Accepted Manuscript

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PII: S0146-6380(18)30154-2
DOI: <https://doi.org/10.1016/j.orggeochem.2018.07.003>
Reference: OG 3748

To appear in: *Organic Geochemistry*

Received Date: 23 May 2018
Revised Date: 28 June 2018
Accepted Date: 8 July 2018

Please cite this article as: Zhu, G., Zhang, Y., Zhang, Z., Li, T., He, N., Grice, K., Neng, Y., Greenwood, P., High abundance of alkylated diamondoids, thiadiamondoids and thioaromatics in recently discovered sulfur-rich LS2 condensate in the Tarim Basin, *Organic Geochemistry* (2018), doi: <https://doi.org/10.1016/j.orggeochem.2018.07.003>

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High abundance of alkylated diamondoids, thiadiamondoids and thioaromatics in recently discovered sulfur-rich LS2 condensate in the Tarim Basin

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2520.

Abstract

Molecular and stable sulfur isotopic ($\delta^{34}\text{S}$) analysis of petroleum recently discovered in the Bachu uplift of the Tarim Basin (China) was conducted to characterize the oil and assist future regional petroleum correlation studies. Sulfur rich condensate from the Lower Ordovician – Upper Cambrian reservoir rock in the LS2 well showed abundant aromatic hydrocarbons and organic sulfur compounds. Extensive distributions of alkylated caged hydrocarbons (i.e., diamondoids) and caged sulfur compounds (thiadiamondoids), including many additional isomers not previously detected in petroleum, were resolved by GC $\times$ GC-MS analysis. The thiadiamondoid products and thioaromatics (i.e., benzothiophenes, dibenzothiophenes), also detected in LS2, products were attributed to a major thermochemical sulfate reduction (TSR) event, which resulted in elevated H_2S (3.66%) and dry gas in the condensate. TSR might also have contributed to the generally heavier $\delta^{34}\text{S}$ values of the benzothiophenes (+26 to +28 ‰) compared to dibenzothiophenes (+20 to +27 ‰). The LS2 reservoir has no sulfate evaporites and the temperature (144 °C) is relatively low for TSR, implying that it is a secondary reservoir for migrated TSR-derived gas, possibly derived from deeper and hotter (>200 °C) Cambrian strata.

Keywords: Thiaadamantane; Adamantane; Condensate; Deep strata; Thermochemical Sulfate Reduction; Exploration

1. Introduction

The Tarim Basin is the largest oil- and gas-bearing basin in China and continues to afford tremendous exploration opportunities. A new and potentially lucrative petroleum play was confirmed in the LS2 well drilled a few years ago in the Bachu uplift of the Tarim Basin (Fig. 1). The Lower Ordovician - Upper Cambrian dolomite reservoir at a depth of 5,741-5,830 m is now producing commercially viable condensate. This resource, like most petroleum recovered

from deep Tarim Basin strata, is condensate-rich and has high H₂S content (3.66%). H₂S concentrations > 3% are typically attributed to thermochemical sulfate reduction (TSR), a high temperature redox reaction between hydrocarbons and inorganic sulfate (Orr, 1974; Krouse et al., 1988; Claypool and Maneini, 1989; Heydari and Moore, 1989; Machel et al., 1995; Machel, 1998; Worden et al., 1995; 2000; Carrigan et al., 1998; Hao et al., 2008; Zhang et al., 2008a).

To further evaluate the sources and TSR impacts on the LS2 petroleum, as well as provide useful organic geochemical data for regional petroleum correlation studies, we conducted detailed molecular and stable sulfur isotopic analyses on the LS2 condensate with particular focus on characterisation of abundant caged and organic sulfur compounds (OSCs) in the LS2 condensate. Several distinctive organic sulfur products (e.g., thiols, isoprenoid thiophenes, thioaromatics, thiadiamondoids) can be diagnostic of TSR (Cai et al., 2005; 2016; Zhang et al., 2005; Worden and Cai, 2006), although some of these products can also originate by diagenetic sulfurization (Sinningh Damste and de Leeuw, 1990). These products can show varied sensitivity to TSR and the $\delta^{34}\text{S}$ values of thioaromatic products may help identify the early stages of TSR (Amrani et al., 2012). The organic geochemical information acquired was integrated with the lithology and mineral composition of the LS2 reservoir.

2. Materials and methods

2.1 Well location and physical properties of condensate samples

The LS2 petroleum reservoir is located in the LS2 structure of the Luonan structural belt on the Maigaiti slope in the southwest depression of the Tarim Basin (Fig. 1a). It was drilled in 2016 to a depth of 6,080 m and produced light crude oil with low density, viscosity, wax and sulfur content. Daily gas and oil production rates are ~215,000 m³ and 3 m³, respectively. For the present study, condensate samples were taken from the Ordovician Penglaiba (O_{1p})

Formation at 5,741-5,830 m in the well (Fig. 1b-d). The physical and bulk geochemical character of four separately analysed petroleum samples were relatively stable with an average oil density of 0.826 g/cm³; viscosity between 1.084 MPa to 1.131 MPa; freezing point < -30 °C; wax content 1.2% to 1.4%; sulfur content 2.1% to 3.2%; high H₂S content (3.27-4.05%); colloid content 0.13% to 0.84% and asphaltene content 0.23% to 0.79%.

