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Title: The sulfur isotopic compositions of individual sulfur compounds and their genetic links in the Lower Paleozoic petroleum pools of the Tarim Basin, NW China

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Abstract: During thermochemical sulfate reduction (TSR), H<sub>2</sub>S generated by reactions between hydrocarbons and aqueous sulfate back-reacts with remaining oil-phase compounds forming new organosulfur compounds (OSC) that have similar  $\delta^{34}\text{S}$  values as the original sulfate. Using compound specific sulfur isotope analysis (CSSIA) of alkylthiaadamantanes (TAs), alkylidibenzothiophenes (DBTs), alkylbenzothiophenes (BTs) and alkylthiolanes (TL), we have here attempted to differentiate OSCs due to primary generation and those due to thermochemical sulfate reduction in oils from the Tarim Basin, China. These oils were generated from Cambrian source rocks and accumulated in Cambrian and Ordovician reservoirs. Based on compound specific sulfur isotope and carbon isotope data, TAs concentrations and DBT/phenanthrene ratios, the oils fall into four groups, reflecting different extents of source rock signal, alteration by TSR, mixing events, and secondary generation of H<sub>2</sub>S. Thermally stable TAs, produced following TSR, rapidly dominate kerogen-derived TAs at low to moderate degrees of TSR. Less thermally stable TLs and BTs were created as soon as TSR commenced, rapidly adopted TSR- $\delta^{34}\text{S}$  values, but they do not survive at high concentrations unless TSR is advanced and ongoing. The presence of TLs and BTs shows that TSR is still active. Secondary DBTs were produced in significant amounts sufficient to dominate kerogen-derived DBTs, only when TSR was at an advanced extent. The difference in sulfur isotopes between (i) TLs and DBTs and (ii) BTs and DBTs and (iii) TAs and DBTs, represents the extent of TSR while the presence of TAs at greater than 20  $\mu\text{g/g}$  represents the occurrence of TSR. The output of this study shows that compound specific sulfur isotopes of different organosulfur compounds, with different thermal stabilities and formation pathways, not only differentiate between oils of TSR and non-TSR origin, but can also reveal information about relative timing of secondary charge events and migration pathways.

Dear editor,

We have made revision on our previous version, and are resubmitting this new version entitled “The sulfur isotopic compositions of individual sulfur compounds and their genetic links in the Lower Paleozoic petroleum pools of the Tarim Basin, NW China”, hoping that this version can be accepted and published in this GCA.

Best regards

Yours sincerely,

Prof Dr Chunfang Cai

Feb. 16, 2016

## Commentary on changes made to the paper following review and editorial

Overall, we have made many changes to the paper in response to the reviewers' and editor's comments.

To summarize the main points:

- a) We have revised the Discussion section to help the reader follow the line of the argument.
- b) Specifically, we have reorganized the Discussion with new titled sub-sections to better let the reader understand the interpretation of the sulfur isotope data from the various groups of compounds.
- c) We have added new synthesis diagrams (Figs. 8 and 9) to help the reader understand the main groupings of the oil geochemistry data and appreciate the main sites and timing of TSR and directions oil migration.
- d) We have added a new table (table 1) that illustrates the molecular structure of the different types of organosulfur compounds and summarizes their origins and evolution.
- e) We have moved two of the previous tables to appendices that can be an online resource.
- f) We have improved the bivariate plots (Figs. 3, 4, 5 and 7) by judicious use of color and keeping the colors of oil groups the same as Figure 6.
- g) We have rewritten the abstract, reducing it from the original 434 words to 294 words and making sure that we better convey what we have done and why and the main conclusions.
- h) We have cleaned up the conclusions to focus on the most important points (and so reduced the number of conclusions from 8 to 6)
- i) We have generally made great efforts to clean up the English, the structure and logic-flow throughout the paper (and especially in the Discussion).

The following represents our specific changes made in response to the reviewers' and editor's comments. Our text is in blue, the reviewers' writing is in black:

### Reviewer #1:

1. Q1: Lines 23-26:

R1: We accept the revision in English expression.

2. The sentence in our previous MS: “The less thermally stable alkylthiolanes (thiolanes) and alkylbenzothiophenes (BTs) are produced at the onset of TSR, while alkylthiaadamantanes (TAs) and alkyl dibenzothiophenes (DBTs) are produced only when TSR proceeds to higher extents.”

Comment: Q2: I'm not sure that this statement is true. I believe that both the less thermally stable thiolanes and benzothiophenes and the more thermally stable thiaadamantanes and dibenzothiophenes are produced at all stages of TSR evolution.

R2: Thanks, we change this sentence to “Thermally stable TAs, produced following TSR, rapidly dominate kerogen-derived TAs at low to moderate degrees of TSR. Less thermally stable TLs and BTs were created as soon as TSR commenced and rapidly adopting its  $\delta^{34}\text{S}$  values but do not survive at high concentrations unless TSR is advanced and ongoing. The presence of TLs and BTs shows that TSR is still active.” in lines 32-36.

- Q3: The apparent enrichment of the less stable compounds to early onset of TSR is due to the

greater degree of preservation at lower reservoir temperatures

R3: We conclude that the enrichment is due to more rapid generation of the less stable compounds to early onset of TSR than more stable OSCs. The stable compounds “DBTs were produced in significant amounts only when TSR was at an advanced extent.” In line 35-36.

Q4: Only the more stable compounds can persist at the higher temp.

R4: Less thermally stable TLs and BTs “do not survive at high concentrations unless TSR is advanced and ongoing” in lines 32-35. In fact, less stable thiolanes are found in the extensive TSR altered oils in well ZS1C in this study and from Smackover Fm at Big Escambia Creek. It seems to us that they are in chemical balance between H<sub>2</sub>S and both TLs and BTs.

## **Reviewer #2:**

### **General remarks:**

The manuscript presents large amount of important new data as well as incorporating the results into the Tarim Basin petroleum systems. The results of the present study show that CSSI of different OSCs, with different thermal stabilities and formation pathways, not only differentiate between oils of TSR and non-TSR origin, but can also reveal information about the relative timing of secondary charge events and migration pathways. The conclusions drawn are helpful in many cases not only to separate the sub-basins but in addition to indicate mixing as well as timing.

It is therefore that I find this manuscript fitting the scope of GCA. Following my specific suggestions.

### **Specific remarks and suggestions:**

After extensive reading of the long paper and some early trial at editing it seems to me that two main problems have to be taken care off.

Q5: a) Some streamlining of the discussion and b) some table in specific table 1 needs to be appendixes.

R5: We have rewritten discussion so that it is shorter and more easily understood. We have added new sub-sections for clarity and reorganized the text.

We have rearranged the discussion, now presenting it in a more logical order: 1) starting with interpretation of TLs and BTs sulfur isotopes, followed by 2) TAs sulfur isotopes for all oils, 3) DBTs and TLs sulfur isotopes for group II oils and 4) finally DBTs sulfur isotopes for group III oils compared with group IV oils.

We moved the classification and explanation of oil groups from discussion section to the

final part of the results section, Previous Section 5.3 has been moved and changed as 5.1. Section 5.2 was changed and separated to 5.3 and 5.4 to help the reader follow the argument. Previous section 5.4 has been deleted because it repeated previous 5.1.1 or 5.2.1 of the new version.

We moved previous tables 1 and 4 to appendixes as Table S1 and S2. In addition, we enlarged Fig. 1 inset to show the important details more clearly. Table 1 and Figures 8-9 are newly added to help understand the discussion. New Table 1 shows relative stabilities of the OSCs found in this study. New Fig. 8 shows the key characteristics of the four groups. New Fig. 9 shows oil migration and mixing plus the distribution of oil groups in cross.

Q6: In addition figures 2-5 and 7 must be redrawn to make sure that in the Journal format one can follow with ease the points discussed. This is obvious as for figures 3,4,5 and 7 appear in black & white in the PDF while the legends indicate color-coding?

R6: We have redrawn all these figs and used the same color scheme as original Fig. 6.

Q7: I have also noted for the editor some points on the PDF. Please see that these notations are not transferred with my name.

R7: We changed as recommended.

**In conclusion I do recommend accepting the manuscript for publication with the editor's discretion.**

1 **Sulfur isotopic compositions of individual organosulfur**  
2 **compounds and their genetic links in the Lower Paleozoic**  
3 **petroleum pools of the Tarim Basin, NW China**

4

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20

21 **Abstract**

22 During thermochemical sulfate reduction (TSR), H<sub>2</sub>S generated by reactions between hydrocarbons and  
23 aqueous sulfate back-reacts with remaining oil-phase compounds forming new organosulfur compounds  
24 (OSC) that have similar  $\delta^{34}\text{S}$  values to the original sulfate. Using compound specific sulfur isotope  
25 analysis (CSSIA) of alkylthiaadamantanes (TAs), alkylthiobenzothiophenes (BTs), alkylbenzothiophenes  
26 (BTs) and alkylthiolanes (TL), we have here attempted to differentiate OSCs due to primary generation  
27 and those due to TSR in oils from the Tarim Basin, China. These oils were generated from Cambrian  
28 source rocks and accumulated in Cambrian and Ordovician reservoirs. Based on compound specific  
29 sulfur isotope and carbon isotope data, TAs concentrations and DBT/phenanthrene ratios, the oils fall into  
30 four groups, reflecting different extents of source rock signal, alteration by TSR, mixing events, and  
31 secondary generation of H<sub>2</sub>S. Thermally stable TAs, produced following TSR, rapidly dominate  
32 kerogen-derived TAs at low to moderate degrees of TSR. Less thermally stable TLs and BTs were  
33 created as soon as TSR commenced, rapidly adopted TSR- $\delta^{34}\text{S}$  values, but they do not survive at high  
34 concentrations unless TSR is advanced and ongoing. The presence of TLs and BTs shows that TSR is  
35 still active. Secondary DBTs were produced in significant amounts sufficient to dominate  
36 kerogen-derived DBTs, only when TSR was at an advanced extent. The difference in sulfur isotopes  
37 between (i) TLs and DBTs and (ii) BTs and DBTs and (iii) TAs and DBTs, represents the extent of TSR  
38 while the presence of TAs at greater than 20  $\mu\text{g/g}$  represents the occurrence of TSR. The output of this  
39 study shows that compound specific sulfur isotopes of different organosulfur compounds, with different  
40 thermal stabilities and formation pathways, not only differentiate between oils of TSR and non-TSR origin,  
41 but can also reveal information about relative timing of secondary charge events and migration pathways.

42

43 Key words: TSR; thiaadamantanes; compound specific sulfur isotopes; carbon isotopes; petroleum;  
44 Tarim Basin.

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46

## 47 1. Introduction

48 Thermochemical sulfate reduction (TSR), a process whereby sulfate minerals and petroleum react  
49 together at temperatures  $\sim > 120^{\circ}\text{C}$ , is considered to result in elevated  $\text{H}_2\text{S}$  concentrations ( $>10\%$ ) in  
50 many deep carbonate gas reservoirs around the world (Orr, 1974; Krouse et al., 1988; Machel et al., 1995;  
51 Sassen et al., 1988; Worden and Smalley, 1996; Cai et al. 2001; 2003). Back reaction of TSR- $\text{H}_2\text{S}$  with  
52 hydrocarbon compounds generates a variety of organic sulfur compounds including thiols (mercaptans),  
53 thiolanes (TLs), alkyl-2-thiaadamantanes (TAs) and alkylbenzothiophenes (BTs) (Orr, 1974; Powell and  
54 MacQueen, 1984; Hanin et al., 2002; Cai et al., 2003; 2009b; 2010; 2015a & b; Wei et al., 2007; 2011;  
55 2012; Amrani et al., 2006; 2012; Walters et al., 2015; Gvirtzman et al, 2015).

56 TSR is generally considered to occur in a closed system; thus  $\text{H}_2\text{S}$  concentration, and the indices  
57  $\text{H}_2\text{S}/(\text{H}_2\text{S}+\text{C}_{1-6})$  and  $\text{CO}_2/(\text{CO}_2+\text{C}_{1-6})$  have been previously used to evaluate the extent of TSR (Krouse et  
58 al., 1988; Worden et al., 1996; Cai et al., 2003; 2004; 2013). However, some case studies have shown  
59 that: (i)  $\text{H}_2\text{S}$  may have migrated from deeper reservoirs (Manzano et al., 1997; Cai et al., 2005), (ii)  $\text{H}_2\text{S}$   
60 may have locally elevated concentrations due to exsolution (phase separation) from formation water (Cai  
61 et al., 2013; 2015b; Jenden et al., 2015), or (iii)  $\text{H}_2\text{S}$  may have reacted with available metals in the  
62 reservoir leading to sulfide mineral growth (Worden et al., 2000; 2003). In such cases,  $\text{H}_2\text{S}$   
63 concentration and  $\text{H}_2\text{S}/(\text{H}_2\text{S}+\text{C}_{1-6})$  cannot be used as a proxy for the extent of TSR within a reservoir.  
64 New proxies to determine the extent of TSR would thus help in the broader understanding of TSR  
65 reactions, gas phase geochemistry and subsequent  $\text{H}_2\text{S}$ -hydrocarbon reactions.

66 Gas chromatography (GC) followed by measurement of  $^{34}\text{S}/^{32}\text{S}$  ratio by multi-collector  
67 inductively-coupled plasma mass spectrometry (MC-ICP-MS) enable Compound Specific Sulfur Isotope  
68 Analysis (CSSIA; Amrani et al., 2009). Amrani et al. (2012) employed this technique to study a suite of  
69 oils from the Gulf of Mexico (Smackover Formation) and found that for TSR-influenced oils, BTs had  
70 significantly and consistently higher  $\delta^{34}\text{S}$  values (up to  $\sim 30\text{‰}$ ) relative to alkyl-dibenzothiophenes (DBTs).  
71 These  $\delta^{34}\text{S}$  differences between BTs and DBTs were interpreted to reflect TSR-altered compounds versus  
72 the original kerogen-derived, or less TSR-altered, compounds represented by more thermally stable DBTs.



73 Therefore, the  $\delta^{34}\text{S}$  difference between BTs and DBTs was suggested to be a sensitive proxy for TSR  
74 (Amrani et al., 2012).

75 The presence of alkylthiaadamantanes (TAs) was suggested as a molecular proxy for TSR as they  
76 were detected from TSR-altered Smackover petroleum (Hanin et al., 2002). Some Smackover oil  
77 samples were shown to have 2-thiaadamantanes with  $\delta^{34}\text{S}$  values from 21 to 22 ‰ (Hanin et al., 2002).  
78 These  $\delta^{34}\text{S}$  values are reasonably close to those of the  $\text{H}_2\text{S}$  in this area from +14.8 to +17.1 ‰ and the  
79 parent Jurassic evaporites (+16 to +24 ‰) (Wei et al., 2011; 2012). It was proposed that oils can be  
80 regarded as being TSR-altered if they contain >54 ppm TAs (or 1-cage thiadiamondoids) or >150 ppm  
81 total thiadiamondoids (Wei et al., 2012). The concentrations of thiadiamondoids and TAs were reported  
82 to increase with extent of TSR (Wei et al., 2012), and have thus also been suggested as useful proxies of  
83 the extent of TSR (Wei et al., 2012). Gvirtzman et al. (2015) conducted a CSSIA study on TAs and  
84 2-cage thiadiamondoids from oil samples from the Smackover Formation. Depending on the degree of  
85 TSR, the  $\delta^{34}\text{S}$  values of individual TAs varied significantly (~30 ‰) between the different oil samples but  
86 tended to be similar to those of BTs. Minute amounts of TAs may form during primary source rock  
87 diagenesis, or oil generation, but the advent of TSR dramatically increases their concentration (Wei et al.,  
88 2012). These newly-generated TAs, with  $\delta^{34}\text{S}$  similar to host sulfate minerals, are considered to rapidly  
89 overwhelm the initial  $\delta^{34}\text{S}$  signal of the source rock-derived TAs (Gvirtzman et al., 2015). Table 1  
90 summarizes the main OSC groups, their associated thermal stabilities, and their  $\delta^{34}\text{S}$  patterns.

