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**Sulfur Speciation in Rod Wax Deposits from an Oil Producing
Well, Eastern Anadarko Basin, Oklahoma: A Sulfur K-Edge
XANES Spectroscopy Study***

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ABSTRACT

The study investigates four samples of wax deposits formed at different depths (temperatures) along the sucker pump rods of an oil producing well. The deposits are characterized by sulfur K-edge XANES spectroscopy, elemental and HTGC analyses. The sulfur species distribution and their variation with respect to the hydrocarbons and temperature of deposit occurrence are presented. The results demonstrate: (1) compositional variability in both sulfur containing compounds and n-alkanes; (2) presence of various oxidation states sulfur species (di-/polysulfidic, thiophenic/sulfidic, sulfoxide, sulfone, sulfonic acid and sulfate); (3) a distinct shift in relative abundance of oxidized to reduced forms with depth (temperature) of wax deposit occurrence; (4) relatively constant proportion of thiophenic/sulfidic sulfur species in all deposits. Temperature-solubility controlled deposition of different sulfur-containing petroleum fractions as well as *in-situ* auto-oxidation processes in the deposits are discussed as two possible processes contributing to observed sulfur distributions.

Key words: wax, asphaltene, sulfur, XANES, production geochemistry, Anadarko, Viola oil, Oklahoma.

INTRODUCTION

The application of geochemistry to solving petroleum production problems has developed during the last ten years as a new branch of petroleum geochemistry, and is often referred to as production geochemistry (Slentz, 1981; England *et al.*, 1987; Curtis and McBane, 1989; Smalley and England, 1992; McCaffrey *et al.* 1996). An old and still not well understood and resolved production problem is the wax (“paraffin”) and asphaltene deposition occurring in petroleum production equipment (e.g., well tubings, pipelines, stock tanks). The solid deposits cause reduction of diameter and plugging of well equipment and pipelines, which ultimately results in an increased cost of the produced oil and gas (e.g., Leontaritis, 1996).

As defined in a number of studies, petroleum wax refers to the hydrocarbons (mainly n-alkanes, but also iso- and cycloalkanes and alkylaromatics) that are with sufficiently high molecular weight (HMW) to be solids at room temperature (e.g., Wright and Mitchell, 1921; Reistle, 1932; Sachanen, 1950; Mozes, 1982; Carlson *et al.*, 1993). Naturally formed wax deposits in oil producing wells and pipelines, on the other hand, represent complex mixtures of both hydrocarbons and non-hydrocarbons. The deposits are generally considered to be dominated by hydrocarbons, mainly n-C₂₀₊ alkanes, with various proportions of the heteroatom-enriched resin and asphaltene fractions, trapped oil, inorganic material and water (e.g., Reistle, 1932; Carnahan, 1989; Misra *et al.*, 1995). Wax fractions precipitated from oils in laboratory have also been shown to represent mixtures of hydrocarbons with resins and asphaltenes, and to be characterized with a various heteroatom content (0.5 to 5.6 wt.% sulfur, 0.2 to 1.9 wt.% nitrogen; Musser and Kilpatrick, 1998). This suggests that at least a part of the polar fractions precipitate together with the hydrocarbons.

The main factors controlling wax and asphaltene deposition in oil producing equipment are temperature and pressure changes that decrease the carrying capacity of the oil acting as a solvent for its heavy molecular weight fractions (Carnahan, 1989). Deposited organic solid mixtures show a large compositional variability depending on the initial oil composition and the specific pressure-temperature conditions of production. Variability in hydrocarbon composition of organic solid deposits has been observed between different fields, between different wells of the same field (Westrich *et al.*, 2000), and along the wax deposit profile formed in the same well or pipeline (Tchouparova, 1999). The compositional characteristics of even the major groups components known to be present in the wax deposits are not completely elucidated, and even less well understood are the properties of the complex mixtures they form under different conditions (Boduzynski, 1988). This lack of sufficient knowledge represents a major problem in predicting the onset of wax deposition, the amount and physical properties of the deposits and in developing efficient remedial and/or preventive methods and technology.

The sample setting and methods used in the present study target to investigate whether a compositional variability in sulfur species distribution exists in wax deposits naturally formed at different depths (temperatures) down the sucker pump rods of the same oil producing well. The same set of samples was initially characterized for changes in hydrocarbon composition as a function of temperature of deposition and compared with experimental results using a cold finger apparatus (Tchouparova, 1999; Chouparova *et al.*, 2000). Further experimental results demonstrated that variations in hydrocarbon distributions of wax deposits significantly influence their solubility, and presence of relatively small proportions of polar fractions in the deposit mixtures could drastically change their solubility and the choice of “best” solvent for remediation (Tchouparova, 1999; Chouparova and Philp, 2000). These results led to the questions about polar

fractions composition and distribution in deposits formed at different temperatures, and their effect on deposit's solubility. The present study is viewed as a further step in attempting to answer some of these questions.

Rod wax deposits formed in different wells were compositionally characterized in the early studies of Reistle (1932) and Nathan (1955). Sulfur speciation in heavy petroleum fractions (resins and asphaltenes), source rocks and coals based on sulfur K-edge XANES spectroscopy were presented in the studies of Spiro *et al.* (1984), George and Gorbaty (1989), Waldo *et al.* (1991), Huffman *et al.* (1991), Gorbaty *et al.* (1992), Taghiei *et al.* (1992), Adam *et al.* (1993), Kasrai *et al.* (1994), Snape *et al.* (1994), Nelson *et al.* (1995), Sarret *et al.* (1999). The method has several advantages, particularly useful for analysis of solid or semi-solid at room temperature samples such as the wax deposits: it is a non-destructive, element specific technique, which permits a variability in the physical state of samples for analysis (e.g., solid, liquid). The sulfur K-edge XANES spectra are sensitive to the oxidation state, electronic structure and three-dimensional arrangement and symmetry of atoms around the absorbing site (e.g., Waldo *et al.*, 1991; Vairavamurthy *et al.*, 1994). Thus, the method provides information about the distribution of different sulfur functional groups in the samples. In addition to the qualitative speciation, the relative proportions of sulfur forms with different oxidation states can be determined and their changes in wax deposits formed at different temperatures to be followed in a quantitative manner. These results are compared with elemental analysis results and changes in n-alkane distributions in the deposits, and discussion of several possible explanations of the observed trends is presented.

EXPERIMENTAL

Samples

The wax deposit samples were collected from the sucker pump rods of well Mosteller 1-21 (T10N, R3W, section 21) located at the easternmost part of Anadarko Basin, Cleveland Co, Oklahoma (Figure 1). Oil was produced from this well by pumping from the Viola Formation carbonate reservoir (Ordovician). Summaries of the uncovered Ordovician sequence and the recompletion history together with the initial test fluid data for the studied well are presented in Tables 1 and 2. The samples were collected after the well was clogged with waxes and oil production had to stop for cleaning operations. The rods were taken to the surface and at that time samples from the deposits plugging the tubings were collected for analysis. The samples were taken in a sequence of increasing depth and covered a depth range of 6000-7000 feet. This depth interval corresponds to a temperature interval from 20°C to 45-55°C considering that the maximum recorded temperature at total depth of 9568 ft is 138°F (59°C). Wax deposits were not observed along the deepest level rods, which suggests that the cloud point of the oil is at a temperature lower than the Viola reservoir temperature.

