. Interestingly, the recoveries of biomarkers from HT-SFE of *Posidonia* shale is not as pronounced as those of regular aliphatic and aromatic hydrocarbons when compared to the recoveries from Soxhlet extraction. The different origins of aliphatic and aromatic hydrocarbons from that of biomarkers in geological samples may have played important roles for this observation. Since the aliphatic and aromatic hydrocarbons are produced by pyrolysis of highly polymeric kerogen, whereas biomarkers are deposited onto OM in the sediments originally, it is apprehensible that relatively less percent of biomarkers has

Comp	Soxhlet	50°C SFE	150°C SFE	250°C SFE	350°C SFE
C ₁₀ +C ₁₁ +C ₁₂ ^(a)	13.9	41.1(296)	46.7(336)	48.3(347)	51.3(369)
C ₂₀ +C ₂₁ +C ₂₂ ^(a)	15.8	16.1(102)	20.5(130)	21.8(138)	23.5(149)
C ₃₀ +C ₃₁ +C ₃₂ ^(a)	4.67	3.14(67)	5.42(116)	6.02(129)	6.43(138)
Naphthalene	10.7	12.8(120)	15.1(141)	19.1(179)	25.9(242)
M-Nas ^(b)	31.3	29.0(93)	37.3(191)	47.2(151)	68.9(220)
DM-Nas ^(b)	32.3	26.7(82)	36.5(113)	50.0(155)	86.3(267)
TM-Nas ^(b)	16.9	13.8(82)	20.7(122)	28.1(166)	62.4(369)
Phenanthrene	4.61	2.30(50)	3.23(70)	4.82(105)	10.2(221) ^(c)
M-PHs ^(b)	7.72	3.97(51)	6.29(82)	9.57(124)	25.3(328) ^(d)
DM-PHs ^(b)	4.59	2.85(62)	4.70(102)	6.86(149)	27.9(608) ^(e)
Hopanes ^(b)	8.29	4.40(53)	9.80(118)	10.4(125)	10.6(128)
M-aro.steranes ^(b)	16.1	7.50(47)	16.9(105)	17.3(107)	17.3(107)
T-aro.steranes ^(b)	18.2	8.26(45)	15.4(85)	15.88(87)	15.92(87)

(a): n-alkanes

(b): Total

(c): Total of phenanthrene and anthracene at 350°C extraction for SFE

(d): Total of methyl-phenanthrenes and methyl-anthracenes at 350°C extraction for SFE

(e): Total of dimethyl-phenanthrenes and dimethyl-anthracenes at 350°C extraction for SFE

Table 36. Accumulative recovery of hydrocarbons and biomarkers (ppm) from single Soxhlet extraction and triplicate HT-SFE, as well as % relative recovery from HT-SFE to recovery from Soxhlet extraction (in parenthesis)

stronger interactions with OM and is 'trapped' in internal voids of polymeric structures of OM than the aliphatic and aromatic hydrocarbons. Therefore, based on the hypothesis of the impact of HT-SFE, which is the rearrangement of macromolecular of matrix under high temperature condition and the penetration of the supercritical fluid into the rearranged matrix (opened pore), it is reasonable that HT-SFE has more pronounced effect on the release of aliphatic and aromatic hydrocarbon than on that of the biomarkers. This observation is consistent with the results achieved in section 9.1 that only very small amount of biomarkers were recovered from SFE at high temperature. Therefore, HT-SFE has less impact on biomarkers than regular hydrocarbons due to different origins of those compounds.

CONCLUSION

Stepwise HT-SFE has been used for the first time as a tool for speciation studies, and indeed, it has been proven to be a valuable technique. The thermal maturity inversion of the hopanes at elevated extraction temperature of HT-SFE proves the presence of the 'trapped' species in ancient sediment. The release of some low molecular weight compounds is suggested to be due to thermodesorption processes, whilst, that of higher molecular weight compounds is a combined effect of both solubility of analytes in supercritical CO₂ and in some cases thermodesorption in HT-SFE. A better understanding of speciation of organic compounds in sediment by stepwise HT-SFE can greatly help organic geochemists to better understand the origin and fate of organic matter in the environment, and the formation of petroleum.

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APPENDIX

SFE OF POSIDONIA SHALE AT 50°C				
A				
Weight of sample=2.9170g				
Weight of IS (squalane)=18.99ug				
Density of supercritical CO ₂ = 0.904 g/ml				
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	4283891	1844819	15.1
	C11	4623922	1844819	16.3
	C12	4189958	1844819	14.8
	C13	3823573	1844819	13.5
	C14	3675752	1844819	13.0
	C15	3533800	1844819	12.5
	C16	2978866	1844819	10.5
	C17+PRI	9750872	1844819	34.4
	C18	2180062	1844819	7.69
	PHY	3313807	1844819	11.7
	C19	1875711	1844819	6.62
	C20	1744080	1844819	6.15
	C21	1540413	1844819	5.44
	C22	1311501	1844819	4.63
	C23	1181093	1844819	4.17
	C24	1282066	1844819	4.52
	C25	1205947	1844819	4.26
	C26	972809	1844819	3.43
	C27	639826	1942985	2.14
	C28	575744	1942985	1.93
	C29	459422	1942985	1.54
	C30	475893	1942985	1.59
	C31	459637	1942985	1.54
	C32	338073	1942985	1.13
	C33	301338	1942985	1.01
	TOTAL ALKANES			200
NAPHTHALENES	NAPHTHALENE	4224046	1957683	14.0
	C-1 MN	4940056	1957683	16.4
	C-2 MN	4155524	1957683	13.8
	TOTAL MN			30.2
	1-E,2-EN	953596	1957683	3.17
	2,6,2,7DMN	1478662	1957683	4.92
	1,3,1,7DMN	1962452	1957683	6.53
	1,6DMN	2292046	1957683	7.62
	1,4,1,3,1,5DMN	1582572	1957683	5.26
	1,8DMN	578787	1957683	1.92
	TOTAL DMN			29.4
	1,3,7TMN	793775	1957683	2.64
	1,3,6TMN	1188973	1957683	3.95
	1,4,6,1,3,5TMN	732235	1957683	2.43
	2,3,6TMN	430579	1957683	1.43
	1,2,7,1,6,7,1,2,6TMN	1065976	1957683	3.54
	1,2,5TMN	483466	1957683	1.61
	TOTAL TMN			15.6
	TOTAL NAPHS			89.3
PHENANTHRENES	PHENANTHRENE	710131	1980872	2.33
	ANTHRACENE	N/A	N/A	N/A
	3-MP	245370	1980872	0.806
	2-MP	340930	1980872	1.12
	2-MA	N/A	N/A	N/A
	9-MP	409369	1980872	1.35
	1-MP	473891	1980872	1.56
	1-MP+1-MA	N/A	N/A	N/A
	9MA	N/A	N/A	N/A
	TOTAL MP			4.83
	TOTAL MP+MA	N/A	N/A	N/A
	TOTAL DMP	1104747	2191102	3.28
	TOTAL DMP+DMA	N/A	N/A	N/A
	TOTAL PHENAS			10.4

	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C29αβ	1505278	19092828	0.513
	C29βα	384068	19092828	0.131
	C30αβ	2654074	19092828	0.905
	C30βα	579851	19092828	0.198
	C31αβ(S)	1017457	19092828	0.347
	C31αβ(R)	738870	19092828	0.252
	C32αβ(S)	570661	19092828	0.195
	C32αβ(R)	539758	19092828	0.184
	C33αβ(S)	922032	19092828	0.314
	C33αβ(R)	872944	19092828	0.298
	C34αβ(S)	636336	19092828	0.217
	C34αβ(R)	560255	19092828	0.191
	C35αβ(S)	461264	19092828	0.157
	C35αβ(R)	656423	19092828	0.224
	TOTAL			4.13
MONO AROMATICS	5β(H)C27(20S)	1178705	17928903	0.428
	5β(H)C27(20R)	1409133	17928903	0.512
	*	4117681	17928903	1.50
	**	7691768	17928903	2.79
	5α(H)C29(20S)	2217305	16531754	0.873
	***	3304025	16531754	1.30
	5α(H)C29(20R)	1370081	17928903	0.497
	TOTAL			7.90
TRI AROMATICS	C26(20S)	2639131	17912782	0.959
	C26(20R)+C27(20S)	5697980	17912782	2.07
	C28(20S)	3505362	16533543	1.38
	C27(20R)	2949211	16533543	1.16
	C28(20R)	4711166	17912782	1.71
	TOTAL			7.28
	*. 5α(H)C27(20S) + 5β(H)C28(20S)			
	** 5α(H)C27(20R)+5α(H)C28(20S)+5β(H)C28(20R)+5βC29(20S)			
	***.5α(H)C28(20R)+5β(H)C29(20R)			

SFE OF POSIDONIA SHALE AT 150°C					
A					
Weight of sample=2.9170g					
Weight of IS (squalane)=9.50ug					
Density of supercritical CO ₂ =0.548 g/ml					
	Comp	Pk Area	IS Pk Area	(ug/g)	
ALKANES	C10	1149996	1891235	1.98	
	C11	1149484	1891235	1.98	
	C12	1361626	1891235	2.34	
	C13	1296803	1891235	2.23	
	C14	1558053	1891235	2.68	
	C15	1628773	1891235	2.80	
	C16	1510781	1891235	2.60	
	C17+PRI	5942556	1891235	10.2	
	C18	1256515	1891235	2.16	
	PHY	2373445	1891235	4.09	
	C19	1256798	1891235	2.16	
	C20	1066072	1891235	1.84	
	C21	934666	1891235	1.61	
	C22	824212	1891235	1.42	
	C23	846046	1891235	1.46	
	C24	907867	1891235	1.56	
	C25	1070210	1891235	1.84	
	C26	915646	1891235	1.58	
	C27	701537	2018419	1.13	
	C28	538463	2018419	0.869	
	C29	416292	2018419	0.672	
	C30	474438	2018419	0.766	
	C31	584451	2018419	0.943	
	C32	434846	2018419	0.702	
	C33	370690	2018419	0.598	
	TOTAL ALKANES			52.3	
NAPHTHALENES	NAPHTHALENE	1635352	1991456	2.67	
	C-1 MN	2435230	1991456	3.98	
	C-2 MN	3102477	1991456	5.07	
	TOTAL MN			9.06	
	1-E,2-EN	670295	1991456	1.10	
	2,6,2,7DMN	878814	1991456	1.44	
	1,3,1,7DMN	1516841	1991456	2.48	
	1,6DMN	1784153	1991456	2.92	
	1,4,1,3,1,5DMN	1021265	1991456	1.67	
	1,8DMN	552495	1991456	0.904	
	TOTAL DMN			10.5	
	1,3,7TMN	727756	1991456	1.19	
	1,3,6TMN	1117281	1991456	1.83	
	1,4,6,1,3,5TMN	783355	1991456	1.28	
	2,3,6TMN	367170	1991456	0.600	
	1,2,7,1,6,7,1,2,6TMN	986992	1991456	1.61	
	1,2,5TMN	567435	1991456	0.928	
	TOTAL TMN			7.44	
	TOTAL NAPHS			29.7	
PHENANTHRENES	PHENANTHRENE	635335	1991456	1.04	
	ANTHRACENE	N/A	N/A	N/A	
	3-MP	276987	1991456	0.453	
	2-MP	324860	1991456	0.531	
	2-MA	N/A	N/A	N/A	
	9-MP	406568	1991456	0.665	
	1-MP	455178	1991456	0.744	
	1-MP+1-MA	N/A	N/A	N/A	
	9MA	N/A	N/A	N/A	
	TOTAL MP			2.39	
	TOTAL MP+MA	N/A	N/A	N/A	
	TOTAL DMP	1367045	2244457	1.98	
	TOTAL DMP+DMA	N/A	N/A	N/A	
	TOTAL PHENAS			5.42	

	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C29 α β	3413264	17621152	0.631
	C29 β α	947073	17621152	0.175
	C30 α β	5640892	17621152	1.04
	C30 β α	1514693	17621152	0.280
	C31 α β (S)	2146581	17621152	0.397
	C31 α β (R)	1563474	17621152	0.289
	C32 α β (S)	1193539	17621152	0.221
	C32 α β (R)	1091130	17621152	0.202
	C33 α β (S)	1808808	17621152	0.334
	C33 α β (R)	1663944	17621152	0.308
	C34 α β (S)	1090089	17621152	0.201
	C34 α β (R)	1020645	17621152	0.189
	C35 α β (S)	881146	17621152	0.163
	C35 α β (R)	1110555	17621152	0.205
	TOTAL			4.64
MONO AROMATICS	5 β (H)C27(20S)	2071651	16304585	0.414
	5 β (H)C27(20R)	2441839	16304585	0.488
	*	7977374	16304585	1.59
	**	13954622	13294352	3.42
	5 α (H)C29(20S)	4633555	13294352	1.14
	***	6076383	13294352	1.49
	5 α (H)C29(20R)	2221513	13294352	0.544
	TOTAL			9.08
TRI AROMATICS	C26(20S)	3848588	13294352	0.943
	C26(20R)+C27(20S)	7528625	13294352	1.84
	C28(20S)	4673130	13294352	1.14
	C27(20R)	3983417	13294352	0.976
	C28(20R)	4511652	13294352	1.11
	TOTAL			6.01
	*: 5 α (H)C27(20S) + 5 β (H)C28(20S)			
	**: 5 α (H)C27(20R) + 5 α (H)C28(20S) + 5 β (H)C28(20R) + 5 β C29(20S)			
	***: 5 α (H)C28(20R) + 5 β (H)C29(20R)			

SFE OF POSIDONIA SHALE AT 250°C				
A				
Weight of sample=2.9170g				
Weight of IS (squalane)=9.50ug				
Density of supercritical CO ₂ = 0.366 g/ml				
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	617669	3118361	0.645
	C11	633621	2958193	0.698
	C12	627204	2958193	0.691
	C13	736245	2997951	0.800
	C14	651157	1891235	1.12
	C15	639108	2997951	0.694
	C16	588064	2997951	0.639
	C17+PRI	1942637	2997951	2.11
	C18	525008	2958193	0.578
	PHY	871341	2958193	0.959
	C19	581530	2958193	0.640
	C20	407417	2958193	0.449
	C21	461597	2958193	0.508
	C22	426517	2958193	0.470
	C23	453427	2958193	0.499
	C24	519280	2958193	0.572
	C25	567284	3118361	0.592
	C26	563034	2958193	0.620
	C27	387012	3118361	0.404
	C28	306989	3118361	0.321
	C29	262861	3118361	0.275
	C30	225887	3118361	0.236
	C31	252785	3118361	0.264
	C32	241186	3118361	0.252
	C33	173545	3118361	0.181
	TOTAL ALKANES			15.2
NAPHTHALENES	NAPHTHALENE	4198832	3031734	4.51
	C-1 MN	6397547	3031734	6.87
	C-2 MN	5443648	3031734	5.85
	TOTAL MN			12.7
	1-E,2-EN	1520106	3031734	1.63
	2,6,2,7DMN	3025655	3031734	3.25
	1,3,1,7DMN	3673801	3031734	3.95
	1,6DMN	3704639	3031734	3.98
	1,4,1,3,1,5DMN	2366867	3031734	2.54
	1,8DMN	842260	3031734	0.905
	TOTAL DMN	842260		16.3
	1,3,7IMN	1568953	3031734	1.69
	1,3,6TMN	1907526	3031734	2.05
	1,4,6,1,3,5TMN	1327454	3031734	1.43
	2,3,6TMN	930143	3031734	1.00
	1,2,7,1,6,7,1,2,6TMN	2210473	3031734	2.37
	1,2,5TMN	784096	3031734	0.842
	TOTAL TMN			9.38
	TOTAL NAPHS			42.9
PHENATHRENES	PHENATHRENE	1759473	3099096	1.85
	ANTHRACENE	N/A	N/A	N/A
	3-MP	583001	3099096	0.613
	2-MP	726144	3099096	0.763
	2-MA	N/A	N/A	N/A
	9-MP	774567	3099096	0.814
	1-MP	1533381	3099096	1.61
	1-MP+1-MA	N/A	N/A	N/A
	9MA	N/A	N/A	N/A
	TOTAL MP			3.80
	TOTAL MP+MA	N/A	N/A	N/A
	TOTAL DMP	2370911	3099096	2.49
	TOTAL DMP+DMA	N/A	N/A	N/A
	TOTAL PHENAS			8.14