91 The focus of the present study is the Tarim Basin in China, where  $\text{H}_2\text{S}$  has been interpreted to be the  
92 result of TSR in Cambrian and Ordovician reservoirs, with  $\delta^{34}\text{S}$  values of 15 to 22 ‰ and 33 ‰  
93 respectively (Cai et al., 2001a; 2009b and 2015b; Jia et al., 2015). TSR-induced oxidation of  
94 hydrocarbons has been independently supported by  $\delta^{13}\text{C}$  values from TSR calcite in Ordovician reservoirs  
95 ranging from -6.0 to -9.4 ‰ (Cai et al., 2001) and from -3.6 to -17.7 ‰ (Jia et al., 2015). However,  
96 present-day  $\text{H}_2\text{S}$  concentrations may have been diluted by a late charge of methane-dominated,  $\text{H}_2\text{S}$ -poor  
97 gas (Wang et al., 2014; Cai et al., 2015b). Thus,  $\text{H}_2\text{S}$  concentrations may not relate to the actual extent of  
98 TSR in the Lower Paleozoic Tarim reservoirs.

99 Cai et al. (2009a & b; 2015a) proposed that the Tarim Basin oils were generated from Cambrian  
100 source rocks, and, except for the ZS1C oil, do not show significant differences in whole oil and DBTs  
101  $\delta^{34}\text{S}$  values (Cai et al., 2009b; 2015a; Li et al., 2015). Thiols and thiolanes were found in several oils  
102 from different wells (Cai et al., 2009b; Li et al., 2012). TAs were reported only in the TZ83 oil from the  
103 Lower Ordovician, which was interpreted to be a byproduct of TSR (Jiang et al., 2008; Cai et al., 2009b).  
104 More recently, Cai (2013) and Zhang et al. (2015) speculated that the ZS1C oil has TAs derived from a  
105 similar origin to thiols and thiolanes. DBTs from ZS1C originated from TSR, as shown by their high  
106 concentrations and enriched  $^{34}\text{S}$  values (Li et al., 2015; Cai et al., 2015a & b; Zhu et al., 2015; Zhang et al.,  
107 2015). This evidence led Zhang et al. (2015) to propose that some other oils, with abnormally high  
108 DBTs from Cambrian, Ordovician and Carboniferous reservoirs in this area (Cai et al., 2009b and Li et al.,  
109 2012), may have mixed with a Cambrian oil similar to the ZS1C oil. Conversely, specific DBTs in the  
110 Lower Ordovician TZ83 oil, found at elevated concentrations, were proposed to have an *in situ* TSR  
111 origin (Cai et al., 2009b). However, this TZ83 oil was found to have  $\delta^{34}\text{S}$  values of individual DBTs  
112 compounds close to those of non-TSR altered oils and Cambrian kerogen; consequently it was concluded  
113 that TZ83 DBTs originated directly from source rocks rather from TSR (Cai et al., 2015a).

114 Using the Tarim Basin as a case study, the work presented here seeks to address the following  
115 research questions:

- 116 1) Are TAs and high concentrations of DBTs exclusively limited to TSR-altered oils?
- 117 2) How do  $\delta^{34}\text{S}$  values vary between, and within, groups of compounds such as TAs, DBTs,  
118 BTs and thiolanes?
- 119 3) Can Compound Specific Sulfur Isotope Analyses (CSSIA) of TAs, DBTs, BTs and thiolanes  
120 be used to reveal the extent of TSR in oil samples from the Tarim Basin?
- 121 4) Can an integrated analysis of  $\delta^{34}\text{S}$  of TAs and DBTs with  $\delta^{13}\text{C}$  of *n*-alkanes be used to  
122 resolve questions of mixing of oils from various source rocks?

123 To address these questions,  $\text{H}_2\text{S}$ , bulk oil, individual sulfur compounds from oils and in the Cambrian  
124 and Ordovician reservoirs were measured for  $\delta^{34}\text{S}$  values and TAs concentrations, and  $\delta^{13}\text{C}$  was measured  
125 for whole oils, their fractions and individual *n*-alkanes.

126

## 127 **2. Geological setting**

128 The Tazhong Uplift is located in the middle of the Tarim Basin (Fig. 1) and is an inherited structural  
129 high. Its tectonic history began with extensional movement during the Neoproterozoic and then oceanic  
130 spreading during the Cambrian to Early Ordovician. At the end of Early Ordovician, a few large  
131 NW-trending basement-involved thrust faults developed, dividing the Central Tarim area, and resulting in  
132 the formation of the present structural configuration and carbonate platform. The Tazhong area was  
133 uplifted and exposed to surface for about 10 Ma during the early Late Ordovician, leading to the  
134 development of an extensive unconformity between the Upper and Lower Ordovician successions (Wu et  
135 al., 2012b). Fault No.1 was active during the Caledonian Orogeny at the end of the Ordovician and cut  
136 Ordovician, Cambrian and late Neoproterozoic (Ediacaran) strata and pre-Ediacaran basement (Cai et al.,  
137 2009a). This fault was reactivated during subsequent orogenies. Continuous compressive stress  
138 resulted in the development of NNE strike-slip faults at the end of the Devonian (Figs. 1 & 2a; Wu et al.,  
139 2009). As a result, Devonian, Silurian, and even Ordovician strata were locally eroded and formed a  
140 major unconformity (Lin et al., 2009).

141 The sedimentary fill consists of Neoproterozoic beach to shallow marine facies siliciclastic and  
142 carbonate rocks. The Lower Cambrian is composed of thick, platform facies dolomites with intercalated  
143 dark mudstones in the middle and upper parts and phosphatic shales and siliceous rocks in the lower part.  
144 The overlying Middle Cambrian contains supratidal, anhydrite-bearing dolomites and bedded anhydrite.  
145 Bedded anhydrite has a cumulative thickness of 20 m to 98 m in the east, and is thicker in the west (Cai et  
146 al., 2015b). The Upper Cambrian Qiulitage Formation is composed of platform facies micritic dolomite  
147 and siliceous dolomite (Shao et al., 2002). The Lower Ordovician is predominantly composed of thick,  
148 platform facies dolomite in the lower part and limestone in the upper part. The Upper Ordovician is  
149 represented by reef and shoal facies packstone and bioclastic limestone and slope facies limestone and  
150 marlstone (Cai et al., 2009a). Silurian to Carboniferous strata are composed of marine sandstone and  
151 mudstone. The Permian consists of sandstone and mudstone with intercalated volcanic rock; the  
152 Mesozoic and Cenozoic sections are predominantly composed of terrestrial sandstones and mudstones.

153 Petroleum has thus far been produced from Carboniferous, Silurian, Lower Ordovician ( $O_{1y}$ ), Middle  
154 and Upper Ordovician ( $O_{2yj}$  and  $O_{3l}$ ), Middle Cambrian Awatage Fm. ( $Cam_{2a}$ ), as well as Lower Cambrian  
155 Wusonggeer Fm. ( $Cam_{1w}$ ) and Xiaoerbulake Fm. ( $Cam_{1x}$ ) reservoirs (Fig. 2a & b). The main source  
156 rock is considered to be in the Cambrian with oil migration accompanied by hot brines (Cai et al., 2009a  
157 & b; 2015a and references therein) via the NW-trending basement-involved thrust faults and NNE  
158 strike-slip faults (Cai et al., 2001b; 2008; LÜ et al., 2004; Jia et al., 2015).

159

### 160 **3. Samples and methods**

#### 161 *3.1. Sample collection and $H_2S$ and bulk oil $\delta^{34}S$ measurement*

162 Gas and oil samples were collected at well head separators from Cambrian and Ordovician reservoirs  
163 from fifty wells in the Tazhong area. ZS1-Z and ZS1-L oils were produced from the same well ZS1, but  
164 from different depths.

165 The methods for determination of  $H_2S$  concentrations and  $\delta^{34}S$  measurement of  $H_2S$  and bulk oil in  
166 gas were reported previously in Cai et al. (2001a & b; 2009b). In brief,  $H_2S$ -bearing gas from the well  
167 head was bubbled through 2L glass jars containing zinc acetate (3g) to precipitate as ZnS. The solution  
168 with ZnS was put aside overnight and then filtered with a 0.45 $\mu$ m filter on site. In the laboratory, ZnS  
169 was transformed to  $Ag_2S$  by adding HCl and passing the evolved  $H_2S$  under an inert atmosphere through  
170  $AgNO_3$  solution at a pH of 4. Samples of oil (1 to 4g) were combusted in a Parr bomb apparatus at ~25  
171 atm oxygen to oxidize organically bound sulfur to sulfate. Dissolved sulfate was then precipitated as  
172  $BaSO_4$ . Samples of formation water (20 to 50ml) were bubbled through  $N_2$  at temperature of ~50°C for  
173 1 hour to precipitate  $H_2S$  as ZnS and then  $BaCl_2$  was added to the water to collect  $BaSO_4$ .

174  $Ag_2S$  and  $BaSO_4$  were converted to  $SO_2$  by combustion in a quartz tube for isotopic analysis using  
175 the method of Bailey and Smith (1972). Isotopic determinations were carried out using a Thermo  
176 Finnigan Delta S mass spectrometer, calibrated by a series of International Atomic Energy Agency  
177 standards. Results are presented as  $\delta^{34}S$  relative to the Vienna Canyon Diablo Troilite (VCDT) standard.  
178 The reproducibility for  $\delta^{34}S$  measurement is  $\pm 0.3$  ‰.

#### 179 *3.3 Quantification of alkyl 2-thiaadamantanes*

180       Asphaltenes were removed by precipitation with *n*-hexane followed by filtration. The  
181 de-asphalted oils were then separated into saturate, aromatic and organic sulfur compound fractions  
182 using column chromatography with a mixture of silica gel and silver nitrate as stationary phase, with  
183 *n*-hexane, dichloromethane, and a mixture of dichloromethane and methanol (9:1, v/v) as eluents,  
184 respectively. The organic sulfur compound fraction was concentrated to about 200  $\mu$ l for gas  
185 chromatography–mass spectrometry analysis.

186       Organic sulfur compound fractions were analyzed using a Micromass Platform II spectrometer  
187 coupled to a Hewlett–Packard 6890 gas chromatograph. Chromatographic separation was achieved  
188 using a 30 m  $\times$  0.25 mm i.d. fused silica capillary column coated with a 0.25  $\mu$ m film of HP-5MS. The  
189 oven temperature started at 60  $^{\circ}$ C (2 min) and was increased to 315  $^{\circ}$ C at 3  $^{\circ}$ C/min, followed by a 15 min  
190 hold. Helium was used as carrier gas at a flow rate of 1.0 ml/min. The transfer line temperature was  
191 250  $^{\circ}$ C and the ion source temperature was 200  $^{\circ}$ C. The ion source was operated in the electron  
192 ionization (EI) mode at 70 eV. Full scan and SIM GC–MS analysis was performed to identify biomarker  
193 compounds. In full-scan GC–MS, the scan time was set at 1 s for a mass range of 50–550. During  
194 SIM–GC–MS analysis of thiadiamondoids, ions were monitored at *m/z* 154, 168, 182, 196, 210 and 224  
195 for thiaadamantanes, *m/z* 206, 220, 234 and 248 for thiadamantanes, *m/z* 258, 272, 286 and 300 for  
196 2-thiatriamantanes and *m/z* 152 for the D16-adamantane standard.

#### 197 *3.4 Liquid column chromatography for $\delta^{34}$ S analysis of organic sulfur compounds (OSCs)*

198       Liquid chromatographic (LC) separation of total sulfides (including thiadamantanes and thiolanes) was  
199 achieved according to Wei et al (2012) and modified by Gvirtzman et al. (2015): liquid chromatography  
200 on silver nitrate-impregnated silica gel was used to fractionate oils and condensates into chemical classes.  
201  $\text{Ag}^+$  ions react with sulfides to form strong complexes, and then the sulfides are replaced by acetone,  
202 which forms a stronger complex with  $\text{Ag}^+$ , to elute as the sulfidic fraction. About 0.9 g of silver  
203 nitrate-impregnated silica gel (Aldrich 10 wt% on silica gel +230 mesh, activated at 105  $^{\circ}$ C for 2 h) and  
204 1.5 g silica gel (Merck, 40 ml, 230-400, activated at 225  $^{\circ}$ C for 24 hrs) were loaded into a 17cm long glass  
205 column (volume 5  $\text{cm}^3$ ). About 150 mg of oil was loaded on the top of the column and sequentially  
206 eluted with 15 ml hexane (“saturate” fraction), 40 ml dichloromethane (“aromatic” fraction) and 15 ml

207 acetone (“sulfidic” fraction). The silver-nitrate column was used for separating the sulfides from the  
208 petroleum sample. Care was taken to avoid drying the sulfidic fraction during evaporation and  
209 concentration to smaller volumes down to 50-150 µl.

### 210 3.5 GC-MC-ICP-MS analysis of $\delta^{34}\text{S}$ of specific compounds

211 Compound specific S isotope analysis of the “aromatic” or “sulfidic” fractions was conducted with  
212 GC-MC-ICPMS based on a similar system to that developed by Amrani et al. (2009) and modified by  
213 Gvirtzman et al. (2015) . The system employs chromatographic separation (Agilent DB5-MS, 30 m,  
214 0.25 mm, 0.25 µm thickness) by gas chromatography (GC, Clarus 580, Perkin Elmer or Trace GC,  
215 ThermoFischer) equipped with a heated transfer line and subsequent  $^{34}\text{S}/^{32}\text{S}$  ratio measurements by  
216 multicollector inductively coupled plasma mass spectrometry (MC-ICPMS-Neptune *plus*, ThermoFischer).  
217  $\text{SF}_6$  gas (in helium) was used for calibration and injected at the beginning and end of each injection. The  
218  $\text{SF}_6$  was calibrated with a mixture of in-house standards (see details in Gvirtzman et al, 2015) that in turn  
219 was calibrated against NIST standards NBS-127 ( $\text{BaSO}_4$ ;  $\delta^{34}\text{S} = 21.1 \text{ ‰}$ ) and IAEA-S-1 ( $\text{Ag}_2\text{S}$ ;  $-0.3 \text{ ‰}$ ).  
220 Calibration of the  $\text{SF}_6$  against the in-house standard mixture was done every 3-5 samples. One microliter  
221 of sample solution was injected to the inlet at a constant temperature of 320°C. Helium was used as  
222 carrier gas at a constant flow rate of 1.5 ml/min. The oven temperature program of the GC was: 60°C for  
223 5 min, 60 to 320°C at 10°C/min, and maintained at 320°C for 20 min.

224 Results of isotopic analyses are expressed in conventional  $\delta^{34}\text{S}$  notation as per mil (‰) relative to the  
225 V-CDT standard:

$$226 \quad \delta^{34}\text{S} = \left( \frac{{}^{34}\text{R}_{\text{sample}}}{{}^{34}\text{R}_{\text{std}}} \right) - 1$$

227 where  ${}^{34}\text{R}$  is the integrated  $^{34}\text{S}/^{32}\text{S}$  ion-current ratio of the sample and standard peaks. Data  
228 processing employed algorithms that are implemented in Visual Basic code within Microsoft Excel (Ricci  
229 et al., 1994; Sessions et al., 2001). Ion currents were integrated by the Neptune software (v. 3.1.0.27) in  
230 189-ms increments and exported to Excel in ASCII format. Further details about the peak integration,  
231 calibration and processing can be found in Amrani et al. (2009, 2012). Specific details about the

232 identification and  $\delta^{34}\text{S}$  analysis of the thiaadamantanes, BTs and DBTs isomers can be found in Gvirtzman  
233 et al. (2015). The mean standard deviation of  $\delta^{34}\text{S}$  values for the aromatic fraction was typically better  
234 than 1 ‰ ( $1\sigma$ ). In a several cases, with co-elutions of peaks, it exceeded 2 ‰ ( $1\sigma$ ). For thiadamantanes  
235 in the sulfidic fraction, the precision was usually worse than for the aromatic fraction because of  
236 co-elution of compounds and noisy background and mean standard deviation can exceed 2 ‰ ( $1\sigma$ ). The  
237 accuracy of the analyses of petroleum samples was estimated to be better than 2 ‰.