XANES Spectroscopy

The sulfur K-edge XANES spectra were collected at X-19A beam line of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (Upton, NY). The X-ray beam was diffracted by a Si (111) double crystal monochromator, which passes a narrow energy band that is focused to a ca. 0.8 mm x 0.8 mm beam spot size at the sample. The spectra were

collected as fluorescence excitation spectra using a Lytle fluorescence detector. The overall energy resolution is estimated to be 0.5 eV at 2.5 keV photon energy (Vairavamurthy *et al.*, 1994). Samples for analysis were prepared as thin films sealed in Mylar (2.5 μm film thickness) bags and mounted in a helium-purged sample chamber to minimize the attenuation of the X-ray beam by air. A sulfate standard was analyzed periodically to evaluate variations in X-ray energy.

Sulfur functional groups determination was performed by comparing the spectra with peak energy positions of standard sulfur compounds (Vairavamurthy *et al.*, 1994; Vairavamurthy, 1998). Due to close energy positions of the peak maxima, a distinction between organic disulfidic and polysulfidic sulfur and between thiophenic and sulfidic sulfur forms was not possible for the studied samples. Quantification of sulfur species was performed on baseline-corrected normalized spectra by a non-linear least-square analysis (WinXAS software) using a linear combination of spectra of different sulfur standards as described in Waldo *et al.*, (1991), Vairavamurthy *et al.* (1997) and Vairavamurthy (1998). Deconvolution of the XANES spectra was carried out using several Gaussian peaks at energy positions of known standard sulfur compounds and arctangent step functions representing the transition to the continuum for unoxidized and oxidized sulfur forms, respectively. The fitting with experimental spectra of wax deposits, representing a mixture of components, was performed manually by varying both scaling and energy-offset parameters. The peaks combination that gave the best fit was considered to indicate the actual composition. Peak areas were normalized to the corresponding arctangent step functions and a correction applied for the increase in peak area with increasing oxidation state, based on the linear relationship known to exist between sulfur oxidation state and the energy of white line peak maxima (e.g., Waldo *et al.*, 1991; Vairavamurthy *et al.*, 1994, 1998). The peak areas thus

obtained were used as a measure of the amount of different sulfur functional groups and for determining their proportions relative to the total sulfur content in each wax deposit.

Elemental analysis

Elemental analyses were performed by Quantitative Technologies, Inc. (QTI). Carbon, hydrogen and nitrogen were determined using a 240 Perkin-Elmer CHN Elemental analyzer. The samples were combusted in a pure oxygen environment. The product gases (CO₂, H₂O, N₂) were separated under steady state conditions and measured as a function of thermal conductivity. Total sulfur was determined by titrating the sulfate obtained after oxidation by combustion in presence of hydrogen peroxide.

High-temperature gas chromatography (HTGC) analysis

The analysis was performed on a GC 8000 Top series gas chromatograph with an on-column injector system and a flame ionization detector, equipped with a 25 m x 0.32 mm i.d. HT5 column bonded with a non-polar (5% phenyl equiv. Polysiloxane-carborane) phase and with film thickness of 0.1 µm. Oven temperature was programmed from 40°C to 400°C at 4°C/min with a final hold time of 25 min. Detector temperature was set at 410°C to prevent condensation effects. Samples were dissolved in hot p-xylene before injection. The quantitation of components was performed using deuterated C₃₆ alkane as an internal standard. Peak integration was carried out on baseline subtracted chromatograms in order to adjust for the baseline increase due to column bleed.

RESULTS

n-Alkane distributions by HTGC analysis

HTGC chromatograms of rod waxes 2 and 6 (Figure 2) present the n-alkane distributions in two deposits formed at different depths along the well rods. The deposit formed at the deeper location (# 6) shows a significant shift in the maximum of n-alkane carbon number distribution towards the higher molecular weight homologues as compared to the shallower deposit (# 2; nC₃₄ to nC₅₁ alkanes). Such shifts in carbon number distribution of n-alkanes were reported for waxes precipitated in laboratory at progressively increasing temperatures (Ronningsen *et al.*, 1991; Tchouparova, 1999) and for petroleum distillates of increasing boiling points (Krishna *et al.*, 1989; Srivastava *et al.*, 1993). The consistency between previous laboratory observations and the field example discussed in the present study suggests temperature to be a main factor controlling wax deposition in the well. The preferential occurrence of HMWHC in deposits formed at higher temperature conditions, below the oil cloud point, relates to the higher melting points and corresponding lower solubility of HMW homologues. Thus, upon reduction in temperature, the solubility of n-alkanes in the oil decreases and the higher molecular weight homologues are the first to precipitate from solution followed by progressively lower molecular weight components.

Elemental analysis results

The elemental analysis results demonstrate that the deepest deposit (# 7) is markedly different from the shallower ones, and characterized with a lower H/C atomic ratio (av. 1.55) and three to four times higher S/C (0.0048) and N/C (0.0037) atomic ratios, compared to the shallower samples (1.90-1.95, 0.0006-0.0014, 0.0009-0.0016, respectively; Table 2, Figure 3). These data

suggest higher abundances of aromatic, condensed structures, and depletion of aliphatic/naphthenic compounds in the deepest deposit relative to the shallower ones. It is worth noting that similar atomic ratios have been reported for natural bitumens such as wurtzilite, ingramite, gilsonite, tabbyite and grahamite (Hunt *et al.*, 1954; Curiale, 1983; Landis and Castaño, 1995). The H/C atomic ratio values for the shallower deposits (# # 2, 4, and 6) are higher than the statistically average value of 1.85 for conventional oils (Hunt, 1995) and fall in the ranges reported for hydrocarbon dominated macro- and microcrystalline waxes (1.85-2.05) by Musser and Kilpatrick (1998). The elemental composition data also indicate higher variations in the nitrogen and sulfur contents of the sample series (Table 3). Within each sample, nitrogen and to some extent sulfur content exhibit significant variations suggestive for a heterogeneous distribution of these elements in the samples.

A significantly lower carbon and hydrogen contents are observed in the deepest deposit (# 7) compared to the shallower ones (Table 3). Three independent analyses on different parts of the sample were performed with similar results. Thus, a large portion (58.6 wt. %) of the sample is unaccounted by these elements. Oxygen is unlikely to be liable for such a large part of the sample and presence of an inorganic material appears to be more probable. Considering that the deepest deposit is formed at a temperature close to the cloud point of the oil, where most of the hydrocarbons are expected to be still in oil solution, presence of even small amounts of inorganic material would constitute a substantial portion of the solid deposit. The nature of the inorganic material could be small particles from the Viola carbonate reservoir and/or corrosion products from the well as indicated by the results from other studies on the same wax deposit series (Chouparova *et al.*, in preparation).

Sulfur speciation by K-edge XANES spectroscopy

XANES spectra of the rod wax samples are presented in Figure 4. Qualitatively, the spectra suggest presence of organic di- or polysulfidic, thiophenic or sulfidic, sulfoxide, sulfone, and sulfate sulfur species in the wax deposits. Elemental sulfur standard has an energy position falling within the peak energy range of different organic di- and polysulfidic compounds (0.5 eV, Vairavamurthy, 1998), and therefore its presence in the samples can not be ruled out. The spectra also demonstrate that there are significant variations in the relative proportions of different sulfur species among the deposits formed at different depths (temperatures). For example, it is apparent that the peak corresponding to di- or polysulfidic sulfur forms is dominant in the deepest deposit (# 7) and appears only as a shoulder of the sulfidic/thiophenic sulfur peak that becomes predominant in the shallower samples.