Mesozoic formations were missing from the entire Bachu uplift (Fig. 1b), while Devonian and Silurian sections were also absent from the LS2 well (Fig. 1c). The Ordovician LS2 strata were deposited as marine sediments and mainly consist of the Lower Ordovician Penglaiba Formation (O1p), which unconformably overlies Carboniferous strata. The Penglaiba Formation mainly comprised thick bedded grey dolomitic limestone, and some light grey limestone with thin beds of grey dolomitic conglomerates also occur in middle and lower sections. The Carboniferous and Permian strata are typical marine-terrigenous units (e.g., thick bed marlstones, calcareous mudstones and mudstones). Paleogene to Quaternary sedimentation was dominated by continental sandstone and mudstone.

The thermal gradient through the formation varied from highs of 28-34°C/km in Cambrian/Ordovician strata (moderated in Cambrian to lower end of this range by 600-1000 m gypsum and salt layers having relatively high thermal conductivity) to ~25°C/km in the Mesozoic and Cenozoic due to the development of post Paleozoic intracratonic and subsequent foreland phases in the basin (Qiu et al., 2012).

2.2 GC×GC-TOFMS Analysis

Whole oil samples were analysed on a Leco Corporation GC×GC-TOFMS instrument equipped with two Agilent GCs interfaced to a Pegasus 4D TOF mass spectrometer. A 50 m × 0.2 mm × 0.5 µm J&W DB-petro capillary column and a 3 m × 0.1 mm × 0.1 µm DB-17ht capillary column were used for the first and second dimension GC, respectively. The

concentrations of diamondoids, thiadiamondoids and other products were quantified on the basis of peak areas relative to an internal standard (D₁₆-adamantane). Further details of the sample pretreatment procedures and operating conditions for the GC×GC-TOFMS analysis of gas condensate can be found elsewhere (Zhu et al., 2013b).

2.3 Carbon isotopes of gaseous hydrocarbons

Carbon isotope analysis of the hydrocarbon constituents of the natural gas samples, collected in steel bottles at the production well site, were measured using a GC interfaced to a Thermo Scientific Delta V Advantage isotope ratio mass spectrometer. All $\delta^{13}\text{C}$ values are given in per mil (‰, VPDB) according to delta notation with standard deviation of $\pm 0.10\text{‰}$.

2.4 $\delta^{34}\text{S}$ measurement of OSCs

Compound specific sulfur isotope analysis (CSSIA) of the aromatic fraction (isolated by liquid chromatography) of the LS2 oils was conducted using an Agilent 6890 GC coupled to a Thermo Neptune Plus multi-collector inductively coupled plasma mass spectrometer (ICP-MS) as described by Greenwood et al (2018). The OSCs were separated on the GC with a DB-5 MS column (30 m $\times$ 0.25 mm i.d. $\times$ 0.1 μm film thickness). $\delta^{34}\text{S}$ values (‰) of the most abundant alkylated benzothiophene and dibenzothiophene products were measured relative to the international sulfur isotope standard Vienna Canyon Diablo Troilite (VCDT). Reported values represent the average of duplicate analyses and the variance of the two measured values was expressed as standard variation (SV $\pm$).

The OSCs were identified based on correlation of their GC elution position with published data (e.g., Garcia et al., 2002; Asif et al., 2009). Methyl dibenzothiophene isomers were identified, but isomeric assignment of higher molecular-weight alkyl dibenzothiophenes (and

alkyl benzothiophenes) was not attempted and are simply referred to as isomers i-iv (i.e., $\delta^{34}\text{S}$ data were measured for up to four different isomers of some OSCs).

3. Results and discussion

3.1 Molecular composition of LS condensates

GC×GC-MS analysis of the LS2 condensates identified more than 5,000 compounds with signal-to-noise ratios >100 in the LS2 condensate. The two-dimensional (2D) contour chromatogram and corresponding 3D peak plot from GC×GC-MS analysis of the LS2 condensates are shown in Fig. 2a and b, respectively. The C_6 to C_{20} products included several distinctive series of aliphatic hydrocarbons (i.e., linear and cyclic alkanes), aromatic hydrocarbons (benzenes, naphthalenes, fluorenes, phenanthrenes), caged hydrocarbons (adamantanes, diamantanes, triamantanes), caged-sulfur compounds (thiaadamantanes, thiadamantanes) and other organic sulfur compounds (benzothiophenes, dibenzothiophenes, phenanthrothiophenes). The alkylated diamondoid (D; Table 1) and thiadiamondoid (TD; Table 2) products included many more isomers than previously detected in petroleum. The notably large distributions of these product series are separately discussed in detail below.