### 238 *3.6 Stable carbon isotope analyses of whole oils and oil fractions*

239 Stable carbon isotopic compositions of whole oils, saturates and aromatics were determined  
240 following procedures similar to those described by Sofer (1980). Carbon dioxide was prepared by  
241 combusting (850°C, 2 h) aliquots (0.5–1 mg) of petroleum samples in clean, evacuated quartz tubes  
242 containing Cu(II)O, Ag and Cu metals. Following combustion, the samples were allowed to cool slowly  
243 (1 °C/min) to room temperature in order to ensure reduction of any nitrous oxides. The resultant CO<sub>2</sub>  
244 was separated cryogenically and carbon isotope ratios were measured using a VG SIRA 12 mass  
245 spectrometer. All data were corrected for <sup>17</sup>O effects (Craig, 1957) and reported in conventional delta ( $\delta$ )  
246 notation in per mil (‰) relative to VPDB. Accuracy and reproducibility of carbon isotopic data were  
247 assessed by replicate analysis of the international standard NBS 22. The mean of eight replicates  
248 (-29.60 ‰) was identical within experimental error to the value reported by Gonfiantini et al. (1995) and  
249 gave a precision of  $\pm 0.04$  ‰.

### 250 *3.7 Compound specific stable carbon isotope analyses*

251 For compound specific  $\delta^{13}\text{C}$  analyses, a method similar to Li et al. (2010) was used. Normal  
252 alkanes were isolated from the saturated hydrocarbon fractions of the oils with 5Å molecular sieves.  
253 Subsequently the analyses were carried out on a Micromass IsoPrime mass spectrometer attached to a HP  
254 6890 GC. A 60 m  $\times$  0.25 mm i.d. capillary column coated with 0.25  $\mu\text{m}$  5% phenylmethylsilicone  
255 stationary phase was fitted to the GC. The GC oven was programmed from 50°C to 310°C at 3 °C/min  
256 with initial and final holding times of 1 min and 30 min, respectively. Helium was used as the carrier gas  
257 at a flow rate of 1 ml/min with the injector operating at constant flow.

258 The  $\delta^{13}\text{C}$  values were calculated by the integration of the masses 44, 45 and 46 ion current counts of  
259 the  $\text{CO}_2$  peaks produced by the combustion (copper oxide reaction furnace at 850 °C) of hydrocarbons  
260 separated by GC. A  $\text{CO}_2$  reference gas (calibrated relative to the PeeDee Belemnite (‰, PDB) with a  
261 known  $\delta^{13}\text{C}$  value was pulsed into the mass spectrometer and the isotopic composition of samples was  
262 reported in the  $\delta$  notation relative to the reference gas. The average values of at least two runs for each  
263 sample have here been reported and only results with a standard deviation of less than 0.3 ‰ were used.

## 264 **4. Results**

### 265 *4.1 H<sub>2</sub>S and bulk oil sulfur concentrations and $\delta^{34}\text{S}$ values*

266  $\text{H}_2\text{S}$  was detected in almost all Ordovician and Cambrian reservoirs with concentrations in the gas  
267 phase from 0.05 to 11% and an average of 2.59% (n=34; Table S1). The  $\text{H}_2\text{S}$  in Ordovician reservoirs has  
268  $\delta^{34}\text{S}$  values from 13.3 to 23.4 ‰ with an average of 16.8 ‰ (n=15, Table S1), which is significantly  
269 lighter than that in the underlying Lower Cambrian reservoir from well ZS1 at the depth of 6,580 to 6,835  
270 m (33.0 ‰).

271 Oil samples from the Cambrian and Ordovician reservoirs have sulfur concentrations from 0.05 to  
272 0.69% with an average of 0.24 and  $\delta^{34}\text{S}$  from 13.2 to 25.9 ‰ with an average of 17.7 ‰ (n=33, Table S1).  
273 Oil samples from Ordovician reservoirs have  $\delta^{34}\text{S}$  values that are uncorrelated with either sulfur  
274 concentrations or with the associated  $\text{H}_2\text{S}$  concentrations (Figs. 3a & b). Most oils from Ordovician  
275 reservoirs, have bulk  $\delta^{34}\text{S}$  values close to the associated  $\text{H}_2\text{S}$   $\delta^{34}\text{S}$  values (Fig. 3c). In contrast, three oils  
276 from Cambrian reservoirs in wells ZS1 and ZS5 have  $\delta^{34}\text{S}$  value of 18.1 to 25.9 ‰; the average (22.3 ‰)  
277 is about 11 ‰ lower than the  $\text{H}_2\text{S}$   $\delta^{34}\text{S}$  value in the Lower Cambrian reservoir.

### 278 *4.2 Concentrations of alkyl 2-thiaadamantanes and DBTs*

279 All oils analyzed were found to contain alkyl 2-thiaadamantanes (TAs) with total TAs concentrations  
280 ranging from 2.2 to 1,937  $\mu\text{g/g}$  oil (n=24). Cambrian ZS1C oil has the highest total TAs concentration  
281 which is associated with the highest  $\text{H}_2\text{S}$  concentration (11%) found in this area (Table S1). The TAs  
282 detected include 21 compounds from  $\text{C}_0$  to  $\text{C}_5$  2-thiaadamantanes, among which 1, 5-DM  
283 2-thiaadamantane has the highest concentration, and shows co-variation with total TAs (Table 2). On



284 average, TAs are composed of 15% C<sub>1</sub> 2-thiaadamantanes, 38% C<sub>2</sub> 2-thiaadamantanes, 30% C<sub>3</sub>  
285 2-thiaadamantanes and 14% C<sub>2</sub> 2-thiaadamantanes.

286 The oils with total TAs concentrations greater than 100 µg/g oil include ZS1C, ZG46, TZ83, ZG6  
287 and ZG5 samples (TZ201C oil was not analyzed). Total TAs concentration displays no correlation with  
288 the associated H<sub>2</sub>S concentration (Fig. 4a), however, they display a crude positive linear correlation with  
289 bulk oil δ<sup>34</sup>S values for all the oils produced from the Ordovician with R<sup>2</sup> of 0.27 (n=20) (Fig. 4b).

290 DBTs concentrations range from 590 to 32,288 µg/g oil with an average of 3,786 µg/g (n=18; Table  
291 S1). DBT to phenanthrene (DBT/Phen) ratios show a wide range from 0.05 to 23.6 with an average of  
292 3.01 (n=32). For the Ordovician oils, DBT/Phen has an average of 2.57, and broadly correlates with the  
293 TAs concentrations with a R<sup>2</sup> of 0.46 (Fig. 5a); DBTs have a mean concentration of 1,886 µg/g oil, and  
294 show poorer correlations to both TAs concentrations and the DBT/Phen ratio with R<sup>2</sup> of 0.33 and 0.37,  
295 respectively (Figs. 5b & c). For the oils in the Cambrian reservoirs, ZS1C oil show the highest  
296 DBT/Phen ratio and DBTs concentration among all oils analyzed, and three other oils (ZS1-Z, ZS1-L and  
297 ZS5) have DBT/Phen ratios less than 0.5, significantly lower than ZS1C oil and an average of the  
298 Ordovician oils.

### 299 **4.3 δ<sup>34</sup>S values of individual OSCs and their relationships to TAs concentrations and DBT/Phen**

300 Individual OSCs from 16 oils from Cambrian and Ordovician reservoirs have a wide distribution of  
301 δ<sup>34</sup>S values, ranging from +12.3 ‰ to +41.8 ‰ (Table 4; Figs. 6a & b). The averaged δ<sup>34</sup>S values are  
302 25.8 ‰ for BTs, 20.2 ‰ for DBTs, 29.8 ‰ for TAs and 24.4 ‰ for thiolanes. The maximum difference  
303 between individual compounds within the same oil reaches up to 17.2 ‰ in the ZG46 oil. The following  
304 features can be summarized from Figs. 6A & B:

305 1) Except for ZG46, TZ201 and ZG8 oils, oils produced from Ordovician reservoirs have variable  
306 DBT/Phen ratios, from 1.3 in ZG432 oil to 6.6 in TZ83 oil (Table S1). However, they have small  
307 variations in DBTs δ<sup>34</sup>S values, mainly from 15.5 to 20.5 ‰ with averages from 16.2 to 19.4 ‰ (Table 3).  
308 Individual and averaged DBTs δ<sup>34</sup>S values do not show correlation with DBT/Phen ratios but are close to  
309 those from the ZS1-L and ZS5 Cambrian oils, which are from 16.6 to 23.0 ‰ for individual compounds

310 and 21.6 ‰ and 17.9 ‰ on average. The DBTs  $\delta^{34}\text{S}$  values of Ordovician oils are significantly  $^{34}\text{S}$   
311 depleted compared to those of ZG46, ZS1C and TZ201C oils with averages from 24.1 to 36.2 ‰. DBTs  
312 in ZS1C oil have  $\delta^{34}\text{S}$  values (from 34.3 to 38.5 ‰) that are higher and less variable than the ZG46 oil  
313 (24.6 to 32.2 ‰) and TZ201C oil (19.6 to 29.2 ‰).

314 2) ZS1-L oil has BTs  $\delta^{34}\text{S}$  values similar to those of DBTs, with differences ( $\delta^{34}\text{S}_{\text{BTs}} - \delta^{34}\text{S}_{\text{DBTs}}$ ) at an  
315 average <2 ‰. All other oils analyzed have BTs  $\delta^{34}\text{S}$  values higher than the DBTs  $\delta^{34}\text{S}$  values, and the  
316 difference in average values ranges from 2.8 ‰ in TZ83 oil to 7.7 ‰ in ZG8 oil. All oils, except ZG46,  
317 TZ201C and ZG432, have the highest  $\delta^{34}\text{S}$  value for 1-MeDBT among the DBTs, which is generally close  
318 to, or slightly lower than, the lowest  $\delta^{34}\text{S}$  values for BTs.

319 3) Different to other oils, TZ201C and ZG46 oils display an increase in  $\delta^{34}\text{S}$  values with increasing  
320 carbon number for BTs and DBTs with the maximum differences of 14.1 ‰ and 15.6 ‰ for TZ201 oil,  
321 9.6 ‰ and 7.4 ‰ for ZG46 oil, respectively.

322 4) TAs have  $\delta^{34}\text{S}$  values close to, or slightly higher than, BTs  $\delta^{34}\text{S}$  values. ZS1C, ZG46 and  
323 TZ201C oils have TAs  $\delta^{34}\text{S}$  values from 35.5 to 41.8 ‰, which are significantly higher than those of  
324 Phanerozoic seawater sulfates and any resulting sulfate-mineral-bearing evaporites. TAs  $\delta^{34}\text{S}$  values  
325 from five other oils from Ordovician reservoirs show a relatively small range from 22.3 to 25.6 ‰ and are  
326 significantly heavier than the DBTs  $\delta^{34}\text{S}$  values, which range from 15.7 to 20.5 ‰.

327 5) TAs  $\delta^{34}\text{S}$  values do not show correlation with their concentrations for any of the eight oils that  
328 were analyzed.

329 6) ZG46 and TZ201C oils have thiolane  $\delta^{34}\text{S}$  values with a mean of 20.9 ‰ similar to other  
330 Ordovician oils with a mean of 23.1 ‰ which is different from TAs and DBTs  $\delta^{34}\text{S}$  values of these oils.  
331 Ordovician oils have thiolane  $\delta^{34}\text{S}$  values ranging from 19.6 to 25.0 ‰, which are thus significantly lower  
332 than those of ZS1C oil (36.0 to 38.5 ‰).

333 7) ZG46 and TZ201 oils have thiolane  $\delta^{34}\text{S}$  values that are close to dimethylbenzothiophene  
334 (DMeBT) but about 10 ‰  $^{34}\text{S}$  depleted compared to other BTs. All other Ordovician oils have thiolane  
335  $\delta^{34}\text{S}$  values close to those of the BTs with a mean of 22.3 ‰ and the  $\delta^{34}\text{S}$  of  $\text{H}_2\text{S}$  gas in this area which

336 ranges mainly from 15 to 23 ‰.

#### 337 **4.4 $\delta^{13}\text{C}$ values of bulk oils and individual *n*-alkanes and relationship to TAs concentrations**

338 Six oils were analyzed for individual  $\text{C}_{14}$  -  $\text{C}_{33}$  *n*-alkane  $\delta^{13}\text{C}$  values in this study and another eight  
339 were collated from Li et al. (2015) and Cai et al. (2015a) (Table S2). Of these, ZS1C oil is most  
340 enriched in  $^{13}\text{C}$  whilst ZS1-Z oil is most  $^{13}\text{C}$  depleted. Of the Ordovician oils, TZ83-O<sub>1</sub> oil is most  
341 enriched in  $^{13}\text{C}$ .

342 Oils from Ordovician reservoirs have bulk  $\delta^{13}\text{C}$  values from -32.5 to -30.3 ‰ (n=20) and saturate  
343 fractions from -32.7 to -30.3 ‰ (n=15) (Table S1). All the oils from Ordovician reservoirs, except ZG46  
344 and TZ201C oils, have TAs concentrations that positively correlate with bulk oil and saturated fraction  
345  $\delta^{13}\text{C}$  values with correlation coefficient  $R^2$  of 0.43 and 0.56, respectively (Figs. 7a & b). Oils produced  
346 from both the Cambrian (ZS5, ZS1-Z and ZS1-L oils) and Ordovician (ZG432 oil) show similarly low  
347 TAs concentrations and  $^{13}\text{C}$  depleted bulk oils and *n*-alkanes (Tables S1 and S2).

348 The *n*-alkane  $\delta^{13}\text{C}$  values, DBT/Phen ratio and TAs concentrations of TZ201C and ZG46 oils range  
349 between equivalent values from ZS1C and ZG432 oils.

#### 350 **4.5 $\delta^{34}\text{S}$ values of anhydrite and barite**

351 Anhydrite in Middle and Lower Cambrian rock samples from wells ZS5 and BT5 was analyzed and  
352 gave  $\delta^{34}\text{S}$  values from 28.9 to 34.1 ‰ (n=5; Table 4). The values are close to those in wells TC1 and F1  
353 (26.8 ‰ and 33.7 ‰, respectively; Cai et al., 2002), but considerably higher than those from the Upper  
354 Cambrian in well TZ75 from 14.4 to 19.8 ‰ (Jia et al., 2015).

355 Significantly, barite from Upper Ordovician rock from ZG51 has a  $\delta^{34}\text{S}$  value of 46.1 ‰, which is  
356 close to values reported from wells TZ12 and TZ162 (from 42.1 to 46.6 ‰; Table 4; Cai et al., 2008).

#### 357 **4.6 Classification of the oil samples into discrete groups**

358 The oils analyzed can be classified into four groups (Fig. 8):

- 359 • Group I oil is represented by ZS1C (Fig. 6a), which was produced from a Cambrian  
360 reservoir. This oil has the highest DBT/Phen ratio and TAs concentration. It also has the  
361 most  $^{34}\text{S}$  enriched TAs, DBTs, BTs and thiolanes, and the most  $^{13}\text{C}$  enriched *n*-alkanes.