Quantitative estimates of the relative proportions of different sulfur functional groups were obtained after deconvolution and fitting of the spectra. An example of XANES spectrum deconvolution into arctangent and Gaussian functions, and fitting with the data is presented in Figure 5. Best fit with the experimental data was achieved only when using an additional compound (2481.6-2481.9 eV), tentatively identified as sulfonic acid. The quantitative estimates of the relative proportions of sulfur species in the deposits are presented in Figure 6, and demonstrate several distinct trends of change in their distribution with depth (temperature) of deposit occurrence. The sulfidic or thiophenic sulfur forms are present in a significant and relatively constant proportion (33-39%) in all samples. Di- or polysulfidic sulfur species constitute 47% of total sulfur in the deepest deposit and show a clear tendency of gradual decrease in relative abundance (from 47% to 8%) towards the deposits formed at shallower depths (Figure 6). A distinct inverse trend is evident for the oxidized sulfur species (sulfoxide, sulfone, and sulfonic

acid), which gradually increase in proportion from the deepest to the shallowest deposit (Figure 6). The sulfate distribution shows relatively higher variability in relative proportion, although it generally increases towards shallower samples. The ratio of total oxidized to total reduced sulfur forms increases from deeper to shallower samples and parallels the decrease in total sulfur amount.

DISCUSSION

The results of present study demonstrate a significant compositional variability in both hydrocarbon and sulfur-containing mixtures present in the solid wax deposits formed at different depths (temperatures) of the studied well. The significant shift towards higher molecular weight n-alkane mixtures in deeper samples strongly suggests that temperature induced solubility differences are controlling the hydrocarbon compositional variation in the deposits of studied well. Interestingly, the distribution of sulfur species demonstrates a significant variability and distinct trends of change in deposits formed at different depths (temperatures). The trend of decreasing di- or polysulfidic sulfur with decreasing depth correlates, on one hand, with a trend of decreasing amount of total sulfur, S/C, N/C atomic ratios, and, on another, with a trend of increase in the relative proportions of oxidized sulfur forms (sulfoxide, sulfone, sulfonic acid (?), sulfate), and the atomic H/C ratio (Figures 3, 6 and Table 3). Several possible reasons will be discussed that could account for these observations.

Since temperature is most likely the main controlling factor for the hydrocarbon compositional differences in the deposits of studied well, temperature induced differences in the solubility of sulfur containing high molecular weight compounds and fractions in the oil could be one

explanation for the observed trends in sulfur species distribution. The sulfur-containing compounds with different functional groups and molecular weight are distributed among petroleum fractions with different solubilities (asphaltene, resin, aromatic) reflecting variations in the extent of intermolecular versus intramolecular sulfur cross linking (e.g., Sinninghe Damste *et al.*, 1987, 1990; Schouten *et al.*, 1995). For example, di- or polysulfidic intermolecular linkages have been reported in the structures of both resins and asphaltenes of oils (e.g., Sinninghe-Damste *et al.*, 1990; Speight, 1991; Hofmann *et al.*, 1991; Adam *et al.*, 1993; Sarret *et al.*, 1999), and they contribute to the low solubility of these fractions. Macromolecules consisting of hydrocarbon units (isoprenoid, monocyclic alkanes) extending to C₃₀₋₄₀ and above, and cross linked with mono-, di- or polysulfidic bridges have been identified in the least polar part of resin fractions of high-sulfur oils (Adams *et al.*, 1993) and in solid hydrocarbons (Ruble and Philp, 1995). Aliphatic and naphthenic sulfides and thiophenes have been identified as major components in aromatic, resin and asphaltene oil fractions and bitumens (Payzant *et al.*, 1983; Schmid *et al.*, 1987; Strausz *et al.*, 1990). Series of aliphatic and cyclic sulfoxides have been reported in resin and aromatic petroleum fractions (Payzant *et al.*, 1983; Strausz *et al.*, 1990) and in bitumens generated by hydrous pyrolysis experiments (Nelson *et al.*, 1995). Thus, the observed trends in di-/polysulfidic, sulfidic/thiophenic, and sulfoxide sulfur distributions in studied wax deposits could result from their predominant incorporation in fractions with different molecular weight and solubility that precipitate to a different extent under different temperatures.

The large relative abundance of reduced di- or polysulfidic sulfur forms in the deepest deposit is intriguing (Figure 6 and Table 3). Such large abundance of these sulfur functionalities has not been observed in previous studies on sulfur speciation of heavy petroleum fractions, such as resins (Waldo *et al.*, 1991; Adam *et al.*, 1993) and asphaltenes (George and Gorbaty, 1989;

Waldo *et al.*, 1991; Kasrai *et al.*, 1994), or coals (Spiro *et al.*, 1984; Taghiei *et al.*, 1992; Gorbaty *et al.*, 1992). Since polysulfides are extremely reactive in both oxidation and reduction reactions (Orr and Sinninghe Damste, 1990), a high abundance of di- or polysulfidic sulfur functional groups in the deposits could rather be attributed to their existence as intermolecular linkages in the asphaltenic macromolecular structures, for example, than to organically non-bound compounds. A decreasing proportion of the least oil soluble asphaltenes/resins, containing di- or polysulfidic linkages in their structure, and an increasing contribution of precipitated aromatic and saturated hydrocarbons from deeper to shallower deposits is one possible explanation for such a distribution. Inorganic material present in the wax deposits (e.g., reservoir rock particles, corrosion products) could be an alternative source of di-/polysulfides.

It should be noted that re-incorporation of active sulfur species (e.g., elemental sulfur, hydrogen sulfide) into reservoired oils, as discussed by Aizenshtat *et al.* (1995), is a possibility supported by some geological evidence presented below that could account for the high abundance of di-/polysulfidic species in the studied deposits. One possible source of hydrogen sulfide could be related to laterally (S-SW to N-NE) and/or vertically migrated oils and/or gas/gas condensates containing hot hydrogen sulfide. Support for such a possibility comes from the known production of sour crudes and gases in several fields in southern Oklahoma (Latham, 1968; Wroblewski, 1975) in addition to the strong geochemical evidence for mixing of oils on a regional scale (Donovan, 1974; Ferguson, 1981; Burruss and Hatch, 1989) and migration of anomalously hot fluids identified in the Silurian/Devonian Hunton group in the Anadarko Basin (Schwalm and Burruss, 1996). The reaction of thermally generated hydrogen sulfide with high gravity oils and condensates was associated with the preferential formation of high-thiol oils (Ho *et al.*, 1974), which upon oxidation could lead to formation of disulfides (Reid, 1960). Hydrogen

sulfide reaction with oxygen in formation waters could also result in elemental sulfur formation, and laboratory experiments have demonstrated the formation of alkylated thiolanes by reaction of n-alkane with elemental sulfur (Schmid *et al.*, 1987).