	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C29 α β	758678	9577063	0.258
	C29 β α	110538	10487286	0.034
	C30 α β	515427	9577063	0.175
	C30 β α	94040	10487286	0.029
	C31 α β (S)	236435	10720959	0.072
	C31 α β (R)	173118	10720959	0.053
	C32 α β (S)	116180	10487286	0.036
	C32 α β (R)	126843	10487286	0.039
	C33 α β (S)	146197	10487286	0.045
	C33 α β (R)	170902	10487286	0.053
	C34 α β (S)	79465	10720959	0.024
	C34 α β (R)	99046	10720959	0.030
	C35 α β (S)	71510	10720959	0.022
	C35 α β (R)	80576	10720959	0.024
	TOTAL			0.896
MONO AROMATICS	5 β (H)C27(20S)	91088	10487286	0.028
	5 β (H)C27(20R)	124923	10194547	0.040
	*	379797	10194547	0.121
	**	633153	9577063	0.215
	5 α (H)C29(20S)	210870	10464261	0.066
	***	274414	10464261	0.085
	5 α (H)C29(20R)	108026	10487286	0.034
	TOTAL			0.589
TRI AROMATICS	C26(20S)	276929	9577063	0.094
	C26(20R)+C27(20S)	538440	9577063	0.183
	C28(20S)	284286	9577063	0.097
	C27(20R)	270341	9577063	0.092
	C28(20R)	306555	9577063	0.104
	TOTAL			0.570
	* 5 α (H)C27(20S) + 5 β (H)C28(20S)			
	** 5 α (H)C27(20R) + 5 α (H)C28(20S) + 5 β (H)C28(20R) + 5 β C29(20S)			
	*** 5 α (H)C28(20R) + 5 β (H)C29(20R)			

SFE OF POSIDONIA SHALE AT 350°C					
A					
Weight of sample=2.9170g					
Weight of I.S (squalane)=18.99ug					
Density of supercritical CO ₂ = 0.281 g/ml					
	Comp	Pk Area	IS Pk Area		(ug/g)
ALKANES	C10	241833	2592683		0.607
	C11	534635	2583694		1.35
	C12	519004	2583694		1.31
	C13	658351	2583694		1.66
	C14	536985	2583694		1.35
	C15	502636	2583694		1.27
	C16	348962	2583694		0.879
	C17	397814	2583694		1.00
	C18	283745	2592683		0.712
	C19	248348	2583694		0.626
	C20	351153	2583694		0.885
	C21	281372	2592683		0.707
	C22	295820	2592683		0.743
	C23	237290	2592683		0.596
	C24	218261	2592683		0.548
	C25	190351	2592683		0.478
	C26	232321	2721253		0.556
	C27	189423	2721253		0.453
	C28	143615	2721253		0.344
	C29	136612	2721253		0.327
	C30	136560	2721253		0.327
	C31	70693	2721253		0.169
	C32	68924	2721253		0.165
	C33	N.D.			0.000
	TOTAL ALKANES				17.1
NAPHTHALENES	NAPHTHALENE	3692112	2705006		8.89
	C-1 MN	6179746	2705006		14.9
	C-2 MN	3447790	2705006		8.30
	TOTAL MN				23.2
	1-E,2-EN	1349039	2705006		3.25
	2,6,2,7DMN	3908736	2705006		9.41
	1,3,1,7DMN	4253575	2705006		10.2
	1,6DMN	2587705	2705006		6.23
	1,4,1,3,1,5DMN	2382883	2705006		5.73
	1,8DMN	1115248	2705006		2.68
	TOTAL DMN				37.5
	1,3,7TMN	2792404	2705006		6.72
	1,3,6TMN	2580611	2705006		6.21
	1,4,6,1,3,5TMN	1921517	2705006		4.62
	2,3,6TMN	2154413	2705006		5.19
	1,2,7:1,6,7:1,2,6TMN	3506992	2705006		8.44
	1,2,5TMN	719182	2705006		1.73
	TOTAL TMN				32.9
	TOTAL NAPHS				103
PHENANTHRENES	PHENANTHRENE	1589813	2592683		3.99
	ANTHRACENE	922424	2592683		2.32
	3-MP	912426	2592683		2.29
	2-MP	1031254	2592683		2.59
	2-MA	1279351	2592683		3.21
	9-MP	862508	2592683		2.17
	1-MP	N/A	N/A		N/A
	1-MP+1-MA	1430506	2592683		3.59
	9MA	381664	2592683		0.958
	TOTAL MP	N/A	N/A		N/A
	TOTAL MP+MA				14.8
	TOTAL DMP	N/A	N/A		N/A
	TOTAL DMP+DMA	6470314	2592683		16.2
	TOTAL PHENAS				37.36

	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C29 α β	423231	18799275	0.147
	C29 β α	119218	18799275	0.041
	C30 α β	121481	18799275	0.042
	C30 β α	75507	18799275	0.026
	C31 α β (S)	36655	18799275	0.013
	C31 α β (R)	76114	18799275	0.026
	C32 α β (S)	11531	18799275	0.004
	C32 α β (R)	52154	18799275	0.018
	C33 α β (S)	N/A	N/A	N/A
	C33 α β (R)	N/A	N/A	N/A
	C34 α β (S)	N/A	N/A	N/A
	C34 α β (R)	N/A	N/A	N/A
	C35 α β (S)	N/A	N/A	N/A
	C35 α β (R)	N/A	N/A	N/A
	TOTAL			0.317
MONO AROMATICS	5 β (H)C27(20S)	N/A	N/A	N/A
	5 β (H)C27(20R)	N/A	N/A	N/A
	*	N/A	N/A	N/A
	**	N/A	N/A	N/A
	5 α (H)C29(20S)	N/A	N/A	N/A
	***	N/A	N/A	N/A
	5 α (H)C29(20R)	N/A	N/A	N/A
	TOTAL			N/A
TRI AROMATICS	C26(20S)	24520	18799275	0.008
	C26(20R)+C27(20S)	44652	18799275	0.015
	C28(20S)	20149	18799275	0.007
	C27(20R)	23758	18799275	0.008
	C28(20R)	30678	18799275	0.011
	TOTAL			0.050
	*: 5 α (H)C27(20S) + 5 β (H)C28(20S)			
	**: 5 α (H)C27(20R)+5 α (H)C28(20S)+5 β (H)C28(20R)+5 β C29(20S)			
	*** 5 α (H)C28(20R)+5 β (H)C29(20R)			

SFE OF POSIDONIA SHALE AT 50°C				
B				
Weight of sample=3.0013g				
Weight of IS (squalane)=18.99ug				
Density of supercritical CO ₂ = 0.904 g/ml				
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	6645735	3137149	13.4
	C11	7298764	3137149	14.7
	C12	4832393	3137149	9.75
	C13	6049371	3137149	12.2
	C14	6383777	3137149	12.9
	C15	6479585	3137149	13.1
	C16	6143604	3137149	12.4
	C17+PRI	18968448	3137149	38.3
	C18	4563772	3137149	9.20
	PHY	6340940	3137149	12.8
	C19	3731484	3137149	7.53
	C20	3192676	3137149	6.44
	C21	2723071	3137149	5.49
	C22	2132458	3137149	4.30
	C23	2162638	3137149	4.36
	C24	2001981	3137149	4.04
	C25	1710910	3137149	3.45
	C26	1631891	3137149	3.29
	C27	932582	3137149	1.88
	C28	673334	3137149	1.88
	C29	626963	3137149	1.36
	C30	621649	3252616	1.22
	C31	686879	3252616	1.34
	C32	503052	3252616	0.979
	C33	486786	3252616	0.947
	TOTAL ALKANES			197
NAPHTHALENES	NAPHTHALENE	8901098	4365790	12.9
	C-1 MN	9998820	4365790	14.5
	C-2 MN	10371594	4365790	15.0
	TOTAL MN			29.5
	1-E,2-EN	1934977	4365790	2.80
	2,6,2,7DMN	2828655	4365790	4.10
	1,3,1,7DMN	4230445	4365790	6.13
	1,6DMN	4568165	4365790	6.62
	1,4,1,3,1,5DMN	3341949	4365790	4.84
	1,8DMN	1545861	4365790	2.24
	TOTAL DMN			26.7
	1,3,7TMN	1560133	4365790	2.26
	1,3,6TMN	2427486	4365790	3.52
	1,4,6,1,3,5TMN	1558479	4365790	2.26
	2,3,6TMN	889399	4365790	1.29
	1,2,7,1,6,7,1,2,6TMN	2226052	4365790	3.23
	1,2,5TMN	983905	4365790	1.43
	TOTAL TMN			14.0
	TOTAL NAPHS			83.1
PHENANTHRENES	PHENANTHRENE	1483752	4373503	2.15
	ANTHRACENE	N/A	N/A	N/A
	3-MP	441580	4373503	0.639
	2-MP	554167	4373503	0.802
	2-MA	N/A	N/A	N/A
	9-MP	660907	4373503	0.956
	1-MP	841547	4373503	1.22
	1-MP+1-MA	N/A	N/A	N/A
	9MA	N/A	N/A	N/A
	TOTAL MP			3.61
	TOTAL MP+MA	N/A	N/A	N/A
	TOTAL DMP	2168783	4373503	3.14
	TOTAL DMP+DMA	N/A	N/A	N/A
	TOTAL PHENAS			12.5

	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C29 α β	2745842	33441710	0.520
	C29 β α	615351	33332139	0.117
	C30 α β	5460970	33441710	1.03
	C30 β α	1202182	33441710	0.227
	C31 α β (S)	2137325	33332139	0.406
	C31 α β (R)	1558419	33332139	0.296
	C32 α β (S)	1184718	33332139	0.225
	C32 α β (R)	1184052	33332139	0.225
	C33 α β (S)	2103667	33441710	0.398
	C33 α β (R)	2016253	33441710	0.381
	C34 α β (S)	1480777	33441710	0.280
	C34 α β (R)	1224751	33441710	0.232
	C35 α β (S)	1127899	33441710	0.213
	C35 α β (R)	1569736	33441710	0.297
	TOTAL			4.85
MONO AROMATICS	5 β (H)C27(20S)	1929384	31483024	0.388
	5 β (H)C27(20R)	2438240	31483024	0.490
	*	6828664	31483024	1.37
	**	14127236	31483024	2.84
	5 α (H)C29(20S)	4148854	31483024	0.834
	***	6270943	31483024	1.26
	5 α (H)C29(20R)	2524306	31483024	0.507
	TOTAL			7.69
TRI AROMATICS	C26(20S)	5141517	31450347	1.03
	C26(20R)+C27(20S)	11339565	31450347	2.28
	C28(20S)	6800739	39744391	1.08
	C27(20R)	6250150	39744391	0.995
	C28(20R)	10212420	31450347	2.05
	TOTAL			7.45
	*. 5 α (H)C27(20S) + 5 β (H)C28(20S)			
	** 5 α (H)C27(20R)+5 α (H)C28(20S)+5 β (H)C28(20R)+5 β C29(20S)			
	*** 5 α (H)C28(20R)+5 β (H)C29(20R)			

SFE OF POSIDONIA SHALE AT 150°C					
B					
Weight of sample=3.0013g					
Weight of IS (squalane)=9.50ug					
Density of supercritical CO ₂ = 0.548 g/ml					
	Comp	Pk Area	IS Pk Area		(ug/g)
ALKANES	C10	1051697	1864254		1.79
	C11	1141274	1864254		1.94
	C12	1329507	1864254		2.26
	C13	1417340	1864254		2.41
	C14	1604071	1864254		2.72
	C15	1541864	1864254		2.72
	C16	1528565	1864254		2.60
	C17+PRI	6341933	1864254		10.8
	C18	1261266	1864254		2.14
	PHY	2578042	1864254		4.38
	C19	1090642	1864254		1.85
	C20	992355	1864254		1.68
	C21	920489	1864254		1.56
	C22	880471	1864254		1.49
	C23	852501	1864254		1.45
	C24	1009170	1864254		1.71
	C25	878148	1864254		1.49
	C26	1199362	1864254		2.04
	C27	756049	1864254		1.28
	C28	597415	2016526		0.938
	C29	454152	2016526		0.713
	C30	503777	2016526		0.791
	C31	567750	2016526		0.891
	C32	480271	2016526		0.754
	C33	521670	2016526		0.819
	TOTAL ALKANES				53.2
NAPHTHALENES	NAPHTHALENE	1756509	2006502		2.77
	C-1 MN	2335690	2006502		3.68
	C-2 MN	3316281	2006502		5.23
	TOTAL MN				8.92
	1-E,2-EN	610507	2006502		0.963
	2,6,2,7DMN	801004	2006502		1.26
	1,3,1,7DMN	1384203	2006502		2.18
	1,6DMN	1707578	2006502		2.69
	1,4,1,3,1,5DMN	1347678	2006502		2.13
	1,8DMN	593796	2006502		0.937
	TOTAL DMN				10.2
	1,3,7TMN	630161	2006502		0.994
	1,3,6TMN	1025670	2006502		1.62
	1,4,6,1,3,5TMN	759051	2006502		1.20
	2,3,6TMN	328255	2006502		0.518
	1,2,7,1,6,7,1,2,6TMN	1010204	2006502		1.59
	1,2,5TMN	503162	2006502		0.794
	TOTAL TMN				6.71
	TOTAL NAPHS				28.6
PHENANTHRENES	PHENANTHRENE	437240	2030415		0.682
	ANTHRACENE	N/A	N/A		N/A
	3-MP	231083	2030415		0.360
	2-MP	284052	2030415		0.443
	2-MA	N/A	N/A		N/A
	9-MP	368072	2030415		0.574
	1-MP	548988	2030415		0.856
	1-MP+1-MA	N/A	N/A		N/A
	9MA	N/A	N/A		N/A
	TOTAL MP				2.23
	TOTAL MP+MA	N/A	N/A		N/A
	TOTAL DMP	1081117	2030415		1.69
	TOTAL DMP+DMA	N/A			N/A
	TOTAL PHENAS				4.60

	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C29 α β	9008688	48802729	0.584
	C29 β α	2085712	48802729	0.135
	C30 α β	15243042	48802729	0.989
	C30 β α	3201706	48802729	0.208
	C31 α β (S)	6047396	48802729	0.392
	C31 α β (R)	4552257	48802729	0.295
	C32 α β (S)	3107218	48802729	0.202
	C32 α β (R)	2949348	48802729	0.191
	C33 α β (S)	4976224	48802729	0.323
	C33 α β (R)	4643633	48802729	0.301
	C34 α β (S)	2772858	48802729	0.180
	C34 α β (R)	2711428	48802729	0.176
	C35 α β (S)	2107005	48802729	0.137
	C35 α β (R)	2624173	48802729	0.170
	TOTAL			4.28
MONO AROMATICS	5 β (H)C27(20S)	5846325	42423554	0.436
	5 β (H)C27(20R)	7073953	42423554	0.528
	*	22513911	42423554	1.68
	**	39989398	42423554	2.98
	5 α (H)C29(20S)	14952771	42423554	1.12
	***	21084130	42423554	1.57
	5 α (H)C29(20R)	8007240	42423554	0.597
	TOTAL			8.91
TRI AROMATICS	C26(20S)	12092257	34016936	1.13
	C26(20R)+C27(20S)	23977502	33937653	2.24
	C28(20S)	15567397	33937653	1.45
	C27(20R)	13141739	34016936	1.22
	C28(20R)	16627104	34016936	1.55
	TOTAL			7.58
	*: 5 α (H)C27(20S) + 5 β (H)C28(20S)			
	**: 5 α (H)C27(20R) + 5 α (H)C28(20S) + 5 β (H)C28(20R) + 5 β C29(20S)			
	***: 5 α (H)C28(20R) + 5 β (H)C29(20R)			

