PS The Identification and Origin of Diamondoid and Thiadiamondoid Products from Condensate of LS2 Well, Tarim Basin: Significance for Oil Exploration Potential of Ultra-Deep Strata*

Guangyou Zhu[1], Ying Zhang[1], and Zhiyao Zhang[1]

Search and Discovery Article #11195 (2019)**
Posted February 18, 2019

*Adapted from poster presentation given at 2018 AAPG Annual Convention & Exhibition, Salt Lake City, Utah, May 20-23, 2018
**Datapages © 2019 Serial rights given by author. For all other rights contact author directly. DOI:10.1306/11195Zhu2019

[1]PetroChina Research Institute of Petroleum Exploration and Development, Beijing, China (zhuguangyou@petrochina.com.cn)

Abstract

High gas production was discovered in 2016 from the LS2 well in Bachu Uplift of the Tarim Basin, China, identifying a promising new region for petroleum exploration. The very sulfur-rich petroleum condensate contained high concentrations of H_2S (3.66%) and distinctive organic sulfur compounds useful for future oil correlations. Here we report the detection of vast distributions of thiophenic, sulfidic and diamondoid products which were resolved by comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry (GC×GC-TOFMS), including a much larger number of alkylated diamondoid and thiadiamondoid isomers than previously reported from petroleum analyses. These caged molecular structures are typical secondary petroleum products of thermochemical sulphate reduction (TSR). A $d^{34}S$ distinction between OSCs reflecting a varied sensitivity to TSR (i.e., $d^{34}S_{BT-DBT}$ ~ 4 ‰) and hydrocarbon gases reflecting a dry composition (C_1/C_{1+} ~ 1) and ^{13}C enrichment with $\delta^{13}C$ values (e.g., C_1 ~ -34 ‰ and C_2 ~ -30 ‰) up to 8 ‰ heavier than non-TSR impacted Tazhong condensates - represent further evidence of TSR impacts on the LS2 condensate. The LS2 well lacks SO_4^{2-} evaporites to directly have supported TSR, implying it is a secondary reservoir of migrated gas. Furthermore, the reservoir temperature (144° C) is relatively low for TSR. The $d^{34}S$ values of the oil and gas are typical of deeper Cambrian strata which contain high quality Xiaoerblak ($\in_{1x}$) dolomites, thick evaporites and experienced temperatures greater than 200° C from which TSR derived petroleum could have migrated through fracture adjustment of the late Himalayan period. This discovery suggests the Cambrian salt layers may be a productive source of condensate rich petroleum warranting further exploration.

20-23 May 2018 • Salt Lake City, Utah
AAPG ACE 2018 ANNUAL CONVENTION & EXHIBITION

The Identification and Origin of Diamondoid and Thiadiamondoid Products from Condensate of LS2 Well, Tarim Basin: Significance for Oil Exploration Potential of Ultra-deep Strata

Guangyou Zhu[1*], Ying Zhang[1], Zhiyao Zhang[1]
E-mail address: zhuguangyou@petrochina.com.cn (G. Y. Zhu)
1. PetroChina Research Institute of Petroleum Exploration and Development, Beijing, China.

PetroChina

Introduction

The petroleum recently discovered in the Bachu uplift of the Tarim Basin (China) has been characterized for its molecular and stable isotopic composition to evaluate its source and thermochemical sulfate reduction (TSR) impact as well as to assist future regional petroleum correlation studies. The S-rich condensate from the LS2 well comprised a very wide distribution of alkylated thiophenic and diamondoid/thiadiamondoid products. A wide array of aromatic products was resolved by GC×GC-TOFMS, including much more additional isomers than those have been previously detected in any petroleum. The organic sulfur products were attributed to TSR, a major occurrence of which was also supported by the relatively high abundances of H_2S (3.66%); a ^{34}S distinction between OSCs reflecting a varied sensitivity to TSR (i.e., benzothiophenes with ^{34}S values 4‰ heavier than dibenzothiophenes) and a dry composition of hydrocarbon gases (C_1/C_{1+} ~1) which were ^{13}C enriched (^{13}C values up to +8‰) compared to non-TSR impacted Tazhong condensates. The LS2 reservoir has no sulfate evaporites and temperatures (144 °C) relatively low for TSR, implying it was a secondary reservoir into which the TSR derived gas had migrated. The ^{34}S values of the oil and gas were typical of deeper Cambrian strata which contain high quality Xiaoerblak (ϵ_{1x}) dolomites and thick evaporates; experienced temperatures greater than 200 °C; and was subject to late Himalayan fracture adjustment through which TSR-derived petroleum could have subsequently migrated. This new petroleum discovery suggests the Cambrian salt layers of the Tarim Basin may be a potential new petroleum resource warranting further exploration.