3.1.1 Diamondoid hydrocarbons

GC×GC-TOFMS analysis of the LS2 condensate identified extensive series of alkylated-adamantanes, diamantanes and triamantanes (Table 1; and highlighted by black, pink and green circles, respectively, in Fig. 2a). These caged, diamond-like hydrocarbon structures can form by thermal cracking of polycycloalkane C-C bonds. The respective series are best highlighted by the selected GC×GC mass chromatograms shown in Fig. 3.

Alkyl adamantanes (extending to C₆) showed higher concentrations than the diamantanes, whilst just three triamantanes were detected in trace amounts (≤ 0.04 mg/g) – consistent with a general trend of decreasing abundance with increasing molecular weight (MW). At least 116 parent or alkylated adamantanes (Fig. 3a), 42 alkyl diamantanes (Fig. 3b) and three triadamantanes (Fig. 3c) were resolved, which represents a much larger number of these products than previously detected in petroleum by GC $\times$ GC-MS analyses. The concentrations of different alkyl-diamondoid products (i.e., total concentration of all isomers), the numbers of isomers of each product, and their identities based on comparison to previous data are given in Table 2.

Mass spectra of selected compounds can be found in Supplementary Information (Fig. S2). Consistent molecular ion detection allowed confident assignment of size/MW (i.e., alkyl size or group), but specific isomeric assignments based on GC-MS or GC $\times$ GC-MS correlation to previous studies (e.g., Wingert, 1992; Wei et al., 2006; Jiang et al., 2008; Zhu et al., 2013b; 2015a; 2015b; 2015c) could be confidently made for only 23 of the alkyl-A detected. As an example, a C₆ alkyl-adamantane isomer (116a of Fig. 4e) was confidently assigned as 2-n-hexyladamantane based on an identical mass spectrum compared to that reported by Zhu et al. (2013a; Figs. 4f and g). The exact isomeric configuration or identity of the other 93 alkyl-As detected in the LS2 condensate could not be unequivocally established. More comprehensive identification of these products will require dedicated preparation and analysis of authentic standards.

3.1.2 Thiadiamondoids

The LS2 condensate also comprised a large array of thiadiamondoids (highlighted by red circle in Fig. 2a). Thiaadamantanes (TAs) in petroleum samples are commonly attributed to

reservoir TSR (Wei et al., 2012). They form by the high temperature reaction of hydrocarbon compounds with sulfates and then H₂S. All of the alkylated thiadiamondoids in LS2 were of the 2-thiadiamantane form. Interestingly, the parent or unsubstituted 2-thiadiamantane was undetected whilst unsubstituted 3-thiadiamantane was confirmed.

The high concentrations and broad distributions of the alkyl thiadiamondoids detected in LS2, like the alky-diamondoids, included a much larger range of products than previously reported from petroleum. Detailed examination of the C₂- and C₃- alkylated 2-thiaadamantanes in LS2 can be made from the selected GCGC mass chromatograms in Fig. 5 and the mass spectra of selected products can be found in Fig. S3 (Supplementary Information). Six C₂ substituted 2-thiaadamantanes were detected (Fig. 5a, **3_{TA}**-**8_{TA}**). Three were assigned as 5,7- (**3_{TA}**), 1,5- (**4_{TA}**) and 1,3- (**5_{TA}**) dm-2-TA's, respectively, based on mass spectral correlation to previously reported data (Jiang et al., 2008). The isomeric identity of the other three C₂-2-TA's (peaks **6_{TA}**-**8_{TA}**; Fig. 5) could not be assigned, although **7_{TA}** and **8_{TA}** are likely the same as two C₂-2-TA's observed by GC-GC-MS analysis of deep Cambrian oils from Tarim Basin (Zhu, et al., 2016a).

Eight C₃ alkyl-2-TAs with similar 2D retention position (reflecting similar structures) are highlighted by the *m/z* 196 chromatogram in Fig. 5b - although substitution positions and actual isomeric identities could not be confirmed. These eight products probably include the six isomerically undefined C₃ alkyl-2-thiaadamantanes previously reported from GCxGC-MS analysis of other petroleums (Jiang et al., 2008; Wei et al., 2012; Zhu et al., 2016a). The mass spectra (**a-f**) of these established products compare closest to peaks **9_{TA}**-**13_{TA}** and **15_{TA}** of the LS2 condensate (Fig. 5b).

The concentrations of the thiaadamantanes and other thiophenics and thioaromatics (i.e., benzothiophenes and dibenzothiophenes) products common of TSR are given in Table 2 along with the numbers of thiadiamondoid product isomers and those isomeric identities confirmed through comparison to previous mass spectral data.

3.2 Stable Sulfur Isotope Analysis

$\delta^{34}\text{S}$ values of alkylated benzothiophenes (BTs) from GC-ICP-MS analysis of the aromatic fraction of LS2 condensate (Table 3) were in the range 25.6‰ to 28.4‰ (Ave = 26.8‰), whilst the alkylated dibenzothiophenes (DBTs) were generally lighter, ranging from 21.3‰ to 27.4‰ (Ave = 22.6‰). The lower concentrations of the caged-sulfur compounds precluded their $\delta^{34}\text{S}$ measurements.