SFE OF POSIDONIA SHALE AT 250°C				
B				
Weight of sample=3.0013g				
Weight of LS (squalane)=9.50ug				
Density of supercritical CO ₂ = 0.366 g/ml				
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	377165	2282068	0.523
	C11	346374	2282068	0.480
	C12	397539	2282068	0.551
	C13	487191	2282068	0.676
	C14	422339	2282068	0.586
	C15	413888	2282068	0.574
	C16	404611	2282068	0.561
	C17+PRI	1536311	2282068	2.13
	C18	363523	2282068	0.504
	PHY	644948	2282068	0.895
	C19	367141	2282068	0.509
	C20	358516	2282068	0.497
	C21	308857	2282068	0.428
	C22	296479	2282068	0.411
	C23	324518	2282068	0.450
	C24	410971	2282068	0.570
	C25	341681	2282068	0.474
	C26	341082	2282068	0.473
	C27	225919	2282068	0.313
	C28	332358	2282068	0.461
	C29	162796	2282068	0.226
	C30	174558	2282068	0.242
	C31	225831	2282068	0.313
	C32	130513	2304760	0.179
	C33	138258	2304760	0.190
	TOTAL ALKANES			13.2
NAPHTHALENES	NAPHTHALENE	2995464	2308722	4.11
	C-1 MN	3424470	2308722	4.70
	C-2 MN	3519708	2308722	4.83
	TOTAL MN			9.52
	1-E,2-EN	901880	2308722	1.24
	2,6,2,7DMN	1621827	2308722	2.22
	1,3,1,7DMN	2067453	2308722	2.83
	1,6DMN	2367069	2308722	3.25
	1,4,1,3,1,5DMN	1674471	2308722	2.30
	1,8DMN	953976	2308722	1.31
	TOTAL DMN			13.1
	1,3,7TMN	885776	2308722	1.21
	1,3,6TMN	1045920	2308722	1.43
	1,4,6,1,3,5TMN	807143	2308722	1.11
	2,3,6TMN	500732	2308722	0.687
	1,2,7,1,6,7,1,2,6TMN	1197096	2308722	1.64
	1,2,5TMN	509089	2308722	0.698
	TOTAL TMN			6.78
	TOTAL NAPHS			33.6
PHENANTHRENES	PHENANTHRENE	1148831	2399943	1.52
	ANTHRACENE	N/A	N/A	N/A
	3-MP	332150	2399943	0.438
	2-MP	385353	2399943	0.508
	2-MA	N/A	N/A	N/A
	9-MP	475307	2399943	0.627
	1-MP	1140488	2399943	1.50
	1-MP+1-MA	N/A	N/A	N/A
	9MA	N/A	N/A	N/A
	TOTAL MP			3.08
	TOTAL MP+MA	N/A	N/A	N/A
	TOTAL DMP	1260401	2399943	1.66
	TOTAL DMP+DMA	N/A	N/A	N/A
	TOTAL PHENAS			6.25

	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C29 α β	1951565	45800188	0.135
	C29 β α	261680	45800188	0.018
	C30 α β	1240798	45800188	0.086
	C30 β α	206093	45800188	0.014
	C31 α β (S)	592474	45800188	0.041
	C31 α β (R)	441198	45800188	0.030
	C32 α β (S)	269039	45800188	0.019
	C32 α β (R)	296966	45800188	0.021
	C33 α β (S)	301378	45800188	0.021
	C33 α β (R)	370632	45800188	0.026
	C34 α β (S)	157120	45800188	0.011
	C34 α β (R)	206616	45800188	0.014
	C35 α β (S)	135549	45800188	0.009
	C35 α β (R)	167791	45800188	0.012
	TOTAL			0.456
MONO AROMATICS	5 β (H)C27(20S)	286992	45800188	0.020
	5 β (H)C27(20R)	358727	45800188	0.025
	*	1100007	45800188	0.076
	**	1862599	45800188	0.129
	5 α (H)C29(20S)	608002	45800188	0.042
	***	562911	45800188	0.039
	5 α (H)C29(20R)	286482	45800188	0.020
	TOTAL			0.350
TRI AROMATICS	C26(20S)	1132495	44812919	0.080
	C26(20R)+C27(20S)	1756969	44812919	0.124
	C28(20S)	989412	44812919	0.070
	C27(20R)	937240	44812919	0.066
	C28(20R)	907679	44812919	0.064
	TOTAL			0.404
	* 5 α (H)C27(20S) + 5 β (H)C28(20S)			
	** 5 α (H)C27(20R) + 5 α (H)C28(20S) + 5 β (H)C28(20R) + 5 β C29(20S)			
	*** 5 α (H)C28(20R) + 5 β (H)C29(20R)			

SFE OF POSIDONIA SHALE AT350°C				
B				
Weight of sample= 3.0013g				
Weight of IS (squalane)=18.99ug				
Density of supercritical CO ₂ = 0.281 g/ml				
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	476561	3082218	0.978
	C11	604238	3109705	1.23
	C12	552104	3109705	1.12
	C13	634104	3109705	1.29
	C14	458454	3109705	0.933
	C15	413959	3109705	0.842
	C16	348349	3082218	0.715
	C17	392475	3082218	0.806
	C18	195157	3082218	0.401
	C19	206741	3095263	0.423
	C20	266112	3095263	0.544
	C21	251100	3095263	0.513
	C22	206084	3095263	0.421
	C23	247289	3095263	0.506
	C24	213455	3095263	0.436
	C25	227237	3095263	0.465
	C26	257731	3095263	0.527
	C27	163746	3095263	0.335
	C28	187732	3095263	0.384
	C29	174301	3095263	0.356
	C30	139856	3095263	0.286
	C31	154434	3095263	0.316
	C32	125618	3095263	0.257
	C33	N.D.		0.000
	TOTAL ALKANES			14.1
NAPHTHALENES	NAPHTHALENE	3299356	3058639	6.83
	C-1 MN	7568049	3058639	15.7
	C-2 MN	4770786	3058639	9.87
	TOTAL MN			25.5
	1-E,2-EN	1723913	3058639	3.57
	2,6,2,7DMN	4839113	3058639	10.0
	1,3,1,7DMN	5692463	3058639	11.8
	1,6DMN	3550031	3058639	7.34
	1,4,1,3,1,5DMN	3031297	3058639	6.27
	1,8DMN	1436531	3058639	2.97
	TOTAL DMN			41.9
	1,3,7TMN	4004946	3058639	8.28
	1,3,6TMN	4341704	3058639	8.98
	1,4,6,1,3,5TMN	2802356	3058639	5.80
	2,3,6TMN	2862114	3058639	5.92
	1,2,7,1,6,7,1,2,6TMN	5054060	3058639	10.5
	1,2,5TMN	724790	3058639	1.50
	TOTAL TMN			40.9
	TOTAL NAPHS			115
PHENANTHRENES	PHENANTHRENE	1946732	3082229	4.00
	ANTHRACENE	796431	3082229	1.63
	3-MP	1291918	3082229	2.65
	2-MP	1668016	3082229	3.42
	2-MA	835195	3082229	1.71
	9-MP	1569189	3082229	3.22
	1-MP	N/A	N/A	N/A
	1-MP+1-MA	3130860	3082229	6.43
	9MA	251719	3123383	0.510
	TOTAL MP	N/A	N/A	N/A
	TOTAL MP+MA			17.9
	TOTAL DMP	N/A	N/A	N/A
	TOTAL DMP+DMA	12430341	3082229	25.5
	TOTAL PHENAS			49.1

	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C29αβ	729425	51808388	0.089
	C29βα	171912	51808388	0.021
	C30αβ	180864	51808388	0.022
	C30βα	96732	51808388	0.012
	C31αβ(S)	42244	52162268	0.005
	C31αβ(R)	91448	51808388	0.011
	C32αβ(S)	22327	52162268	0.003
	C32αβ(R)	69486	52162268	0.008
	C33αβ(S)	N/A	N/A	N/A
	C33αβ(R)	N/A	N/A	N/A
	C34αβ(S)	N/A	N/A	N/A
	C34αβ(R)	N/A	N/A	N/A
	C35αβ(S)	N/A	N/A	N/A
	C35αβ(R)	N/A	N/A	N/A
	TOTAL			0.171
MONO AROMATICS	5β(H)C27(20S)	N/A	N/A	N/A
	5β(H)C27(20R)	N/A	N/A	N/A
	*	N/A	N/A	N/A
	**	N/A	N/A	N/A
	5α(H)C29(20S)	N/A	N/A	N/A
	***	N/A	N/A	N/A
	5α(H)C29(20R)	N/A	N/A	N/A
	TOTAL			N/A
TRI AROMATICS	C26(20S)	34335	51810806	0.004
	C26(20R)+C27(20S)	80560	51810806	0.010
	C28(20S)	36446	52162268	0.004
	C27(20R)	28441	52162268	0.003
	C28(20R)	47825	52162268	0.006
	TOTAL			0.028
	*: 5α(H)C27(20S) + 5β(H)C28(20S)			
	** 5α(H)C27(20R)+5α(H)C28(20S)+5β(H)C28(20R)+5βC29(20S)			
	*** 5α(H)C28(20R)+5β(H)C29(20R)			

SFE OF POSIDONIA SHALE AT 50°C				
C				
Weight of sample=2.9967g				
Weight of IS (squalane)=18.99µg				
Density of supercritical CO ₂ = 0.904 g/ml				
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	2198543	1011354	13.8
	C11	2213465	1011354	13.9
	C12	1823103	1011354	11.4
	C13	2095294	1011354	13.1
	C14	2108676	1011354	13.2
	C15	2200026	1011354	13.8
	C16	2064952	1011354	12.9
	C17+PRI	6534248	1011354	40.9
	C18	1656305	1011354	10.4
	PHY	2327777	1011354	14.6
	C19	1331338	1011354	8.34
	C20	1020462	1011354	6.39
	C21	849574	1011354	5.32
	C22	664851	1011354	4.17
	C23	640342	1011354	4.01
	C24	644207	1011354	4.04
	C25	532974	1011354	3.34
	C26	433202	1011354	2.71
	C27	309641	1011354	1.94
	C28	301090	1011354	1.89
	C29	271541	1011354	1.70
	C30	285163	1011354	1.79
	C31	165245	1011354	1.04
	C32	124995	1011354	0.783
	C33	106987	1011354	0.670
	TOTAL ALKANES			206
NAPHTHALENES	NAPHTHALENE	1862860	1035504	11.4
	C-1 MN	2344099	1035504	14.3
	C-2 MN	2110834	1035504	12.9
	TOTAL MN			27.3
	1-E,2-EN	416329	1035504	2.55
	2,6,2,7DMN	665369	1035504	4.07
	1,3,1,7DMN	907746	1035504	5.56
	1,6DMN	874310	1035504	5.35
	1,4,1,3,1,5DMN	725457	1035504	4.44
	1,8DMN	327468	1035504	2.00
	TOTAL DMN			24.0
	1,3,7TMN	307996	1035504	1.88
	1,3,6TMN	455135	1035504	2.79
	1,4,6,1,3,5TMN	299557	1035504	1.83
	2,3,6TMN	192784	1035504	1.18
	1,2,7,1,6,7,1,2,6TMN	448430	1035504	2.74
	1,2,5TMN	214988	1035504	1.32
	TOTAL TMN			11.7
	TOTAL NAPHS			74.4
PHENANTHRENES	PHENANTHRENE	431900	1134383	2.41
	ANTHRACENE	N/A	N/A	N/A
	3-MP	121779	1134383	0.680
	2-MP	131118	1134383	0.732
	2-MA	N/A	N/A	N/A
	9-MP	162543	1134383	0.908
	1-MP	203634	1134383	1.14
	1-MP+1-MA	N/A	N/A	N/A
	9MA	N/A	N/A	N/A
	TOTAL MP			3.46
	TOTAL MP+MA	N/A	N/A	N/A
	TOTAL DMP	378638	1134383	2.12
	TOTAL DMP+DMA	N/A	1134383	N/A
	TOTAL PHENAS			7.99

	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C29 α β	7525220	89230864	0.534
	C29 β α	1819715	89230864	0.129
	C30 α β	13567265	89230864	0.964
	C30 β α	3039272	89230864	0.216
	C31 α β (S)	5346868	89230864	0.380
	C31 α β (R)	3951015	89230864	0.281
	C32 α β (S)	3030250	89230864	0.215
	C32 α β (R)	2761979	89230864	0.196
	C33 α β (S)	4204554	89230864	0.299
	C33 α β (R)	4255124	89230864	0.302
	C34 α β (S)	2821230	89230864	0.200
	C34 α β (R)	2682211	89230864	0.190
	C35 α β (S)	1956968	89230864	0.139
	C35 α β (R)	2724109	89230864	0.193
	TOTAL			4.24
MONO AROMATICS	5 β (H)C27(20S)	4514693	82430906	0.347
	5 β (H)C27(20R)	5903060	82430906	0.454
	*	16633256	82430906	1.28
	**	31321627	82430906	2.41
	5 α (H)C29(20S)	9714047	82430906	0.747
	***	15449281	82430906	1.19
	5 α (H)C29(20R)	6523614	82430906	0.502
	TOTAL			6.92
TRI AROMATICS	C26(20S)	13131149	72842098	1.14
	C26(20R)+C27(20S)	31807715	72842098	2.77
	C28(20S)	19713367	72842098	1.71
	C27(20R)	20881996	72842098	1.82
	C28(20R)	29903037	72842098	2.60
	TOTAL			10.0
	*. 5 α (H)C27(20S) + 5 β (H)C28(20S)			
	** 5 α (H)C27(20R)+5 α (H)C28(20S)+5 β (H)C28(20R)+5 β C29(20S)			
	*** 5 α (H)C28(20R)+5 β (H)C29(20R)			