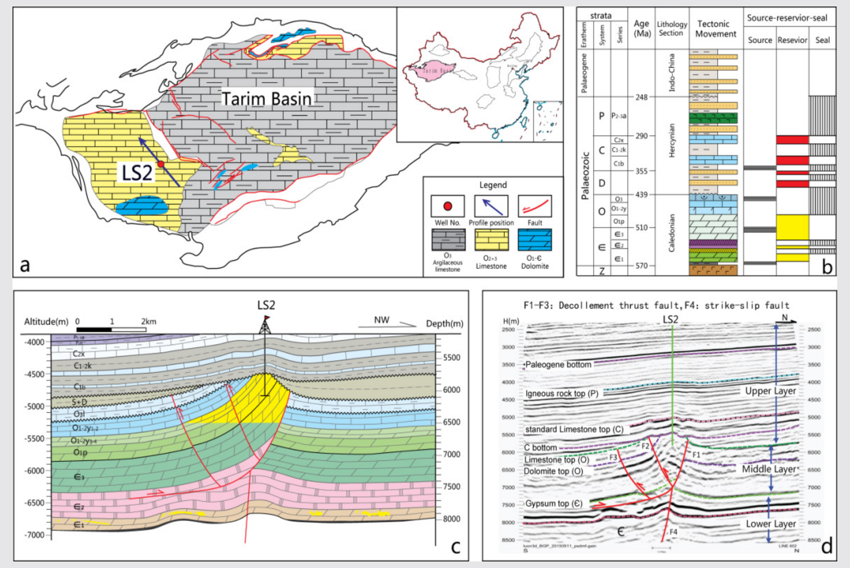

Fig. 1. Geological information of LS2 Well and gas reservoir in Bachu uplift of Tarim Basin, China.

a, Paleogeologic map of Tarim Basin with LS2 location;
b, Stratigraphic column of Maigaiti slope in Bachu area;
c, Structural profile of LS2;
d, Seismic profile and structural model of LS2.

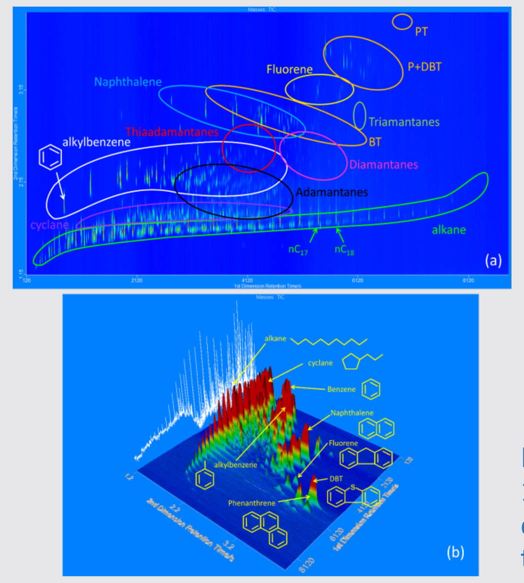

Fig. 2. GC×GC-TOFMS chromatogram of the LS2 condensate.

a, GC×GC-TOFMS color contour chromatogram;
b, GC×GC-TOFMS 3D plot.

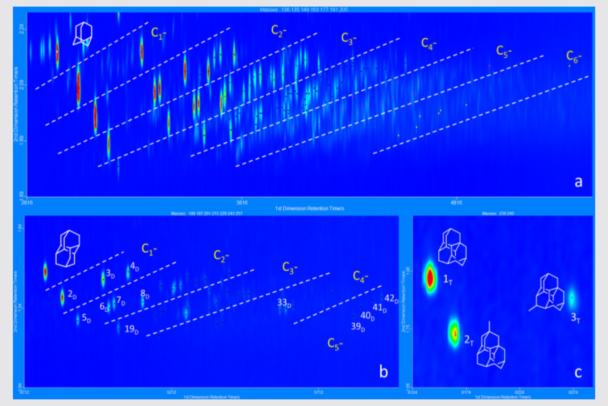

Fig. 3. Diamondoid hydrocarbons with 1-3 cages highlighted by selected mass chromatograms from the GC×GC-MS analysis of the LS2 condensate:

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.

