Diamondoids and thiadiamondoids generated from hydrothermal pyrolysis of crude oil and TSR experiments

Yanyan Peng1,2,3, Chunfang Cai1,2,3,4, Chenchen Fang6, Liangliang Wu5, Jinzhong Liu5, Peng Sun4 & Dawei Liu1,2,3

Diamondoid compounds are widely used to reflect thermal maturation of high mature source rocks or oils and oil cracking extents. However, diamondoids and thiadiamondoids were demonstrated to have newly been generated and decomposed in our hydrothermal pyrolysis of crude oil and TSR experiments. Our results show that adamantanes and diamantanes are generated primarily within the maturity range 0.48–2.1% and 1.2–3.0% EasyRo, respectively. Their formation is enhanced and the decomposition of diamantanes obviously lags at elevated temperatures compared with anhydrous experiments. MDI, EAI, DMAI-1, DMDI-2 may serve as reliable maturity proxies at > ca.1.0% EasyRo, and other isomerization indices (TMAI-1, TMAI-2 and DMAI-2) are effective for the highly mature organic matter at EasyRo > 2.0%. The extent of oil cracking (EOC) calculated from the broadly used (3- + 4-) MD method (Dahl et al. in Nature 399:54–56, 1999) is proven to overestimate, especially for highly cracked samples due to the new generation of (3- + 4-) MD. Still, it can be corrected using a new formula at < 3.0% EasyRo. Other diamondoid-related indices (e.g., EAI, DMDI-2, As/DSs, As/MDs, DMAs/DMDs, and DMAs/MDs) can also be used to estimate EOC. However, these indices cannot be applied to TSR-altered petroleum. TSR is experimentally confirmed to generate diamantanes and thiadamantanes at 1.81% EasyRo likely via direct reactions of reduced S species with hydrocarbons and accelerate the decomposition of diamantanes at > 2.62% EasyRo compared with thermal chemical alteration (TCA). More studies are needed to assess specific mechanisms for the formation of thiadiamondoids under natural conditions.

Nanometer-sized polycyclic diamondoid hydrocarbons (also polymantanes) appear in petroleum (crude oil and condensates), coal and sedimentary rock in the geosphere1–8, and are considered to form during early diagenesis7,8,9. Results of numerous laboratory syntheses suggest that diamondoids can generate in mudstone and shale source rocks by carbonium ion rearrangements of specific strained polycyclic alkane precursors under thermal stress in the presence of strong Lewis acids acting as catalysts4,11,12. Diamondoids have high thermal stability because they possess a unique ring system composed of cages with three or more fused chair cyclohexane rings. They are considered stable when other hydrocarbons are being cracked down. Therefore, diamondoids provide a measure of the degree of thermal maturation using their isomerization proxies, and (3- + 4-) methyl diamondoid (3- + 4-MD) concentrations can be used to reflect oil cracking extents5.

However, diamondoids have been formed by the pyrolysis of crude oils13 and all four oil fractions14–16, as well as compounds, such as C16, C18, C22, C34 and C36 n-alkanes17 and β-ionone18 without catalysis. All these pyrolysis experiments were conducted in dry conditions, ignoring the effect of water on oil cracking. It is typically

1Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, People’s Republic of China. 2Innovation Academy for Earth Science, Chinese Academy of Sciences, Beijing 100029, People’s Republic of China. 3College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing 100049, People’s Republic of China. 4Key Laboratory of Exploration Technologies for Oil and Gas Resources of Ministry of Education, Yangtze University, Wuhan 430100, Hubei, People’s Republic of China. 5State Key Laboratory of Organic Geochemistry (SKLOG), Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, People’s Republic of China. 6PetroChina Research Institute of Petroleum Exploration and Development, Beijing 100083, People’s Republic of China. 7Email: cai_cf@mail.iggcas.ac.cn
recognized that as a ubiquitous substance in sedimentary basins, water can react with organic compounds to provide hydrogen atoms and may have been involved in quite many reactions\textsuperscript{12–22}; hydrothermal pyrolysis of organic matter at elevated temperatures have been shown to generate gases more similar to natural gases\textsuperscript{23}.

On the other hand, diamondoid has been proposed to create by thermochemical sulfate reduction (TSR), a process whereby aqueous sulfate and petroleum compounds react at high temperatures (≥ 120 °C) to result in elevated H\textsubscript{2}S concentrations in many carbonate reservoirs\textsuperscript{26–29}. This is based on the evidence that TSR-altered oils and condensates in the Cambrian and Ordovician in the Tarim basin and Smackover Formation in the US Gulf Coast have much higher concentrations of diamondoids than non- or minor TSR-altered oils which experienced higher heating.

The diamondoid isomerization ratios are used to assess the thermal maturity of crude oils and source rocks\textsuperscript{30–32} based on the more stable thermodynamic properties of bridge carbon substitution in isomers\textsuperscript{4,10,33}. There are nine isomerization indices: MAI [1-MA/(1-MA + 2-MA)]; EAI [1-EA/(1-EA + 2-EA)]; DMAI-1 [1,3-DMA/(TMA + 1,3,4-TMA)]; TMAI-2 [1,3,5-TMAI/(1,3,5-TMA + 1,3,6-TMA)]; MDI [4-MD/(4-MD + 1-MD + 3-MD)]; DMDI-1 [4,9-DMD/(4,9-DMD + 3,4-DMD)]; and DMDI-2 [4,9-DMD/(4,9-DMD + 4,8-DMD)]\textsuperscript{31,10,13,30,32,34}.

However, the maturity scopes for the application of each index are still controversial. Also, the isomerization of diamondoids is proposed to enhance due to TSR. As a result, diamondoid-based proxies cannot be used to reflect maturity and lithology in the TSR active areas\textsuperscript{25}. However, these proposals have not been confirmed from simulation experiments and the mechanisms for the generation of diamondoids from TSR remain confused.