SFE OF POSIDONIA SHALE AT 150°C				
C				
Weight of sample=2.9967g				
Weight of IS (squalane)=9.50ug				
Density of supercritical CO ₂ =				
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	722182	1677144	1.37
	C11	751567	1677144	1.42
	C12	856213	1677144	1.62
	C13	983442	1677144	1.86
	C14	1103917	1677144	2.09
	C15	1194706	1677144	2.26
	C16	1052141	1677144	1.99
	C17+PRI	4837781	1677144	9.14
	C18	948756	1677144	1.79
	PHY	1936697	1677144	3.66
	C19	778774	1677144	1.47
	C20	644284	1677144	1.22
	C21	610435	1677144	1.15
	C22	591230	1677144	1.12
	C23	620661	1677144	1.17
	C24	774798	1677144	1.46
	C25	692173	1677144	1.31
	C26	658033	1677144	1.24
	C27	393475	1677144	0.744
	C28	468176	1835240	0.809
	C29	350831	1835240	0.606
	C30	408567	1835240	0.706
	C31	461883	1835240	0.798
	C32	394920	1835240	0.682
	C33	384615	1835240	0.664
	TOTAL ALKANES			42.4
NAPHTHALENES	NAPHTHALENE	781585	1845936	1.34
	C-1 MN	1670955	1845936	2.87
	C-2 MN	2323470	1845936	3.99
	TOTAL MN			6.86
	1-E,2-EN	505480	1845936	0.868
	2,6,2,7DMN	648422	1845936	1.11
	1,3,1,7DMN	1227330	1845936	2.11
	1,6DMN	1443990	1845936	2.48
	1,4,1,3,1,5DMN	955734	1845936	1.64
	1,8DMN	378830	1845936	0.651
	TOTAL DMN			8.86
	1,3,7TMN	641258	1845936	1.10
	1,3,6TMN	864635	1845936	1.48
	1,4,6,1,3,5TMN	777884	1845936	1.34
	2,3,6TMN	269893	1845936	0.464
	1,2,7,1,6,7,1,2,6TMN	885524	1845936	1.52
	1,2,5TMN	415390	1845936	0.713
	TOTAL TMN			6.62
	TOTAL NAPHS			23.7
PHENANTHRENES	PHENANTHRENE	694639	2048214	1.08
	ANTHRACENE	N/A	N/A	N/A
	3-MP	238554	2048214	0.369
	2-MP	279824	2048214	0.433
	2-MA	N/A	N/A	N/A
	9-MP	430851	2048214	0.667
	1-MP	565782	2048214	0.876
	1-MP+1-MA	N/A	N/A	N/A
	9MA	N/A	N/A	N/A
	TOTAL MP			2.34
	TOTAL MP+MA	N/A	N/A	N/A
	TOTAL DMP	1217800	2048214	1.88
	TOTAL DMP+DMA	N/A	N/A	N/A
	TOTAL PHENAS			5.30

	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C29 α β	20438113	51153676	1.27
	C29 β α	3718802	58145263	0.203
	C30 α β	32318326	51153676	2.00
	C30 β α	6636024	59677131	0.353
	C31 α β (S)	12970529	75632117	0.544
	C31 α β (R)	9439336	75632117	0.396
	C32 α β (S)	6695584	59677131	0.356
	C32 α β (R)	6642711	59677131	0.353
	C33 α β (S)	11202618	75632117	0.470
	C33 α β (R)	10343064	75632117	0.434
	C34 α β (S)	5914472	75632117	0.248
	C34 α β (R)	5460603	75632117	0.229
	C35 α β (S)	4471634	75632117	0.187
	C35 α β (R)	5587634	75632117	0.234
	TOTAL			7.27
MONO AROMATICS	5 β (H)C27(20S)	7768941	51099706	0.482
	5 β (H)C27(20R)	9807571	51099706	0.608
	*	32382149	51099706	2.01
	**	59996759	51099706	3.72
	5 α (H)C29(20S)	19142998	53221587	1.14
	***	24971813	53221587	1.49
	5 α (H)C29(20R)	11474850	51099706	0.712
	TOTAL			10.2
TRI AROMATICS	C26(20S)	18157211	51059086	1.13
	C26(20R)+C27(20S)	39240214	50832119	2.45
	C28(20S)	24675621	50832119	1.54
	C27(20R)	25201073	62763100	1.27
	C28(20R)	29518435	62763100	1.49
	TOTAL			7.88
	*: 5 α (H)C27(20S) + 5 β (H)C28(20S)			
	** : 5 α (H)C27(20R)+ 5 α (H)C28(20S)+ 5 β (H)C28(20R)+ 5 β C29(20S)			
	***: 5 α (H)C28(20R)+ 5 β (H)C29(20R)			

SFE OF POSIDONIA SHALE AT 250°C				
C				
Weight of sample=2.9967g				
Weight of IS (squalane)=9.50ug				
Density of supercritical CO ₂ = 0.366 g/ml				
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	577586	4865198	0.376
	C11	661871	4865198	0.431
	C12	502603	4865198	0.327
	C13	717437	486519	0.468
	C14	742624	486519	0.485
	C15	719116	486519	0.469
	C16	647211	486519	0.422
	C17+PRI	2174223	486519	1.42
	C18	531369	486519	0.347
	PHY	874004	4865198	0.569
	C19	647614	4865198	0.422
	C20	646804	4865198	0.421
	C21	560668	4865198	0.365
	C22	496284	4865198	0.323
	C23	494065	4865198	0.322
	C24	636367	4865198	0.415
	C25	645920	4865198	0.421
	C26	646020	4865198	0.421
	C27	514343	4865198	0.335
	C28	422979	5006265	0.268
	C29	303383	5006265	0.192
	C30	303809	5006265	0.192
	C31	247495	5006265	0.157
	C32	206899	5006265	0.131
	C33	196268	5006265	0.124
	TOTAL ALKANES			9.83
NAPHTHALENES	NAPHTHALENE	5212289	4922950	3.36
	C-1 MN	6391448	4922950	4.12
	C-2 MN	5125473	4922950	3.30
	TOTAL MN			7.42
	1-E,2-EN	1585647	4922950	1.02
	2,6,2,7DMN	3207364	4922950	2.07
	1,3,1,7DMN	3769434	4922950	2.43
	1,6DMN	4239943	4922950	2.73
	1,4,1,3,1,5DMN	2778997	4922950	1.79
	1,8DMN	1504324	4922950	0.969
	TOTAL DMN			11.0
	1,3,7TMN	1678905	4922950	1.08
	1,3,6TMN	2005133	4922950	1.29
	1,4,6,1,3,5TMN	1425126	4922950	0.918
	2,3,6TMN	1046848	4922950	0.674
	1,2,7,1,6,7,1,2,6TMN	2425125	4922950	1.56
	1,2,5TMN	922057	4922950	0.594
	TOTAL TMN			6.12
	TOTAL NAPHS			27.9
PHENANTHRENES	PHENANTHRENE	2233527	5043922	1.40
	ANTHRACENE	N/A	N/A	N/A
	3-MP	757095	5043922	0.476
	2-MP	932095	5043922	0.586
	2-MA	N/A	N/A	N/A
	9-MP	912878	5043922	0.574
	1-MP	2104370	5043922	1.32
	1-MP+1-MA	N/A	N/A	N/A
	9MA	N/A	N/A	N/A
	TOTAL MP			2.96
	TOTAL MP+MA	N/A	N/A	N/A
	TOTAL DMP	3714174	5043922	2.33
	TOTAL DMP+DMA	N/A	N/A	N/A
	TOTAL PHENAS			6.70

	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C29 α β	3456806	70154582	0.156
	C29 β α	538658	71906001	0.024
	C30 α β	2080874	70154582	0.094
	C30 β α	366333	71906001	0.016
	C31 α β (S)	1101988	71906001	0.049
	C31 α β (R)	808703	71906001	0.036
	C32 α β (S)	480951	71906001	0.021
	C32 α β (R)	542265	71906001	0.024
	C33 α β (S)	564518	71906001	0.025
	C33 α β (R)	734448	71906001	0.032
	C34 α β (S)	318976	71906001	0.014
	C34 α β (R)	457589	71906001	0.020
	C35 α β (S)	260942	71906001	0.012
	C35 α β (R)	358024	71906001	0.016
	TOTAL			0.538
MONO AROMATICS	5 β (H)C27(20S)	281886	71906001	0.012
	5 β (H)C27(20R)	360601	71906001	0.016
	*	1167914	71906001	0.051
	**	1983851	71906001	0.087
	5 α (H)C29(20S)	659772	71906001	0.029
	***	970283	71906001	0.043
	5 α (H)C29(20R)	363575	71906001	0.016
	TOTAL			0.255
TRI AROMATICS	C26(20S)	1918204	67972302	0.089
	C26(20R)+C27(20S)	3088830	70154582	0.140
	C28(20S)	1563857	67972302	0.073
	C27(20R)	1696208	70154582	0.077
	C28(20R)	1756940	70154582	0.079
	TOTAL			0.458
	*. 5 α (H)C27(20S) + 5 β (H)C28(20S)			
	** 5 α (H)C27(20R)+5 α (H)C28(20S)+5 β (H)C28(20R)+5 β C29(20S)			
	*** 5 α (H)C28(20R)+5 β (H)C29(20R)			

SFE OF POSIDONIA SHALE AT350°C					
C					
Weight of sample=2.9967g					
Weight of IS (squalane)=18.99ug					
Density of supercritical CO ₂ = 0.281 g/ml					
	Comp	Pk Area	IS Pk Area	(ug/g)	
ALKANES	C10	426805	3473377	0.779	
	C11	474523	3473377	0.866	
	C12	471703	3473377	0.861	
	C13	539973	3473377	0.985	
	C14	416276	3473377	0.759	
	C15	407072	3473377	0.743	
	C16	313815	3473377	0.573	
	C17	538010	3473377	0.982	
	C18	192708	3473377	0.352	
	C19	249257	3473377	0.455	
	C20	230512	3473377	0.421	
	C21	210902	3473377	0.385	
	C22	218082	3473377	0.398	
	C23	208228	3473377	0.380	
	C24	196216	3473377	0.358	
	C25	170593	3473377	0.311	
	C26	190250	3473377	0.347	
	C27	125455	3473377	0.229	
	C28	129844	3473377	0.237	
	C29	127041	3473377	0.232	
	C30	103020	3473377	0.188	
	C31	96277	3473377	0.176	
	C32	75821	3473377	0.138	
	C33	N.D.		0.000	
	TOTAL ALKANES			11.2	
NAPHTHALENES	NAPHTHALENE	2532860	3477672	4.62	
	C-1 MN	5426571	3477672	9.89	
	C-2 MN	3513337	3477672	6.40	
	TOTAL MN			16.3	
	1-E,2-EN	1341344	3477672	2.44	
	2,6,2,7DMN	3584771	3477672	6.53	
	1,3,1,7DMN	4433352	3477672	8.08	
	1,6DMN	3132061	3477672	5.71	
	1,4,1,3,1,5DMN	2454455	3477672	4.47	
	1,8DMN	1278008	3477672	2.33	
	TOTAL DMN			29.6	
	1,3,7TMN	3053176	3477672	5.56	
	1,3,6TMN	3365160	3477672	6.13	
	1,4,6,1,3,5TMN	2230620	3477672	4.06	
	2,3,6TMN	2331234	3477672	4.25	
	1,2,7,1,6,7,1,2,6TMN	4082484	3477672	7.44	
	1,2,5TMN	853893	3477672	1.56	
	TOTAL TMN			29.0	
	TOTAL NAPHS			79.5	
PHENANTHRENES	PHENANTHRENE	1500215	3473377	2.74	
	ANTHRACENE	806236	3473377	1.47	
	3-MP	1061289	3473377	1.94	
	2-MP	1308536	3473377	2.39	
	2-MA	931555	3473377	1.70	
	9-MP	1496309	3473377	2.73	
	1-MP	N/A	N/A	N/A	
	1-MP+1-MA	2785786	3473377	5.08	
	9MA	292171	3473377	0.533	
	TOTAL MP	N/A	N/A	N/A	
	TOTAL MP+MA			14.4	
	TOTAL DMP	N/A	N/A	N/A	
	TOTAL DMP+DMA	11669902	3473377	21.3	
	TOTAL PHENAS			39.9	

	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C29 α β	2130380	141849526	0.095
	C29 β α	554045	139899675	0.025
	C30 α β	627004	139899675	0.028
	C30 β α	319791	139899675	0.014
	C31 α β (S)	170137	139899675	0.008
	C31 α β (R)	332751	139899675	0.015
	C32 α β (S)	76456	140883025	0.003
	C32 α β (R)	260333	140883025	0.012
	C33 α β (S)	N/A	N/A	N/A
	C33 α β (R)	N/A	N/A	N/A
	C34 α β (S)	N/A	N/A	N/A
	C34 α β (R)	N/A	N/A	N/A
	C35 α β (S)	N/A	N/A	N/A
	C35 α β (R)	N/A	N/A	N/A
	TOTAL			0.201
MONO AROMATICS	5 β (H)C27(20S)	N/A	N/A	N/A
	5 β (H)C27(20R)	N/A	N/A	N/A
	*	N/A	N/A	N/A
	**	N/A	N/A	N/A
	5 α (H)C29(20S)	N/A	N/A	N/A
	***	N/A	N/A	N/A
	5 α (H)C29(20R)	N/A	N/A	N/A
	TOTAL			N/A
TRI AROMATICS	C26(20S)	48890	140883025	0.002
	C26(20R)+C27(20S)	115781	140883025	0.005
	C28(20S)	181877	140883025	0.008
	C27(20R)	56882	140883025	0.003
	C28(20R)	196012	140883025	0.009
	TOTAL			0.027
	*: 5 α (H)C27(20S) + 5 β (H)C28(20S)			
	** : 5 α (H)C27(20R)+5 α (H)C28(20S)+5 β (H)C28(20R)+5 β C29(20S)			
	***: 5 α (H)C28(20R)+5 β (H)C29(20R)			

THERMODESORPTION OF POSIDONIA SHALE AT 50C				
A				
Weight of sample=2.9914g				
Weight of I.S. (squalane)=9.50ug				
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	N.D.		0.0000
	C11	N.D.		0.0000
	C12	N.D.		0.0000
	C13	N.D.		0.0000
	C14	N.D.		0.0000
	C15	N.D.		0.0000
	C16	N.D.		0.0000
	C17+PRI	N.D.		0.0000
	C18	N.D.		0.0000
	PHY	N.D.		0.0000
	C19	N.D.		0.0000
	C20	N.D.		0.0000
	C21	N.D.		0.0000
	C22	N.D.		0.0000
	C23	N.D.		0.0000
	C24	N.D.		0.0000
	C25	N.D.		0.0000
	C26	N.D.		0.0000
	C27	N.D.		0.0000
	C28	N.D.		0.0000
	C29	N.D.		0.0000
	C30	N.D.		0.0000
	C31	N.D.		0.0000
	C32	N.D.		0.0000
	C33	N.D.		0.0000
	TOTAL ALKANES			0.0000
NAPHTHALENES	NAPHTHALENE	N.D.		0.0000
	C-1 MN	N.D.		0.0000
	C-2 MN	N.D.		0.0000
	TOTAL MN			0.0000
	1-E,2-EDMN	N.D.		0.0000
	2,6,2,7DMN	N.D.		0.0000
	1,3,1,7DMN	N.D.		0.0000
	1,6DMN	N.D.		0.0000
	1,4,1,3,1,5DMN	N.D.		0.0000
	1,8DMN	N.D.		0.0000
	TOTAL DMN			0.0000
	1,3,7TMN	N.D.		0.0000
	1,3,6TMN	N.D.		0.0000
	1,4,6,1,3,5TMN	N.D.		0.0000
	2,3,6TMN	N.D.		0.0000
	1,2,7,1,6,7,1,2,6TMN	N.D.		0.0000
	1,2,5TMN	N.D.		0.0000
	TOTAL TMN			0.0000
	TOTAL NAPHS			0.0000
PHENATHALENES	PHENATHLENE	N.D.		0.0000
	ANTHRASENE	N.D.		0.0000
	3-MP	N.D.		0.0000
	2-MP	N.D.		0.0000
	2-MA	N.D.		0.0000
	9-MP	N.D.		0.0000
	1-MP	N.D.		0.0000
	1-MP+1-MA	N.D.		0.0000
	9MA	N.D.		0.0000
	TOTAL MP	N.D.		0.0000
	TOTAL MP+MA	N.D.		0.0000
	TOTAL DMP	N.D.		0.0000
	TOTAL DMP+DMA	N.D.		0.0000
	TOTAL PHENAS			0.0000