3.3 Origin of H_2S and organic sulfur compounds

The high 3.6% H_2S content of the condensate is indicative of TSR (Zhu et al., 2015a; 2016a). The thiadiazolones and thiophenes (e.g., BTs, DBTs, PTs) in the LS2 condensate are common products of TSR, which was also likely responsible for the ~4‰ heavier $\delta^{34}\text{S}$ values of BTs compared to DBTs. Differences in TSR production rates of BTs and DBTs, and hence also their $\delta^{34}\text{S}$ values, have been shown to be sensitive to early stages of TSR (Amrani et al, 2012). BT and DBT produced by the reaction of H_2S with hydrocarbons during TSR will gradually approach $\delta^{34}\text{S}$ values near the sulfate utilized by TSR. Mineral sulfates are generally enriched in ^{34}S compared to reduced sulfur from seawater sulfates utilized by organic sulfurization processes. ^{34}S -enriched OSCs from TSR will add to the existing pool of these compounds and as BT is produced more quickly than DBT, its overall $\delta^{34}\text{S}$ value (i.e., of all BT sourced from both seawater reduced sulfate and mineral sulfate) will approach the $\delta^{34}\text{S}$ of the mineral sulfate faster.

TSR can also increase the accumulation, dry coefficient [$\text{C}_1/(\text{C}_1 \text{ to } \text{C}_5)$] and $\delta^{13}\text{C}$ values of hydrocarbon gases (Zhu et al., 2015d, 2015e). The gas composition of the LS2 condensate is methane 67.6-68.7%; ethane 0.4-0.7%; N_2 6.6-6.8%; CO_2 20.1-20.2%. A dry coefficient of

0.98 was typical of dry gas (Dai et al., 2008).

The $\delta^{13}\text{C}_1$ value of methane (-34.1‰) in LS2 was 4‰ lighter than ethane (-30.1‰). These $\delta^{13}\text{C}$ values were both $\geq 5\%$ heavier than corresponding thermally derived Ordovician gases from the nearby Tazhong uplift, which were not impacted by TSR (Zhu et al., 2014). TSR derived hydrocarbon gases are ^{13}C enriched due to the preferential TSR consumption of the lighter ^{12}C (Lu et al., 2011). The H_2S content of the Tazhong gases (<2%; Zhu et al., 2014) was also much lower than LS2.

No evaporites, the principal inorganic reactant for subsurface TSR, have been detected in any LS2 strata. The major lithologies of the reservoir are limestones and dolomites. A formation temperature of 145 °C (64.23 MPa) measured at 5,737 m in the LS2 well was also at the lower range required to initiate TSR. The apparent absence of in-reservoir TSR, implies the condensate migrated from a remote source able to support TSR.

The deeper Cambrian strata are a likely source for the LS2 condensate. A thick evaporite layer developed in the Tarim Basin during the Lower-Middle Cambrian, followed by deposition of high quality source rock in the Yuertusi Formation (ϵ_{1y}). Reservoir development in the Xiaoerblak Formation (ϵ_{1x}) during the Lower Cambrian (Zhu et al., 2016b), together with good-quality regional seal provided by thick (350-400 m) middle Cambrian gypsum and mudstone units widely distributed in lagoon facies in central and western areas of the Tarim Basin, completed the key elements of an effective source-reservoir-seal (Zhu et al., 2015d).

Deep (8,000-9,000 m) Cambrian reservoirs in this part of the Tarim Basin were predicted to be at temperatures of 200-220°C based on geothermal modelling, which identified an enhanced thermal gradient (2.5°C/100 m) during the Palaeogene (Fig. 6) due to rapidly subsiding strata. Under such high maturity conditions, petroleum hydrocarbons would have been extensively cracked (Pan et al., 2010; Zhu et al., 2012), reducing their average molecular weight (and gas dryness) and increasing their thermal reactivity with the sulfate-rich dolomite

reservoirs in the Xiaerblak Formation (ϵ_{1x}). Secondary reaction by TSR generated H_2S with organic compounds in the Cambrian strata could have contributed the wide range of sulfidic (e.g., thiadiamondoids) and thioaromatic (e.g., benzothiophenes) compounds detected in the LS2 condensate. The development of strike-slip faults through the Ordovician basement may have released trapped Cambrian petroleum and allowed migration to secondary reservoirs, as in the LS2 well.

4. Conclusions

LS2 condensate shows several features indicative of TSR including dry gas composition with light $\delta^{13}C$ values, high H_2S content and high concentrations of thiadiamondoids and other OSCs with distinctive $\delta^{34}S$ values. However, the absence of evaporitic minerals in the well identifies the LS2 unit as a secondary reservoir into which the TSR-impacted condensate migrated. The source of the condensate is likely deeper Cambrian strata that have the necessary elements to support TSR (evaporites, organic-rich intervals and temperatures $> 200^\circ C$), with faults through the Ordovician overlay providing source-reservoir connectivity.