Thiadiamondoids are diamond-like compounds with a sulfide bond located within the cage structure. Hanin et al.\textsuperscript{35} found that alkylated 2-thiaadamanatanes were present only in TSR-altered oils and thus proposed that alkylated 2-thiaadamanatanes might have been formed by acid-catalyzed rearrangement of tricyclic sulfide. Wei et al.\textsuperscript{36} showed a linear correlation between the concentrations of thiadiamonds and diamondoids in support of their diamondoids origin. Some laboratory experiments were carried out to understand the origin of the thiadiamonds. There may be at least two distinct mechanisms for the formation of thiadiamonds, one under relatively low temperatures and the other at high temperatures. Wei et al.\textsuperscript{37} found that trace amounts of dimethyl-2-thiaadamanatanes were produced by montmorillonite K10-catalyzed rearrangement of thiocholester at 200 °C. Such an origin of dimethyl-2-thiaadamanatanes may have occurred in extractable organic matter or been bound in kerogen of source rocks during early diagenesis. Thiadiamonds are also shown to form from reactions between diamondoids or diamondoidithiols and sulfate or sulfur species at ≥ 350 °C\textsuperscript{37,38}. However, no detectable thiadiamonds were generated from the experiments of a diamondoid-enriched condensate with CaSO\textsubscript{4} or S\textsubscript{0} at 360 °C for 20 h or 40 h\textsuperscript{38}, suggesting that no thiadiamonds have been generated under a lab condition similar to natural geologic environments.

In the present study, hydrothermal pyrolysis and TSR experiments were carried out under the same experimental conditions as those of anhydrous pyrolysis of Fang et al.\textsuperscript{13}. The objectives of this study are to: (1) clarify the effect of water on yields of diamondoids; (2) ascertain whether TSR will lead to the new generation of diamondoids and thiadiamonds; (3) calibrate the reliable EasyRo maturity range of isomerization-related diamondoid proxies; (4) develop diamondoid-related indices to reflect oil cracking extents (EOCs). This study will have a broad application in petroleum evaluation and thus exploration.

Experimental methods and samples
Sample preparation. A typical black oil (53.1% saturated, 16.0% aromatic, 15.4% resin, 3.86% asphaltene, and 12% other components) was collected from the HD23 well of the Tarim Basin, NW China, used by Fang et al.\textsuperscript{13,16}. The oil contains well-preserved, mono-modal distribution of n-alkanes, and abundant biomarkers and has not undergone obvious biodegradation and thermal degradation. This oil is in the early stage of the oil generation window (Ro of 0.6%–0.8%) as indicated by some maturity proxies, such as the methylphenanthrene index (MPI) = 0.62, %Rc (= 0.60 * MPI-1 + 0.37) = 0.74; C\textsubscript{29} steranes ββ/(ββ + αα) = 0.67, C\textsubscript{29} steranes 20S/(20S + 20R) = 0.47, and C\textsubscript{31} hopanes 22S/(22S + 22R) = 0.53. More details can be found in Fang et al.\textsuperscript{16}. Quantitative analysis showed that this oil contained relatively low concentrations of adamantanes and diamantanes (359 μg/g for adamantanes and 79.8 μg/g for diamantanes). Therefore, this oil is suitable to study the evolution of diamondoids during thermal maturation.

Another oil sample (ZS1-L oil) was obtained from the ZS1 well in the Tarim basin. This oil has a low sulfur content of 0.18%, API gravity of 48.3°, viscosity of 1.60 mPa·s, density of 0.789 g/cm\textsuperscript{3} at 20 °C and is composed of saturates (84.2%), aromatics (5.5%), resins (4.6%) and asphaltene (5.8%). The diamondoids and thiaadmantanes concentrations of ZS1-L oil are about 1861 μg/g (1697 μg/g for As, 127 μg/g for Ds and 79.8 μg/g for diamantanes and adamantanes). Therefore, this oil is suitable to study the evolution of diamondoids during thermal maturation.

Another oil sample (ZS1-L oil) was obtained from the ZS1 well in the Tazhong of the Tarim basin. This oil has a low sulfur content of 0.18%, API gravity of 48.3°, viscosity of 1.60 mPa·s, density of 0.789 g/cm\textsuperscript{3} at 20 °C and is composed of saturates (84.2%), aromatics (5.5%), resins (4.6%) and asphaltene (5.8%). The diamondoids and thiaadmantanes concentrations of ZS1-L oil are about 1861 μg/g (1697 μg/g for As, 127 μg/g for Ds and 37 μg/g for (3- + 4-) MD), 19 μg/g, respectively. ZS1-L oil produced from the Cambrian, which experienced higher heating, show much less thiadiamondoid (<20 μg/g), less DBT/Phen ratios (<2.0) and they have δ\textsuperscript{34}S value of +23.3% and most 13\textsuperscript{C} depleted n-alkanes, implying the lowest (negligible) degree of TSR alteration\textsuperscript{25}.

To eliminate the effect of original diamondoids on the quantification of the diamondoid generated during oil cracking, both HD23 oil and ZS1-L oil were evaporated in a fume hood for 120 h before the pyrolysis experiment to remove the original adamantanes according to the method described by Fang et al.\textsuperscript{13}. GC–MS–MS and GC–MS showed that no adamantanes and thiaadmantanes have remained in the evaporated oil. That means both thiaadmantanes and adamantanes had been volatilized before experiments. Inorganic reagents, including MgSO\textsubscript{4}, with δ\textsuperscript{34}S of +3.75‰, elemental S with δ\textsuperscript{34}S of −6.3‰, CaSO\textsubscript{4}·2H\textsubscript{2}O with δ\textsuperscript{34}S of +21.3‰, sodium chloride (NaCl) and magnesium chloride (MgCl\textsubscript{2}), were purchased from Sigma–Aldrich (St. Louis, MO) and are analytical grade (>99.9% purity).

Confined pyrolysis experiments. Pyrolysis experiments were conducted using two methods, gold tubes and quartz tubes, depending on the volumes of the oils. For TSR experiments, the liquid chromatographic (LC)
separation of thiadiamondoids needs to recover sufficient pyrolysates (pyrolysis products). Hence, gold tubes were used for hydrothermal experiments and quartz tubes were used for TSR experiments. The thermal matur-ation of samples was calculated using the Easy%Ro approach developed by Sweeney and Burnham[39]. The pyrolysates were collected and analyzed using GC–MS and GC–MS–MS.

**Quartz tube pyrolysis experiments.** 110 mm-long quartz tubes with 20 mm internal diameter, 1 mm thick wall, giving a total reactor volume of approximately 25 mL, were used for the TSR Experiments. Before loading the tubes, each tube was cleaned using distilled milli-Q water and heated to 450 °C. The solid or liquid reactants were accurately loaded or injected into tubes by a small funnel with an outside diameter slightly smaller than the inner diameter of the quartz tubes. After that, the other end of the tubes was sealed under vacuum conditions. Finally, the tubes with samples loaded were put into autoclaves and desired temperature programs were carried out. After the desired temperature or time was reached, each autoclave was quenched to room temperature before being opened.