HOPANES	Comp	Pk Area	IS Pk Area	(ug/g)
	C29 $\alpha\beta$	N.D.		0.0000
	C29 $\beta\alpha$	N.D.		0.0000
	C30 $\alpha\beta$	N.D.		0.0000
	C30 $\beta\alpha$	N.D.		0.0000
	C31 $\alpha\beta$ (S)	N.D.		0.0000
	C31 $\alpha\beta$ (R)	N.D.		0.0000
	C30 $\beta\beta$	N.D.		0.0000
	C32 $\alpha\beta$ (S)	N.D.		0.0000
	C32 $\alpha\beta$ (R)	N.D.		0.0000
	C33 $\alpha\beta$ (S)	N.D.		0.0000
	C33 $\alpha\beta$ (R)	N.D.		0.0000
	C34 $\alpha\beta$ (S)	N.D.		0.0000
	C34 $\alpha\beta$ (R)	N.D.		0.0000
	C35 $\alpha\beta$ (S)	N.D.		0.0000
	C35 $\alpha\beta$ (R)	N.D.		0.0000
	TOTAL			0.0000
MONO AROMATICS	5 β (H)C27(20S)	N.D.		0.0000
	5 β (H)C27(20R)	N.D.		0.0000
	*	N.D.		0.0000
	**	N.D.		0.0000
	5 α (H)C29(20S)	N.D.		0.0000
	***	N.D.		0.0000
	5 α (H)C29(20R)	N.D.		0.0000
	TOTAL			0.0000
TRI AROMATICS	C26(20S)	N.D.		0.0000
	C26(20R)+C27(20S)	N.D.		0.0000
	C28(20S)	N.D.		0.0000
	C27(20R)	N.D.		0.0000
	C28(20R)	N.D.		0.0000
	TOTAL			0.0000
	*: 5 α (H)C27(S) + 5 β (H)C28(S)			
	**: 5 α (H)C27(20R)+5 α (H)C28(20S)+5 β (H)C28(20R)+5 β C29(20S)			
	***: 5 α (H)C28(20R)+5 β (H)C29(20R)			

THERMODESORPTION OF POSIDONIA SHALE AT 150C				
A				
Weight of sample=2.9914g				
Weight of LS (squalane)=9.50ug				
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	3325892	2046875	5.16
	C11	4840251	2046875	7.51
	C12	3575546	2046875	5.55
	C13	1903363	2046875	2.95
	C14	891211	2046875	1.38
	C15	439363	2046875	0.682
	C16	N.D.		0.0000
	C17+PRI	N.D.		0.0000
	C18	N.D.		0.0000
	PHY	N.D.		0.0000
	C19	N.D.		0.0000
	C20	N.D.		0.0000
	C21	N.D.		0.0000
	C22	N.D.		0.0000
	C23	N.D.		0.0000
	C24	N.D.		0.0000
	C25	N.D.		0.0000
	C26	N.D.		0.0000
	C27	N.D.		0.0000
	C28	N.D.		0.0000
	C29	N.D.		0.0000
	C30	N.D.		0.0000
	C31	N.D.		0.0000
	C32	N.D.		0.0000
	C33	N.D.		0.0000
	TOTAL ALKANES			23.24
NAPHTHALENES	NAPHTHALENE	767470	2046875	1.1907
	C-1 MN	N.D.		0.0000
	C-2 MN	N.D.		0.0000
	TOTAL MN			0.0000
	1-E,2-EDMN	N.D.		0.0000
	2,6,2,7DMN	N.D.		0.0000
	1,3,1,7DMN	N.D.		0.0000
	1,6DMN	N.D.		0.0000
	1,4,1,3,1,5DMN	N.D.		0.0000
	1,8DMN	N.D.		0.0000
	TOTAL DMN			0.0000
	1,3,7TMN	N.D.		0.0000
	1,3,6TMN	N.D.		0.0000
	1,4,6,1,3,5TMN	N.D.		0.0000
	2,3,6TMN	N.D.		0.0000
	1,2,7,1,6,7,1,2,6TMN	N.D.		0.0000
	1,2,5TMN	N.D.		0.0000
	TOTAL TMN			0.0000
	TOTAL NAPHS			1.19
PHENATHALENES	PHENATHLENE	N.D.		0.0000
	ANTHRASENE	N.D.		0.0000
	3-MP	N.D.		0.0000
	2-MP	N.D.		0.0000
	2-MA	N.D.		0.0000
	9-MP	N.D.		0.0000
	1-MP	N.D.		0.0000
	1-MP+1-MA	N.D.		0.0000
	9MA	N.D.		0.0000
	TOTAL MP	N.D.		0.0000
	TOTAL MP+MA	N.D.		0.0000
	TOTAL DMP	N.D.		0.0000
	TOTAL DMP+DMA	N.D.		0.0000
	TOTAL PHENAS			0.0000

HOPANES	Comp	Pk Area	IS Pk Area	(ug/g)
	C29αβ	N.D.		0.0000
	C29βα	N.D.		0.0000
	C30αβ	N.D.		0.0000
	C30βα	N.D.		0.0000
	C31αβ(S)	N.D.		0.0000
	C31αβ(R)	N.D.		0.0000
	C30ββ	N.D.		0.0000
	C32αβ(S)	N.D.		0.0000
	C32αβ(R)	N.D.		0.0000
	C33αβ(S)	N.D.		0.0000
	C33αβ(R)	N.D.		0.0000
	C34αβ(S)	N.D.		0.0000
	C34αβ(R)	N.D.		0.0000
	C35αβ(S)	N.D.		0.0000
	C35αβ(R)	N.D.		0.0000
	TOTAL			0.0000
MONO AROMATICS	5β(H)C27(20S)	N.D.		0.0000
	5β(H)C27(20R)	N.D.		0.0000
	*	N.D.		0.0000
	**	N.D.		0.0000
	5α(H)C29(20S)	N.D.		0.0000
	***	N.D.		0.0000
	5α(H)C29(20R)	N.D.		0.0000
	TOTAL			0.0000
TRI AROMATICS	C26(20S)	N.D.		0.0000
	C26(20R)+C27(20S)	N.D.		0.0000
	C28(20S)	N.D.		0.0000
	C27(20R)	N.D.		0.0000
	C28(20R)	N.D.		0.0000
	TOTAL			0.0000
	*. 5α(H)C27(S) + 5β(H)C28(S)			
	**. 5α(H)C27(20R)+5α(H)C28(20S)+5β(H)C28(20R)+5βC29(20S)			
	***. 5α(H)C28(20R)+5β(H)C29(20R)			

THERMODESORPTION OF POSIDONIA SHALE AT 250C				
	A			
	Weight of sample=2.9914g			
	Weight of I.S.(squalane)=9.50ug			
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	1329137	936604	4.51
	C11	731252	936604	2.48
	C12	3220426	936604	10.92
	C13	3384789	936604	11.48
	C14	2687111	936604	9.11
	C15	2245334	936604	7.61
	C16	1555200	936604	5.27
	C17+PRI	1395089	936604	4.73
	C18	533278	860246	1.97
	PHY	299492	931652	1.02
	C19	307498	936604	1.04
	C20	186224	936604	0.631
	C21	N/D		0.0000
	C22	N/D		0.0000
	C23	N/D		0.0000
	C24	N/D		0.0000
	C25	N/D		0.0000
	C26	N/D		0.0000
	C27	N/D		0.0000
	C28	N/D		0.0000
	C29	N/D		0.0000
	C30	N/D		0.0000
	C31	N/D		0.0000
	C32	N/D		0.0000
	C33	N/D		0.0000
	TOTAL ALKANES			60.77
NAPHTHALENES	NAPHTHALENE	5730437	931652	19.53
	C-1 MN	5758147	931652	19.63
	C-2 MN	4420071	931652	15.07
	TOTAL MN			34.70
	1-E,2-EDMN	892096	931652	3.04
	2,6,2,7DMN	1427597	931652	4.87
	1,3,1,7DMN	1471464	931652	5.02
	1,6DMN	1405244	931652	4.79
	1,4,1,3,1,5DMN	1041998	931652	3.55
	1,8DMN	499301	931652	1.70
	TOTAL DMN			22.97
	1,3,7TMN	335284	931652	1.14
	1,3,6TMN	246810	931652	0.841
	1,4,6,1,3,5TMN	192501	931652	0.656
	2,3,6TMN	113098	931652	0.386
	1,2,7,1,6,7,1,2,6TMN	309083	931652	1.05
	1,2,5TMN	120978	931652	0.412
	TOTAL TMN			4.49
	TOTAL NAPHS			81.69
PHENATHALENES	PHENATHLENE	377657	931652	1.29
	ANTHRASENE	N/D		0.0000
	3-MP	62702	931652	0.214
	2-MP	36003	931652	0.123
	2-MA	N/D		0.0000
	9-MP	73980	931652	0.252
	1-MP	98717	931652	0.337
	1-MP+1-MA	N/D		0.0000
	9MA	N/D		0.0000
	TOTAL MP	N/D		0.925
	TOTAL MP+MA	N/D		0.0000
	TOTAL DMP	N/D		0.0000
	TOTAL DMP+DMA	N/D		0.0000
	TOTAL PHENAS			2.21

HOPANES	Comp	Pk Area	IS Pk Area	(ug/g)
	C29 α B	N.D.		0.0000
	C29 β A	N.D.		0.0000
	C30 α B	N.D.		0.0000
	C30 β A	N.D.		0.0000
	C31 α B(S)	N.D.		0.0000
	C31 α B(R)	N.D.		0.0000
	C30 β B	N.D.		0.0000
	C32 α B(S)	N.D.		0.0000
	C32 α B(R)	N.D.		0.0000
	C33 α B(S)	N.D.		0.0000
	C33 α B(R)	N.D.		0.0000
	C34 α B(S)	N.D.		0.0000
	C34 α B(R)	N.D.		0.0000
	C35 α B(S)	N.D.		0.0000
	C35 α B(R)	N.D.		0.0000
	TOTAL			0.0000
MONO AROMATICS	5 β (H)C27(20S)	N.D.		0.0000
	5 β (H)C27(20R)	N.D.		0.0000
	*	N.D.		0.0000
	**	N.D.		0.0000
	5 α (H)C29(20S)	N.D.		0.0000
	***	N.D.		0.0000
	5 α (H)C29(20R)	N.D.		0.0000
	TOTAL			0.0000
TRI AROMATICS	C26(20S)	N.D.		0.0000
	C26(20R)+C27(20S)	N.D.		0.0000
	C28(20S)	N.D.		0.0000
	C27(20R)	N.D.		0.0000
	C28(20R)	N.D.		0.0000
	TOTAL			0.0000
	* 5 α (H)C27(S) + 5 β (H)C28(S)			
	** 5 α (H)C27(20R)+5 α (H)C28(20S)+5 β (H)C28(20R)+5 β C29(20S)			
	*** 5 α (H)C28(20R)+5 β (H)C29(20R)			

THERMODESORPTION OF POSIDONIA SHALE AT 350C					
A					
Weight of sample=2.9914g					
Weight of LS (squalane)=9.50ug					
	Comp	Pk Area	IS Pk Area		(ug/g)
ALKANES	C10	648082	2754192		0.747
	C11	1111707	2754192		1.28
	C12	1049199	2754192		1.21
	C13	1389535	2754192		1.60
	C14	1451336	2754192		1.67
	C15	2166972	2754192		2.50
	C16	2625044	2754192		3.03
	C17+PRI	3295018	2754192		3.80
	C18	2802766	2754192		3.23
	PHY	498666	1655836		0.956
	C19	2573645	2754192		2.97
	C20	1859756	2754192		2.14
	C21	1499145	2754192		1.73
	C22	1186554	2754192		1.37
	C23	832847	2754192		0.960
	C24	720728	2754192		0.831
	C25	457003	2754192		0.527
	C26	355326	2754192		0.410
	C27	165321	2754192		0.191
	C28	118457	2754192		0.137
	C29	N.D.			0.0000
	C30	N.D.			0.0000
	C31	N.D.			0.0000
	C32	N.D.			0.0000
	C33	N.D.			0.0000
	TOTAL ALKANES				31.29
NAPHTHALENES	NAPHTHALENE	5437719	2728368		6.33
	C-1 MN	11937962	2728368		13.90
	C-2 MN	7325723	2728368		8.53
	TOTAL MN				22.42
	1-E,2-EDMN	2932719	2728368		3.41
	2,6,2,7DMN	9530583	2728368		11.09
	1,3,1,7DMN	10567470	2728368		12.30
	1,6DMN	8122654	2728368		9.45
	1,4,1,3,1,5DMN	6387935	2728368		7.44
	1,8DMN	2802399	2728368		3.26
	TOTAL DMN				46.96
	1,3,7TMN	6485947	2728368		7.55
	1,3,6TMN	7114875	2728368		8.28
	1,4,6,1,3,5TMN	4733671	2728368		5.51
	2,3,6TMN	4914779	2728368		5.72
	1,2,7,1,6,7,1,2,6TMN	9737580	2728368		11.33
	1,2,5TMN	1914245	2728368		2.23
	TOTAL TMN				40.62
	TOTAL NAPHS				116.34
PHENATHALENES	PHENATHLENE	4769823	2754192		5.50
	ANTHRASENE	2015190	2754192		2.32
	3-MP	2581118	2754192		2.98
	2-MP	2879243	2754192		3.32
	2-MA	2451999	2754192		2.83
	9-MP	2901804	2754192		3.35
	1-MP	N/A			N/A
	1-MP+1-MA	5146807	2754192		5.93
	9MA	507507	2754099		0.585
	TOTAL MP				N/A
	TOTAL MP+MA				18.99
	TOTAL DMP	N/A	N/A		N/A
	TOTAL DMP+DMA	17366724	2754192		20.03
	TOTAL PHENAS				46.84

HOPANES	Comp	Pk Area	IS Pk Area	(ug/g)
	C29αβ	N.D.		0.0000
	C29βα	N.D.		0.0000
	C30αβ	N.D.		0.0000
	C30βα	N.D.		0.0000
	C31αβ(S)	N.D.		0.0000
	C31αβ(R)	N.D.		0.0000
	C30ββ	N.D.		0.0000
	C32αβ(S)	N.D.		0.0000
	C32αβ(R)	N.D.		0.0000
	C33αβ(S)	N.D.		0.0000
	C33αβ(R)	N.D.		0.0000
	C34αβ(S)	N.D.		0.0000
	C34αβ(R)	N.D.		0.0000
	C35αβ(S)	N.D.		0.0000
	C35αβ(R)	N.D.		0.0000
	TOTAL			0.0000
MONO AROMATICS	5β(H)C27(20S)	N.D.		0.0000
	5β(H)C27(20R)	N.D.		0.0000
	*	N.D.		0.0000
	**	N.D.		0.0000
	5α(H)C29(20S)	N.D.		0.0000
	***	N.D.		0.0000
	5α(H)C29(20R)	N.D.		0.0000
	TOTAL			0.0000
TRI AROMATICS	C26(20S)	N.D.		0.0000
	C26(20R)+C27(20S)	N.D.		0.0000
	C28(20S)	N.D.		0.0000
	C27(20R)	N.D.		0.0000
	C28(20R)	N.D.		0.0000
	TOTAL			0.0000
	*: 5α(H)C27(S) + 5β(H)C28(S)			
	**: 5α(H)C27(20R)+5α(H)C28(20S)+5β(H)C28(20R)+5βC29(20S)			
	***: 5α(H)C28(20R)+5β(H)C29(20R)			