- 362           • Group II oils, including TZ201 and ZG46 (Fig. 6b), come from Lower Ordovician  
363           reservoirs, and have a range of characteristics between Group I and Group IV oils,  
364           including significantly higher TAs concentrations and more <sup>34</sup>S enriched TAs and DBTs  
365           than Group III, and IV oils. Thiolanes from this group of oils have an average  $\delta^{34}\text{S}$  value  
366           of 20.9 ‰, which is significantly lighter than that of the Group I oil (37.4 ‰) but close to  
367           those of Group III and IV oils (23.1 ‰).
- 368           • Group III oils, including TZ83, ZG43, ZG431, ZG5, ZG501, ZG8, ZG511, ZG12, ZG11,  
369           ZG22, ZG462, ZG6, ZG7 and possibly ZG54 (Fig. 6b), come from Ordovician reservoirs,  
370           have TAs concentrations >22  $\mu\text{g/g}$ , and most have DBT/Phen ratios that are > 2.0. Group  
371           III oils have  $\delta^{13}\text{C}$  values that range between those from Group I and Group IV oils, but have  
372           similar DBTs  $\delta^{34}\text{S}$  values to the Group IV oils.
- 373           • Group IV oils, include ZG432, TZ821-1, ZG13 and possibly ZG54 oils (Fig. 6a) produced  
374           from Ordovician reservoirs and ZS5, ZS1-Z and ZS1-L oils produced from Cambrian  
375           reservoirs. These oils have TAs concentrations of <20  $\mu\text{g/g}$ , DBT/Phen ratios < 2.0 and  
376           they have most <sup>3</sup>C depleted *n*-alkanes. This group can be further divided into group IV  
377           oils (ZG432, TZ821-1, ZG13 and ZS5) with similar thiolanes and BTs  $\delta^{34}\text{S}$  values but  
378           significantly <sup>34</sup>S enriched relative to the DBTs, and group IV oils (ZS1-Z and ZS1-L) with  
379           similar BTs and DBTs  $\delta^{34}\text{S}$  values.

380

## 381 **5. Discussion**

### 382 ***5.1 Thiolanes and benzothiophenes sulfur isotopes and origins***

#### 383 *5.1.1 Thiolanes $\delta^{34}\text{S}$ represents recent or ongoing TSR and H<sub>2</sub>S-oil reaction*

384           Thiolanes, because of their low thermal stability and high rates of formation (Table 1; Sinninghe  
385           Damsté and De Leeuw, 1990), represent reaction of hydrocarbons with the instantaneous H<sub>2</sub>S, or the last  
386           portion of H<sub>2</sub>S that the oils have encountered (Amrani et al., 2009, Gvirtzman et al., 2015). No  
387           significant sulfur isotope fractionation has been found to occur during the incorporation of reduced sulfur

388 into DBTs and organic sulfides (Amrani et al., 2006; Gvirtzman et al., 2015). We can therefore infer the  
389  $\delta^{34}\text{S}$  of the TSR-derived  $\text{H}_2\text{S}$ , by using the thiolanes'  $\delta^{34}\text{S}$  values, to be 22.5 ‰ on average (calculated  
390 from Group II, III and IV Ordovician oils) which is about 5 ‰ higher than that of averaged kerogen and  
391 kerogen-derived DBTs.

392 Group I oil has thiolane  $\delta^{34}\text{S}$  values almost as high as those for TAs, DBTs and BTs (Figs. 6 and 8).  
393 The small variation in the  $\delta^{34}\text{S}$  values of Group I (ZS1C) oil indicates that all these organic sulfur species  
394 were derived from advanced and ongoing TSR alteration that replaced or overwhelmed their original  $\delta^{34}\text{S}$   
395 values. A similar scenario was proposed previously for the extensively-TSR altered Smackover oils in  
396 Big Escambia Creek and South State Line wells (Amrani et al., 2012; Gvirtzman et al., 2015). Group III  
397 and IV Ordovician oils have a mean thiolane  $\delta^{34}\text{S}$  value of 23.1 ‰, which is 5.6 ‰  $^{34}\text{S}$  enriched compared  
398 to that of averaged DBTs of this oil, but close to TSR- $\text{H}_2\text{S}$  in the Ordovician, suggesting that the thiolanes  
399 were generated by TSR- $\text{H}_2\text{S}$  incorporation in the Ordovician *in situ*, as proposed by Cai et al. (2009b).  
400 Group II oils show similar thiolane  $\delta^{34}\text{S}$  values to that of Group III and IV oils, and thus have a similar  
401 sulfur origin as will be discussed later in more details.

#### 402 5.1.2 Benzothiophene $\delta^{34}\text{S}$ represents recent or ongoing TSR and $\text{H}_2\text{S}$ -oil reaction

403 BTs, especially the more alkylated species, are more thermally-stable than thiolanes, but are much less  
404 stable than DBTs and TAs (Table 1; Amrani et al., 2009; Gvirtzman et al., 2015). Therefore, DBTs will  
405 change their  $\delta^{34}\text{S}$  values more slowly in response to secondary generation or charge of  $\text{H}_2\text{S}$  than BTs (Fig  
406 9). This is consistent with BTs having  $^{34}\text{S}$  enriched values as a function of their increasing degree of  
407 alkylation or thermal stabilities (Fig. 6b). This indicates that less stable BTs species change their  $\delta^{34}\text{S}$   
408 values to greater degrees and are closer to the thiolanes and the source  $\text{H}_2\text{S}$   $\delta^{34}\text{S}$  value of  $\sim 22.5$  ‰ while  
409 the more stable (more alkylated) BTs are closer to DBTs. Laboratory heating experiments with  $^{34}\text{S}$   
410 depleted elemental S and  $^{34}\text{S}$  enriched petroleum sample have shown similar CSSI pattern for the BTs,  
411 with the less stable BTs getting closer the elemental S  $\delta^{34}\text{S}$  value while the more alkylated BTs and DBTs  
412 almost unchanged (Gvirtzman et al., 2015).

413

## 414 ***5.2 Origin of TAs and their use as a proxy to indicate TSR extents***

### 415 *5.2.1 Cambrian Reservoirs*

416 Given the elevated  $\delta^{34}\text{S}$  values of group I ZS1C oil in the Cambrian reservoir, DBTs were probably  
417 generated from the incorporation of TSR- $\text{H}_2\text{S}$ , as proposed by Cai et al. (2015a), Li et al. (2015) and  
418 Zhang et al. (2015). TAs from this oil have a similar origin, as indicated by the concentration of 1,937  
419  $\mu\text{g/g}$  being significantly higher than the TSR limit as proposed by Wei et al. (2012) and their TAs  $\delta^{34}\text{S}$   
420 values ranging from 38.4 to 41.4 ‰. The  $\delta^{34}\text{S}$  values are, on average, 22 ‰ higher than the proposed  
421 source rock kerogen  $\delta^{34}\text{S}$  values (10.4 to 21.6 ‰; Cai et al., 2009a and 2015a), indicating that the TAs are  
422 unlikely to have been derived from these source rocks. Moreover, the  $\delta^{34}\text{S}$  values of TAs of Group I  
423 ZS1C oil are 2 to 8 ‰ higher than those of the  $\text{H}_2\text{S}$  in well ZS1 (33.0 ‰) and the Cambrian seawater  
424 sulfate (from 28.9 to 33.7 ‰ with an average of 31.5 ‰; Table 4). The difference in  $\delta^{34}\text{S}$  values may  
425 plausibly result from two processes:

426 1) The incorporated TSR- $\text{H}_2\text{S}$  was generated from a local,  $^{34}\text{S}$ -enriched sulfate, either from TSR  
427 residual sulfates (after being reduced to very limited concentrations in a closed system during advanced  
428 stages of TSR), or inherited from the local environment with limited sulfate supply to sulfate-reducing  
429 bacteria during deposition and early diagenesis. No sedimentary or early diagenetic anhydrite has been  
430 found to have enriched  $\delta^{34}\text{S}$  values (Table 4), indicating that the  $^{34}\text{S}$  enriched sulfate may be residual  
431 following advanced TSR. This option is supported by the fracture-filling barite and formation water in  
432 the Ordovician from different locations having similar  $\delta^{34}\text{S}$  values to the TAs (from 37 to 42 ‰; Table 4),  
433 although they are not spatially associated.

434 2) Sulfur isotope fractionation occurred during TSR- $\text{H}_2\text{S}$  incorporation into TAs or a different and  
435 unknown process occurred that created TAs enriched in  $^{34}\text{S}$ , and the residual  $\text{H}_2\text{S}$  was  $^{34}\text{S}$ -depleted.  
436 However, a recent study has shown that the formation of TAs from the reaction of elemental sulfur and  
437 adamantane at elevated temperatures, has only small and negative fractionation (up to 3 ‰) relative to the  
438 initial S (Gvirtzman et al., 2015).

439 Further work needs to be undertaken to clarify the origin of the elevated  $\delta^{34}\text{S}$  values in TAs of Group

440 I ZS1C oil, the fracture-filling sulfate in the reservoir and dissolved sulfate in the formation water.

441 Group IV Cambrian oils with low concentrations of TAs (2.2 to 19.0  $\mu\text{g/g}$ ) have no  $\delta^{34}\text{S}$  values  
442 available, thus their origin cannot be positively identified. However, a case study from North America  
443 showed that TAs, in a slightly TSR-altered Smackover Formation oil from Sugar Ridge, have  
444 concentrations of 87  $\mu\text{g/g}$ , and  $\delta^{34}\text{S}$  values from 0 to 6.2 ‰ (Gvirtzman et al., 2015). These  $\delta^{34}\text{S}$  values  
445 are significantly lower than those of another oil from the Smackover Formation with TAs of 1,282  $\mu\text{g/g}$   
446 from South State Line well (from 21.6 to 26.5 ‰) and lower than that of coeval Jurassic seawater sulfates  
447 during the deposition of the source rock (18 to 22 ‰) (Claypool et al., 1980; Wei et al., 2012; Gvirtzman  
448 et al., 2015). The Smackover example suggests that some of the TAs in low TAs concentration oils were  
449 derived from the source rock. Thus, by analogy it is reasonable to conclude that part, if not all, of the  
450 TAs in the three Group IV Cambrian oils from the Tarim Basin were derived from Lower Cambrian source  
451 rocks. This proposal is supported by these oils having the lowest TAs concentrations,  $\text{H}_2\text{S}$   
452 concentrations less than 0.04% and lowest bulk oil  $\delta^{34}\text{S}$  values, saturates and individual *n*-alkane  $\delta^{13}\text{C}$   
453 values of all the oils analyzed (Tables S1 & S2 and Cai et al., 2015b), and by their BTs and DBTs  $\delta^{34}\text{S}$   
454 values close to the Cambrian source rocks (Fig. 6a and Cai et al., 2015a).

### 455 5.2.2 Ordovician Reservoirs

456 Individual TAs  $\delta^{34}\text{S}$  values of Group III oils, from 22.2 to 26.6 ‰, are close to the coeval Ordovician  
457 seawater sulfate (Claypool et al., 1980), but significantly  $^{34}\text{S}$  enriched relative to source rock kerogen  
458 (from 10.5 to 20.4 ‰) and  $^{34}\text{S}$ -depleted compared to Group I ZS1C oil, indicating that the TAs were  
459 probably generated by TSR *in situ* (i.e. in their present day reservoir).

460 The positive correlation between TAs concentrations and the  $\delta^{13}\text{C}$  values of bulk oil and saturates of  
461 group IV and III oils from the Ordovician (Figs. 7a & b) may be explained by two possible hypotheses:

462 1) Mixing of the heavily TSR-altered Group I oil (ZS1C) with non-TSR-altered oil Group IV oil, as  
463 suggested by Zhang et al. (2015).

464 2)  $^{13}\text{C}$  depleted saturates were preferentially oxidized and thus residues become  $^{13}\text{C}$  enriched with  
465 increasing extent of TSR.

466 Hypothesis 1 seems unlikely to be valid. Group I oil has DBTs  $\delta^{34}\text{S}$  values that are significantly  
467 higher than these oils; thus, if mixing had occurred, a positive correlation would be expected between  
468 DBTs  $\delta^{34}\text{S}$  values and both TAs concentrations and DBT/Phen ratios. The absence of such correlations  
469 (non-correlations not illustrated, but see data in Tables S1 and 3) argues against mixing.

470 Hypothesis 2 seems to be more feasible. Group IV ZG432 and TZ821-1 oils may not be  
471 significantly altered by TSR, as indicated by low TAs concentrations of 18.0 and 18.9  $\mu\text{g/g}$  and  
472 correspondingly low *n*-alkane  $\delta^{13}\text{C}$  values from -33.2 to -35.0 ‰ and -33.4 to -35.1 ‰. These  $\delta^{13}\text{C}$   
473 values are very close to those of minimal-TSR Group IV ZS5 oil in this study and Group IV ZS1-Z and  
474 YM2 oils from Cai et al. (2015a), with no TSR-induced preferential oxidization of  $^{12}\text{C}$ -rich *n*-alkanes.

475 Group III oils (TZ83, ZG5, ZG43, ZG8 and ZG431) have been altered by TSR to different degrees  
476 and thus have higher concentrations of TAs (>22  $\mu\text{g/g}$ ) and slightly higher *n*-alkane  $\delta^{13}\text{C}$  values than  
477 Group IV oils. Thus, if the elevated TAs concentrations resulted from TSR, it is plausible that the shift  
478 in  $\delta^{13}\text{C}$  value could have the same origin. If these oils had mixed with ZS1C oil (hypothesis 1) then we  
479 would have expected to find a positive correlation between TAs concentrations and TAs  $\delta^{34}\text{S}$  values  
480 because Group I ZS1C oil has highly  $^{34}\text{S}$  enriched TAs (Figs 6 & 8). Although these oils contain variable  
481 TAs concentrations, from 22 to 140  $\mu\text{g/g}$ , the differences in averaged TAs  $\delta^{34}\text{S}$  values are within 2 ‰,  
482 thus it is unlikely for these oils to have mixed with Group I ZS1C oil. This lack of mixing also is  
483 supported by DBTs  $\delta^{34}\text{S}$  values (See section 5. 4).

484 Overall, therefore, the positive correlation between TAs concentrations and alkane  $\delta^{13}\text{C}$  values  
485 indicates that these parameters can be used to reveal the extent of TSR in the Ordovician reservoirs.

### 486 ***5.3 Origin of Group II Ordovician oils***

#### 487 ***5.3.1 DBTs $\delta^{34}\text{S}$ values suggest mixing origin for Group II Ordovician oils***

488 It has been proposed that  $^{13}\text{C}$ -enriched, methane-dominated dry gas migrated upwards from the  
489 Cambrian during the Himalayan orogeny during the Neogene along several intersections between NNW  
490 strike-slip fault and No.1 fault-slope (Figs. 1B and 2A), resulting in elevated gas/oil ratios and oil wax  
491 contents (Pang et al., 2013; Wang et al., 2014; Cai et al., 2015b). It is possible that Group I oil also



492 up-migrated from the Cambrian along similar pathways during this period and mixed with other oils  
493 (Zhang et al., 2015).