Distribution of diamondoids and OSCs

GC×GC-MS analysis of the LS2 condensates identified more than 5,000 compounds with > 100 signal-to-noise ratios 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. These caged, diamond like hydrocarbon structures can form following the thermal cracking of polycycloalkane C-C bonds. The respective series are best highlighted by the selected GC×GC mass chromatograms shown in Fig. 3.

Selected mass chromatograms from the GC-GC-TOFMS analysis of the LS2 condensate can clearly resolve many different alkyl-diamondoid products. The different GC-GC regions in which distinctive distributions of adamantanes, diamantanes and triamantanes eluted were highlighted in Fig. 2a. These three product groups each comprised a series of products with various alkyl substitutions the extent of which was determined by molecular ion size and GC-MS correlation to previous studies. The adamantanes showed the largest abundances and distribution of these products, extending up to C_6-A's, followed by the alkylated diamantanes and then the triamantanes of which just three were detected (Fig. 3&4).

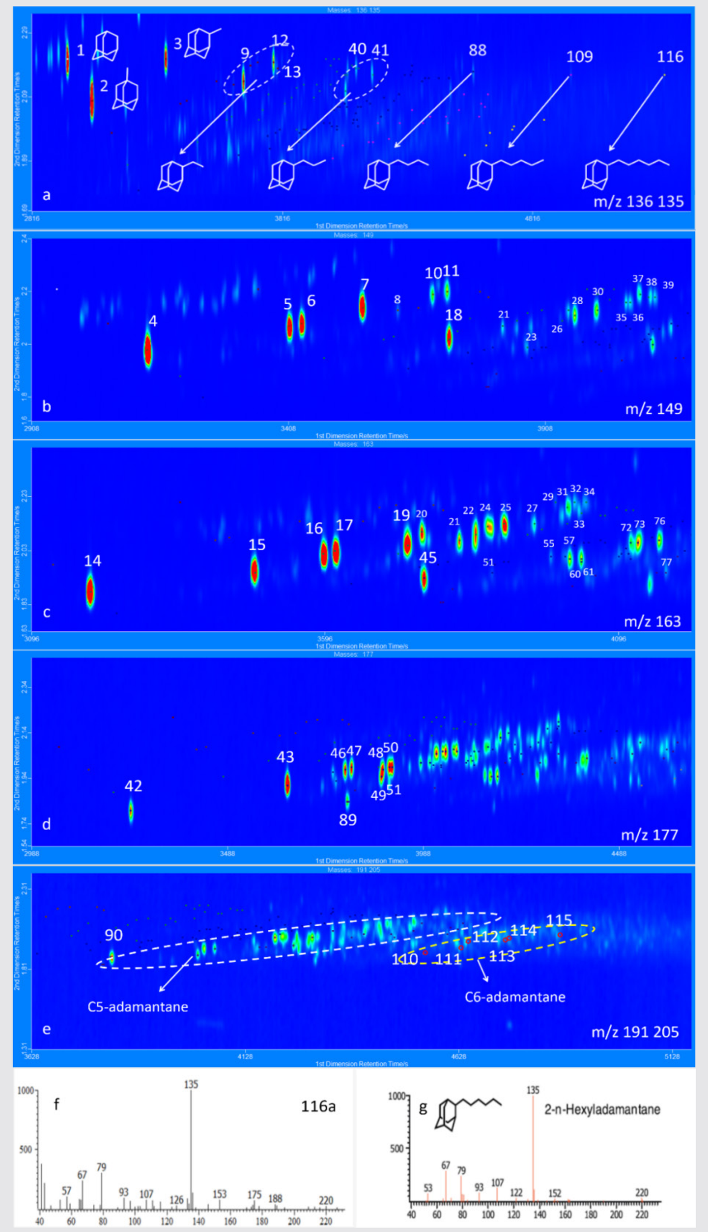

Fig. 4. Respective alkylated series of adamantanes highlighted by the following GC×GC mass chromatograms.

a, 135+136 Da showing A, C_1-A's and C_{2-6}-A's with ion 135 Da; b, 149 Da showing C_2-A's; c, 163 Da showing C_3-A's; d, 177 Da showing C_4-A's; e, 191, 205 Da showing both C_5-A's and C_6-A's. The different alkyl-A products are numbered; f, mass spectra of C_6-adamantane isomer (product 116A in a); g, mass spectra of 2-n-Hexyladamantane.