THERMODESORPTION OF POSIDONIA SHALE AT 50C				
	B			
	Weight of sample=3.0150g			
	Weight of I.S (squalane)=9.50ug			
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	N.D.		0.0000
	C11	N.D.		0.0000
	C12	N.D.		0.0000
	C13	N.D.		0.0000
	C14	N.D.		0.0000
	C15	N.D.		0.0000
	C16	N.D.		0.0000
	C17+PRI	N.D.		0.0000
	C18	N.D.		0.0000
	PHY	N.D.		0.0000
	C19	N.D.		0.0000
	C20	N.D.		0.0000
	C21	N.D.		0.0000
	C22	N.D.		0.0000
	C23	N.D.		0.0000
	C24	N.D.		0.0000
	C25	N.D.		0.0000
	C26	N.D.		0.0000
	C27	N.D.		0.0000
	C28	N.D.		0.0000
	C29	N.D.		0.0000
	C30	N.D.		0.0000
	C31	N.D.		0.0000
	C32	N.D.		0.0000
	C33	N.D.		0.0000
	TOTAL ALKANES			0.0000
NAPHTHALENES	NAPHTHALENE	N.D.		0.0000
	C-1 MN	N.D.		0.0000
	C-2 MN	N.D.		0.0000
	TOTAL MN			0.0000
	1-E,2-EDMN	N.D.		0.0000
	2,6,2,7DMN	N.D.		0.0000
	1,3,1,7DMN	N.D.		0.0000
	1,6DMN	N.D.		0.0000
	1,4,1,3,1,5DMN	N.D.		0.0000
	1,8DMN	N.D.		0.0000
	TOTAL DMN			0.0000
	1,3,7TMN	N.D.		0.0000
	1,3,6TMN	N.D.		0.0000
	1,4,6,1,3,5TMN	N.D.		0.0000
	2,3,6TMN	N.D.		0.0000
	1,2,7,1,6,7,1,2,6TMN	N.D.		0.0000
	1,2,5TMN	N.D.		0.0000
	TOTAL TMN			0.0000
	TOTAL NAPHS			0.0000
PHENATHALENES	PHENATHLENE	N.D.		0.0000
	ANTHRASENE	N.D.		0.0000
	3-MP	N.D.		0.0000
	2-MP	N.D.		0.0000
	2-MA	N.D.		0.0000
	9-MP	N.D.		0.0000
	1-MP	N.D.		0.0000
	1-MP+1-MA	N.D.		0.0000
	9MA	N.D.		0.0000
	TOTAL MP	N.D.		0.0000
	TOTAL MP+MA	N.D.		0.0000
	TOTAL DMP	N.D.		0.0000
	TOTAL DMP+DMA	N.D.		0.0000
	TOTAL PHENAS			0.0000

HOPANES	Comp	Pk Area	IS Pk Area	(ug/g)
	C29 α β	N.D.		0.0000
	C29 β α	N.D.		0.0000
	C30 α β	N.D.		0.0000
	C30 β α	N.D.		0.0000
	C31 α β (S)	N.D.		0.0000
	C31 α β (R)	N.D.		0.0000
	C30 β β	N.D.		0.0000
	C32 α β (S)	N.D.		0.0000
	C32 α β (R)	N.D.		0.0000
	C33 α β (S)	N.D.		0.0000
	C33 α β (R)	N.D.		0.0000
	C34 α β (S)	N.D.		0.0000
	C34 α β (R)	N.D.		0.0000
	C35 α β (S)	N.D.		0.0000
	C35 α β (R)	N.D.		0.0000
	TOTAL			0.0000
MONO AROMATICS	5 β (H)C27(20S)	N.D.		0.0000
	5 β (H)C27(20R)	N.D.		0.0000
	*	N.D.		0.0000
	**	N.D.		0.0000
	5 α (H)C29(20S)	N.D.		0.0000
	***	N.D.		0.0000
	5 α (H)C29(20R)	N.D.		0.0000
	TOTAL			0.0000
TRI AROMATICS	C26(20S)	N.D.		0.0000
	C26(20R)+C27(20S)	N.D.		0.0000
	C28(20S)	N.D.		0.0000
	C27(20R)	N.D.		0.0000
	C28(20R)	N.D.		0.0000
	TOTAL			0.0000
	*: 5 α (H)C27(S) + 5 β (H)C28(S)			
	**: 5 α (H)C27(20R)+5 α (H)C28(20S)+5 β (H)C28(20R)+5 β C29(20S)			
	***: 5 α (H)C28(20R)+5 β (H)C29(20R)			

THERMODESORPTION OF POSIDONIA SHALE AT 150C				
B				
Weight of sample=3.0150g				
Weight of LS (squalane)=9.50ug				
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	12532094	4576673	8.63
	C11	11194092	4576673	7.71
	C12	6400241	4576673	4.41
	C13	3308778	4576673	2.28
	C14	1377171	4576673	0.948
	C15	685788	4576673	0.472
	C16	N.D.		0.0000
	C17	N.D.		0.0000
	C18	N.D.		0.0000
	PHY	N.D.		0.0000
	C19	N.D.		0.0000
	C20	N.D.		0.0000
	C21	N.D.		0.0000
	C22	N.D.		0.0000
	C23	N.D.		0.0000
	C24	N.D.		0.0000
	C25	N.D.		0.0000
	C26	N.D.		0.0000
	C27	N.D.		0.0000
	C28	N.D.		0.0000
	C29	N.D.		0.0000
	C30	N.D.		0.0000
	C31	N.D.		0.0000
	C32	N.D.		0.0000
	C33	N.D.		0.0000
	TOTAL ALKANES			24.44
NAPHTHALENES	NAPHTHALENE	3637617	4575673	2.50
	C-1 MN	N.D.		0.0000
	C-2 MN	N.D.		0.0000
	TOTAL MN			0.0000
	1-E,2-EDMN	N.D.		0.0000
	2,6,2,7DMN	N.D.		0.0000
	1,3,1,7DMN	N.D.		0.0000
	1,6DMN	N.D.		0.0000
	1,4,1,3,1,5DMN	N.D.		0.0000
	1,8DMN	N.D.		0.0000
	TOTAL DMN			0.0000
	1,3,7TMN	N.D.		0.0000
	1,3,6TMN	N.D.		0.0000
	1,4,6,1,3,5TMN	N.D.		0.0000
	2,3,6TMN	N.D.		0.0000
	1,2,7,1,6,7,1,2,6TMN	N.D.		0.0000
	1,2,5TMN	N.D.		0.0000
	TOTAL TMN			0.0000
	TOTAL NAPHS			2.50
PHENATHALENES	PHENATHLENE	N.D.		0.0000
	ANTHRASENE	N.D.		0.0000
	3-MP	N.D.		0.0000
	2-MP	N.D.		0.0000
	2-MA	N.D.		0.0000
	9-MP	N.D.		0.0000
	1-MP	N.D.		0.0000
	1-MP+1-MA	N.D.		0.0000
	9MA	N.D.		0.0000
	TOTAL MP	N.D.		0.0000
	TOTAL MP+MA	N.D.		0.0000
	TOTAL DMP	N.D.		0.0000
	TOTAL DMP+DMA	N.D.		0.0000
	TOTAL PHENAS			0.0000

HOPANES	Comp	Pk Area	IS Pk Area	(ug/g)
	C29 α β	N.D.		0.0000
	C29 β α	N.D.		0.0000
	C30 α β	N.D.		0.0000
	C30 β α	N.D.		0.0000
	C31 α β (S)	N.D.		0.0000
	C31 α β (R)	N.D.		0.0000
	C30 β β	N.D.		0.0000
	C32 α β (S)	N.D.		0.0000
	C32 α β (R)	N.D.		0.0000
	C33 α β (S)	N.D.		0.0000
	C33 α β (R)	N.D.		0.0000
	C34 α β (S)	N.D.		0.0000
	C34 α β (R)	N.D.		0.0000
	C35 α β (S)	N.D.		0.0000
	C35 α β (R)	N.D.		0.0000
	TOTAL			0.0000
MONO AROMATICS	5 β (H)C27(20S)	N.D.		0.0000
	5 β (H)C27(20R)	N.D.		0.0000
	*	N.D.		0.0000
	**	N.D.		0.0000
	5 α (H)C29(20S)	N.D.		0.0000
	***	N.D.		0.0000
	5 α (H)C29(20R)	N.D.		0.0000
	TOTAL			0.0000
TRI AROMATICS	C26(20S)	N.D.		0.0000
	C26(20R)+C27(20S)	N.D.		0.0000
	C28(20S)	N.D.		0.0000
	C27(20R)	N.D.		0.0000
	C28(20R)	N.D.		0.0000
	TOTAL			0.0000
	*: 5 α (H)C27(S) + 5 β (H)C28(S)			
	**: 5 α (H)C27(20R)+5 α (H)C28(20S)+5 β (H)C28(20R)+5 β C29(20S)			
	***: 5 α (H)C28(20R)+5 β (H)C29(20R)			

THERMODESORPTION OF POSIDONIA SHALE AT 250C					
B					
Weight of sample=3.0150g					
Weight of LS.(squalane)=9.50ug					
	Comp	Pk Area	IS Pk Area		(ug/g)
ALKANES	C10	1092483	1718436		2.00
	C11	1073144	1718436		1.97
	C12	5210319	1718436		9.55
	C13	6100970	1718436		11.19
	C14	6087863	1718436		11.16
	C15	5650964	1718436		10.36
	C16	4711298	1718436		8.64
	C17+PRI	6744681	1718436		12.37
	C18	2222541	1718436		4.08
	PHY	678439	1718436		1.24
	C19	1560609	1718436		2.86
	C20	857222	1718436		1.57
	C21	N.D.			0.0000
	C22	N.D.			0.0000
	C23	N.D.			0.0000
	C24	N.D.			0.0000
	C25	N.D.			0.0000
	C26	N.D.			0.0000
	C27	N.D.			0.0000
	C28	N.D.			0.0000
	C29	N.D.			0.0000
	C30	N.D.			0.0000
	C31	N.D.			0.0000
	C32	N.D.			0.0000
	C33	N.D.			0.0000
	TOTAL ALKANES				76.99
NAPHTHALENES	NAPHTHALENE	10279879	1718436		18.85
	C-1 MN	13284703	1718436		24.36
	C-2 MN	10541217	1718436		19.33
	TOTAL MN				43.69
	1-E,2-EDMN	2373692	1718436		4.35
	2,6,2,7DMN	4103425	1718436		7.52
	1,3,1,7DMN	4738488	1718436		8.69
	1,6DMN	4624410	1718436		8.48
	1,4,1,3,1,5DMN	3259510	1718436		5.98
	1,8DMN	1549753	1718436		2.84
	TOTAL DMN				37.86
	1,3,7TMN	1226223	1718436		2.25
	1,3,6TMN	997678	1718436		1.83
	1,4,6,1,3,5TMN	800249	1718436		1.47
	2,3,6TMN	472467	1718436		0.866
	1,2,7,1,6,7,1,2,6TMN	1294634	1718436		2.37
	1,2,5TMN	512240	1718436		0.939
	TOTAL TMN				9.72
	TOTAL NAPHS				110.12
PHENATHALENES	PHENATHLENE	1656946	1718436		3.04
	ANTHRASENE	N.D.			0.0000
	3-MP	306924	1718436		0.563
	2-MP	310056	1718436		0.569
	2-MA	N.D.			0.0000
	9-MP	340903	1718436		0.625
	1-MP	442973	1718436		0.812
	1-MP+1-MA	N.D.			0.0000
	9MA	N.D.			0.0000
	TOTAL MP	N.D.			2.57
	TOTAL MP+MA	N.D.			0.0000
	TOTAL DMP	N.D.			0.0000
	TOTAL DMP+DMA	N.D.			0.0000
	TOTAL PHENAS				5.61

HOPANES	Comp	Pk Area	IS Pk Area	(ug/g)
	C29 α β	N.D.		0.0000
	C29 β α	N.D.		0.0000
	C30 α β	N.D.		0.0000
	C30 β α	N.D.		0.0000
	C31 α β (S)	N.D.		0.0000
	C31 α β (R)	N.D.		0.0000
	C30 β β	N.D.		0.0000
	C32 α β (S)	N.D.		0.0000
	C32 α β (R)	N.D.		0.0000
	C33 α β (S)	N.D.		0.0000
	C33 α β (R)	N.D.		0.0000
	C34 α β (S)	N.D.		0.0000
	C34 α β (R)	N.D.		0.0000
	C35 α β (S)	N.D.		0.0000
	C35 α β (R)	N.D.		0.0000
	TOTAL			0.0000
MONO AROMATICS	5 β (H)C27(20S)	N.D.		0.0000
	5 β (H)C27(20R)	N.D.		0.0000
	*	N.D.		0.0000
	**	N.D.		0.0000
	5 α (H)C29(20S)	N.D.		0.0000
	***	N.D.		0.0000
	5 α (H)C29(20R)	N.D.		0.0000
	TOTAL			0.0000
TRI AROMATICS	C26(20S)	N.D.		0.0000
	C26(20R)+C27(20S)	N.D.		0.0000
	C28(20S)	N.D.		0.0000
	C27(20R)	N.D.		0.0000
	C28(20R)	N.D.		0.0000
	TOTAL			0.0000
	*. 5 α (H)C27(S) + 5 β (H)C28(S)			
	**. 5 α (H)C27(20R)+5 α (H)C28(20S)+5 β (H)C28(20R)+5 β C29(20S)			
	***. 5 α (H)C28(20R)+5 β (H)C29(20R)			

THERMODESORPTION OF POSIDONIA SHALE AT 350C				
B				
Weight of sample=3.0150g				
Weight of IS (squalane)=9.50ug				
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	648082	2754192	0.741
	C11	1111707	2754192	1.27
	C12	1049199	2754192	1.20
	C13	1389535	2754192	1.59
	C14	1451336	2754192	1.66
	C15	2166972	2754192	2.48
	C16	2625044	2754192	3.00
	C17+PRI	3295018	2754192	3.77
	C18	2802766	2754192	3.21
	PHY	498666	1655836	0.949
	C19	2573645	2754192	2.94
	C20	1859756	2754192	2.13
	C21	1499145	2754192	1.72
	C22	1186554	2754192	1.36
	C23	832847	2754192	0.953
	C24	720728	2754192	0.825
	C25	457003	2754192	0.523
	C26	355326	2754192	0.407
	C27	165321	2754192	0.189
	C28	118457	2754192	0.136
	C29	N.D.		0.0000
	C30	N.D.		0.0000
	C31	N.D.		0.0000
	C32	N.D.		0.0000
	C33	N.D.		0.0000
	TOTAL ALKANES			31.05
NAPHTHALENES	NAPHTHALENE	5437719	2728368	6.28
	C-1 MN	11937962	2728368	13.79
	C-2 MN	7325723	2728368	8.46
	TOTAL MN			22.25
	1-E,2-EDMN	2932719	2728368	3.39
	2,6,2,7DMN	9530583	2728368	11.01
	1,3,1,7DMN	10567470	2728368	12.20
	1,6DMN	8122654	2728368	9.38
	1,4,1,3,1,5DMN	6387935	2728368	7.38
	1,8DMN	2802399	2728368	3.24
	TOTAL DMN			46.59
	1,3,7TMN	6485947	2728368	7.49
	1,3,6TMN	7114875	2728368	8.22
	1,4,6,1,3,5TMN	4733671	2728368	5.47
	2,3,6TMN	4914779	2728368	5.68
	1,2,7,1,6,7,1,2,6TMN	9737580	2728368	11.25
	1,2,5TMN	1914245	2728368	2.21
	TOTAL TMN			40.31
	TOTAL NAPHS			115.43
PHENATHALENES	PHENATHLENE	4769823	2754192	5.46
	ANTHRASENE	2015190	2754192	2.31
	3-MP	2581118	2754192	2.95
	2-MP	2879243	2754192	3.29
	2-MA	2451999	2754192	2.81
	9-MP	2901804	2754192	3.32
	1-MP	N/A		N/A
	1-MP+1-MA	5146807	2754192	5.89
	9MA	507507	2754099	0.581
	TOTAL MP			N/A
	TOTAL MP+MA			18.84
	TOTAL DMP	N/A	N/A	N/A
	TOTAL DMP+DMA	17366724	2754192	19.87
	TOTAL PHENAS			46.47