494 Group II TZ201C and ZG46 oils, produced from Ordovician reservoirs, are likely to be mixtures  
495 between ZS1C TSR-altered Cambrian oil and a non-TSR altered Ordovician oil, such as ZG432 oil.  
496 These two oils have TAs concentrations and  $\delta^{34}\text{S}$  values ranging between those of other Ordovician oils  
497 and Group I ZS1C oil (Fig. 6 and Table 3). A simple calculation (Table 5) shows that the differences  
498 between: (i) the mixture of Group IV ZG432 oil and Group I ZS1C oil in a proportion of 9:1 and (ii)  
499 Group II ZG46 oil are within  $\pm 0.4\%$  in saturate fraction and most of  $\text{C}_{15}\text{-C}_{28}$   $n$ -alkane  $\delta^{13}\text{C}$  values, and  
500  $0.9\%$  for averaged DBTs  $\delta^{34}\text{S}$  values. This calculation supports the interpreted mixing between Group  
501 IV ZG432 and Group I ZS1C oils to have resulted in Group II ZG46 oil. Group II TZ201C oil has  
502 geochemical characteristics that are broadly similar to the Group II ZG46 oil (Table S1 and Fig. 6), and  
503 thus may also have a similar mixed origin. This proposal is further supported by geological evidence  
504 which shows that wells ZG46 and TZ201C are located near to the intersection between No. ZG8  
505 strike-slip and No.10 fault (Fig. 1B). It seems that oil and gas may have up-migrated along different  
506 pathways with up-migration of Group I oil along No. ZG8 strike-slip and No.10 fault in the southern  
507 Tazhong Uplift (Figs. 1B and 9) and up-migration of the gas along the northern boundary. The  
508 migration may have occurred during the Late Cretaceous to Neogene (Cai et al., 2009b and references  
509 therein).

### 510 **5.3.2 Thiolanes $\delta^{34}\text{S}$ values suggest “in situ” TSR or $\text{H}_2\text{S}$ charge for Group II Ordovician oils**

511 Since Group II oils have TAs and DBTs that probably derived from mixing of Group I oil with a  
512 non-TSR affected oil, they should have had thiolanes contributed from Group I oil. However, Group II  
513 oils have thiolane and DMeBTs  $\delta^{34}\text{S}$  values about  $17\%$  lower than Group I oil and close to groups III and  
514 IV oils but DBTs and TAs  $\delta^{34}\text{S}$  values significantly higher than Group III and IV oils. These  
515 observations suggest two sequential steps for the abnormal CSSI record of Group II oils. First, there was  
516 a charge from Group I Cambrian oil that entered Group II oil reservoirs and changed the OSCs  $\delta^{34}\text{S}$  values  
517 by mixing, as discussed above. Second, a new generation of OSCs from  $^{34}\text{S}$ -depleted  $\text{H}_2\text{S}$  (around  $22.5\%$

518 as discussed in section 5.1) in the Ordovician (“*in-situ*”) changed the  $\delta^{34}\text{S}$  values of the mixed oils of  
519 Group II. Since thiolanes are the least thermally stable of all the sulfur compounds measured in this  
520 study, their  $\delta^{34}\text{S}$  will respond rapidly and intensively to a charge of  $\text{H}_2\text{S}$  or *in-situ* TSR. Gradually, with  
521 prolonged TSR or  $\text{H}_2\text{S}$  exposure, other more thermally-stable compounds will change their  $\delta^{34}\text{S}$  values  
522 toward that of the external sulfur source as shown by the average thiolane  $\delta^{34}\text{S}$  value of 22.5 ‰ for all  
523 Ordovician oils. This scenario is supported by Group II oils having  $\delta^{34}\text{S}$  values of the first DMeBT, the  
524 least thermally stable BTs analyzed, similar to thiolanes and BTs of Group III and IV Ordovician oils,  
525 indicating that all these oils have a similar sulfur source, probably from  $\text{H}_2\text{S}$  of *in-situ* TSR.

#### 526 ***5.4 DBTs $\delta^{34}\text{S}$ values suggest high sulfur source rock and incipient-TSR origin for Group III***

##### 527 ***Ordovician oils***

528 Group III and IV Ordovician oils do not show obvious mixing features. Group III oils show  
529 individual DBTs  $\delta^{34}\text{S}$  values close to those of Group IV oils (Fig. 6a & b), those of other non- or  
530 minor-TSR altered oils reported previously (Cai et al., 2015a and Li et al., 2015), and Cambrian kerogens  
531 from 10.4 to 21.6 ‰ with an average of 17.3 ‰ (n=9; Cai et al., 2009a; 2015a). These new data further  
532 support the interpretation that the DBTs found in oils produced from both Cambrian and Ordovician  
533 reservoirs were not considerably TSR-altered and instead were probably derived directly from Cambrian  
534 source rocks. However, this proposal seems to contradict the positive correlation between the DBT/Phen  
535 ratio and TAs concentrations (Fig. 5a) since TAs concentrations reflect TSR extents. Thus, an increase  
536 in the DBT/Phen ratio may result from increasing amounts of DBTs generated during TSR if the  
537 phenanthrene concentrations remained constant. However, the DBT/Phen ratio has been found to  
538 decrease with increasing maturity of oil (Zhang et al., 2015), and neither TAs concentration nor the  
539 DBT/Phen ratio are significantly correlated with DBTs concentrations (Fig. 5b & c). Thus, it seems that  
540 both increasing maturity and extent of TSR are responsible for the elevated DBT/Phen ratio.

541 If TSR resulted in an increase of DBTs concentration from 1,923  $\mu\text{g/g}$  in Group IV ZG13 non-TSR  
542 oil to 2,526  $\mu\text{g/g}$  in Group III TZ83 oil, then this extra amount of DBTs (603  $\mu\text{g/g}$ ) should have  $\delta^{34}\text{S}$   
543 values that are 5.2 ‰ higher than the non-TSR altered DBTs. Isotope mass balance calculations. by

544 adding TSR-derived DBTs (about one quarter of the total DBTs) to Group IV ZG13 oil, lead to a positive  
545 shift of about 1.2 ‰ in  $\delta^{34}\text{S}$  value of total DBTs as in Group III TZ83 oil. That is, the mixing of small  
546 proportions of TSR-derived DBTs is expected to change the total DBTs values by only a small amount  
547 and DBTs in Group III oils that remain dominated by kerogen-derived DBTs. This is the most likely  
548 reason why Group III and IV oils have variable TAs concentrations and extents of TSR but show broadly  
549 similar DBTs  $\delta^{34}\text{S}$  values. Thus, it can be concluded that the high DBTs concentrations in Group III oils  
550 may have been predominantly derived from high sulfur kerogen in the Cambrian, mixing with small  
551 amounts of TSR-derived DBTs.

552 Group IV Ordovician ZG13 oil in the Tazhong area experienced only a minor degree of TSR, as  
553 indicated by TAs concentrations as low as 15.5  $\mu\text{g/g}$ , but has DBTs concentrations of 1,923  $\mu\text{g/g}$  (Li et al.,  
554 2015). This suggests that such elevated DBTs concentrations can be the result of source rock  
555 depositional conditions and maturation processes with little or no influence of TSR. Group III TZ83 oil  
556 can be interpreted to be the most TSR-altered oil in the Ordovician as it has the highest TAs concentration  
557 (140.2  $\mu\text{g/g}$ ), the most  $^{13}\text{C}$  enriched *n*-alkanes (average of -30.64 ‰) and the highest DBTs concentration  
558 (2,526  $\mu\text{g/g}$ ) of all Ordovician samples. These values can be compared to negligibly TSR-altered Group  
559 IV oil (ZG13) with its TAs concentration of 15.5  $\mu\text{g/g}$ , a low saturates  $\delta^{13}\text{C}$  value of -31.82 ‰ and a  
560 relatively low DBTs concentration 1,923  $\mu\text{g/g}$ . This probably means that TAs and DBTs concentrations  
561 increased by 125  $\mu\text{g/g}$  and by 600  $\mu\text{g/g}$ , respectively, as a result of TSR alteration, which was, however,  
562 not followed by resolvable change in  $\delta^{34}\text{S}$  values of the DBTs.

563 In summary,  $\delta^{34}\text{S}$  values of the DBTs depend on the ratio of TSR- to kerogen-derived DBTs with  
564  $\delta^{34}\text{S}$  value of TSR-DBTs in the Ordovician reservoirs of about 22.5 ‰ and kerogen-derived DBTs  
565 averaged of 17.3 ‰. It is generally assumed that no sulfur isotope fractionation occurs during TSR in  
566 the majority of petroleum basins (Orr, 1974; Cai et al., 2003; 2004). The justification for this assumption  
567 is that the overall rate limiting step in TSR is probably the dissolution of  $\text{CaSO}_4$  to free sulfate ions  
568 (Machel et al., 1995; Worden and Smalley, 1996). No significant sulfur isotope fractionation has also  
569 been found to occur during the incorporation of reduced sulfur into DBTs or organic sulfides (Amrani et

570 al., 2006; Gvirtzman et al., 2015).

571

## 572 **6. Conclusions**

- 573 1. Oils from Ordovician and Cambrian reservoirs in the Tarim Basin, China were generated from  
574 Lower Cambrian source rocks. These oils have been divided into four distinct groups that  
575 represent different extents of TSR alteration and mixing. Group IV represents the lowest  
576 (negligible) degree of TSR-alteration. Group III represents a small degree of TSR alteration.  
577 Group I represents highly TSR-altered oil.
- 578 2. A charge of the Group I highly TSR-altered oil from Cambrian into Ordovician reservoirs with  
579 Group IV oil led to Group II oil. Group II oils experienced further *in-situ* TSR which affected  
580 the  $\delta^{34}\text{S}$  values of the less thermally stable thiolanes and BTs toward  $\text{H}_2\text{S}$  values of Ordovician  
581 reservoirs, but did not significantly affect the  $\delta^{34}\text{S}$  of more thermally stable TAs and DBTs.
- 582 3. The  $\delta^{34}\text{S}$  of thiolanes, because of their low thermal stability and high rates of formation,  
583 represent back-reaction of oil with very recent TSR-generated  $\text{H}_2\text{S}$ . They can therefore be used  
584 as proxy for *in-situ*  $\text{H}_2\text{S}$   $\delta^{34}\text{S}$  value.
- 585 4. Cambrian source rocks in the Tarim Basin contribute low concentrations of TAs (<20  $\mu\text{g/g}$ ).  
586 Therefore, TAs concentrations can be used to reflect extent of TSR. Moreover, because TAs  
587 are mainly formed during TSR, they quickly adopt the TSR- $\text{H}_2\text{S}$   $\delta^{34}\text{S}$  values and preserve them  
588 for prolonged times, even after TSR has ceased or a secondary charge of  $\text{H}_2\text{S}$  has up migrated  
589 into the reservoir.
- 590 5. Source rocks contributed up to 2,000  $\mu\text{g/g}$  DBTs, and thus their  $\delta^{34}\text{S}$  values can be used for  
591 oil-source rock correlation when TSR has not proceeded to a great extent. In TSR-altered oils,  
592 the  $\delta^{34}\text{S}$  values of DBTs are controlled by the ratio between the original DBTs content and the  
593 newly formed DBTs from TSR. In the Tarim Basin, only oils that have experienced high  
594 degrees of TSR have DBTs with  $\delta^{34}\text{S}$  values that approach the parent sulfate in the reservoir.
- 595 6. These results show that CSSI of different OSCs, with different thermal stabilities and formation

596 pathways, not only differentiate between oils of TSR and non-TSR origin, but can also reveal  
597 information about the relative timing of secondary charge events and migration pathways.

598

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## Table Captions

759 Table 1: Summary of the origins and thermal stability of the main sulfur compounds found in the

760 Cambrian and Ordovician oil samples in the Tarim Basin.

761 Table 2: Concentrations of specific alkylthiaadamantane compounds ( $\mu\text{g/g}$ ) in oil samples.

762 Table 3: Sulfur isotope values of alkylbenzothiophenes, alkyl dibenzothiophenes, alkylthiaadamantane,

763 alkylthiophenes and alkylthiolanes compounds and their averages.

764 Table 4: Sulfur isotope values of different occurrence of anhydrite and barite.

765 Table 5: Chemical composition and  $\delta^{34}\text{S}$  and  $\delta^{13}\text{C}$  values of the mixture between ZS432 and ZS1C oil in

766 9:1 by calculation.

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## Figure Captions

770

771 Fig. 1: (A) General map showing the location of the Tarim Basin and the Tazhong Uplift (B) Detailed map  
772 showing geological structures of the Tazhong uplift and locations of some sampled wells with  
773 location of cross sections AB and CD.

774 Fig. 2: (A) Cross section AB showing distribution of oil, gas and water in the Ordovician reservoirs and  
775 faults. Note that wells ZG46 and TZ201C (see Fig. 1) are located near ZG8 fault. (B) Cross section  
776 CD showing oil and gas distribution in the Cambrian.

777 Fig. 3: Variation of whole oil  $\delta^{34}\text{S}$  value vs (A) oil sulfur content, (B)  $\text{H}_2\text{S}$  concentration in separated gas,  
778 and (C)  $\text{H}_2\text{S}$   $\delta^{34}\text{S}$  values.

779 Fig. 4: Relationships of total alkylthiaadamantanes (TAs) concentration of oil in the Ordovician reservoirs  
780 to, (A)  $\text{H}_2\text{S}$  concentration, and (B) bulk oil  $\delta^{34}\text{S}$  value.

781 Fig. 5: Variation of, (A) total TAs concentrations vs DBT/phenanthrene ratios, (B) total TAs  
782 concentrations vs total DBTs concentrations, and (C) total DBTs concentrations vs DBT/phenanthrene  
783 ratios, for oils in the Ordovician reservoirs.

784 Fig. 6: Individual alkylthiaadamantanes (TAs), alkyldibenzothiophenes (DBTs), alkylbenzothiophenes  
785 (BTs) and alkylthiolanes (TIs)  $\delta^{34}\text{S}$  values from oils from the Cambrian and Ordovician reservoirs. TAs  
786 compounds were identified based on Wei et al. (2007; 2012). These oils are divided into Group I (red),  
787 II (brown), III (blue) and IV (green) oils.

788 Fig. 7: Relationships of total alkylthiaadamantanes (TAs) concentrations of oils in the Ordovician  
789 reservoirs compared to, (A) bulk oil  $\delta^{13}\text{C}$  values, and (B) saturates  $\delta^{13}\text{C}$  values. Note that regression  
790 lines and  $R^2$  are for the Ordovician oils only.

791 Fig. 8: Synthesis diagram representing the sulfur isotope values of the main classes of organosulfur  
792 compounds in the four groups of oils discerned in this study.

793 Fig. 9: Cross section with migration of the four discerned groups of oils in the Lower Paleozoic of the  
794 Tarim Basin

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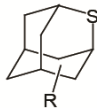
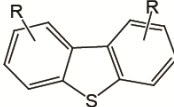
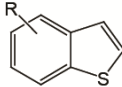
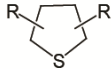
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## Appendices

797 Table S1: H<sub>2</sub>S concentration of associated gas phase (%), sulfur content of oil samples (%), concentrations  
798 of total alkylthiaadamantane and total alkyl dibenzothiophenes (μg/g), dibenzothiophene/phenanthrene  
799 ratio, sulfur isotope ratio of H<sub>2</sub>S and bulk oil and carbon isotope values of saturate, aromatic, resin and  
800 asphaltene fractions and whole oil.