Deep Cambrian strata represent a promising hydrocarbon resource within the Tarim Basin not withstanding their vulnerability to thermal over maturity and TSR alteration, which can degrade oil quality and generate high H_2S levels that are problematic for exploration and production. Our GC $\times$ GC-MS analysis of the LS2 condensate revealed more alkylated thiadiamondoid (and diamondoid hydrocarbon) products than previously detected in any petroleum sample and the broad distribution of these caged structures may assist regional oil exploration and help evaluate the extent of TSR alteration.

Acknowledgements

Dr. Haijun Yang, Yongquan Chen and Baoshou Zhang from the PetroChina Tarim Oilfield Company contributed data and supported the sample collection. This work was financially supported by National Science and Technology Major Project (Item No. 2016ZX05004-004). The $\delta^{34}\text{S}$ measurements were conducted on the Advanced Geochemical Facility for Indian Ocean Research at the University of Western Australia. We are very appreciative of advice from the Assoc Editor (Ken Peters) and reviewers of a previous similar manuscript (Jeremy Dahl and one anonymous) which improved this account of our study

References

- Amrani, A., Deev, A., Sessions, A. L., Tang, Y., Adkins, J., Hill, R., Moldowan, J. M., Wei, Z., 2012. The sulfur-isotopic compositions of benzothiophenes and dibenzothiophenes as a proxy for thermochemical sulfate reduction. *Geochimica et Cosmochimica Acta* 84, 152-164.
- Asif, M., Alexander, R., Fazeelat, T., Pierce, K., 2009. Geosynthesis of dibenzothiophene and alkyl dibenzothiophenes in crude oils and sediments by carbon catalysis. *Organic Geochemistry* 40, 895-901.
- Cai, C.F., Hu, G.Y., Li, H.X., Jiang, L., He, W.X., Zhang, B.S., Jia, L.Q., Wang, T.K., 2015. Origins and fates of H_2S in the Cambrian and Ordovician in Tazhong area, evidence from sulfur isotopes, fluid inclusions and production data. *Marine and Petroleum Geology* 67, 408-418.

- Cai, C.F., Worden, R.H., Wolff, G.A., Bottrell, S., Wang, D.L., Li, X., 2005. Origin of sulfur-rich oils and H₂S in Tertiary lacustrine sections of the Jinxian Sag, Bohai Bay Basin, China. *Applied Geochemistry* 20, 1427-1444.
- Cai, C.F., Xiao, Q.L., Fang, C.C., Wang, T.K., He, W.X., Li, H.X., 2016. The effect of thermochemical sulfate reduction on formation and isomerization of thiadiamondoids and diamondoids in the Lower Paleozoic petroleum pools of the Tarim Basin, NW China. *Organic Geochemistry* 101, 49-62.
- Carrigan, W.J., Jones, P.J., Tobey, M.H., Halpern, H.I., Wender, L.E., Philp, R.P., Allen, J., 1998. Geochemical variations among eastern Saudi Arabian Paleozoic condensates related to different source kitchen areas. *Organic Geochemistry* 29, 785-798.
- Claypool, G.E., Mancini, E.A., 1989. Geochemical relationships of petroleum in Mesozoic reservoirs to carbonate source rocks of Jurassic Smackover Formation, southwestern Alabama. *AAPG Bulletin* 73, 904-924.
- Dai, J.X., Zou, C.N., Zhang, S.C., Li, J., Ni, Y.Y., Hu, G.Y., Luo, X., Tao, S.Z., Zhu, G.Y., Mi, J.K., Li, Z.S., Hu, A.P., Yang, C., Zhou, Q.H., Shuai, Y.H., Zhang, Y., Ma, C.H., 2008. The identification of alkane gas of inorganic and organic. *Science of China* 38, 11, 1329-1341.
- Garcia, C.L., Becchi, M., Grenier-Loustalot, M.F., Paisse, O., and Szymanski, R., 2002. Analysis of aromatic sulfur compounds in gas oils using GC with sulfur chemiluminescence detection and high-resolution MS. *Analytical Chemistry* 74(15), 3849-3857.
- Greenwood, P.F., Mohammed, L., Grice, K., McCulloch, M.T., Schwark, L., 2018. The