HOPANES	Comp	Pk Area	IS Pk Area	(ug/g)
	C29 $\alpha\beta$	N.D.		0.0000
	C29 $\beta\alpha$	N.D.		0.0000
	C30 $\alpha\beta$	N.D.		0.0000
	C30 $\beta\alpha$	N.D.		0.0000
	C31 $\alpha\beta$ (S)	N.D.		0.0000
	C31 $\alpha\beta$ (R)	N.D.		0.0000
	C30 $\beta\beta$	N.D.		0.0000
	C32 $\alpha\beta$ (S)	N.D.		0.0000
	C32 $\alpha\beta$ (R)	N.D.		0.0000
	C33 $\alpha\beta$ (S)	N.D.		0.0000
	C33 $\alpha\beta$ (R)	N.D.		0.0000
	C34 $\alpha\beta$ (S)	N.D.		0.0000
	C34 $\alpha\beta$ (R)	N.D.		0.0000
	C35 $\alpha\beta$ (S)	N.D.		0.0000
	C35 $\alpha\beta$ (R)	N.D.		0.0000
	TOTAL			0.0000
MONO AROMATICS	5 β (H)C27(20S)	N.D.		0.0000
	5 β (H)C27(20R)	N.D.		0.0000
	*	N.D.		0.0000
	**	N.D.		0.0000
	5 α (H)C29(20S)	N.D.		0.0000
	***	N.D.		0.0000
	5 α (H)C29(20R)	N.D.		0.0000
	TOTAL			0.0000
TRI AROMATICS	C26(20S)	N.D.		0.0000
	C26(20R)+C27(20S)	N.D.		0.0000
	C28(20S)	N.D.		0.0000
	C27(20R)	N.D.		0.0000
	C28(20R)	N.D.		0.0000
	TOTAL			0.0000
	*: 5 α (H)C27(S) + 5 β (H)C28(S)			
	**: 5 α (H)C27(20R)+5 α (H)C28(20S)+5 β (H)C28(20R)+5 β C29(20S)			
	***: 5 α (H)C28(20R)+5 β (H)C29(20R)			

THERMODESORPTION OF POSIDONIA SHALE AT 50C				
C				
Weight of sample=3.0267g				
Weight of LS (squalane)=9.50ug				
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	N.D.		0.0000
	C11	N.D.		0.0000
	C12	N.D.		0.0000
	C13	N.D.		0.0000
	C14	N.D.		0.0000
	C15	N.D.		0.0000
	C16	N.D.		0.0000
	C17+PRI	N.D.		0.0000
	C18	N.D.		0.0000
	PHY	N.D.		0.0000
	C19	N.D.		0.0000
	C20	N.D.		0.0000
	C21	N.D.		0.0000
	C22	N.D.		0.0000
	C23	N.D.		0.0000
	C24	N.D.		0.0000
	C25	N.D.		0.0000
	C26	N.D.		0.0000
	C27	N.D.		0.0000
	C28	N.D.		0.0000
	C29	N.D.		0.0000
	C30	N.D.		0.0000
	C31	N.D.		0.0000
	C32	N.D.		0.0000
	C33	N.D.		0.0000
	TOTAL ALKANES			0.0000
NAPHTHALENES	NAPHTHALENE	N.D.		0.0000
	C-1 MN	N.D.		0.0000
	C-2 MN	N.D.		0.0000
	TOTAL MN			0.0000
	1-E,2-EDMN	N.D.		0.0000
	2,6,2,7DMN	N.D.		0.0000
	1,3,1,7DMN	N.D.		0.0000
	1,6DMN	N.D.		0.0000
	1,4,1,3,1,5DMN	N.D.		0.0000
	1,8DMN	N.D.		0.0000
	TOTAL DMN			0.0000
	1,3,7TMN	N.D.		0.0000
	1,3,6TMN	N.D.		0.0000
	1,4,6,1,3,5TMN	N.D.		0.0000
	2,3,6TMN	N.D.		0.0000
	1,2,7,1,6,7,1,2,6TMN	N.D.		0.0000
	1,2,5TMN	N.D.		0.0000
	TOTAL TMN			0.0000
	TOTAL NAPHS			0.0000
PHENATHALENES	PHENATHLENE	N.D.		0.0000
	ANTHRASENE	N.D.		0.0000
	3-MP	N.D.		0.0000
	2-MP	N.D.		0.0000
	2-MA	N.D.		0.0000
	9-MP	N.D.		0.0000
	1-MP	N.D.		0.0000
	1-MP+1-MA	N.D.		0.0000
	9MA	N.D.		0.0000
	TOTAL MP	N.D.		0.0000
	TOTAL MP+MA	N.D.		0.0000
	TOTAL DMP	N.D.		0.0000
	TOTAL DMP+DMA	N.D.		0.0000
	TOTAL PHENAS			0.0000

HOPANES	Comp	Pk Area	IS Pk Area	(ug/g)
	C29 α β	N.D.		0.0000
	C29 β α	N.D.		0.0000
	C30 α β	N.D.		0.0000
	C30 β α	N.D.		0.0000
	C31 α β (S)	N.D.		0.0000
	C31 α β (R)	N.D.		0.0000
	C30 β β	N.D.		0.0000
	C32 α β (S)	N.D.		0.0000
	C32 α β (R)	N.D.		0.0000
	C33 α β (S)	N.D.		0.0000
	C33 α β (R)	N.D.		0.0000
	C34 α β (S)	N.D.		0.0000
	C34 α β (R)	N.D.		0.0000
	C35 α β (S)	N.D.		0.0000
	C35 α β (R)	N.D.		0.0000
	TOTAL			0.0000
MONO AROMATICS	5 β (H)C27(20S)	N.D.		0.0000
	5 β (H)C27(20R)	N.D.		0.0000
	*	N.D.		0.0000
	**	N.D.		0.0000
	5 α (H)C29(20S)	N.D.		0.0000
	***	N.D.		0.0000
	5 α (H)C29(20R)	N.D.		0.0000
	TOTAL			0.0000
TRI AROMATICS	C26(20S)	N.D.		0.0000
	C26(20R)+C27(20S)	N.D.		0.0000
	C28(20S)	N.D.		0.0000
	C27(20R)	N.D.		0.0000
	C28(20R)	N.D.		0.0000
	TOTAL			0.0000
	*: 5 α (H)C27(S) + 5 β (H)C28(S)			
	**: 5 α (H)C27(20R)+5 α (H)C28(20S)+5 β (H)C28(20R)+5 β C29(20S)			
	***: 5 α (H)C28(20R)+5 β (H)C29(20R)			

THERMODESORPTION OF POSIDONIA SHALE AT 150C				
C				
Weight of sample=3.0267g				
Weight of I.S (squalane)=9.50ug				
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	4223143	1249590	10.61
	C11	5129696	1249590	12.88
	C12	3817916	1249590	9.59
	C13	2337422	1249590	5.87
	C14	1063586	1249590	2.67
	C15	486976	1249590	1.22
	C16	N.D.		0.0000
	C17+PRI	N.D.		0.0000
	C18	N.D.		0.0000
	PHY	N.D.		0.0000
	C19	N.D.		0.0000
	C20	N.D.		0.0000
	C21	N.D.		0.0000
	C22	N.D.		0.0000
	C23	N.D.		0.0000
	C24	N.D.		0.0000
	C25	N.D.		0.0000
	C26	N.D.		0.0000
	C27	N.D.		0.0000
	C28	N.D.		0.0000
	C29	N.D.		0.0000
	C30	N.D.		0.0000
	C31	N.D.		0.0000
	C32	N.D.		0.0000
	C33	N.D.		0.0000
	TOTAL ALKANES			42.85
NAPHTHALENES	NAPHTHALENE	1157095	1249590	2.91
	C-1 MN	N.D.		0.0000
	C-2 MN	N.D.		0.0000
	TOTAL MN			0.0000
	1-E,2-EDMN	N.D.		0.0000
	2,6,2,7DMN	N.D.		0.0000
	1,3,1,7DMN	N.D.		0.0000
	1,6DMN	N.D.		0.0000
	1,4,1,3,1,5DMN	N.D.		0.0000
	1,8DMN	N.D.		0.0000
	TOTAL DMN			0.0000
	1,3,7TMN	N.D.		0.0000
	1,3,6TMN	N.D.		0.0000
	1,4,6,1,3,5TMN	N.D.		0.0000
	2,3,6TMN	N.D.		0.0000
	1,2,7,1,6,7,1,2,6TMN	N.D.		0.0000
	1,2,5TMN	N.D.		0.0000
	TOTAL TMN			0.0000
	TOTAL NAPHS			2.91
PHENATHALENES	PHENATHLENE	N.D.		0.0000
	ANTHRASENE	N.D.		0.0000
	3-MP	N.D.		0.0000
	2-MP	N.D.		0.0000
	2-MA	N.D.		0.0000
	9-MP	N.D.		0.0000
	1-MP	N.D.		0.0000
	1-MP+1-MA	N.D.		0.0000
	9MA	N.D.		0.0000
	TOTAL MP	N.D.		0.0000
	TOTAL MP+MA	N.D.		0.0000
	TOTAL DMP	N.D.		0.0000
	TOTAL DMP+DMA	N.D.		0.0000
	TOTAL PHENAS			0.0000

HOPANES	Comp	Pk Area	IS Pk Area	(ug/g)
	C29αβ	N.D.		0.0000
	C29βα	N.D.		0.0000
	C30αβ	N.D.		0.0000
	C30βα	N.D.		0.0000
	C31αβ(S)	N.D.		0.0000
	C31αβ(R)	N.D.		0.0000
	C30ββ	N.D.		0.0000
	C32αβ(S)	N.D.		0.0000
	C32αβ(R)	N.D.		0.0000
	C33αβ(S)	N.D.		0.0000
	C33αβ(R)	N.D.		0.0000
	C34αβ(S)	N.D.		0.0000
	C34αβ(R)	N.D.		0.0000
	C35αβ(S)	N.D.		0.0000
	C35αβ(R)	N.D.		0.0000
	TOTAL			0.0000
MONO AROMATICS	5β(H)C27(20S)	N.D.		0.0000
	5β(H)C27(20R)	N.D.		0.0000
	*	N.D.		0.0000
	**	N.D.		0.0000
	5α(H)C29(20S)	N.D.		0.0000
	***	N.D.		0.0000
	5α(H)C29(20R)	N.D.		0.0000
	TOTAL			0.0000
TRI AROMATICS	C26(20S)	N.D.		0.0000
	C26(20R)+C27(20S)	N.D.		0.0000
	C28(20S)	N.D.		0.0000
	C27(20R)	N.D.		0.0000
	C28(20R)	N.D.		0.0000
	TOTAL			0.0000
	*: 5α(H)C27(S) + 5β(H)C28(S)			
	** : 5α(H)C27(20R)+5α(H)C28(20S)+5β(H)C28(20R)+5βC29(20S)			
	***: 5α(H)C28(20R)+5β(H)C29(20R)			

THERMODESORPTION OF POSIDONIA SHALE AT 250C				
	C			
	Weight of sample=3.0267g			
	Weight of IS (squalane)=9.50ug			
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	2740085	2386489	3.60
	C11	967540	2386489	1.27
	C12	2861257	2386489	3.76
	C13	5349753	2386489	7.04
	C14	6475996	2386489	8.52
	C15	6967266	2386489	9.16
	C16	6310452	2386489	8.30
	C17+PRI	7497127	2386489	9.86
	C18	3335485	2386489	4.39
	PHY	1800541	2414944	2.34
	C19	2429106	2386489	3.19
	C20	1411716	2386489	1.86
	C21	N.D.	2386489	0.0000
	C22	N.D.	2414944	0.0000
	C23	N.D.	2414944	0.0000
	C24	N.D.		0.0000
	C25	N.D.		0.0000
	C26	N.D.		0.0000
	C27	N.D.		0.0000
	C28	N.D.		0.0000
	C29	N.D.		0.0000
	C30	N.D.		0.0000
	C31	N.D.		0.0000
	C32	N.D.		0.0000
	C33	N.D.		0.0000
	TOTAL ALKANES			63.29
NAPHTHALENES	NAPHTHALENE	4442573	2414944	5.77
	C-1 MN	10099965	2414944	13.13
	C-2 MN	8624654	2414944	11.21
	TOTAL MN			24.34
	1-E,2-EDMN	2162645	2414944	2.81
	2,6,2,7DMN	3460657	2414944	4.50
	1,3,1,7DMN	4302103	2414944	5.59
	1,6DMN	4273414	2414944	5.55
	1,4,1,3,1,5DMN	2960464	2414944	3.85
	1,8DMN	1480127	2414944	1.92
	TOTAL DMN			24.23
	1,3,7TMN	1141270	2414944	1.48
	1,3,6TMN	906243	2414944	1.18
	1,4,6,1,3,5TMN	743560	2414944	0.966
	2,3,6TMN	428855	2414944	0.557
	1,2,7,1,6,7,1,2,6TMN	1177456	2414944	1.53
	1,2,5TMN	488649	2414944	0.635
	TOTAL TMN			6.35
	TOTAL NAPHS			60.69
PHENATHALENES	PHENATHLENE	1912931	2414944	2.49
	ANTHRASENE	N.D.		0.0000
	3-MP	353046	2414944	0.459
	2-MP	283602	2414944	0.369
	2-MA	N.D.		0.0000
	9-MP	360255	2414944	0.468
	1-MP	455880	2414944	0.593
	1-MP+1-MA	N.D.		0.0000
	9MA	N.D.		0.0000
	TOTAL MP	N.D.		1.89
	TOTAL MP+MA	N.D.		0.0000
	TOTAL DMP	N.D.		0.0000
	TOTAL DMP+DMA	N.D.		0.0000
	TOTAL PHENAS			4.37

<u>HOPANES</u>	<u>Comp</u>	<u>Pk Area</u>	<u>IS Pk Area</u>	<u>(ug/g)</u>
	C29αβ	N.D.		0.0000
	C29βα	N.D.		0.0000
	C30αβ	N.D.		0.0000
	C30βα	N.D.		0.0000
	C31αβ(S)	N.D.		0.0000
	C31αβ(R)	N.D.		0.0000
	C30ββ	N.D.		0.0000
	C32αβ(S)	N.D.		0.0000
	C32αβ(R)	N.D.		0.0000
	C33αβ(S)	N.D.		0.0000
	C33αβ(R)	N.D.		0.0000
	C34αβ(S)	N.D.		0.0000
	C34αβ(R)	N.D.		0.0000
	C35αβ(S)	N.D.		0.0000
	C35αβ(R)	N.D.		0.0000
	<u>TOTAL</u>			<u>0.0000</u>
<u>MONO AROMATICS</u>	5β(H)C27(20S)	N.D.		0.0000
	5β(H)C27(20R)	N.D.		0.0000
	*	N.D.		0.0000
	**	N.D.		0.0000
	5α(H)C29(20S)	N.D.		0.0000
	***	N.D.		0.0000
	5α(H)C29(20R)	N.D.		0.0000
	<u>TOTAL</u>			<u>0.0000</u>
<u>TRI AROMATICS</u>	C26(20S)	N.D.		0.0000
	C26(20R)+C27(20S)	N.D.		0.0000
	C28(20S)	N.D.		0.0000
	C27(20R)	N.D.		0.0000
	C28(20R)	N.D.		0.0000
	<u>TOTAL</u>			<u>0.0000</u>
	*: 5α(H)C27(S) + 5β(H)C28(S)			
	**: 5α(H)C27(20R)+5α(H)C28(20S)+5β(H)C28(20R)+5βC29(20S)			
	***: 5α(H)C28(20R)+5β(H)C29(20R)			