801 Table S2: Carbon isotope values of C<sub>14</sub> to C<sub>33</sub> normal alkanes of oils.

802

Compound types and description	Structure
<p><b>TAs (Thiaadamantanes):</b> stable compounds in trace concentration in the source kerogen. Created during TSR and rapidly dominates kerogen-derived TAs and survives to the present day</p>	
<p><b>DBTs (Dibenzothiophenes):</b> stable compounds in variable concentration in the source rock. Created during TSR, slowly dominates kerogen-derived DBTs and survives to the present day.</p>	
<p><b>BTs (Benzothiophenes):</b> low stability compounds, created early during TSR but breaks down rapidly. Stability is increasing with alkylation degree. Low alkylated BTs adopts the <i>in-situ</i> H<sub>2</sub>S δ<sup>34</sup>S value rapidly.</p>	
<p><b>TLs (thiolanaes):</b> low stability compounds, created early following TSR but breaks down reflecting sulfur isotope equilibrium between H<sub>2</sub>S and organic S. In the presence of H<sub>2</sub>S they can reach high steady state concentrations. They adopts the <i>in-situ</i> H<sub>2</sub>S δ<sup>34</sup>S value rapidly.</p>	
<p>H<sub>2</sub>S: small quantity derived from kerogen, produced during TSR, but is reactive so can be lost from gas, large quantity produced when TSR is ongoing at an advanced stage</p>	


  
 Increasing thermal stability

**Table 2**

No.	Ion	Well Name	ZS1C	ZG46	TZ83	ZG14-1	ZG511	ZG11	ZG12	TZ44	ZG22	ZG43	ZG431	ZG433C	ZG45	ZG462
		Group-code	I-1	II-2	III-4	III-5	III-6	III-7	III-8	III-9	III-10	III-11	III-12	III-13	III-14	III-15
		Compound ( $\mu\text{g/g}$ . oil)														
1	154	2-thiaadamantane	0.12	0.32	0.51	0.61	0.47	0.32	0.30	0.34	0.50	0.19	0.26	0.90	0.45	1.08
2	168	5-methyl-2-thiaadamantane	35.47	21.03	9.56	3.56	4.55	3.99	3.93	2.33	4.56	3.97	3.05	6.32	4.76	8.55
3	168	1-methyl-2-thiaadamantane	40.80	17.11	8.99	2.92	3.30	2.50	3.43	2.13	2.74	1.96	1.59	3.27	2.37	5.14
4	182	5,7-dimethyl-2-thiaadamantane	80.29	12.28	7.60	2.77	3.73	2.84	5.10	1.84	2.51	2.85	1.45	2.11	3.12	5.08
5	182	1,5-dimethyl-2-thiaadamantane	356.73	53.38	35.74	13.07	14.47	13.52	23.58	8.40	12.20	11.88	6.10	10.22	13.63	20.85
6	182	1,3-dimethyl-2-thiaadamantane	118.32	14.51	7.75	2.28	2.53	1.88	3.54	1.80	1.94	1.42	0.89	1.51	1.57	4.28
7	196	C3-2-thiaadamantane	247.94	15.66	14.45	4.93	6.39	4.50	9.45	3.46	3.77	4.15	1.75	2.11	4.75	6.65
8	196	C3-2-thiaadamantane	274.27	15.75	16.94	5.63	6.22	5.50	10.00	4.08	4.36	4.43	1.97	2.59	5.09	6.43
9	196	C3-2-thiaadamantane	163.05	11.53	7.65	2.45	2.66	2.58	4.36	1.55	2.02	1.93	1.10	1.62	2.40	4.16
10	196	C3-2-thiaadamantane	84.48	8.08	6.02	2.02	2.50	1.99	3.12	1.29	1.71	1.69	0.93	1.48	2.16	3.16
11	210	C4-2-thiaadamantane	89.10	3.33	4.94	1.53	2.05	1.32	2.53	1.30	1.06	1.20	0.48	0.51	1.39	1.55
12	210	C4-2-thiaadamantane	71.97	3.37	3.20	1.04	1.35	1.03	1.62	0.77	0.75	0.79	0.48	0.50	1.04	1.26
13	210	C4-2-thiaadamantane	42.66	2.53	2.16	0.74	1.08	0.65	1.09	0.54	0.59	0.60	0.31	0.40	0.76	1.06
14	210	C4-2-thiaadamantane	84.40	3.53	2.13	0.71	0.82	0.76	1.21	0.53	0.58	0.53	0.30	0.40	0.70	1.07
15	210	C4-2-thiaadamantane	56.59	3.77	4.01	1.11	1.64	1.13	1.90	0.95	1.02	0.97	0.50	0.69	1.29	1.51
16	210	C4-2-thiaadamantane	26.70	1.70	1.26	0.34	0.56	0.46	0.67	0.29	0.33	0.32	0.20	0.29	0.46	0.59
17	210	C4-2-thiaadamantane	61.76	3.15	2.36	0.68	1.00	0.76	1.39	0.53	0.67	0.64	0.35	0.46	0.82	1.20
18	210	C4-2-thiaadamantane	12.49	1.78	1.66	--	--	--	--	--	--	0.39	0.25	--	--	--
19	224	C5-2-thiaadamantane	15.75	0.66	1.03	0.26	0.38	0.23	0.41	0.27	0.21	0.21	0.10	0.13	0.29	0.29
20	224	C5-2-thiaadamantane	21.13	0.74	0.62	0.18	0.26	0.21	0.32	0.18	0.15	0.15	0.09	0.11	0.22	0.26
21	224	C5-2-thiaadamantane	40.71	1.09	1.17	0.33	0.46	0.33	0.63	0.29	0.28	0.28	0.13	0.15	0.37	0.44
22	224	C5-2-thiaadamantane	11.91	0.51	0.42	0.12	0.20	0.13	0.19	0.11	0.11	0.11	0.06	0.08	0.15	0.21
Sum			1936.64	195.79	140.18	47.28	56.61	46.63	78.77	32.96	42.07	40.66	22.32	35.85	47.78	74.80

**Table 2 (continued)**

No.	Ion	Well Name	ZG5	ZG501	ZG6	ZG7	ZG8	ZG13	ZS1-Z	ZS1-L	ZS5	TZ821-1	ZG432	TZ243	ZG106
		Group-code	III-16	III-17	III-18	III-19	III-20	IV-21	IV-22	IV-23	IV-24	IV-25	IV-26	IV-27	IV-28
		Compound (µg/g. oil)													
1	154	2-thiaadamantane	0.09	0.47	0.50	0.96	0.20	0.43	0.33	0.19	0.15	0.31	0.45	0.14	0.09
2	168	5-methyl-2-thiaadamantane	7.17	3.07	6.77	9.62	6.80	2.78	0.06	1.10	0.19	1.27	2.19	0.73	1.33
3	168	1-methyl-2-thiaadamantane	4.42	1.73	6.02	6.51	4.03	1.47	0.07	0.69	0.13	0.89	1.27	0.54	0.77
4	182	5,7-dimethyl-2-thiaadamantane	7.06	2.12	6.49	6.78	4.71	0.84	0.27	1.51	0.15	1.40	1.02	0.78	1.21
5	182	1,5-dimethyl-2-thiaadamantane	30.23	7.61	34.37	28.77	24.34	4.83	0.36	5.15	0.54	4.72	4.84	2.43	4.89
6	182	1,3-dimethyl-2-thiaadamantane	3.77	1.14	8.97	4.58	3.24	0.65	0.08	0.72	0.09	0.78	0.77	0.47	0.51
7	196	C3-2-thiaadamantane	12.39	2.18	17.12	9.76	7.72	0.82	0.22	2.43	0.22	2.30	1.44	1.64	1.72
8	196	C3-2-thiaadamantane	12.89	2.61	23.07	10.51	9.59	1.09	0.18	2.23	0.21	2.25	1.72	1.47	1.80
9	196	C3-2-thiaadamantane	4.70	1.43	7.81	4.60	4.82	0.58	0.12	0.85	0.16	0.92	0.91	0.60	0.68
10	196	C3-2-thiaadamantane	3.99	1.25	5.80	4.34	3.81	0.57	0.09	0.73	0.17	0.72	0.80	0.45	0.56
11	210	C4-2-thiaadamantane	3.88	0.61	7.42	2.77	2.34	0.21	0.07	0.71	0.07	0.78	0.42	0.68	0.49
12	210	C4-2-thiaadamantane	2.08	0.62	4.22	2.01	1.75	0.21	0.07	0.41	0.08	0.45	0.34	0.35	0.26
13	210	C4-2-thiaadamantane	1.63	0.43	3.01	1.63	1.22	0.16	0.05	0.33	0.07	0.31	0.28	0.22	0.19
14	210	C4-2-thiaadamantane	1.32	0.37	3.50	1.24	1.34	0.15	0.05	0.28	0.06	0.28	0.27	0.24	0.17
15	210	C4-2-thiaadamantane	2.80	0.64	4.26	2.51	2.14	0.27	0.07	0.53	0.12	0.49	0.46	0.42	0.31
16	210	C4-2-thiaadamantane	0.86	0.25	1.44	0.85	0.80	0.11	0.03	0.17	0.04	0.15	0.17	0.11	0.10
17	210	C4-2-thiaadamantane	1.76	0.43	2.32	1.55	1.49	0.16	0.04	0.35	0.06	0.30	0.31	0.23	0.20
18	210	C4-2-thiaadamantane	0.92	0.32	--	--	1.04	--	0.02	0.17	0.06	0.16	--	--	--
19	224	C5-2-thiaadamantane	0.66	0.13	1.16	0.51	0.46	0.06	0.02	0.12	0.03	0.13	0.10	0.14	0.07
20	224	C5-2-thiaadamantane	0.42	0.11	0.87	0.35	0.36	0.05	0.02	0.09	0.02	0.08	0.08	0.09	0.05
21	224	C5-2-thiaadamantane	0.85	0.16	1.45	0.64	0.63	0.06	0.02	0.16	0.03	0.14	0.12	0.15	0.09
22	224	C5-2-thiaadamantane	0.29	0.07	0.64	0.26	0.25	0.03	0.01	0.06	0.01	0.05	0.06	0.05	0.04
Sum			104.19	27.75	147.20	100.75	83.06	15.54	2.24	19.00	2.65	18.91	18.02	11.92	15.55

-- No data available



**Table 3**

Compounds	ZS1C	ZG46	TZ201C	TZ83	ZG511	ZG12	ZG43	ZG431	ZG5	ZG501	ZG8	ZS1-L	ZS5	TZ821-1	ZG432	ZG54
Group-code	I-1	II-2	II-3	III-4	III-6	III-8	III-11	III-12	III-16	III-17	III-20	IV-23	IV-24	IV-25	IV-26	--
3/4-MeBT	--	--	--	--	--	--	--	--	--	--	21.2	21.2	--	21.8	26.3	--
DMeBT	40.4	23.2	20.6	22.3	--	--	25.3	23.4	24.2	25.3	20.7	25.2	--	21.5	--	--
DMeBT	--	28.5	26.1	19.6	--	--	23.5	22.1	--	22.2	25.2	--	--	20.4	23.3	--
TMeBT	--	28.8	25.7	21.1	--	--	23.9	22.8	22.0	26.1	22.1	--	--	20.6	23.4	--
TMeBT	--	33.8	30.4	20.0	--	--	24.1	21.9	20.8	24.0	19.7	23.3	33.1	18.8	22.5	--
TMeBT	--	29.0	27.1	20.1	--	--	24.3	23.3	21.0	25.0	20.0	23.6	33.5	20.4	23.7	--
C4-BT	--	38.8	35.0	21.1	--	--	24.6	19.7	22.3	--	21.2	--	--	19.6	21.9	--
C4-BT	--	35.9	33.1	--	--	--	24.0	21.8	--	22.0	19.5	23.3	33.3	20.2	23.7	--
Average	40.4	31.1	28.3	20.7	--	--	24.2	22.1	22.1	24.1	21.2	--	--	20.4	23.5	22.3
DBT	36.9	24.6	19.6	18.4	18.5	20.9	17.4	16.0	18.7	18.5	15.8	23.0	23.0	17.6	17.3	20.8
4-MeDBT	36.7	26.7	21.6	17.6	18.3	18.8	17.9	15.5	17.3	19.9	13.1	22.1	17.9	17.4	17.1	19.1
3/2-MeDBT	36.7	26.3	21.6	18.3	17.4	19.9	17.3	15.6	17.8	19.8	14.7	22.1	21.2	17.8	16.9	20.5
1-MeDBT	38.5	29.0	23.1	19.0	27.8	20.4	20.1	17.7	19.6	20.5	18.0	24.4		18.4	17.7	20.5
4-EtDBT		30.3	25.2	17.0	19.8	18.1	18.9	17.4	18.9	19.7	14.9	22.3	20.7	15.7	19.1	19.2
4,6-DMeDBT	36.0	27.5	23.9	16.9	18.1	18.0	17.4	16.0	16.2	20.1	10.7	20.3	13.0	17.7	17.5	19.5
2,4/2,6/3,6-DMeDBT	36.0	29.1	25.1	17.9	17.6	18.1	17.8	16.1	16.8	20.1	11.9	21.2	16.6	17.8	17.1	20.2
DMeDBT	36.3	29.3	25.4	18.8	17.7	19.4	17.8	15.7	18.3	19.9	14.9	20.8	22.9	17.7	16.5	19.7
TMeDBT	34.3	30.6	26.7	17.0	17.1	16.5	17.9	16.2	16.3	20.1	10.0	19.4	12.3	17.8	17.8	17.4
TMeDBT	34.4	32.0	29.2		16.7	16.1	18.0	15.7	16.7	20.4	11.2	20.3	13.6	17.9	17.5	16.5
Average	36.2	28.5	24.1	17.9	18.9	18.6	18.0	16.2	17.7	19.9	13.5	21.6	17.9	17.6	17.4	19.4
5,7-DMe/3,5,7-TMe-TA	40.4	39.8	37.2	24.7	--	--	22.7	22.5	22.6	22.7	--	--	--	--	--	--
5-Me-TA	38.4	38.8	37.9	24.1	--	--	23.5	24.8	25.2	23.1	--	--	--	--	--	--
1,5-DMe/1,5,7-TMe-TA	39.6	39.8	38.7	25.8	--	--	22.3	25.6	24.9	23.3	--	--	--	--	--	--
1-Me-TA	39.0	37.6	37.8	26.6	--	--			25.0	25.4	--	--	--	--	--	--
1,3-DMe-TA	39.9	40.3	39.3	24.4	--	--			24.6		--	--	--	--	--	--
C2/C3-TA	39.6	36.5	40.2	25.3	--	--	22.8	22.8		22.2	--	--	--	--	--	--

1,3,7-TMe-TA	39.4	--	41.8	25.4	--	--	23.4	26.2	23.2	23.1	--	--	--	--	--	--
1,3,5-TMe-TA	41.4	36.8	--	25.8	--	--	24.6	27.8	23.8	24.5	--	--	--	--	--	--
Average	39.7	38.5	39.0	25.3	--	--	23.2	24.9	24.2	23.5	--	--	--	--	--	--
C7-Thiolane	36.0	20.4	21.1		--	--	--	--	--	--	--	--	--	19.7	--	--
C8-Thiolane	37.0	20.2	21.9	21.7	--	--	--	--	--	--	--	--	--	20.0	--	--
C9-Thiolane	38.5	19.6	20.4	24.3	--	--	23.3	24.0	24.9	--	--	--	--	20.5	--	--
C10-Thiolane	38.3	20.9	22.7	25.0	--	--	23.7	22.9	24.0	--	--	--	--	21.9	--	--
Average	37.4	20.3	21.5	23.7			23.5	23.5	24.4					20.5		23.1

-- No data available; all in VCDT‰.