The inverse and proportional changes of di- or polysulfidic sulfur, on one hand, and oxidized sulfur species such as sulfoxides, sulfones and sulfonic acids, on the other, with depth (temperature) of deposition imply the possibility of autooxidation and conversion of di-/polysulfidic or other reduced sulfur species in the shallower deposits. Sulfoxides and sulfones have been reported as oxidation products of sulfides, and sulfonic acids as final products of thiol oxidation, with di-/polysulfides as intermediates in the process (Reid, 1960). Gorbaty *et al.* (1992) demonstrated that organically bound aliphatic sulfur in different coals is selectively oxidized to sulfoxides and sulfones or sulfonic acids, respectively, while the aromatic sulfur forms are relatively stable to the oxidation conditions. Waldo *et al.* (1991) have shown examples of autooxidation and partial conversion of sulfides to sulfoxides after an extended storage period at ambient conditions in support of the previous conclusions of Okuno *et al.* (1967). Payzant *et al.* (1983), however, concluded that sulfoxides can be present in maltene fractions of the virgin oils and could be considered indicative for in-reservoir mild-oxidative conditions. Sulfate is the only highly oxidized sulfur functional form, which does not show a smooth trend of change with samples depth. Two possible sources of sulfate in the deposits could be related to trapped in the deposits formation water and/or carbonate reservoir particles with sulfate substitution of carbonate minerals (Pingitore *et al.*, 1995).

While an increasing proportion of sulfoxides in the shallower rod wax deposits could be attributed at least partially to their presence in resin and aromatic fractions, the increase in sulfones and sulfonic acids is likely to result from oxidation processes. The oxidation could have

occurred after deposition in the well or after sample collection. However, the distinct trends of change in oxidized sulfur species with depth (temperature) of deposit occurrence suggest an *in-situ* oxidation, most probably controlled by the temperature-solubility induced variability in the overall deposit composition, which creates different chemical (pH, Eh) micro-environments and reactants, and could promote a different extent of oxidation. Oxidation by microorganisms and/or an increasing amount of trapped water in the deposits are some possible options for *in-situ* post-deposition transformations of the sulfur species.

CONCLUSIONS

A series of rod wax deposits formed at different temperatures along the sucker pump rods of the same oil producing well were characterized by sulfur K-edge XANES spectroscopy, elemental and HTGC analyses in order to evaluate the sulfur species distribution and variations with respect to the hydrocarbon composition and temperature of deposit occurrence. The results of this study demonstrate:

1. Compositional variability in both sulfur containing compounds and n-alkane distributions in wax deposits formed at different depths/temperatures in the same well. This compositional variability suggests differences in the solubility of wax deposit profile formed in the same well, and should be considered in the development of more efficient methods for wax deposit remediation.
2. Several clear trends in sulfur species distribution and total sulfur with depth (temperature) of deposit occurrence are apparent in studied samples:

- Thiophenic or sulfidic sulfur species remain relatively constant in proportion in all studied deposits.
- Di- or polysulfidic sulfur species were most abundant in the deepest deposit, formed at the highest temperature below the cloud point of the oil, and significantly decrease (from 47% to 8%) in relative proportion in the shallower deposits.
- Oxidized sulfur species (sulfoxides, sulfones, sulfonic acids, and sulfates) increase in relative abundances with decreasing depth of deposition while di- or polysulfidic sulfur functionalities proportionately decrease.
- The amount of total sulfur decreases from deeper to shallower deposits

3. Two possible explanations for the observed compositional variability and trends in sulfur species distribution with depth (temperature) of deposit occurrence relate to:

- Temperature induced differences in solubility of oil components and fractions leading to precipitation and deposition of the most insoluble hydrocarbons and sulfur species at higher temperatures of deposition.
- *In situ* autooxidation processes that may be taking place in deposits formed at shallower depths of the well, and possibly controlled by the temperature-solubility induced variability in the overall deposit composition that creates different chemical micro-environments and reactants, and could promote a different extent of oxidation.

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FIGURE CAPTIONS:

Figure 1. Location of the studied well in the tectonic framework of Oklahoma. NFZ – Nemaha Fault Zone.

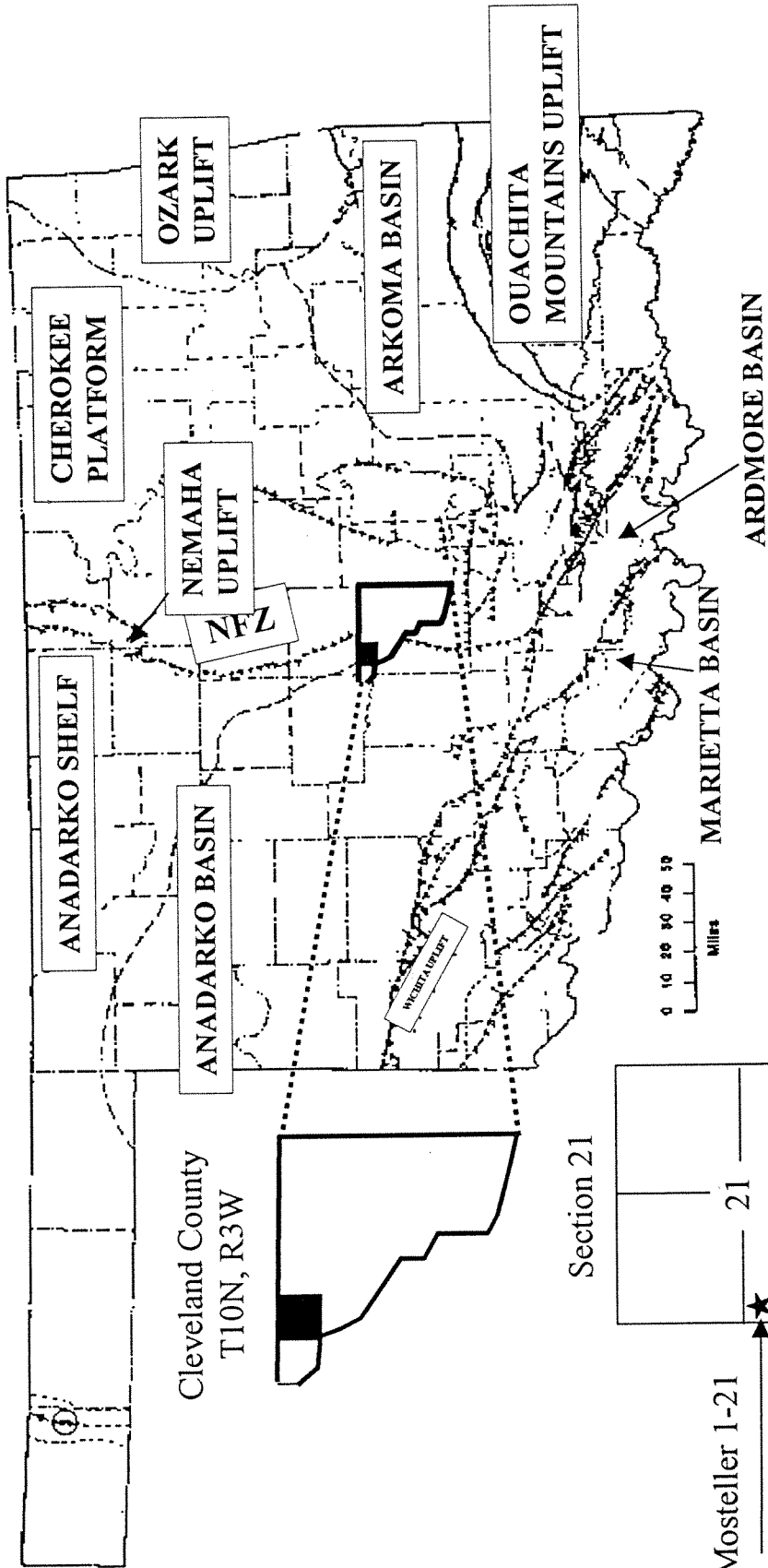
Figure 2. HTGC chromatograms (a) and quantitative results (b) representing the n-alkane distributions in two rod wax deposits collected at different depths. Note the significant shift towards a HMW n-alkane mixture in the deeper deposit. IS – internal standard.