THERMODESORPTION OF POSIDONIA SHALE AT 350C				
	C			
	Weight of sample=3.0267g			
	Weight of I.S. (squalane)=9.50ug			
	Comp	Pk Area	IS Pk Area	(ug/g)
ALKANES	C10	323685	1015295	1.00
	C11	395596	1015295	1.22
	C12	330798	1015295	1.02
	C13	236661	1015295	0.732
	C14	300202	1015295	0.928
	C15	339662	1015295	1.05
	C16	472149	1015295	1.46
	C17+PRI	761089	1015295	2.35
	C18	867884	1015295	2.68
	PHY	127203	1015295	0.393
	C19	545524	1015295	1.69
	C20	462160	1015295	1.43
	C21	372830	1015295	1.15
	C22	285511	1015295	0.883
	C23	268122	1015295	0.829
	C24	146112	1015295	0.452
	C25	457003	1015295	1.41
	C26	108418	1015295	0.335
	C27	49107	1015295	0.152
	C28	23214	1015295	0.072
	C29	10948	1015295	0.034
	C30	N.D.		0.0000
	C31	N.D.		0.0000
	C32	N.D.		0.0000
	C33	N.D.		0.0000
	TOTAL ALKANES			21.28
NAPHTHALENES	NAPHTHALENE	1330838	1015295	4.11
	C-1 MN	2744087	1015295	8.48
	C-2 MN	1564641	1015295	4.84
	TOTAL MN			13.32
	1-E,2-EDMN	777038	1015295	2.40
	2,6,2,7DMN	2531277	1015295	7.83
	1,3,1,7DMN	2732298	1015295	8.45
	1,6DMN	2588570	1015295	8.00
	1,4,1,3,1,5DMN	1907124	1015295	5.90
	1,8DMN	874760	1015295	2.70
	TOTAL DMN			35.28
	1,3,7TMN	1880853	1015295	5.81
	1,3,6TMN	2400332	1015295	7.42
	1,4,6,1,3,5TMN	1687396	1015295	5.22
	2,3,6TMN	1585780	1015295	4.90
	1,2,7,1,6,7,1,2,6TMN	3397303	1015295	10.50
	1,2,5TMN	915464	1015295	2.83
	TOTAL TMN			36.69
	TOTAL NAPHS			89.40
PHENATHALENES	PHENATHLENE	1604225	1015295	4.96
	ANTHRASENE	930787	1015295	2.88
	3-MP	971029	1015295	3.00
	2-MP	1208665	1015295	3.74
	2-MA	591495	1015295	1.83
	9-MP	1404719	1015295	4.34
	1-MP	N/A		N/A
	1-MP+1-MA	2991694	1015295	9.25
	9MA	386696	1015295	1.20
	TOTAL MP			N/A
	TOTAL MP+MA			23.35
	TOTAL DMP	N/A	N/A	N/A
	TOTAL DMP+DMA	6366767	1015295	19.68
	TOTAL PHENAS		1015295	50.87

<u>HOPANES</u>	<u>Comp</u>	<u>Pk Area</u>	<u>IS Pk Area</u>	<u>(ug/g)</u>
	C29αβ	N.D.		0.0000
	C29βα	N.D.		0.0000
	C30αβ	N.D.		0.0000
	C30βα	N.D.		0.0000
	C31αβ(S)	N.D.		0.0000
	C31αβ(R)	N.D.		0.0000
	C30ββ	N.D.		0.0000
	C32αβ(S)	N.D.		0.0000
	C32αβ(R)	N.D.		0.0000
	C33αβ(S)	N.D.		0.0000
	C33αβ(R)	N.D.		0.0000
	C34αβ(S)	N.D.		0.0000
	C34αβ(R)	N.D.		0.0000
	C35αβ(S)	N.D.		0.0000
	C35αβ(R)	N.D.		0.0000
	<u>TOTAL</u>			<u>0.0000</u>
<u>MONO AROMATICS</u>	5β(H)C27(20S)	N.D.		0.0000
	5β(H)C27(20R)	N.D.		0.0000
	*	N.D.		0.0000
	**	N.D.		0.0000
	5α(H)C29(20S)	N.D.		0.0000
	***	N.D.		0.0000
	5α(H)C29(20R)	N.D.		0.0000
	<u>TOTAL</u>			<u>0.0000</u>
<u>TRI AROMATICS</u>	C26(20S)	N.D.		0.0000
	C26(20R)+C27(20S)	N.D.		0.0000
	C28(20S)	N.D.		0.0000
	C27(20R)	N.D.		0.0000
	C28(20R)	N.D.		0.0000
	<u>TOTAL</u>			<u>0.0000</u>
	*: 5α(H)C27(S) + 5β(H)C28(S)			
	** : 5α(H)C27(20R)+5α(H)C28(20S)+5β(H)C28(20R)+5βC29(20S)			
	***: 5α(H)C28(20R)+5β(H)C29(20R)			

SOXHLET EXTRACTION OF POSIDONIA SHALE				
Weight of sample=10.0276g				
Weight of IS (squalane)=18.60ug				
ALKANES	Comp	Pk Area	IS Pk Area	(ug/g)
	C10	1893706	2113856	1.66
	C11	5546372	2113856	4.87
	C12	8422971	2113856	7.39
	C13	10936500	2113856	9.60
	C14	11942701	2113856	10.48
	C15	13282572	2113856	11.66
	C16	12776141	2113856	11.21
	C17	15497178	2113856	13.60
	PR1	23906837	2113856	20.98
	C18	11113766	2113856	9.75
	PHY	15017395	2113856	13.18
	C19	8617595	2113856	7.56
	C20	7290451	2113856	6.40
	C21	6606739	2113856	5.80
	C22	5879979	2113856	5.16
	C23	5530254	2113856	4.85
	C24	5815543	2113856	5.10
	C25	4607578	2113856	4.04
	C26	4898410	2113856	4.30
	C27	3280199	2113856	2.88
	C28	2264025	2113856	1.99
	C29	1772716	2113856	1.56
	C30	1703651	2113856	1.49
	C31	2209030	2113856	1.94
	C32	1413527	2113856	1.24
	C33	1563909	1988676	1.46
	TOTAL ALKANES			170.13
NAPHTHALENES	NAPHTHALENE	11655935	2023116	10.69
	C-1 MN	17981727	2023116	16.49
	C-2 MN	16140208	2023116	14.80
	TOTAL MN			31.28
	1-E,2-EN	3531242	2023116	3.24
	2,6;2,7DMN	5937364	2023116	5.44
	1,3;1,7DMN	8633238	2023116	7.92
	1,6DMN	7778222	2023116	7.13
	1,4;1,3;1,5DMN	6267338	2023116	5.75
	1,8DMN	3042445	2023116	2.79
	TOTAL DMN			32.26
	1,3,7TMN	3366163	2023116	3.09
	1,3,6TMN	4016680	2023116	3.68
	1,4,6;1,3,5TMN	3202526	2023116	2.94
	2,3,6TMN	1660801	2023116	1.52
	1,2,7;1,6,7;1,2,6TMN	4471628	2023116	4.10
	1,2,5TMN	1767750	2023116	1.62
	TOTAL TMN			16.95
	TOTAL NAPHS			91.18
PHENANTHRENES	PHENANTHRENE	5881559	2366338	4.61
	ANTHRACENE	N/A	N/A	N/A
	3-MP	1983481	2366338	1.55
	2-MP	1887523	2366338	1.48
	2-MA	N/A	N/A	N/A
	9-MP	3047496	2366338	2.39
	1-MP	2926153	2366338	2.29
	1-MP+1-MA	N/A	N/A	N/A
	9MA	N/A	N/A	N/A
	TOTAL MP			7.72
	TOTAL MP+MA	N/A	N/A	N/A
	TOTAL DMP	5858507	2366338	4.59
	TOTAL DMP+DMA	N/A	N/A	N/A
	TOTAL PHENAS			16.92

	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C29 α β	1233878	2234852	1.02
	C29 β α	285997	2234852	0.237
	C30 α β	2102319	2234852	1.74
	C30 β α	470254	2234852	0.390
	C31 α β (S)	834260	2234852	0.692
	C31 α β (R)	641835	2234852	0.533
	C30 β β	N/A	2234852	0.0000
	C32 α β (S)	520494	2234852	0.432
	C32 α β (R)	483643	2234852	0.401
	C33 α β (S)	772797	2234852	0.641
	C33 α β (R)	794450	2234852	0.659
	C34 α β (S)	476232	2234852	0.395
	C34 α β (R)	512409	2234852	0.425
	C35 α β (S)	444526	2234852	0.369
	C35 α β (R)	411090	2234852	0.341
	TOTAL			8.29
MONO AROMATICS	5 β (H)C27(20S)	1018907	2366338	0.799
	5 β (H)C27(20R)	1345568	2366338	1.05
	*	3649389	2366338	2.86
	**	7136693	2366338	5.59
	5 α (H)C29(20S)	2418796	2366338	1.90
	***	3763003	2366338	2.95
	5 α (H)C29(20R)	1216935	2366338	0.954
	TOTAL			16.11
TRI AROMATICS	C26(20S)	2718441	2366338	2.13
	C26(20R)+C27(20S)	6617737	2366338	5.19
	C28(20S)	4543700	2366338	3.56
	C27(20R)	3838179	2366338	3.01
	C28(20R)	5500734	2366338	4.31
	TOTAL			18.20
	*: 5 α (H)C27(S) + 5 β (H)C28(S)			
	** : 5 α (H)C27(20R)+5 α (H)C28(20S)+5 β (H)C29(20S)+5 α C29(20R)			
	***: 5 α (H)C28(20R)+5 β (H)C29(20R)			

SFE OF KUPFERSCHIEFER SHALE AT 50°C				
Weight of sample=3.0010g				
Weight of I.S. (squalane)=9.30ug				
Density of supercritical CO ₂ = 0.904 g/ml				
	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C30αβ	513864	24400780	0.065
	C30βα	411885	24498626	0.052
	C31αβ(S)	178285	24561118	0.022
	C31αβ(R)	844158	24561118	0.107
	C32αβ(S)	43938	25071076	0.005
	C32αβ(R)	253141	24639961	0.032
	TOTAL			0.284
MONO AROMATICS	5β(H)C27(20S)	917221	24653383	0.115
	5β(H)C27(20R)	1097641	24653383	0.138
	*	3104450	24653383	0.390
	**	8235820	24653383	1.04
	5α(H)C29(20S)	3330441	24653383	0.419
	***	4868318	24653383	0.612
	5α(H)C29(20R)	2415016	24653383	0.304
	TOTAL			3.01
TRI AROMATICS	C26(20S)	198868	24535437	0.025
	C26(20R)+C27(20S)	435564	24391948	0.055
	C28(20S)	606252	24491534	0.077
	C27(20R)	218735	24575243	0.028
	C28(20R)	535391	24498626	0.068
	TOTAL			0.252
	*: 5α(H)C27(20S) + 5β(H)C28(20S)			
	**: 5α(H)C27(20R)+ 5α(H)C28(20S)+ 5β(H)C29(20S)+ 5αC29(20R)			
	***: 5α(H)C28(20R)+ 5β(H)C29(20R)			
SFE OF KUPFERSCHIEFER SHALE AT 150°C				
Weight of sample=3.0010g				
Weight of I.S. (squalane)=9.30ug				
Density of supercritical CO ₂ = 0.548 g/ml				
	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C30αβ	1353859	64418056	0.065
	C30βα	993643	64395142	0.048
	C31αβ(S)	489184	64533921	0.023
	C31αβ(R)	2275655	64533921	0.109
	C32αβ(S)	115876	64539898	0.006
	C32αβ(R)	664533	64533921	0.032
	TOTAL			0.283
MONO AROMATICS	5β(H)C27(20S)	1772901	64343647	0.085
	5β(H)C27(20R)	2125592	64343647	0.102
	*	6514042	64343647	0.314
	**	17117201	64343647	0.824
	5α(H)C29(20S)	7518506	64343647	0.362
	***	9824536	64343647	0.473
	5α(H)C29(20R)	5043221	64343647	0.243
	TOTAL			2.40
TRI AROMATICS	C26(20S)	540220	64403309	0.026
	C26(20R)+C27(20S)	1186337	64530083	0.057
	C28(20S)	1764983	64205455	0.085
	C27(20R)	649035	64403309	0.031
	C28(20R)	1361114	64205455	0.066
	TOTAL			0.265
	*: 5α(H)C27(20S) + 5β(H)C28(20S)			
	**: 5α(H)C27(20R)+ 5α(H)C28(20S)+ 5β(H)C29(20S)+ 5α(H)C29(20R)			
	***: 5α(H)C28(20R)+ 5β(H)C29(20R)			

SFE OF KUPFERSCHIEFER SHALE AT 250°C				
Weight of sample=3.0010g				
Weight of LS (squalane)=9.30ug				
Density of supercritical CO ₂ = 0.366 g/ml				
	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C30αβ	320258	21745039	0.046
	C30βα	214265	21866588	0.030
	C31αβ(S)	115818	21852161	0.016
	C31αβ(R)	531567	21753122	0.076
	C32αβ(S)	28754	21879840	0.004
	C32αβ(R)	159744	21970590	0.023
	TOTAL			0.195
MONO AROMATICS	5β(H)C27(20S)	161259	21756427	0.023
	5β(H)C27(20R)	226490	21854094	0.032
	*	714147	21854094	0.101
	**	1660929	21854094	0.236
	5α(H)C29(20S)	750033	21854094	0.106
	***	864162	21854094	0.123
	5α(H)C29(20R)	457246	21854094	0.065
	TOTAL			0.686
TRI AROMATICS	C26(20S)	154541	21855175	0.022
	C26(20R)+C27(20S)	319052	21855175	0.045
	C28(20S)	438087	21743899	0.062
	C27(20R)	183178	21855175	0.026
	C28(20R)	388931	21743899	0.055
	TOTAL			0.211
	*: 5α(H)C27(20S)+ 5β(H)C28(20S)			
	**: 5α(H)C27(20R)+5α(H)C28(20S)+ 5β(H)C29(20S)+ 5αC29(20R)			
	***: 5α(H)C28(20R)+ 5β(H)C29(20R)			
SFE OF KUPFERSCHIEFER SHALE AT 350°C				
Weight of sample=3.0010g				
Weight of LS (squalane)=9.30ug				
Density of supercritical CO ₂ = 0.281 g/ml				
	Comp	Pk Area	IS Pk Area	(ug/g)
HOPANES	C30αβ	9475591	222583393	0.132
	C30βα	13068051	222583393	0.182
	C31αβ(S)	694483	224173769	0.010
	C31αβ(R)	10077303	224173769	0.139
	C32αβ(S)	28754	21879840	0.004
	C32αβ(R)	4046066	224173769	0.056
	TOTAL			0.523
MONO AROMATICS	5β(H)C27(20S)	359607	225237899	0.005
	5β(H)C28(20S)	883973	224216033	0.012
	*	1953384	224763855	0.027
	**	6147442	222361189	0.086
	5α(H)C29(20S)	3011704	222455793	0.042
	***	3759960	222455793	0.052
	5α(H)C29(20R)	2439425	222793820	0.034
	TOTAL			0.258
TRI AROMATICS	C26(20S)	4634209	224173769	0.064
	C26(20R)+C27(20S)	7922780	222583393	0.110
	C28(20S)	10581867	222702656	0.147
	C27(20R)	5088125	222702656	0.071
	C28(20R)	11019213	224216033	0.152
	TOTAL			0.545
	*: 5α(H)C27(S) + 5β(H)C28(S)			
	**: 5α(H)C27(20R)+ 5α(H)C28(20S)+ 5β(H)C29(20S)+ 5αC29(20R)			
	***: 5α(H)C28(20R)+ 5β(H)C29(20R)			