- application of compound-specific sulfur isotopes to the oil-source rock correlation of Kurdistan petroleum. *Organic Geochemistry* 117, 22-30.
- Hao, F., Guo, T.L., Zhu, Y.M., Cai, X.Y., Zou, H.Y., Li, P.P., 2008. Evidence for multiple stages of oil cracking and thermochemical sulfate reduction in Puguang gas field, Sichuan Basin, China. *AAPG Bulletin* 92, 611-637.
- Heydari, E., Moore, C.H., 1989. Burial diagenesis and thermochemical sulfate reduction, Smackover Formation, southeastern Mississippi Salt Basin. *Geology* 17, 1080-1084.
- Jiang, N.H., Zhu, G.Y., Zhang, S.C., 2008. Detection of 2-Thiaadamantanes in the oil from Well TZ-83 in Tarim Basin and its geological implication. *China. Science of China* 53, 396-401.
- Krouse, H.R., Viau, C.A., Eliuk, L.S., Ueda, A., Halas, S., 1988. Chemical and isotopic evidence of thermochemical sulphate reduction by light hydrocarbon gases in deep carbonate reservoirs. *Nature* 333, 415-419.
- Lu, H., Greenwood, P., Chen, T., Liu, J., and Peng P.A., 2011. The role of metal sulfates in thermochemical sulfate reduction (TSR) of hydrocarbons: insight from the yields and stable carbon isotopes of gas products. *Organic Geochemistry* 42, 700-706.
- Machel, H.G., 1998. Gas souring by thermochemical sulfate reduction at 140 °C, Discussion. *AAPG Bulletin* 82, 1870-1873.
- Machel, H.G., Krouse, H.R., Sassen, R., 1995. Products and distinguishing criteria of bacterial and thermochemical sulfate reduction. *Applied Geochemistry* 10, 373-389.
- Orr, W.L., 1974. Changes in sulfur content and isotopic-ratios of sulfur during petroleum maturation-study of Big Horn Basin Paleozoic oils. *AAPG Bulletin* 58, 2295-2318.

- Pan, C., Jiang, L., Liu, J., Zhang, S.C., Zhu, G.Y., 2010. The effects of calcite and montmorillonite on oil cracking in confined pyrolysis experiments, *Organic Geochemistry* 41, 7, 611-626.
- Qiu, N., Chang, J., Zuo, Y., Wang, J., Li, H., 2012. Thermal evolution and maturation of lower Paleozoic source rocks in the Tarim Basin, Northwest China. *AAPG Bulletin* 96, 789-821.
- Sinningh Damste, J.S., de Leeuw, J.W., 1990. Analysis, structure and geochemical significance of organically-bound sulphur in the geosphere, State of the art and future research. *Organic Geochemistry* 16, 1077-1101.
- Wei, Z., Moldowan, J.M., Paytan, A., 2006. Diamondoids and molecular biomarkers generated from modern sediments in the absence and presence of minerals during hydrous pyrolysis. *Organic Geochemistry* 37, 8, 891-911.
- Wei, Z., Walters, C.C., Moldowan, J.M., Mankiewicz, P.J., Pottorf, R.J., Xiao, Y., Maze, W., Nguyen, P.T.H., Madincea, M.E., Phan, N.T., Peters, K.E., 2012. Thiadiamondoids as proxies for the extent of thermochemical sulfate reduction. *Organic Geochemistry* 44, 53-70.
- Wingert, W. S. 1992. GC-MS analysis of diamondoid hydrocarbons in Smackover petroluems. *Fuel* 71, 1, 37-43.
- Worden, R.H., Cai, C.F., 2006. Geochemical characteristics of the Zhaolanzhuang sour gas accumulation and thermochemical sulfate reduction in the Jinxian Sag of Bohai Bay Basin by Zhang et al. *Organic Geochemistry* 36, 1717-1730.
- Worden, R.H., Smalley, P.C., Oxtoby, N.H., 1995. Gas souring by thermochemical sulfate

reduction at 140 °C. AAPG Bulletin 79, 854-863.

Worden, R.H., Smalley, P.C., Cross, M.M., 2000. The influence of rock fabric and mineralogy on thermochemical sulfate reduction, Khuff Formation, Abu Dhabi. *Journal of Sedimentary Research* 70, 1210-1221.

Zhang, S.C., Zhu, G.Y., Liang, Y.B., Dai, J.X., Liang, H.B., Li, M.W., 2005. Geochemical characteristics of the Zhaolanzhuang sour gas accumulation and thermochemical sulfate reduction in the Jixian Sag of Bohai Bay basin. *Organic Geochemistry* 36, 1717-1730.

Zhang, T., Ellis, G.S., Walters, C.C., Kelemen, S.R., Wang, K.S., Tang, Y., 2008a. Experimental diagnostic geochemical signatures of the extent of thermochemical sulfate reduction. *Organic Geochemistry* 39, 308-328.

Zhu, G.Y., Chen, F.R., Chen, Z.Y., Zhang, Y., Xing, X., Tao, X.W., Ma, D.B., 2016b. Discovery and basic characteristics of high-quality source rocks found in the Yuertusi Formation of the Cambrian in Tarim Basin, China. *Journal of Natural Gas Geoscience* 1, 21-33.

Zhu, G.Y., Huang, H.P., Wang, H.T., 2015e. Geochemical significance of discovery in Cambrian reservoirs at Well ZS1 of the Tarim Basin, Northwest China. *Energy & Fuels* 29, 1332-1344.

Zhu, G.Y., Wang, H., Weng, N., 2016a. TSR-altered oil with high-abundance thiaadamantanes of a deep-buried Cambrian gas condensate reservoir in Tarim Basin. *Marine and Petroleum Geology* 69, 1-12.