**Table 4**

Well	Strata	Depth (m)	Occurrence	$\delta^{34}\text{S}$ (‰)
TZ75	Upper Cambrian	4830.4	Fracture-filling An	15.2*
TZ75	Upper Cambrian	4804.5	Fracture-filling An	14.4*
TZ75	Upper Cambrian	4939.1	Fracture-filling An	19.8*
BT5	Middle Cambrian	5221.28	An nodule	34.1*
TC1	Middle Cambrian	6993	Bedded An	26.8**
ZS5	Middle Cambrian	6193.84	Bedded An	32.8
ZS5	Middle Cambrian	6222.17	An nodule	31.3
ZS5	Middle Cambrian	6535.73	Bedded An	28.9
ZS5	Lower Cambrian	6557.03	An nodule	33.1
F1	Lower Cambrian	4602	An nodule	33.7**
TZ12	Upper Ordovician	--	Barite	46.6***
TZ12	Upper Ordovician	--	Barite	45.3***
TZ162	Upper Ordovician	5979	Barite	42.1***
ZG51	Upper Ordovician	4500	Barite	46.1

-- No data available; An: anhydrite; \*: from Jia et al. (2015); \*\*: Cai et al. (2002);

\*\*\*: Cai et al. (2008);

**Table 5**

Item No.	Parameters	ZG432 oil (EM1)	ZS1C oil (EM2)	Mixture in 9:1 (Mix)	ZG46 oil	Differences
1	TAs concentration ( $\mu\text{g/g}$ )	18	1937	209	195.8	13.2
2	DBT/Phen ratio	1.3	23.1	3.5	3.9	-0.4
3	Bulk oil $\delta^{13}\text{C}$ (‰)	-32.1	-29.9	-31.8	-31.1	-0.7
4	TAs $\delta^{34}\text{S}$ average (‰)	Too low to be measured	39.7	Not known	38.5	
5	BTs $\delta^{34}\text{S}$ average (‰)	23.5	40.4	Not known due to unknown BTs concentrations	31.1	
6	DBTs $\delta^{34}\text{S}$ average (‰)	17.4	36.2	29.4	28.5	0.9
7	Saturates (‰)	-32.07	-30.4	-31.19	-31.4	-0.2
8	<i>n</i> -C <sub>15</sub> $\delta^{13}\text{C}$ (‰)	-34.82	-28.7	-34.21	-34.28	0.07
9	<i>n</i> -C <sub>19</sub> $\delta^{13}\text{C}$ (‰)	-34.31	-28.6	-33.74	-33.49	-0.25

Note: 1) Mix = (EM1×9+EM2×1)/10 for items 1, 2 & 3;

2) Mix = (EM1×concentration1×9 + EM2×concentration2×1)/(concentration1×9 + concentration2×1) for items 4, 5, 6, 7, 8, 9.

3) DBTs concentration of ZS432 oil relative to ZS1C oil is represented by their DBT/Phen ratio;

4) ZS432 and ZS1C oils have saturates contents of 73.4% and 57.3%, respectively. *n*-C<sub>15</sub> and *n*-C<sub>19</sub> contents in the ZS432 oil relative to ZS1C oil are represented by their saturate fraction contents.

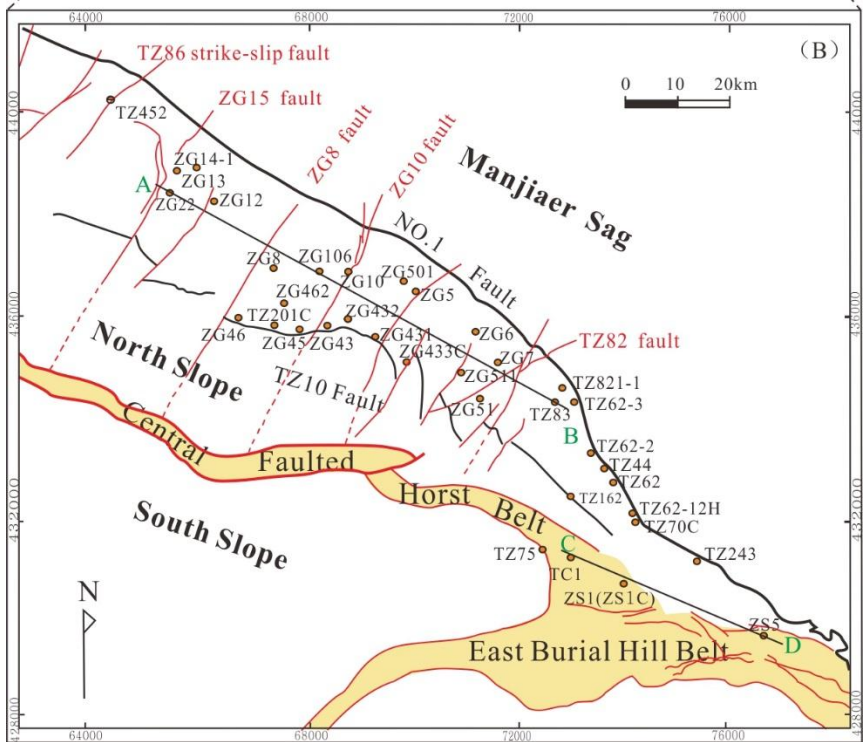
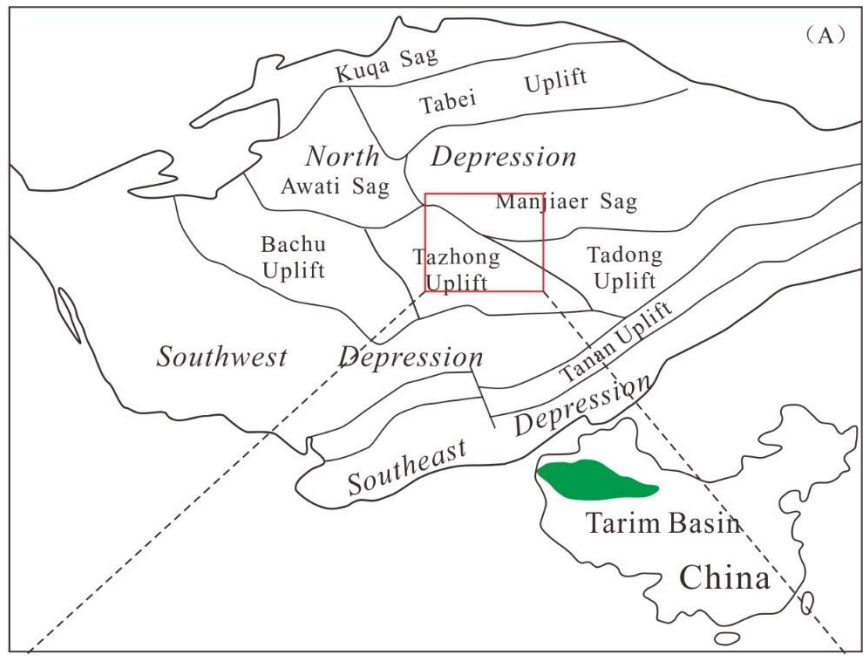


Figure 1

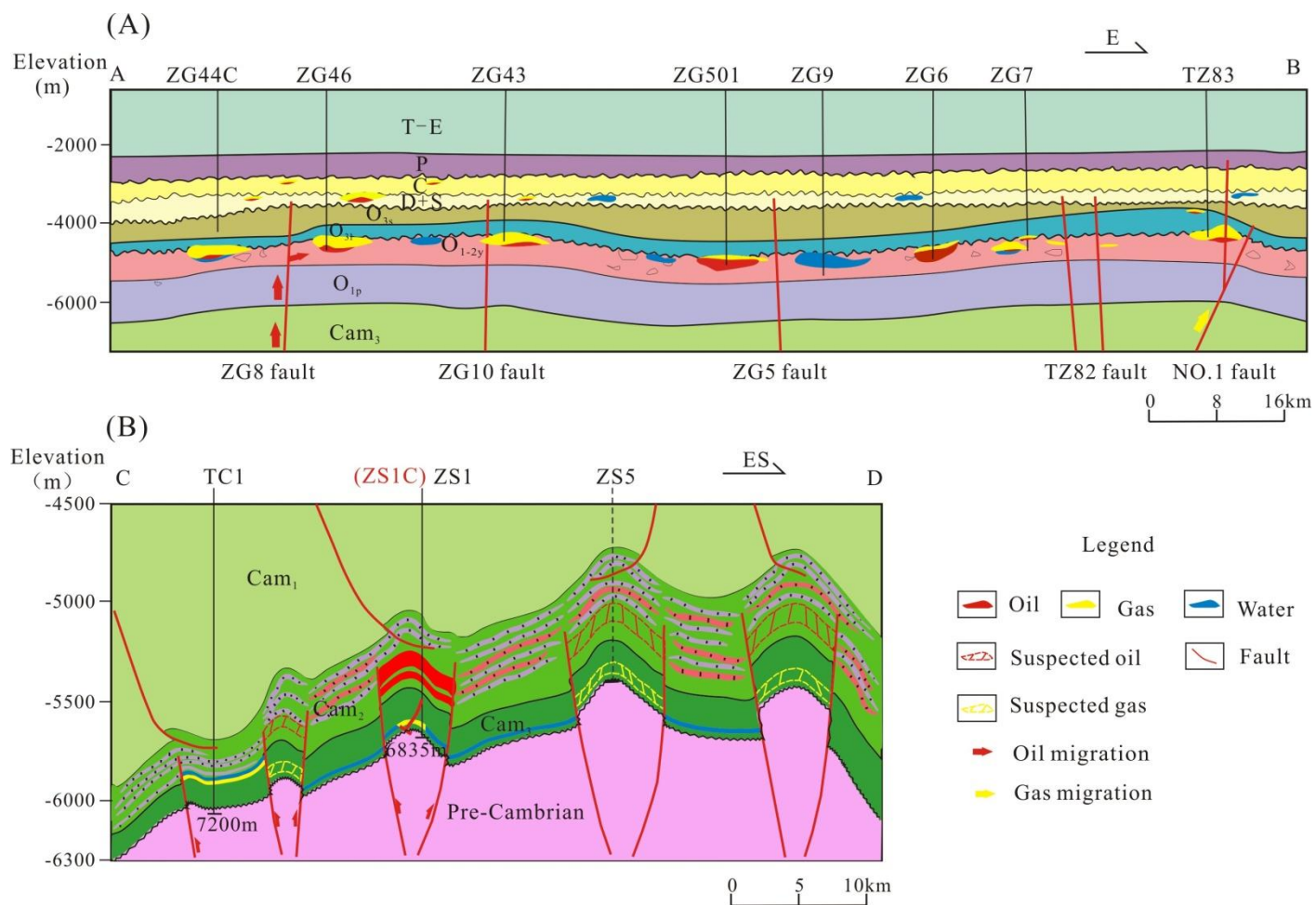


Figure 2

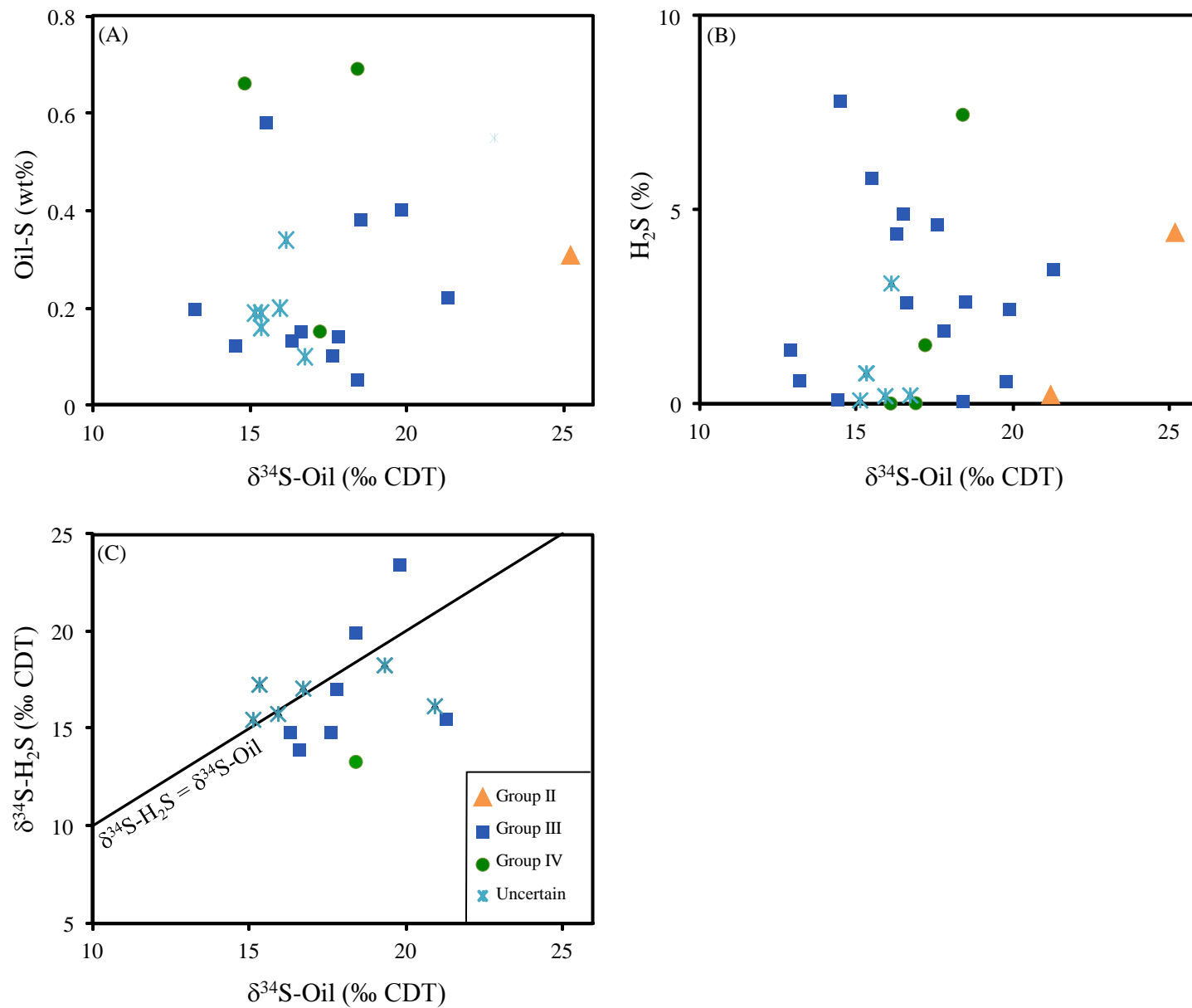


Figure 3



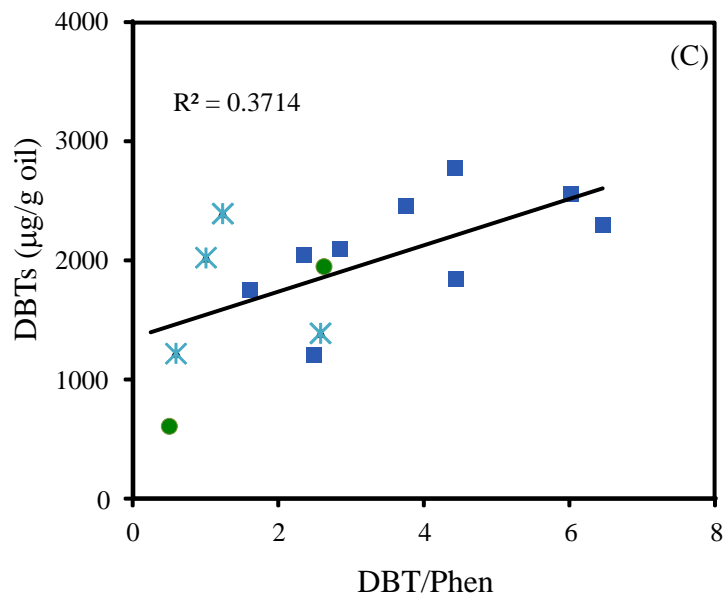
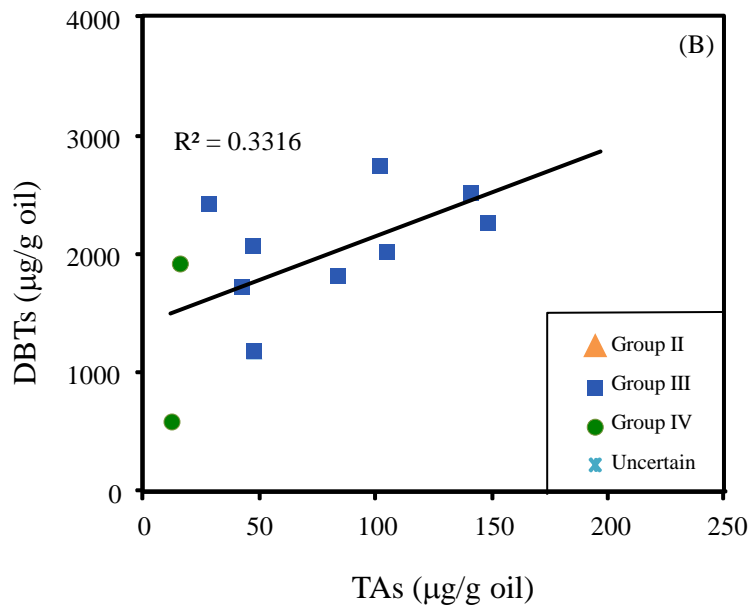
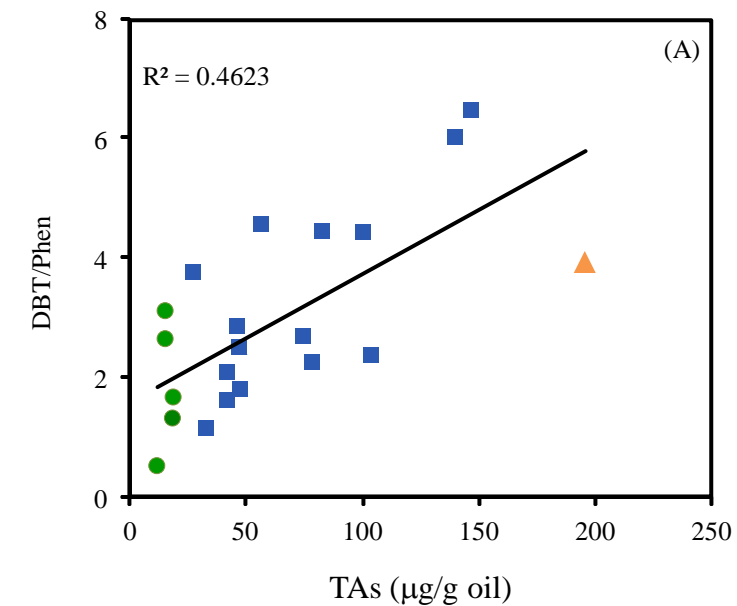