We used the Mg$_2$O$_4$-talc-silica system as a mineral buffer at elevated temperatures to keep the in-situ pH in a narrow range (pH ~ 3)[40]. Thus, each quartz tube was loaded with 30 mg talc, 30 mg silica, 100 mL distilled milli-Q water solution with 5.6 wt.% MgCl$_2$, 10 wt.% NaCl and 0.56 wt.% MgSO$_4$. The approach used to regulate in situ chemical conditions for our study relies on chemical reactions known to proceed rapidly at the temperature and pressure conditions of the experiments[41,42]. More details related to the mineral buffer approach are given by Zhang et al.[40,43]. Subsequently, 100 mg of ZS1-L oil sample, 25 mg elemental S and 100 mg MgSO$_4$ were accurately weighed and transferred to the tubes by a small funnel with an outside diameter slightly smaller than the inner diameter of the quartz tubes (Group 1). Blank experiments (TCA experiments) with 100 mg of ZS1-L oil sample and 100 mL solution (5.6 wt.% MgCl$_2$, 10 wt.% NaCl) were performed in parallel. After being sealed under vacuum conditions, the quartz tubes were placed in stainless steel autoclaves and heated from 336 °C to 600 °C at constant heating rates (20 °C/h). The error of the recorded temperatures is ± 1 °C. When the desired temperature or time was reached, each autoclave was quenched to room temperature before being opened.

After pyrolysis, the tubes were placed in a vacuum glass system connected to the GC inlet and then pulled out. After cracking the quartz tube, gaseous hydrocarbons were released and introduced into the GC system. Part of the gas collected at each temperature was bubbled through a basic 5% AgNO$_3$ solution to convert H$_2$S to Ag$_2$S for isotopic analysis, as discussed in Sect. 2.4. The individual gaseous hydrocarbons were quantified using an Agilent Technologies 6890 N gas chromatograph and the pyrolysates (pyrolysis products) were recovered by repeated sonication with dichloromethane. The organic fraction then LC separated to saturate, aromatic and sulfidic fractions using silver nitrate impregnated silica gel column as described below.

**Gold tube pyrolysis experiments.** Oil pyrolysis in hydrothermal conditions was conducted in sealed gold tubes with an internal diameter of 5 mm and wall thickness of 0.5 mm after the method of Fang et al.[13]. Each tube was between 40 and 50 mm long, giving a total reactor volume of approximately 0.5 mL. One end of each tube was crimped and sealed using an argon arc welder. Before loading the samples, the open-ended tubes were heated to 600 °C to remove any residual organic material. Then, specific amounts of samples (i.e., oil and water with the weight ratio of 1:1) were loaded into the gold tubes, which were subsequently flushed with argon for 5 min and sealed under an argon atmosphere. Individual sealed gold tubes were later placed in separate stainless-steel autoclaves and inserted into a pyrolysis oven. The ovens were heated from 336 to 600 °C at two constant rates of 20 °C/h and 2 °C/h, respectively, under the constant pressure of 50 MPa. After reaching desired reaction temperature and the pressure was released, the tubes were taken out from autoclaves.

Two parallel gold tubes were positioned in each autoclave to quantify diamondoid hydrocarbons and the extent of oil cracking (EOC) in pyrolysates. To remove any potential organic contaminants from the exterior of the gold tubes, they were cleaned in dichloromethane and allowed to air dry. Tubes were cooled for 25–30 min using liquid nitrogen following this cleaning procedure. Upon removing the liquid nitrogen, the first cleaned gold tube for diamondoid analysis was rapidly cut in half and placed in a 4 mL sample vial filled with isooctane to minimize loss of volatile components. The parallel gold tube for EOC analysis was first cut off welded ends and then rapidly cut into four equal pieces. The four tube pieces were quickly placed into a 10 mL sample vial filled with dichloromethane and allowed to soak overnight (12–20 h). The vials containing the gold tube pieces were then sonicated repeatedly to recover the pyrolysates. The vials were then opened for a minimal amount of time to remove the pieces of gold tubing and their transfer to 4 mL sample vial containing dichloromethane. Asphaltenes were then precipitated from the products by adding 50-fold (volume ratio for n-hexane/bitumen) cold n-hexane and removed by centrifugation. Then the absolute amount of liquid hydrocarbon was weighed on residual liquid hydrocarbons.

**TSR control-experiments.** Although anhydrite appears to be the reactive oxidant and is replaced by calcite and dolomite in natural TSR reservoirs,[26–28,44–48] it is generally not used in laboratory TSR studies due to its low solubility,[17,49–51]. Magnesium (Mg$^{2+}$) is always present in natural TSR reservoirs and may play a catalytic role in natural TSR processes. To ensure that the sulfate will be involved in TSR experiments, rather than just elemental S, another group of TSR control-experiments using elemental S and CaSO$_4$·2H$_2$O was conducted (Group 2). Therefore, there are two sulfates with large different sulfur isotope values (MgSO$_4$: 3.74‰; CaSO$_4$·2H$_2$O: 21.3‰) were used in the present study for the comparison of the δ$^{34}$S values of H$_2$S. Group1: See 2.2.1 for details; Group2: 100 mg of ZS1-L oil sample, 25 mg elemental S, 100 mg CaSO$_4$·2H$_2$O and 100 mL solution (5.6 wt.% MgCl$_2$, 10 wt.% NaCl and 0.8 wt.% CaSO$_4$·2H$_2$O). In Group 2 experiments, the pyrolysis temperature and time were 360 °C and 48–840 h, respectively. The experimental conditions are consistent with Group 1.
Quantification of diamondoids (GC–MS–MS) and thiaadamantanes (GC–MS). About 50 µL standards isocetane with n-dodecane-d_{13} and n-hexadecane-d_{14} were injected into the sample vial. The vial was ultrasonically treated for 10 min to improve the dissolution of pyrolysates. Leaving the vial for 12 h to precipitate asphaltenes, a volume of the supernatant was transferred into a 2 ml auto-sampler vial for GC–MS–MS. The identification and measurement of diamondoids using the GC–MS–MS method was described in detail elsewhere.