Zhu, G.Y., Wang, H.T., Weng, N., Huang H.P., Liang, H.B., Ma, S.P., 2013b. Use of comprehensive two-dimensional gas chromatography for the characterization of

- ultra-deep condensate from the Bohai Bay Basin, China. *Organic Geochemistry* 63, 8-17.
- Zhu, G.Y., Wang, H.T., Weng, N., Yang H.J., Zhang, K., Liao, F.R., Yuan, N., 2015c. Geochemistry, origin and accumulation of continental condensate in the ultra-deep-buried Cretaceous sandstone reservoir, Kuqa Depression, Tarim Basin, China. *Marine and Petroleum Geology* 65, 103-113.
- Zhu, G.Y., Wang, T.S., Xie, Z.Y., Xie, B.H., Liu, K.Y., 2015d. Giant gas discovery in the Precambrian deeply buried reservoirs in the Sichuan Basin, China, implications for gas exploration in old cratonic basins. *Precambrian Research* 262, 45-66.
- Zhu, G.Y., Weng, N., Wang, H.T., Yang, H.J., Zhang, S.C., Su, J., Liao, F.R., Zhang, B., Ji, Y.G., 2015a. Origin of diamondoid and sulfur compounds in the Tazhong Ordovician condensate, Tarim Basin, China, implications for hydrocarbon exploration in deep-buried strata. *Marine and Petroleum Geology* 62, 14-27.
- Zhu, G.Y., Zhang, B.T., Yang, H.J., Su, J., Han, J.F., 2014. Origin of deep strata gas of Tazhong in Tarim Basin, China. *Organic Geochemistry* 74, 85-97.
- Zhu, G.Y., Zhang, S.C., Su, J., Huang, H.P., Yang, H.J., Gu, L.J., Zhang, B., Zhu, Y.F., 2012. The occurrence of ultra-deep heavy oils in the Tabei Uplift of the Tarim Basin, NW China. *Organic Geochemistry* 52, 88-102.
- Zhu, G.Y., Zhang, S.C., Su, J., Zhang, B., Yang, H.J., Zhu, Y.F., Gu, L.J., 2013a. Alteration and multi-stage accumulation of oil and gas in the Ordovician of the Tabei uplift, Tarim Basin, NW China, implications for genetic origin of the diverse hydrocarbons. *Marine and Petroleum Geology* 46, 234-250.
- Zhu, G.Y., Zou, C.N., Yang H.J., Wang, K., Zheng, D.M., Zhu, Y.F., Wang, Y., 2015b.

Hydrocarbon accumulation mechanisms and industrial exploration depth of the large area fracture-cavity carbonates in the Tarim Basin, western China. Journal of Petroleum Science and Engineering 133, 889-907.

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Figure Captions

Fig. 1. Geological information for the LS2 well and gas reservoir in Bachu uplift of Tarim

Basin, China. (a) Paleogeologic map of Tarim Basin showing LS2 location; (b) Stratigraphic column of Maigaiti slope in Bachu uplift; (c) Structural profile of LS2; (d) Seismic profile and structural model of LS2.

Fig. 2. GC×GC-TOFMS chromatogram of the LS2 condensate. (a) GC×GC-TOFMS color contour chromatogram; (b) GC×GC-TOFMS 3D plot.

Fig. 3. Diamondoid hydrocarbons with 1-3 cages highlighted by selected mass chromatograms from GC×GC-MS analysis of the LS2 condensate: (a) m/z 135+136+149+163+177+191+205 chromatogram highlighting adamantanes; (b) m/z 188+187+201+215+229+243+257 chromatogram highlighting diamantanes; (c) m/z 240+239 chromatogram highlighting triamantanes.

Fig. 4. Respective alkylated series of adamantanes highlighted by the following GC×GC mass chromatograms. (a) 135+136 Da showing A, C₁-A's and C₂₋₆-A's with ion 135 Da; (b) 149 Da showing C₂-A's; (c) 163 Da showing C₃-A's; (d) 177 Da showing C₄-A's; (e) 191, 205 Da showing both C₅-A's and C₆-A's. The different alkyl-A products are numbered; (f) mass spectrum of C₆-adamantane isomer (product 116_A in a); (g) modified mass spectrum of 2-*n*-hexyladamantane from Zhu et al. (2013a).

Fig. 5. Selected GC×GC mass chromatograms showing the resolved isomer series of (a) C₂ 2-thiaadamantanes; and (b) C₃ 2-thiaadamantanes. Mass spectra of selected products can be found in Supplementary Figure S2.

Fig. 6. Burial and thermal history of Maigaiti slope and LS2 Well.

Table Captions

Table 1. Alkyl diamondoid compounds detected in LS2 condensate. The concentration of different alkyl diamondoids (inclusive of all isomers) is given along with the numbers of isomers detected, which typically represents more isomers than previously detected in petroleum by GC×GC-MS studies

Table 2. Concentration of organic sulfur compounds detected in LS2 condensate. The concentration of different alkyl diamondoids (inclusive of all isomers) is given along with the numbers of isomers detected, which consistently represents more isomers than previously detected in petroleum.

Table 3. Sulfur isotopic compositions of sulfur-containing compounds in LS2 well condensate and sulfur isotope value of kerogens in source rocks of Tarim Basin. SV = standard variation of duplicate analysis.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

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Figure 5.