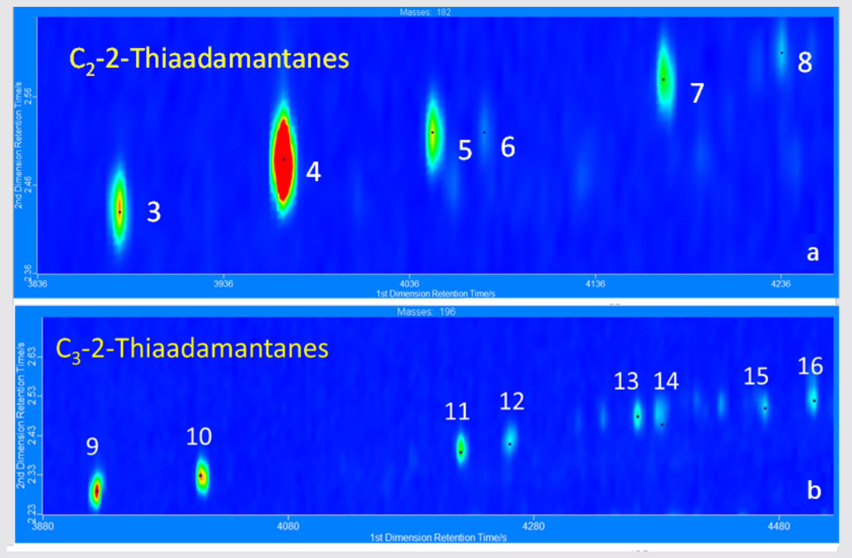

Fig. 6. Selected GC×GC mass chromatograms showing the resolved isomer series of (a) C_2 2-thiaadamantanes; and (b) C_3 2-thiaadamantanes.

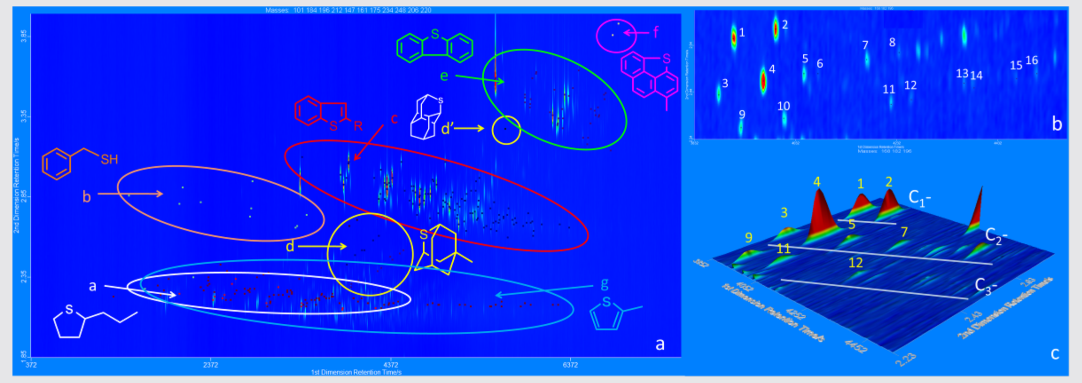

Fig. 5. OSCs detected in the LS2 condensate collectively highlighted in the 2D GCGC contour map.

Extensive distributions of abundant organic sulfur compounds (OSCs) were detected in the LS2 condensate. The different OSCs resolved by GC-GC-MS analysis included tetrahydrothiophenes, alkylthiophenes, benzylmercaptanes, thiaadamantanes, alkylbenzothiophenes, dibenzothiophenes and phenanthrothiophenes. These different OSC groups were all evident in the chromatogram shown in Fig. 4.

Very large distributions of alkyl thiaadamantanes were detected in the LS2 condensate (Figs. 5-6). Interestingly, this included unsubstituted 3-thiadiamantane but not 2-thiadiamantane, whereas all of the alkylated products were of alkly-2-thiadiamantane form.

Origin and source of OSCs

Differences in the TSR associated production rates of BTs and DBTs, and hence also their ^{34}S values, have been shown to be sensitive to early stages of TSR. BT and DBT produced by the reaction of the H_2S from TSR with hydrocarbons will gradually inherit a ^{34}S value close to that of the sulfate utilized by TSR. As BT is produced more quickly than DBT, it's overall ^{34}S value will be quicker to reflect the ^{34}S of the mineral SO_4's. The ^{34}S values of the BTs in LS2 were generally higher than the DBTs, by an average of 4.2‰, and this differential is likely indicative of TSR.