The liquid chromatographic (LC) separation of thiadiamondoids was done according to the method of Wei et al.: LC on silver nitrate-impregnated silica gel was used to fractionate samples into saturate, aromatic, and sulfidic fractions by sequential elution using hexane, dichloromethane, and acetone, respectively. Care was taken to avoid drying the sulfidic fractions during evaporation and concentration to smaller volumes down to 50–150 μl and analyzed for thiaadamantanes using GC–MS method as detailed in Cai et al.

Sulfur isotope analysis. For analysis of δ^{34}S of the H_{2}S (converted to Ag_{2}S) was conducted at the Institute of Geology and Geophysics, Chinese Academy of Sciences. The dried Ag_{2}S and Cu_{2}O were generally mixed in a proportion of 1:10 and then combusted at 1100 °C under vacuum to produce SO_{2}. The resulting SO_{2} was sealed within pyrex tubing and analyzed on a Thermo Delta S mass spectrometer. Sulfur isotope values are expressed as per mil (%) deviations from the sulfur isotope composition of the Vienna Canyon Diablo Troilite (VCDT) using the conventional delta (δ^{34}S) notation. Isotopic results were generally reproducible within ± 0.3‰.

Results

The yield of the individual diamondoid compounds is used to characterize the variation in the absolute amount of diamondoids during the experiments and expresses as the mass of diamondoids generated at each temperature point relative to the initial weight of the oil in each gold tube or quartz tube, according to

\[ Y_i = \frac{M_i}{M_0} \]  

where \( Y_i \) is the yield of the particular diamondoids (e.g., an individual diamondoid compound, a group of compounds, or the total diamondoids); \( M_i \) is the mass (µg) of the relevant diamondoids; \( M_0 \) is the initial mass (g) of the diamondoid-generating substance (original oil mass loaded in the tube).

In this study, 32 diamondoid compounds, including 22 adamantanes and 10 diamantanes were identified by GC–MS–MS, and their concentrations were quantified as in Table 1. Meanwhile, several homologous series of alkylated 2-thiaadamantanes were identified by GC–MS, the tentative peak assignments of alkylated 2-thiaadamantanes were given in Fig. 1.

Hydrothermal experiments of HD23 oil. The first sample was obtained at EasyRo = 0.48% during hydrothermal pyrolysis of an HD23 oil with yields of adamantanes and diamantanes of 137.4 µg/g and 72.4 µg/g, respectively (Supplementary Table S1 and Fig. 2). The yields of adamantanes continue to increase until EasyRo 2.1%, and at > EasyRo 2.1%, adamantanes show a decrease. The yields of diamantanes are rising from EasyRo 0.48% until EasyRo 3.0% (Fig. 2). Adamantanes dominate the generated diamondoids (Fig. 2): adamantanes have concentrations of 137.4–563.9 µg/g, which are three times more than diamantanes (from 72.4–182.1 µg/g) with the maximum value of 563.9 µg/g and 182.1 µg/g at 2.1% EasyRo and 3.0% EasyRo, respectively.

As for individual compounds, the amounts of generated Adamantane (A), Methyladamantane (MA), Ethyladamantane (EA), Dimethyladamantane (DMA) and Trimethyladamantane (TMA) are shown to increase with EasyRo in the range of 0.48–2.1% and rapid decrease in the EasyRo range 2.1–2.5%. The yields of Tetramethyladamantane (TeMA) increase in the EasyRo range 0.48–2.5% and a reversal occurs above the 2.5% EasyRo (Fig. 3 and Supplementary Table S1). Similarly, the yields of different types of diamantanes keep nearly constant in the oil samples from experiments at EasyRo < 1.5% (Fig. 3c,f,i). Subsequently, the yields of Methyladamantane (MD), Dimethyladamantane (DMD) and Trimethyladamantane (TMD) increase in the EasyRo range 1.5–3.0% and a reversal occur above the 3.0% EasyRo (Fig. 3). In addition, adamantanes generated during oil cracking are dominated by DMA, followed by TMA, EA and A, while diamantanes are dominated by MD, DMD, TMD and Diamantane (D).

TSR experiments with ZS1-L oil. H_{2}S and sulfur isotope data. The yields of hydrogen sulfide (H_{2}S) generated in hydrothermal experiments with MgSO_{4} apparently are higher than those with CaSO_{4}2H_{2}O (Table 2). For group 1, the H_{2}S yields increase from 9.57 mmol/g at EasyRo of 0.57 to 17.48 mmol/g at EasyRo of 2.5%, and then decreases slightly to 14.62 mmol/g at EasyRo of 3.87% (Table 2). For group 2, the H_{2}S yields rise from 8.92 mmol/g to 11.47 mmol/g at EasyRo = 1.13–1.69% (Table 2). Moreover, the evolution trends for δ^{34}S of H_{2}S in two groups of experiments are totally different (Table 2 and Fig. 4). The δ^{34}S values of group 1 H_{2}S range from –5.00‰ to –2.45‰ with EasyRo from 0.57‰ to 3.87‰ and show a positive correlation with EasyRo (Table 2). In contrast, the δ^{34}S of H_{2}S generated in group 2 ranged from –5.79‰ to –6.79‰, within ± 1‰ of elsewhere52.

Diamondoids and thiadiamondoids data. For the yields of diamondoids, only diamantanes from the TSR experiments in group 1 are discussed in this study. See “Hydrothermal experiments of HD23 oil” section for details. Adamantanes were evaporatively lost during sample working up, the collected samples show elevated diamantanes yields, and thus only results of diamantanes are listed (Table 3). The yields of total diamantanes and (3- + 4-) MD progressively rises from 129.58 µg/g and 49.11 µg/g before the heating to a maximum of 249.15 µg/g and 79.45 µg/g at EasyRo 1.81%, respectively (Fig. 5d,e). At EasyRo > 1.81%, both (3- + 4-) MD and...
diamantanes show a decrease. Diamantanes generated during TSR are dominated by MD, followed by DMD, TMD and D (Fig. 5a–c). Interestingly, thiadiamondoids including thiaadmantane and methyl thiaadmantanes isomers were detected from the oil after TSR pyrolysis in the 480 °C experiments (1.81% EasyRo) with the maximum yield of diamantanes (Fig. 1).

In the non-TSR or TCA experiments (blank experiments), the maximum yields of total diamantanes and (3- + 4-) MD were 184.95 µg/g and 67.88 µg/g, which are significantly lower than those from TSR experiments, respectively (Fig. 5d,e). In addition, an obvious lag in reversals (2.62% EasyRo) occurred for non-TSR experiments compared to TSR (1.81% EasyRo). Similar to the TSR experiments, diamantanes generated during TCA are dominated by MD, followed by DMD, TMD and D (Fig. 5a–c).