Figure 3. Elemental composition and distribution of H/C, S/C and N/S atomic ratios in wax deposits formed at increasing depths (temperatures). R2, R7 are the shallowest and deepest studied deposits, respectively.

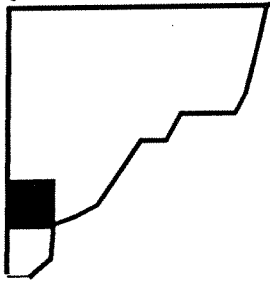
Figure 4. Sulfur K-edge XANES spectra of rod wax deposits occurring at different depths of the well.

Figure 5. An example (R4 wax sample) of typical deconvolution of XANES spectrum into arctangent and Gaussian functions, and fitting with the experimental curve. SA – sulfonic acid.

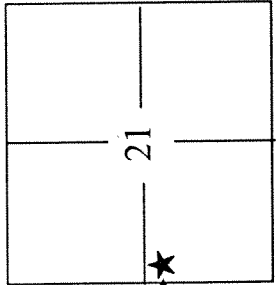
Figure 6. Estimated relative proportions of different sulfur functionalities in studied rod wax deposits (R2, R4, R6, R7). Total sulfur content (wt.% of deposit) – from elemental analysis.



Cleveland County
T10N, R3W

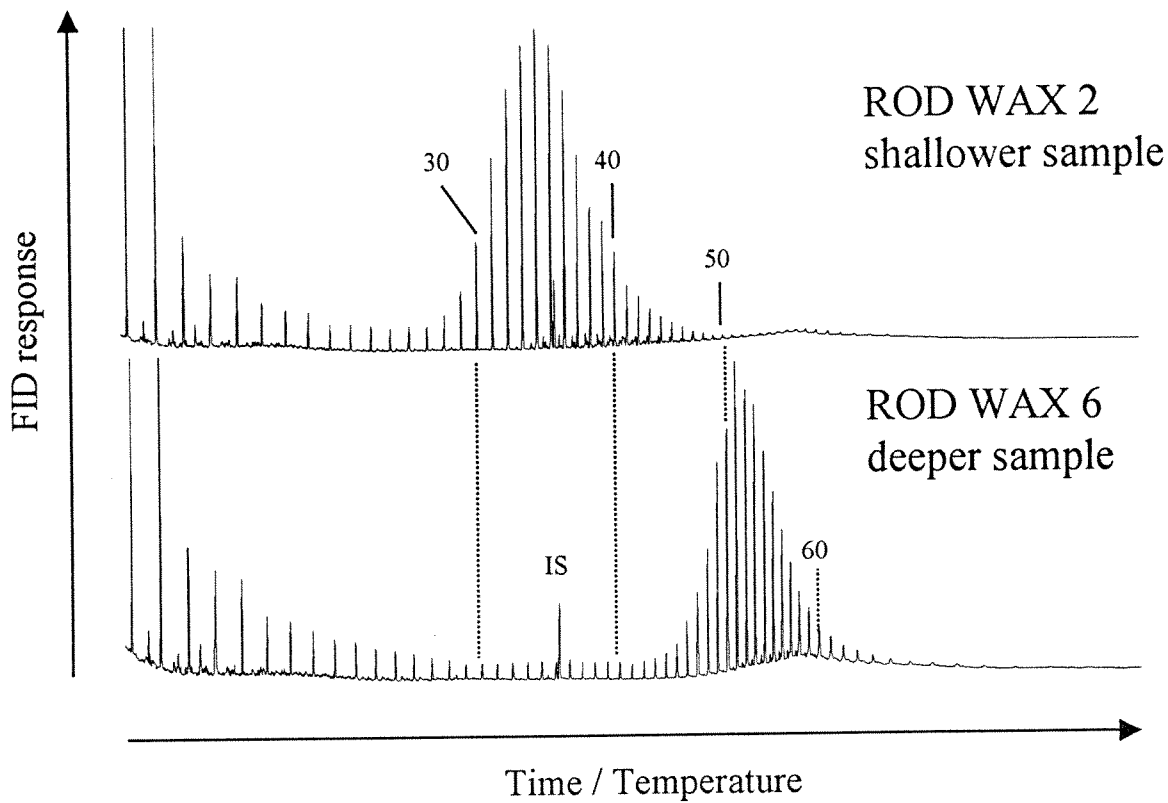


Section 21

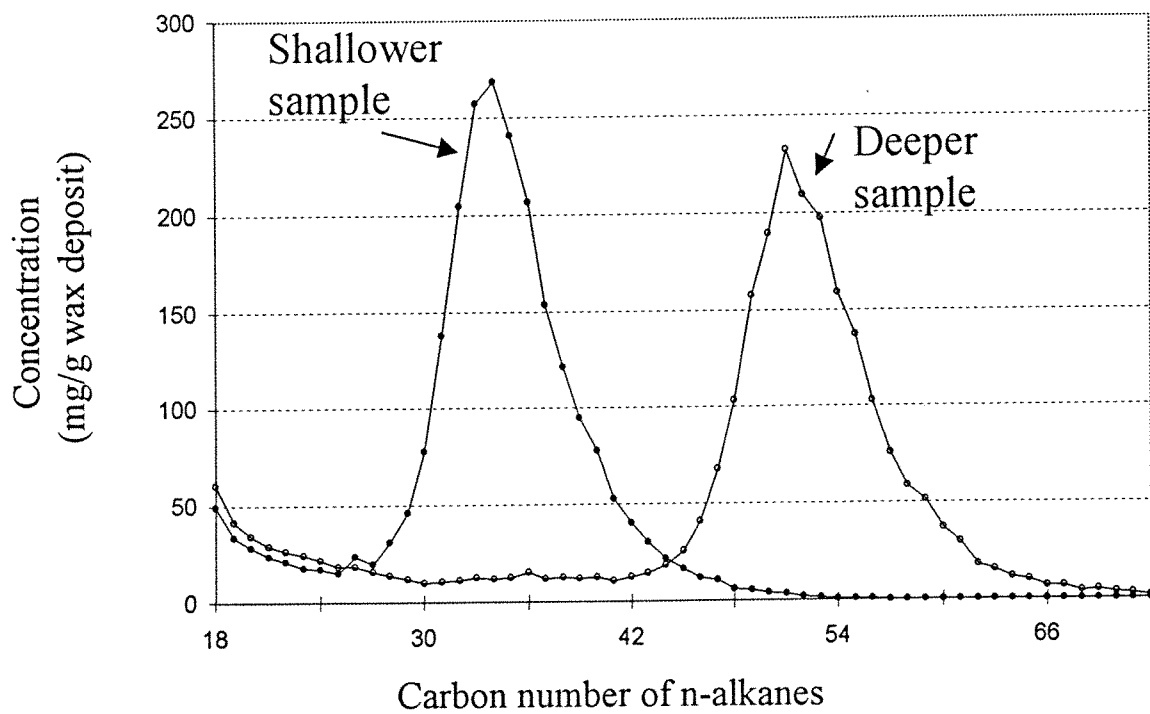


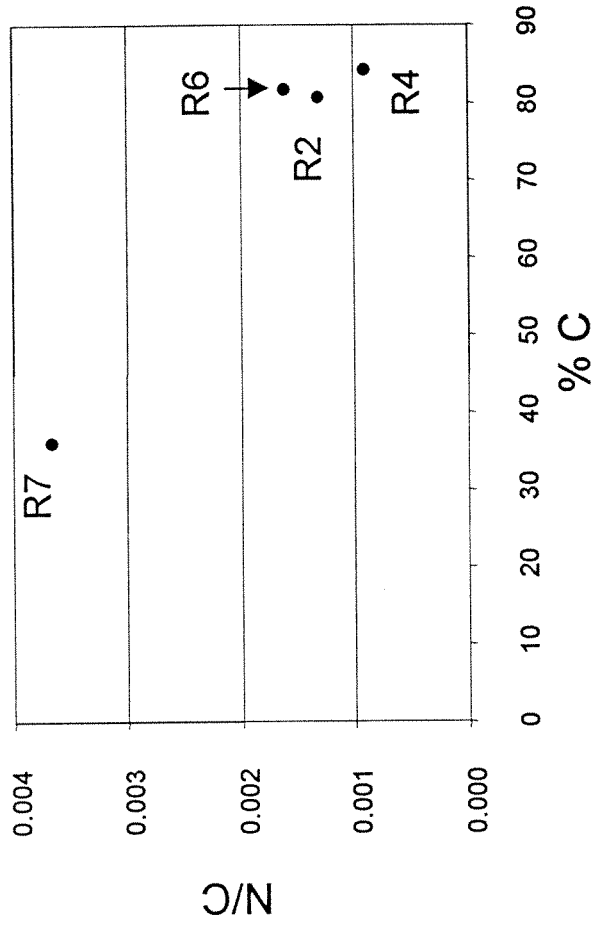
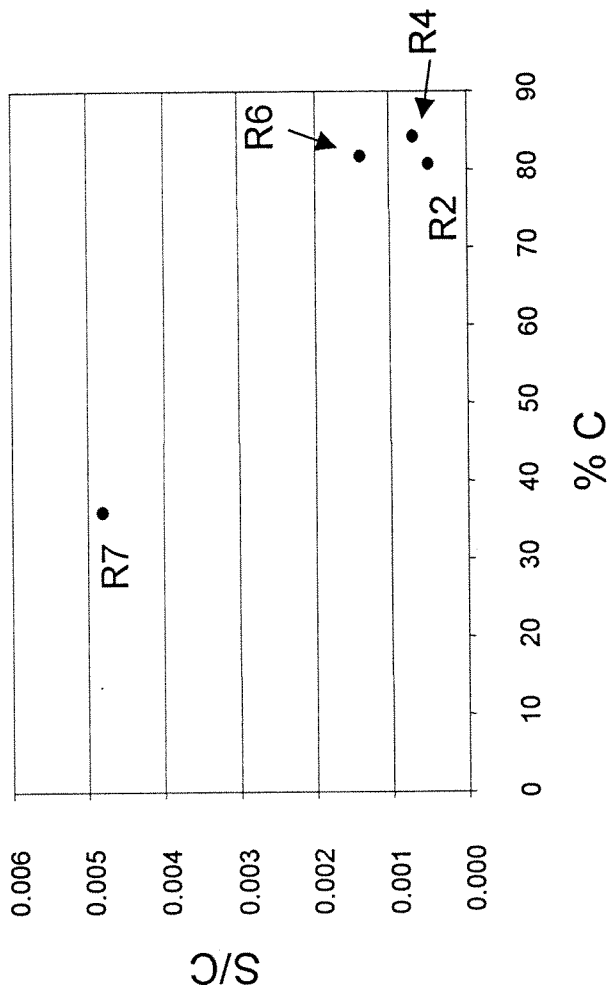
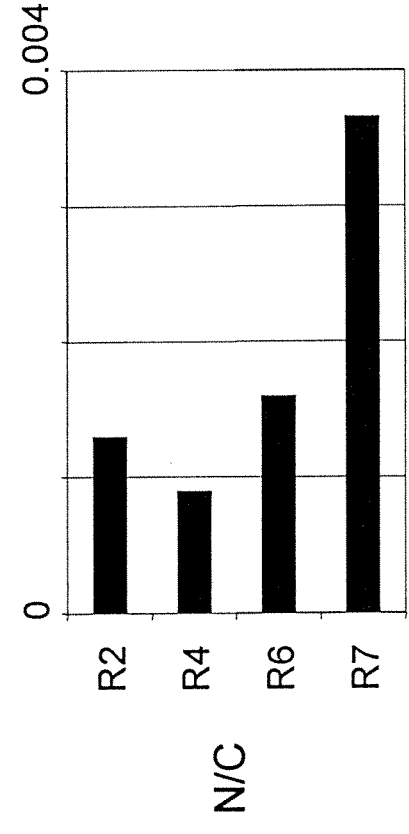
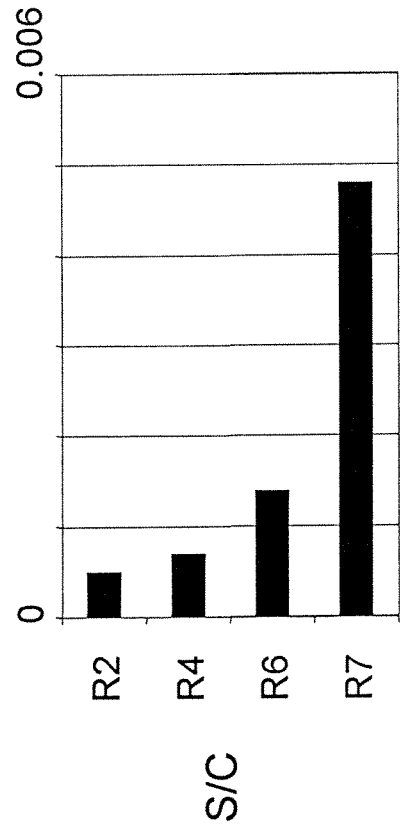
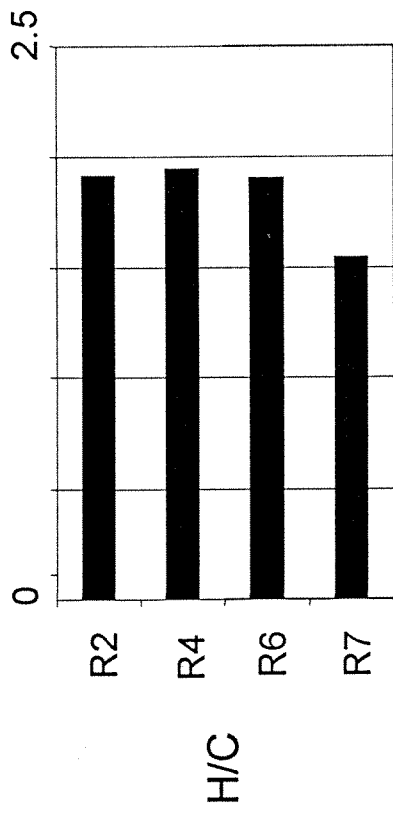
well Mosteller 1-21