The $\delta^{13}C_1$ value of methane in Well LS2 was -34.1‰, which was +4‰ lighter than the coincident ethane. Both the C_1 and C_2 hydrocarbon gases of LS2 had $\delta^{13}C$ values 5%-8% heavier than other non TSR impacted from the nearby Tazhong uplift. The high abundance of OSCs, particularly the TAs, and ^{34}SBT-DBT distinction are evidence for the impact of TSR on this condensate. The temperature of the LS2 dolomite reservoir at the depth sampled (5,736.57 m) was measured to be 144.6 °C (pressure = 64.23 MPa) which is at the lower range for TSR. More significantly, there were no evaporites present in the reservoir. The lack of SO_4^{2-} reactant would preclude the in-reservoir occurrence of TSR. This implies the condensate presently in place migrated from an external location where TSR was supported.

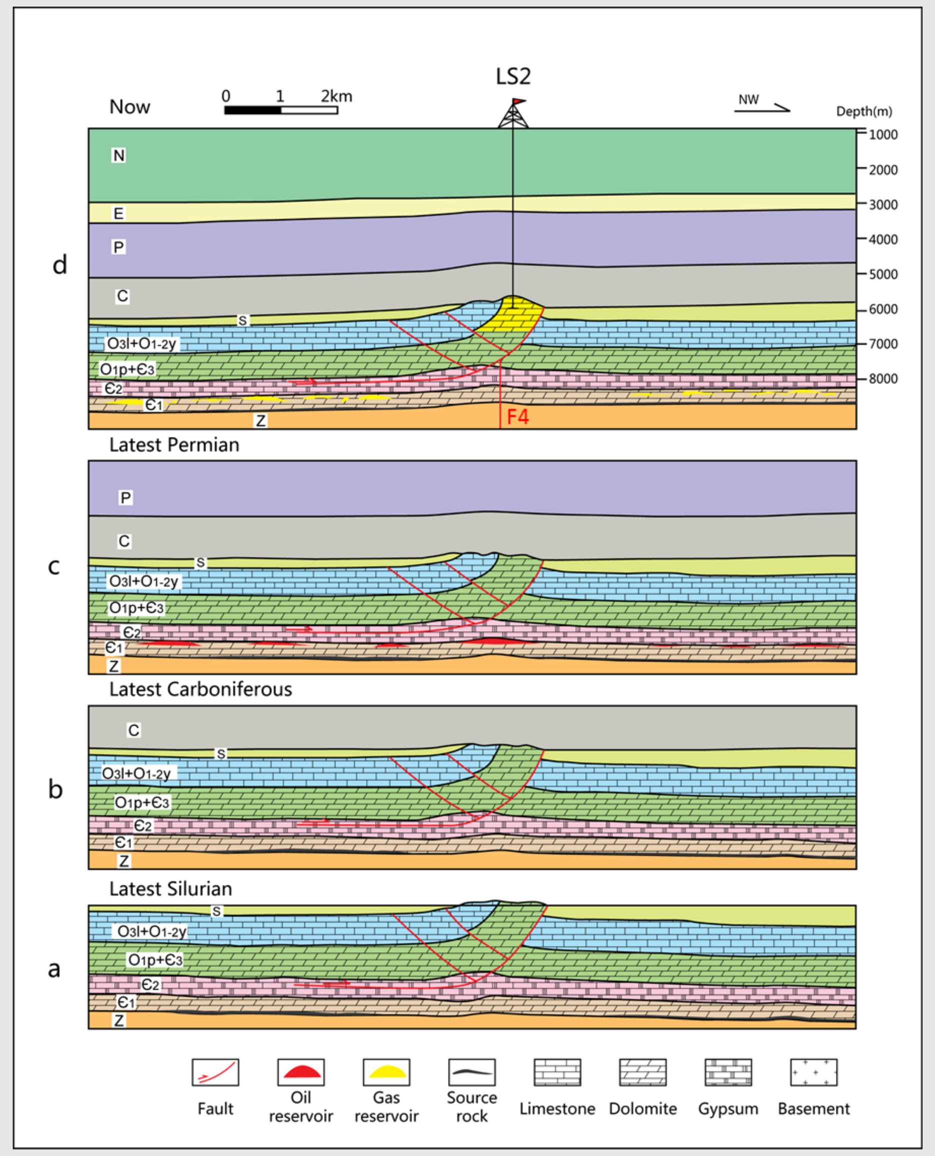

Fig. 7. Oil and gas accumulation evolution map of LS2 well and Bachu uplift, Tarim Basin.

a, LS2 structural formation; b, LS2 stabilization;
c, LS2 subjected and stabilised, the Mesozoic was absent;
maturation of Yuertusi formation (ϵ_{1y}) source rock led to expelling of hydrocarbons which accumulated in large quantities under the Cambrian salt layer;
d, Neogene deposited rapidly; crude oil in Cambrian cracked and generated gas. F4 strike-slip fault was formed connecting deep gas reservoirs from which hydrocarbons migrated and accumulated in the LS2 secondary gas reservoir.