Discussion
Formation and decomposition of diamondoids during hydrothermal pyrolysis of an HD23 oil. Hydrothermal pyrolysis of the HD23 oil shows that both adamantanes and diamantanes were newly generated and decomposed. Still, their yield curves are partially different from the anhydrous: First, diamondoids were generated in a broader range of EasyRo with higher yields at < 1.7% EasyRo during the hydrothermal experiments than the anhydrous (Fig. 6), indicating that water promoted the yields of diamondoids at low EasyRo (< ~ 2.0%). With increasing EasyRo, the differences in the yields of diamondoids between the two became smaller. Among diamondoids, adamantanes show an increase in their yields from 0.48% to 2.1% EasyRo (Fig. 6a), and the range is wider than the range of 1.0–2.1% for the anhydrous experiments. Similarly, diamantanes began to be generated at 0.79% EasyRo from hydrothermal pyrolysis experiments, much lower than 1.7% EasyRo for the anhydrous pyrolysis experiments (Fig. 6b). Second, the decomposition of diamantanes

| Peak number | Diamondoid compound | m/z | Abbreviation |
|-------------|---------------------|-----|--------------|
| 1           | Adamantane          | 136 → 93 | A            |
| 2           | 1-Methyladamantane  | 150 → 135 | 1-MA          |
| 3           | 2-Methyladamantane  | 150 → 135 | 2-MA          |
| 4           | 1-Ethyladamantane   | 164 → 135 | 1-EA          |
| 5           | 2-Ethyladamantane   | 164 → 135 | 2-EA          |
| 6           | 1,3-Dimethyladamantane | 164 → 149 | 1,3-DMA      |
| 7           | 1,4-Dimethyladamantane (cis) | 164 → 149 | 1,4-DMA (cis) |
| 8           | 1,4-Dimethyladamantane (trans) | 164 → 149 | 1,4-DMA (trans) |
| 9           | 1,2-Dimethyladamantane | 164 → 149 | 1,2-DMA      |
| 10          | 2,6- + 2,4-Dimethyladamantane | 164 → 149 | 2,6- + 2,4-DMA |
| 11          | 1-Ethyl3-methyladamantane | 178 → 149 | 1-E,3-MA |
| 12          | 1,3,5-Trimethyladamantane | 178 → 163 | 1,3,5-TMA |
| 13          | 1,3,6-Trimethyladamantane | 178 → 163 | 1,3,6-TMA |
| 14          | 1,3,4-Trimethyladamantane (cis) | 178 → 163 | 1,3,4-TMA (cis) |
| 15          | 1,3,4-Trimethyladamantane (trans) | 178 → 163 | 1,3,4-TMA (trans) |
| 16          | 1,2,3-Trimethyladamantane | 178 → 163 | 1,2,3-TMA |
| 17          | 1-Ethyl3,5-dimethyladamantane | 192 → 163 | 1-E,3,5-DMA |
| 18          | 1,3,5,7-Tetramethyladamantane | 192 → 177 | 1,3,5,7-TeMA |
| 19          | 1,2,5,7-Tetramethyladamantane | 192 → 177 | 1,2,5,7-TeMA |
| 20          | 1,3,5,6-Tetramethyladamantane | 192 → 177 | 1,3,5,6-TeMA |
| 21          | 1,2,3,5-Tetramethyladamantane | 192 → 177 | 1,2,3,5-TeMA |
| 22          | 1-Ethyl3,5,7-trimethyladamantane | 192 → 177 | 1-E,3,5,7-TMA |
| 1.S.-1      | n-Dodecane-d26      | 196 → 82  | n-C12-d26 |
| 23          | Diamantane          | 188 → 131 | D            |
| 24          | 4-Methyldiamantane  | 202 → 187 | 4-MD         |
| 25          | 1-Methyldiamantane  | 202 → 187 | 1-MD         |
| 26          | 3-Methyldiamantane  | 202 → 187 | 3-MD         |
| 27          | 4,9-Dimethyldiamantane | 216 → 201 | 4,9-DMD |
| 28          | 1,4-Dimethyldiamantane + 2,4-Diamethyldiamantane | 216 → 201 | 1,4-DMD + 2,4-DMD |
| 29          | 4,8-Dimethyldiamantane | 216 → 201 | 4,8-DMD |
| 30          | 3,4-Dimethyldiamantane | 216 → 201 | 3,4-DMD |
| 31          | 1,4,9-Trimethyldiamantane | 230 → 215 | 1,4,9-TMD |
| 32          | 3,4,9-Trimethyldiamantane | 230 → 215 | 3,4,9-TMD |
| 1.S.-2      | n-Hexadecane-d34    | 260 → 82  | n-C16-d34 |

Table 1. The detected diamondoid compounds in this study.
and TeMA from the hydrothermal experiments occurred at EasyRo > 3.0% and EasyRo > 2.5%, obviously lagging behind that from the corresponding anhydrous experiments at EasyRo > 2.5% and 2.1%, respectively (Figs. 3 and 6b). This may indicate that water can delay the decomposition of high molecular weight diamondoids during oil thermal cracking.

Figure 1. Mass chromatograms of alkylated thiadiamantanes in the sulfidic fraction of the products from TSR experiments (Group1) at 480 °C. 5-M-2-TA = 5-methyl-2-thiaadmantane; 5,7-DM-2-TA = 5,7-dimethyl-2-thiaadmantane; 1,5-DM-2-TA = 1,5-dimethyl-2-thiaadmantane; 1,3-DM-2-TA = 1,3-dimethyl-2-thiaadmantane; 3,5,7-TM-2-TA = 3,5,7-trimethyl-2-thiaadmantane; 1,5,7-TM-2-TA = 1,5,7-trimethyl-2-thiaadmantane; 1,3,7-TM-2-TA = 1,3,7-trimethyl-2-thiaadmantane; 1,3,5-TM-2-TA = 1,3,5-trimethyl-2-thiaadmantane; 1,3,5,7-TeM-2-TA = 1,3,5,7-tetramethyl-2-thiaadmantane; TeM-2-TA = tetramethyl-2-thiaadmantane.