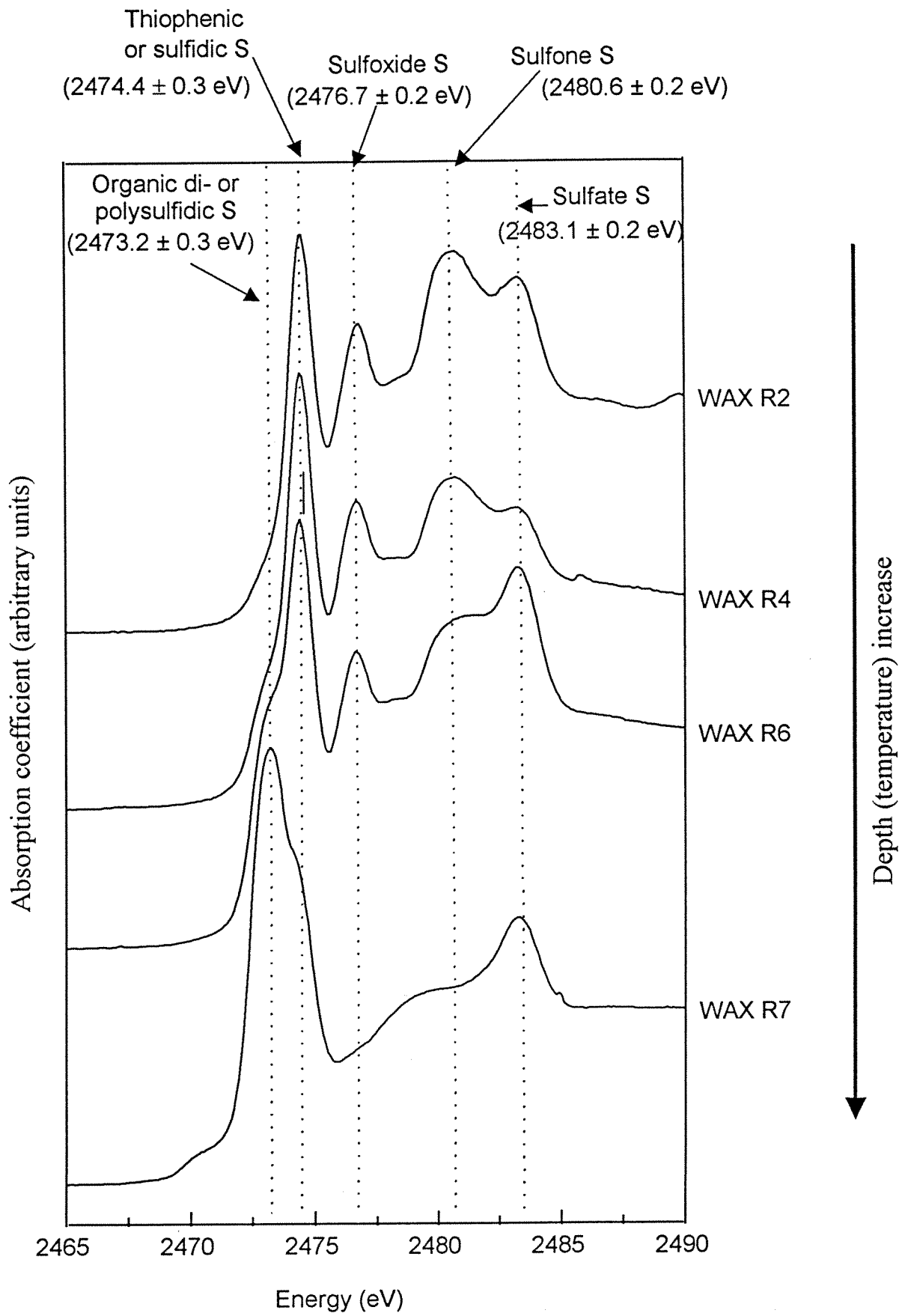
(a)

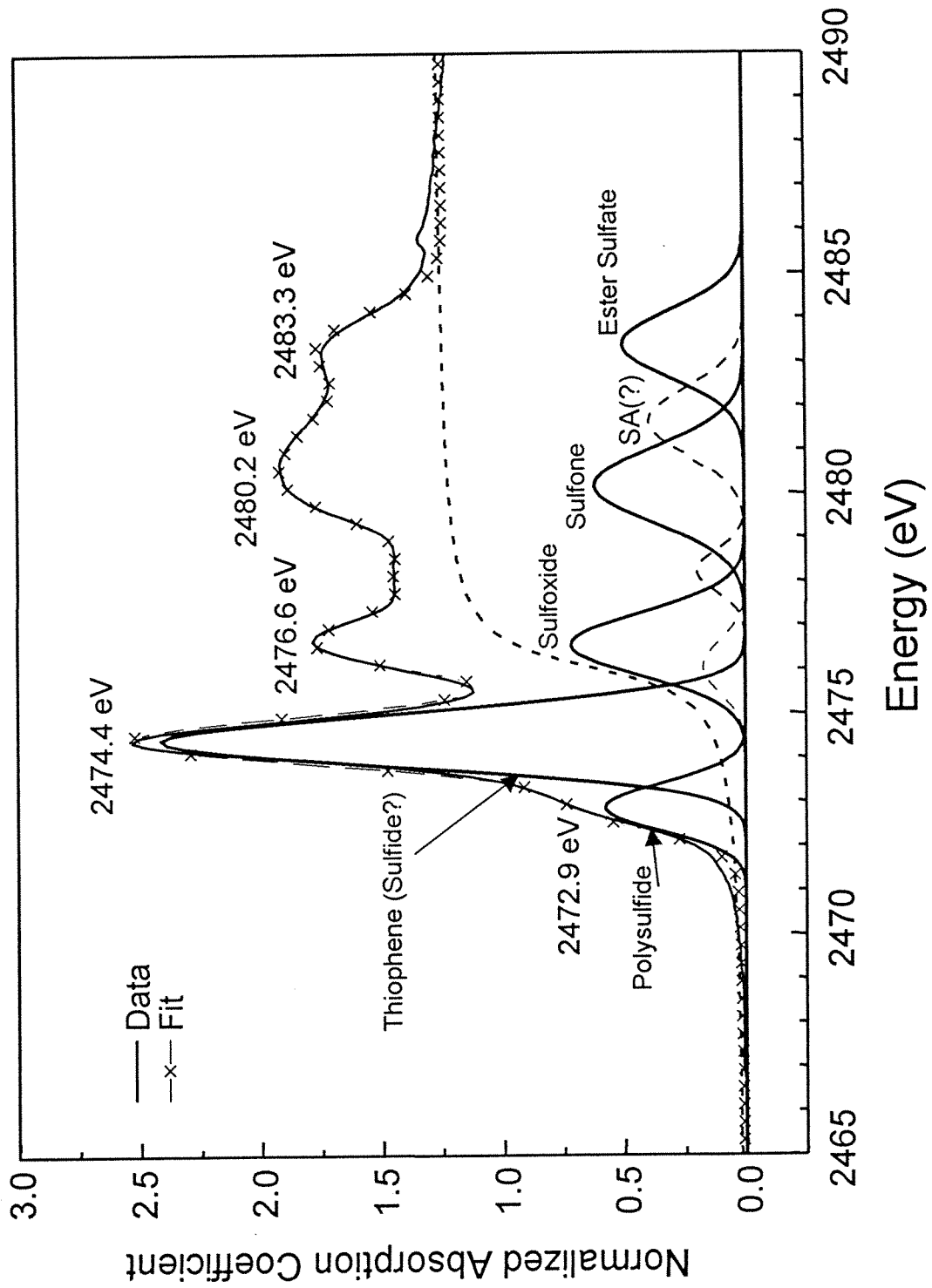


(b)