Figure 5



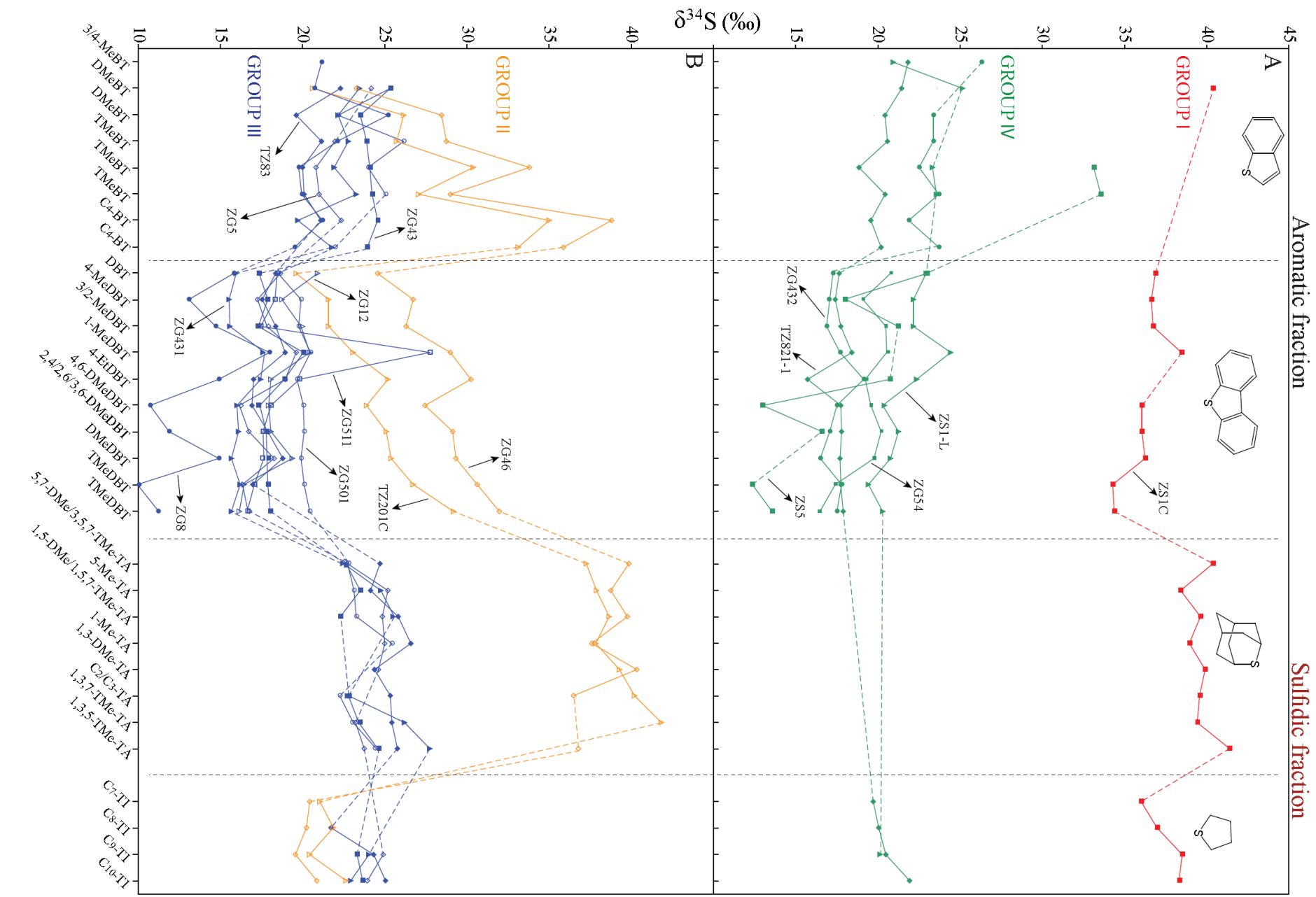


Figure 6

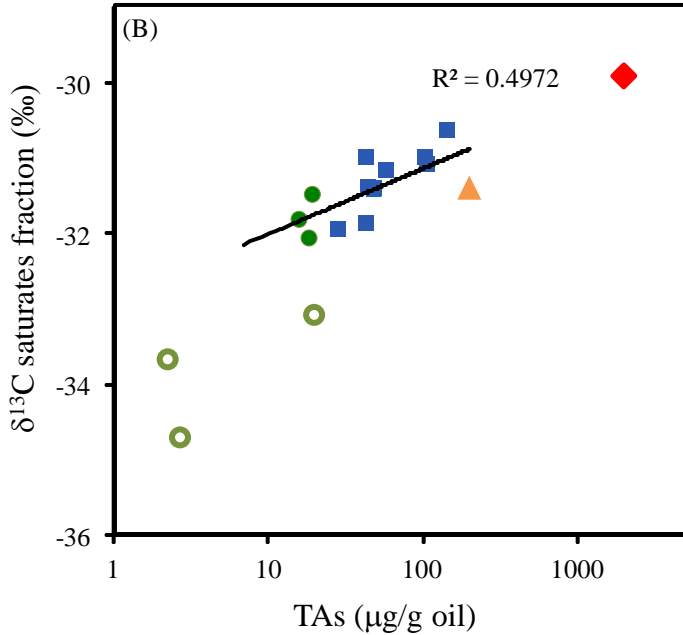
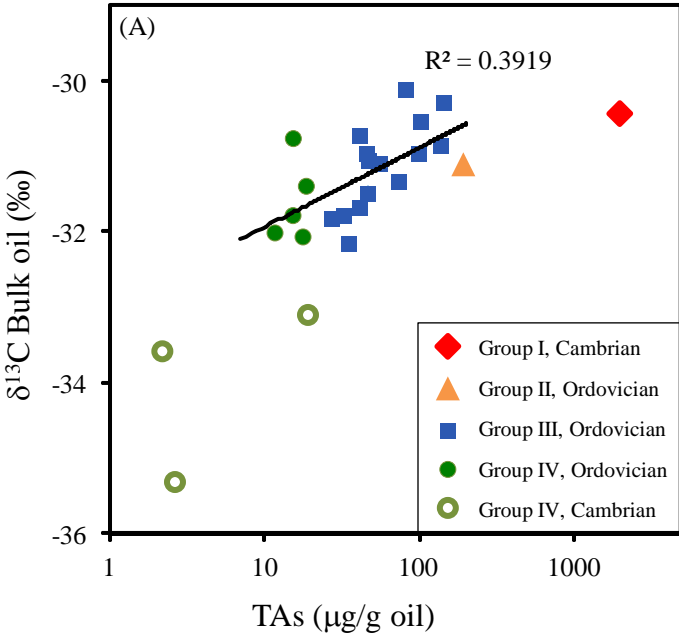


Figure 7

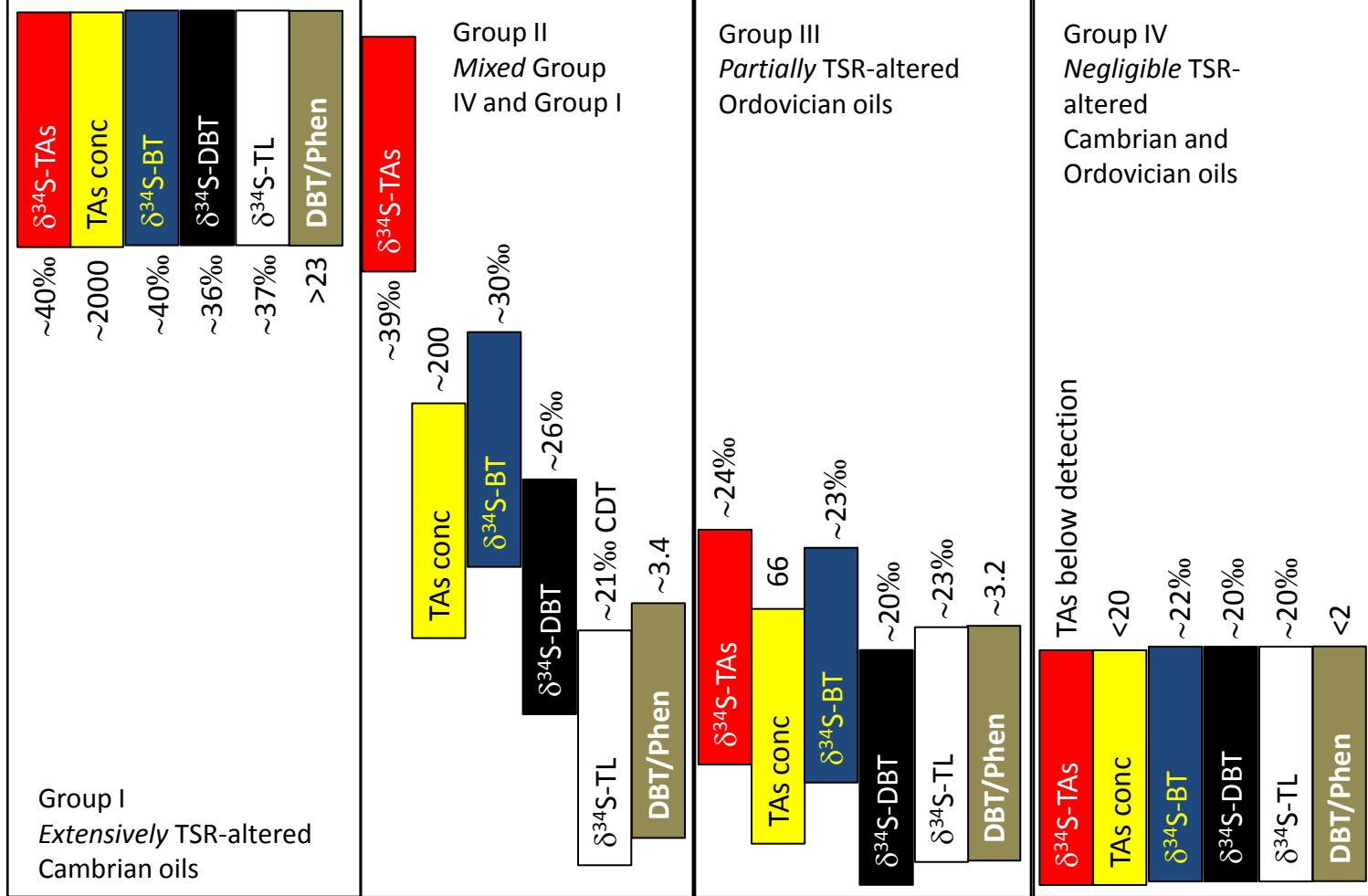
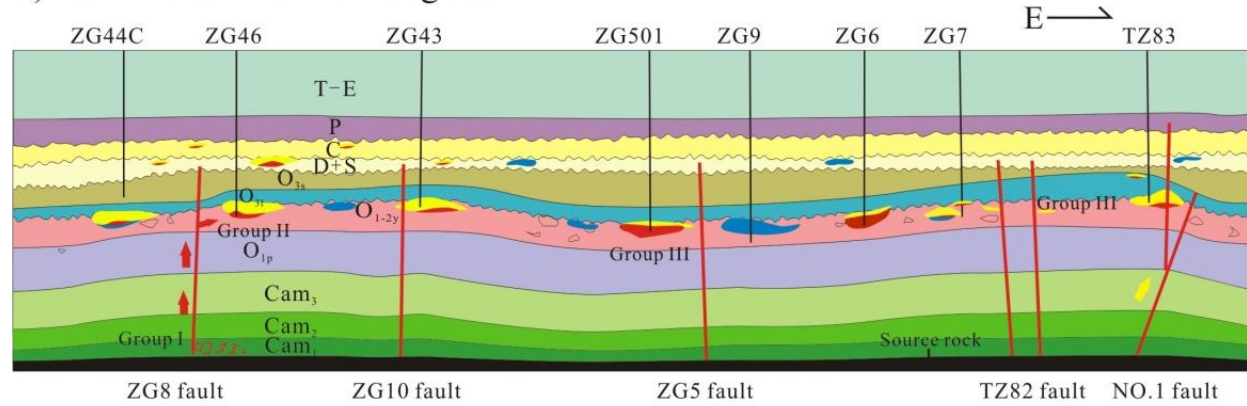
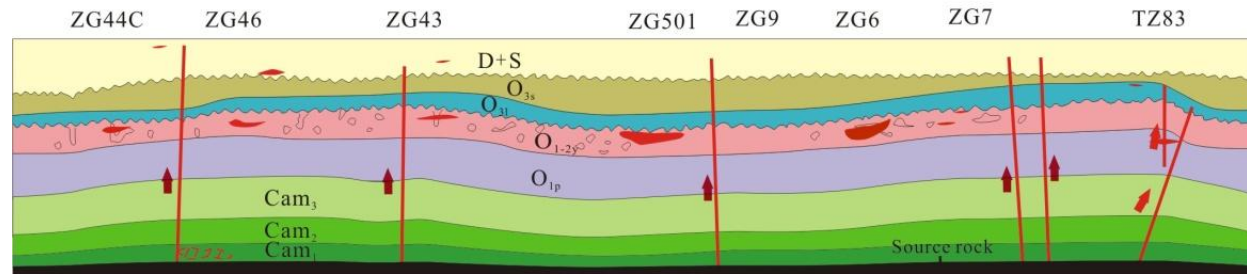


Figure 8

## 2) Late Cretaceous to Neogene



## 1) Late Silurian to early Devonian



Legend  Oil  Gas  Water  Suspected oil  Fault  Oil  Gas

Figure 9

## Appendix

[Click here to download Appendix: Appendix Tables S.docx](#)