Figure 2. Variation in diamondoids yields (µg/g oil) with EasyRo (%) from hydrothermal pyrolysis of oil. (Total = sum of adamantanes and diamantanes).
Larger yields of diamondoids from hydrothermal pyrolysis than the anhydrous (Fig. 6) can be explained as follow. As the result of ionic reactions, hydrothermal pyrolysis of organic matter generates more considerable amounts of intermediate olefinic and isomeric hydrocarbons than the anhydrous pyrolysis. In turn, the olefins and isomeric hydrocarbons will be hydrogenated by rapid free radical reactions, raising the yields of diamondoids during hydrothermal pyrolysis. That is, combining ionic and free radical reactions can accelerate isomerization and cyclization of these olefinic hydrocarbons to generate the relatively high yields of diamondoids under hydrothermal pyrolysis.

It is necessary to discuss which one, hydrothermal or anhydrous pyrolysis, has the products representing maturation of natural samples, considering the more significant differences in EasyRo for decomposition of diamantanes and yields of diamondoids between the two. The EasyRo for the generation and decomposition of the (3- + 4-) MD in this study are close to that of natural samples from both coals and rocks, that is, ca. 1.2% EasyRo vs 1.1% Ro for the generation and 3.0% EasyRo vs ca. 4.0% Ro for the decomposition. In contrast, EasyRo obtained from anhydrous pyrolysis are deviated more from the natural samples, 1.5% for the generation and 2.5% for the decomposition. Ro values are approximately equal to the calculated EasyRo values at EasyRo < 1.5 ~ 2.0%. The differences between Ro and calculated EasyRo are slightly more significant at EasyRo > 1.5 ~ 2.0%, likely due to the change in the chemical composition of solid kerogen with higher maturity levels. This result suggests that hydrothermal pyrolysis has the products closer to the cracking of natural samples, which is supported by the gas produced from the hydrothermal pyrolysis more similar to the natural gas than anhydrous pyrolysis. Moreover, water is ubiquitous in petroleum reservoirs and may provide H and O involved in petroleum generation and evolution, suggesting hydrothermal pyrolysis may represent the maturation of natural samples better than the anhydrous.

**Diamondoids as proxies for thermal maturity.** It is widely accepted those isomerization ratios such as MAI, MDI, EAI, DMAI-1, TMAI-1, TMAI-2, DMDI-1 and DMDI-2 can be used to determine the thermal maturity of highly mature crude oils (Ro > 1.1%)[9,10,30,32,34], and they can be applied for different maturity ranges[16]. Isomerization-related diamondoid ratios are unaffected by thermal maturity levels with EasyRo < 2.0% in anhydrous pyrolysates and used as proxies of thermal maturity at > 2.0% EasyRo[35]. In this study, MDI, EAI, DMAI-1 and DMDI-2 can be applied to reflect maturity at much lower EasyRo from hydrothermal pyrolysis: 1.47–3.5% EasyRo for MDI with R² of 0.8717 (Fig. 7b), 0.86–2.5% EasyRo for EAI with R² of 0.8412 (Fig. 7c), 1.08–3.5% EasyRo for DMAI-1 with R² of 0.8502 (Fig. 7e) and 1.08–3.5% EasyRo for DMDI-2 with R² of 0.9304 (Fig. 7d). This supports that MDI is an effective proxy of maturity at > 1.3% Ro for either source rock extracts or hydro-
However, consistent with Fang et al.\textsuperscript{13}, MAI in this study seems not related to EasyRo (Fig. 7a), and thus cannot be used as a proxy to assess the thermal maturity of oils. MDI, EAI, DMAI-1, DMDI-2 can serve as reliable maturity indicators with broad EasyRo ranges mainly > 1.0%. In contrast, at EasyRo < 1.0%, diamondoid-related proxies including MDI, EAI, DMAI-1, DMDI-2 show no correlations with EasyRo, suggesting that they cannot be used to determine the maturity of oils and thus source rocks. The previous observation supports this proposal that diamondoid concentrations and distributions are dependent on the source rocks instead of maturity within the oil window\textsuperscript{58}.

Other isomerization ratios (e.g., DMAI-2, TMAI-2 and TMAI-1) show good correlations with thermal maturity in the higher EasyRo ranges of 2.08–3.5% with $R^2$ of 0.9617, 0.9752 and 0.8581 (Fig. 7g–i). These ratios seem controlled by the parent organic matter during the generation stage of diamondoids (EasyRo < 2.0%), and thus may reflect the source feature rather than maturity\textsuperscript{16}. They can be used to reflect maturity only at higher maturity levels (> 2.0% EasyRo) as found in Fang et al.\textsuperscript{16} and this study. However, unlike other studies, DMDI-1 does not correlate well with EasyRo values in this study (Fig. 7f), probably due to the relatively sizeable analytical error associated with low concentrations of dimethyldiamantanes in the pyrolysates.

### Table 2

Gas yields (mmol/g oil) and $^{34}$S isotopic ratios of H$_2$S in hydrothermal experiments involving S$^0$, MgSO$_4$, and CaSO$_4$·2H$_2$O. – Indicates not detected; * The blank experiments.

| Temperature (℃) | Time (h) | EasyRo (%) | MgSO$_4$/CaSO$_4$·2H$_2$O (mmol/g oil) | $^{34}$S$_{H_2S}$ | CO$_2$ | $^{34}$S$_{H_2S}$/S$^0$ (%) |
|-----------------|---------|------------|----------------------------------------|----------------|-------|--------------------------|
| 536             | 0.57    | 13.93      | 13.68                                  | 9.66           | 0.38  | 0.71                     | −5.00     |
| 360             | 0.68    | 13.45      | 12.85                                  | 9.42           | 0.47  | 0.73                     | −4.87     |
| 384             | 0.79    | 13.47      | 12.85                                  | 9.49           | 0.44  | 0.74                     | −4.93     |
| 408             | 0.96    | 13.52      | 12.47                                  | 10.57          | 0.54  | 0.85                     | −3.96     |
| 432             | 1.19    | 13.45      | 12.91                                  | 11.04          | 0.63  | 0.86                     | −3.68     |
| 456             | 1.47    | 13.64      | 12.24                                  | 11.36          | 0.84  | 0.93                     | −3.05     |
| 480             | 1.81    | 13.05      | 12.92                                  | 12.28          | 1.07  | 0.95                     | −2.74     |
| 504             | 2.19    | 11.41      | 11.59                                  | 15.12          | 1.15  | 1.31                     | −2.74     |
| 528             | 2.62    | 12.86      | 12.79                                  | 17.43          | 1.70  | 1.36                     | −2.74     |
| 552             | 3.06    | 13.84      | 13.00                                  | 16.96          | 1.93  | 1.30                     | −2.97     |
| 576             | 3.5     | 13.35      | 12.18                                  | 15.58          | 1.99  | 1.28                     | −2.49     |
| 600             | 3.87    | 13.41      | 13.11                                  | 14.62          | 2.14  | 1.12                     | −2.45     |