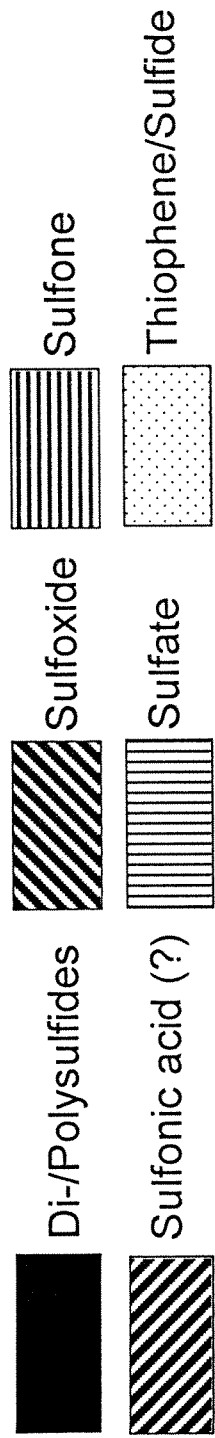
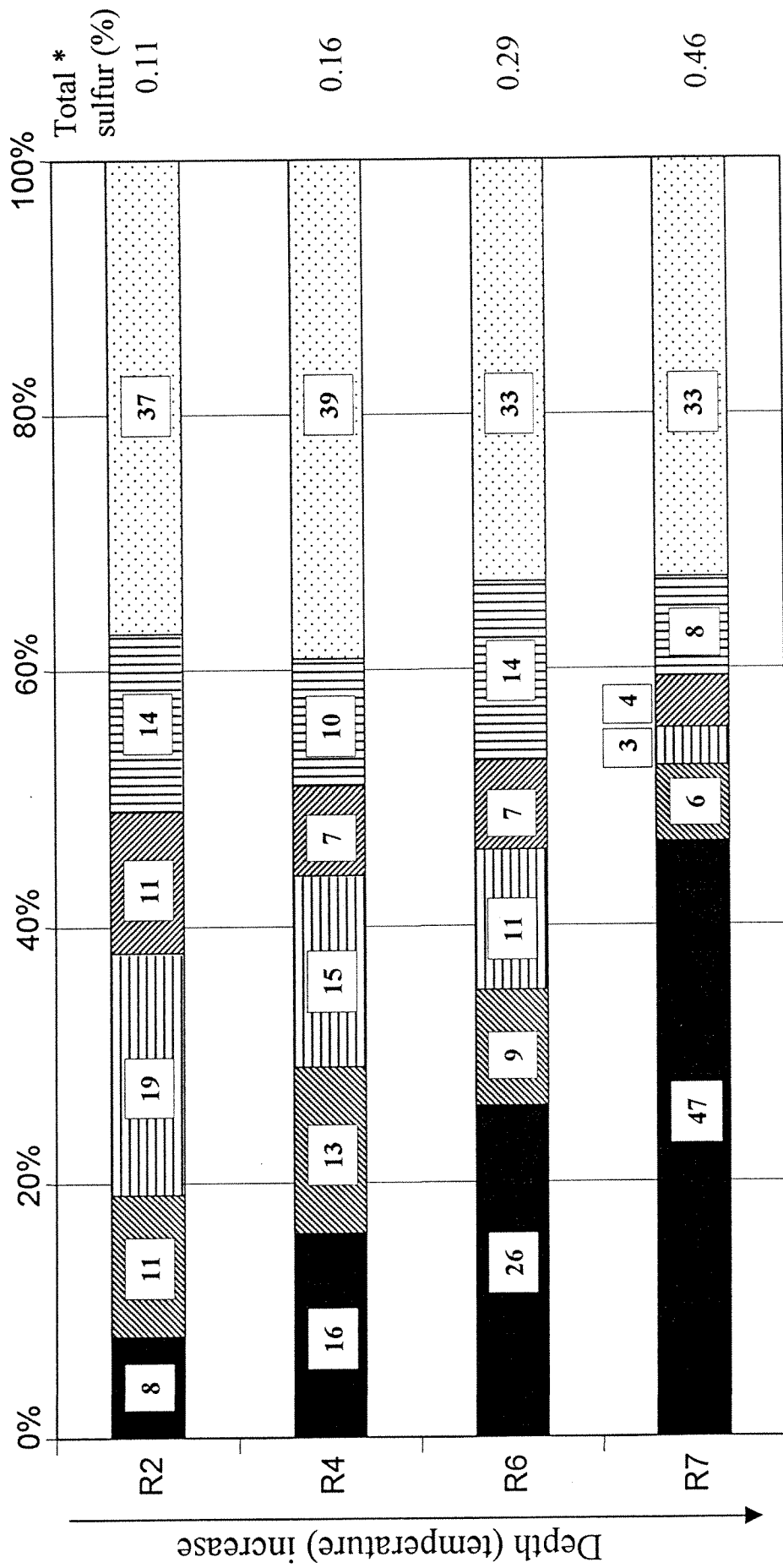


Table 1. Ordovician sequence uncovered by the well.

Group/ Formation	Top of formation feet	Top of formation meters
Sylvan Shale	8192	2497
Viola Group	8288	2526
Simpson Group	8656	2638
Bromide Formation	8656	2638
Tulip Creek Formation	8964	2732
McLish Formation	9075	2766
Oil Creek Formation	9356	2852
Arbuckle Group	9402	2866
Total Depth	9568	2916

Table 2. Summary of recompletion history and initial test fluid data for Mosteller 1-21 well.

Year	Perforation interval (ft.)	Formation	GOR (scf/STB)	Oil Gravity (°API)	Comments
1969	8670-8690	Bromide	352,500	gas	Casing 998-9454 ft
	8966-8979	Tulip Creek	400,000	gas	
	9087-9101	McLish	500,000	gas	
1973	8518-8496	Viola	1880	40.1	Casing 997-9454 ft; no water production; bottom hole plugged at 8550 ft with an iron cast cemented on top.
1980	8308-8442	Viola	35,714	gas	Bottom hole plugged with an iron bridge at 8455 ft.; acid treatment (11,000 gals 15% acid).

Table 3. Elemental analysis results for rod wax deposits R2, R4, R6 and R7.

Sample	C ¹	H ¹	N ¹	S ¹	H/C ²	S/C ²	N/C ²
R2	80.81	12.80	<0.10	<0.10	1.90	<0.0005	0.0011
R2	80.88	13.00	0.13	0.13	1.93	0.0006	0.0014
R4	84.54	13.75	0.05	0.14	1.95	0.0006	0.0005
R4	84.22	13.69	0.12	0.18	1.95	0.0008	0.0012
R6	81.74	13.17	0.13	0.28	1.93	0.0013	0.0014
R6	81.94	12.90	0.16	0.31	1.89	0.0014	0.0017
R7	36.68	4.73	0.11	0.45	1.55	0.0046	0.0026
R7	34.71	4.33	0.16	0.46	1.50	0.0050	0.0040
R7	37.09	4.96	0.19		1.60		0.0044

¹ weight % of deposit; ² atomic ratios