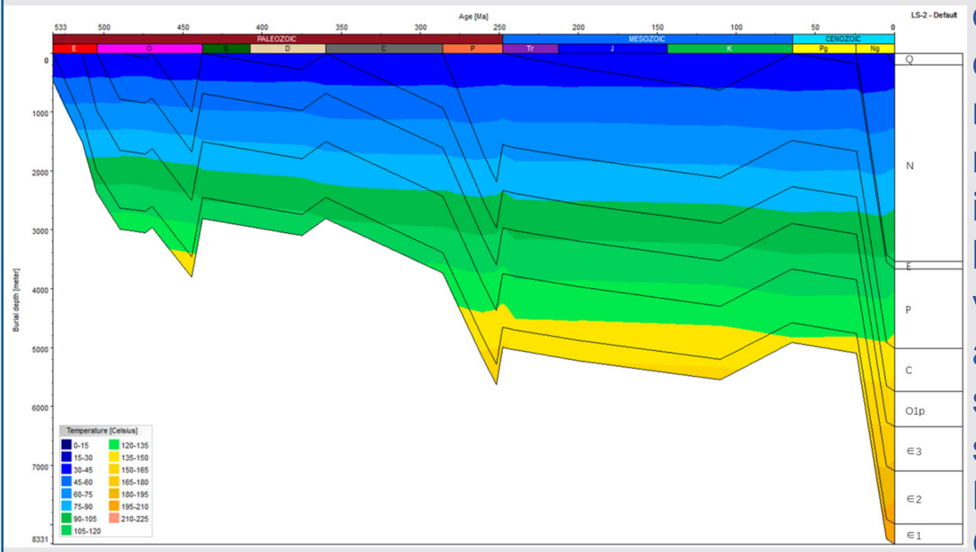

Fig. 8. Burial and thermal history of Maigaiti slope and LS2 Well.

The deeper Cambrian strata is a likely source candidate of the LS2 condensate. The relative consistency of the $^{34}S_{OSCs}$ values measured for the condensate thioaromatic (DBTs: 19.5%-27.4%, Table 7), with the $\delta^{34}S$ value (10.4%-22.3%) of Cambrian kerogens; whereas the $\delta^{34}S$ value (3.8%-6.8%) reported for Ordovician kerogen are quite a bit lighter. The evolution of sedimentation from Cambrian to Ordovician and the hydrocarbon accumulation process of the southwest of Tarim Basin is shown in Fig. 7. A thick layer of evaporate were developed through the Lower middle Cambrian, then high quality source rock was deposited in Yuertusi formation (ϵ_{1y}) and reservoir in Xiaoerblak formation (ϵ_{1x}) during lower Cambrian. These elements composed an effective source-reservoir-seal combination.

Deep Exploration Potential

The discovery of LS2 oil and gas from the Cambrian strata highlights the promising hydrocarbon resource potential of this deep source. The typically high temperatures (>200 °C) of these deep Cambrian sources make the hydrocarbons produced vulnerable to extensive TSR and thermal cracking. These alteration processes can deteriorate oil quality and the high H_2S contents of TSR can be hazardous to drilling and other production activities, thus their potential occurrence should be a careful consideration of any exploration strategies.

Conclusions:

The LS2 gas reservoir has been evaluated as secondary gas reservoir into which a dry and S-rich gas condensate from deeper Cambrian sources has migrated and accumulated following the development of basement faults during the Himalayan period. The condensate and Cambrian source rocks were correlated on the basis of sulfur isotopic compositions. The condensate has also encountered extensive TSR, reflected by high concentrations of H_2S and OSCs. TSR might have also contributed to the measured sulfur isotopic difference of 4% between BTs and DBTs, a dry hydrocarbon gas composition and relatively heavy ^{13}C values of gas hydrocarbons gas. The high temperature and abundance of mineral sulfates of the Cambrian strata were able to support TSR, whereas no mineral sulfate reactants have been detected in the shallower LS2 reservoir with lower temperature. Therefore, Cambrian strata may represent a potentially promising hydrocarbon resource within the Tarim Basin.