**Group 1**: Non-isothermal pyrolysis of ZS1-L oil involving S$^0$ and MgSO$_4$ under constant rate of 20℃/h

**Group 2**: Isothermal pyrolysis of ZS1-L oil involving S$^0$ and CaSO$_4$·2H$_2$O at 360℃ for 48–840 h2

![Figure 4](https://doi.org/10.1038/s41598-021-04270-z)

**Figure 4**: The $^{34}$S isotopic ratios of H$_2$S in hydrothermal experiments involving S$^0$, MgSO$_4$, and CaSO$_4$·2H$_2$O.
Diamondoids as proxies for the extent of oil cracking. Oil cracking involves the thermal breakdown of heavy hydrocarbons to smaller ones, or the process of ultimately converting oil to hydrogen-rich gas and carbon-rich pyrobitumen. In our hydrothermal pyrolysis, we found that the extent of oil cracking (EOC; i.e., the percentage of liquid hydrocarbon converted to gas and pyrobitumen, or \( EOC = (1 - C_0/C_C) \times 100 \% \)) can be calculated as (1  −  C0/Cc) × 100%, in which (3-  + 4-) MD is assumed not to have newly been generated or decomposed during oil cracking (\( C_0 \) and \( C_C \) are concentrations of (3- + 4-) MD before and after oil cracking). However, an increase in the (3- + 4-) MD occurs at ca. 1.2% EasyRo. The decrease in the (3-  + 4-) MD yield is observed at 3.0% EasyRo during oil thermal cracking experiments (Fig. 9a), suggesting the assumption does not apply (Fig. 9b). This finding is supported by other pyrolysis experiments, lending usage of (1−C0/Cc) × 100% is suspect. Based on our results, Dahl’s formula for EOC is only applicable to a very narrow range of maturity (EasyRo < 1.2%), and gives higher values than those obtained from our hydrothermal experiments (Fig. 8a). The differences between the two results become progressively smaller with the increasing extent of oil cracking with the values from 6% to 21% at EasyRo from 0.48% to 1.81% (Fig. 8a). Oil cracking occurs at slower rates with further increasing maturation as reflected in the increase in EasyRo from 1.81% (480 °C) to 3.5% (600 °C) and relatively stable EOC around 90% to 95%. However, at the high maturity (above 500 °C) almost all of the liquid hydrocarbons have been consumed, so the error is around ±5% from 2.19% (504 °C) to 3.5% (600 °C) in the oil pyrolysis experiments.

EOC can also be calculated as (1  −  C0/Cc) × 100%, in which (3- + 4-) MD is assumed not to have newly been generated or decomposed during oil cracking (\( C_0 \) and \( C_C \) are concentrations of (3- + 4-) MD before and after oil cracking). However, an increase in the (3- + 4-) MD occurs at ca. 1.2% EasyRo. The decrease in the (3- + 4-) MD yield is observed at 3.0% EasyRo during oil thermal cracking experiments (Fig. 9a), suggesting the assumption does not apply (Fig. 9b). This finding is supported by other pyrolysis experiments, lending usage of (1−C0/Cc) × 100% is suspect. Based on our results, Dahl’s formula for EOC is only applicable to a very narrow range of maturity (EasyRo < 1.2%), and gives higher values than those obtained from our hydrothermal experiments (Fig. 8a). The differences between the two results become progressively smaller with the increasing extent of oil cracking with the values from 6% to 21% at EasyRo from 0.48% to 1.81% (Fig. 8a). Oil cracking occurs at slower rates with further increasing maturation as reflected in the increase in EasyRo from 1.81% (480 °C) to 3.5% (600 °C) and relatively stable EOC around 90% to 95%. However, at the high maturity (above 500 °C) almost all of the liquid hydrocarbons have been consumed, so the error is around ±5% from 2.19% (504 °C) to 3.5% (600 °C) in the oil pyrolysis experiments.

EOC can also be calculated as (1  −  C0/Cc) × 100%, in which (3- + 4-) MD is assumed not to have newly been generated or decomposed during oil cracking (\( C_0 \) and \( C_C \) are concentrations of (3- + 4-) MD before and after oil cracking). However, an increase in the (3- + 4-) MD occurs at ca. 1.2% EasyRo. The decrease in the (3- + 4-) MD yield is observed at 3.0% EasyRo during oil thermal cracking experiments (Fig. 9a), suggesting the assumption does not apply (Fig. 9b). This finding is supported by other pyrolysis experiments, lending usage of (1−C0/Cc) × 100% is suspect. Based on our results, Dahl’s formula for EOC is only applicable to a very narrow range of maturity (EasyRo < 1.2%), and gives higher values than those obtained from our hydrothermal experiments (Fig. 8a). The differences between the two results become progressively smaller with the increasing extent of oil cracking with the values from 6% to 21% at EasyRo from 0.48% to 1.81% (Fig. 8a). Oil cracking occurs at slower rates with further increasing maturation as reflected in the increase in EasyRo from 1.81% (480 °C) to 3.5% (600 °C) and relatively stable EOC around 90% to 95%. However, at the high maturity (above 500 °C) almost all of the liquid hydrocarbons have been consumed, so the error is around ±5% from 2.19% (504 °C) to 3.5% (600 °C) in the oil pyrolysis experiments.
This implies that these parameters might help assess the extent of oil cracking (EOC2). Note that the isomerization ratio of DMDI-2 has a good correlation with EOC2 throughout the EasyRo range examined, indicating that it may be a reliable proxy for a wide range of maturity.