Figure 6.

Table 1

Alkyl-Diamondoid Products	Conc. (mg/g)	MW	Isomer Number ^A	Assigned Isomers ^B
Adamantane	0.92	136		
C ₁ -adamantane	4.43	150	2 (2)	1-mA (2 _A), 2-mA (3 _A)
C ₂ -adamantane	7.52	164	10 (7)	1-e A (9 _A), 2-eA (12 _A), 1,3-dmA (4 _A), 1,4-dmA(<i>c</i>) (5 _A), 1,4-dmA(<i>t</i>) (6 _A), 1,2-dmA (7 _A)
C ₃ -adamantane	7.92	178	28 (6)	1-e-3-mA (18 _A), 1,3,5-tmA (14 _A), 1,3,6-tmA (15 _A), 1,3,4-tmA(<i>c</i>) (16 _A), 1,3,4-tmA(<i>t</i>) (17 _A), 1,2,3-tmA (19 _A), 2-n-pA (41 _A)
C ₄ -adamantane	4.60	192	47 (5)	1,3,5,7-TetA (42 _A), 1,2,5,7-TetA (43 _A), 1-e-3,5-dmA (45 _A), 2-n-bA (88 _A)
C ₅ -adamantane	0.87	206	21 (2)	1,2,3,5,7-PmA (90 _A), 2-n-penA (109 _A)
C ₆ -adamantane	0.00	230	7 (0)	2-n-hA (116 _A)
Diamantane	0.33	188		
C ₁ -diamantane	0.66	202	3 (3)	4-mD (2 _D), 1-mD (3 _D), 3-mD (4 _D)
C ₂ -diamantane	0.47	216	14 (6)	4,9-dmD (5 _D), 1,2-+2,4-dmD (6 _D), 4,8-dmD (7 _D), 3,4-dmD (8 _D),
C ₃ -diamantane	0.30	230	13 (2)	
C ₄ -diamantane	0.14	244	7 (0)	
Triamantane	0.04	240		
C ₁ -triamantane	0.03	254	2 (4)	9-mT (2 _T), 5-mT (3 _T)

^A total isomer numbers detected in this study; numbers in the brackets represent the isomer numbers from previous GC×GC-MS study (Wei et al., 2006; Zhu et al., 2013b, 2015b, 2015c).

^B product assignment corresponding to GC×GC-MS peaks in Figs. 3a-c (A=adamantane, D=diamantane, T=triamantane); m=methyl, e=ethyl, p=propyl, b=butyl, pen=pentyl, h=hexyl, d=di, t=tri, Tet=tetra, P=penta, (*c*)=cis, (*t*)=trans

Table 2

Compound	Conc. (mg/g)	MW	Isomer Number ^A	Assigned Compounds ^B
Tetrahydrothiophenes	4.1			
Alkylthiophanes	147.6			
Benzylmercaptanes	1.5			
Alkylbenzothiophenes	251.1			
Dibenzothiophenes	187.9			
Phenanthrothiophenes	2.6			
C ₁ -thiaadamantanes	0.1	168	2 (2)	5-m-2-TA (1 _{TA}), 1-m-2-TA (2 _{TA})
C ₂ -thiaadamantanes	0.1	182	6 (3)	5,7-dm-2-TA (3 _{TA}), 1,5-dm-2-TA (4 _{TA}), 1,3-dm-2-TA (5 _{TA})
C ₃ -thiaadamantanes	0.1	196	9 (4)	
Other sulfur-containing compounds	31.5			

^A total isomer numbers detected in this study; numbers in the brackets represent the isomer numbers from previous GC×GC-MS study (Wei et al., 2007; Jiang et al., 2008).

^B abbreviated product symbol in parenthesis following assigned isomer name correspond to GC×GC-MS peak assignments in Fig. 5: TA=thiaadamantane, m=methyl, d=di

Table 3.

OSCs/kerogens	$\delta^{34}\text{S}$ (‰)	SV
C ₂ BTi	28.4	0.8
C ₃ BTi	26.8	0.3
C ₃ BTii	25.9	0.7
C ₃ BTiii	27.1	0.6
C ₃ BTiv	25.6	0.1
C ₄ BTi	27.0	0.3
DBT	21.7	0.3
mDBTi (4mDBT)	21.7	0.3
mDBTii (2&3 mDBT)	22.3	0.1
C ₂ DBTi	19.5	0.1
C ₂ DBTii	23.3	0.4
C ₂ DBTiii	27.4	0.3
C ₃ DBT	23.4	1.5
C ₃ DBTii	21.3	3.6
Ave BT's	26.8	
Ave DBTs	22.6	
Cambrian kerogens	10.4-22.3*	
Ordovician kerogens	3.8-6.8*	

* From Cai et al. (2015).

First characterization of condensate recently discovered in Bachu uplift

Wide distributions of OSC/diamondoid isomers resolved

Includes many additional isomers than previously detected in petroleum

TSR source of condensate correlated with deep Cambrian strata.

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