On the other hand, the concentration ratios of diamondoid pairs are expected to eliminate the effect of matrix changes during the thermal cracking of oil. Some diamondoid concentration ratios (As/Ds, MAs/MDs, DMAs/DMDs, and DMAs/MDs) appear positively correlated with EOC2 at EasyRo from 0.48% to 2.1% (Fig. 10c-f) with regressive equations as follow.

\[
\text{EAI} = 0.0015 \text{EOC2} + 0.2635 \quad r^2 = 0.6355 \quad (\text{EasyRo} < 1.81\%)
\]

\[
\text{DMDI-2} = 0.0024 \text{EOC2} + 0.3177 \quad r^2 = 0.7271
\]

\[
\text{As/Ds} = 0.0115 \text{EOC2} + 1.7478 \quad r^2 = 0.6052 \quad (\text{EasyRo} < 2.1\%)
\]

\[
\text{MAs/MDs} = 0.0083 \text{EOC2} + 0.2543 \quad r^2 = 0.8507 \quad (\text{EasyRo} < 2.1\%)
\]

\[
\text{DMAs/MDs} = 0.0131 \text{EOC2} + 0.5355 \quad r^2 = 0.8054 \quad (\text{EasyRo} < 2.1\%)
\]
Figure 6. Variation in the yields (µg/g oil) of diamondoids generated from hydrothermal and Fang et al.13 anhydrous pyrolysis of the same oil with EasyRo (%): (a) As, (b) Ds, (c) Total, (d) (3-+4-) MD. As = total adamantanes; Ds = total diamantanes.

Figure 7. Plots showing the variation of diamondoid indices (MAI, MDI, DMAI-1, DMAI-2, DMDI-1, EAI, TMAI-1 and TMAI-2) with EasyRo (%) from anhydrous and hydrothermal pyrolysis of oil. MAI = 1-MA/(1-MA + 2-MA), MDI = 4-MD/(4-MD + 1-MD + 3-MD), DMAI-1 = 1,3-DMA/(1,2-DMA + 1,3-DMA), DMAI-2 = 1,3-DMA/(1,2-DMA + 1,4-DMA), DMDI-1 = 3,4-DMD/(4,9-DMD + 3,4-DMD), DMDI-2 = 4,8-DMD/(4,9-DMD + 4,8-DMD), EAI = 2-EA/(1-EA + 2-EA), TMAI-1 = 1,3,5-TMA/(1,3,5-TMA + 1,3,4-TMA), TMAI-2 = 1,3,5-TMA/(1,3,5-TMA + 1,3,6-TMA).
However, the above diamondoid isomerization ratios negatively correlate with EasyRo values of > 2.1% when adamantanesadamananes enter the decomposition stage. The above equations established from hydrothermal pyrolysis are proposed to be used as proxies of the extent of oil cracking during 0.48–2.1% EasyRo for natural petroleum reservoirs.

\[
\text{DMAs/DMDs} = 0.0225 \text{EOC2} + 0.8348 \quad r^2 = 0.6159 \quad (\text{EasyRo < 2.1%})
\]  

(7)
New generation of diamondoids and thiadiamondoids during TSR?  

In group 1 and group 2 experiments, H2S may have been derived from: 1) cracking of ZS1-L oil, 2) elemental sulfur hydrolysis, 3) thermochemical reduction of MgSO4 or CaSO4·2H2O. The H2S is not mainly from cracking of ZS1-L oil because thermal decomposition of ZS1-L oil with a sulfur content of 0.18% can only generate 0.056 mmol/g H2S. Thus, H2S must have mainly derived from the reduction of elemental S, MgSO4 or CaSO4·2H2O. Elemental S may react with water at temperatures as low as 200 °C in the following disproportionation reaction:

$$4S^0 + 4H_2O \rightarrow SO_4^{2-} + 3H_2S + 2H^+$$  \hspace{1cm} (8)

An alternative production pathway for the exceptionally high yields of H2S was via the classical aqueous reaction of elemental S and hydrocarbon shown in Eq. (9):

$$4S^0 + 1.33(-CH_2-) + 2.66H_2O \rightarrow 4H_2S + 1.33CO_2$$  \hspace{1cm} (9)

The H2S/S0 molar ratio can be used to determine the amount of H2S from the conversion of elemental S (Table 2), and thus will approach 0.75 and 1 for Eqs. (8) and (9), respectively.

The results from group 1 experiment at the lowest temperature of 336 °C (0.57% EasyRo) has H2S/S0 molar ratio of around 0.71 and δ34S H2S value of −5‰ (Table 2), being close to that of elemental S (−6.3‰), indicating that nearly all H2S was derived from elemental S. Furthermore, the increasing production of CO2 did not start until above 408 °C, when the H2S/S0 molar ratio began to be greater than 0.75. This inconsistency in the product implies H2S was not produced by elemental sulfur via Eq. (8) from 336–384 °C (0.57–0.79% EasyRo) in group 1. Thus, MgSO4 source has to be considered with an Eq. (10).

$$MgSO_4 + 2H^+ + CH_4 \rightarrow CO_2 + H_2S + 2H_2O + Mg^{2+}$$  \hspace{1cm} (10)

It can be expected that with an increase in temperature, more MgSO4 is involved in TSR reaction, or TSR proceeds to higher degrees. Suppose all H2S was generated from reactions of S0 with hydrocarbons without generation of SO42− (Eq. 9). In that case, the H2S is expected to have the molarity of elemental S of about 12.79 mmol (26.8 mg), which is lower than H2S from experiments at 504 °C to 600 °C. Hence, the conversion of elemental S

Figure 10. Relationships between diamondoid-related proxies and EOC2 (%): (a) EAI; (b) DMDI-2; (c) DMAs/MDs, (d) DMDAs/DMDs, (e) As/Ds, (f) MAs/MDs. Triangles indicate data from EasyRo > 3.0%.
is insufficient for the generation of H$_2$S from 504 °C to 600 °C, suggesting that MgSO$_4$ in group 1 experiments must have been involved in the reaction. On the other hand, the H$_2$S/S$^0$ molar ratio gradually increases until it reaches a maximum of 1.36 at 528 °C (2.62% EasyRo) with the temperature increasing, then gradually decreases to 1.12 (Table 2). Meanwhile, the $\delta^{34}$S value of H$_2$S show rise from −5% to −2.45%, getting closer to the $\delta^{34}$S value of MgSO$_4$ (δ$^{34}$S of +3.75%), suggesting that the H$_2$S may have significantly derived from the reduction of MgSO$_4$ in the aqueous experiments following Eq. (10).

Note that some of the H$_2$S is expected to react with hydrocarbons to form OSCs such as thiols, (poly)sulfides, thioephens, and benzothioephens, thus free H$_2$S amount is expected to be lower than that of decrease in reactants MgSO$_4$ and elemental sulfur and more incorporation may have occurred and thus shows a decreasing trend at EasyRo = 2.5–3.87% (Table 2).

In contrast, no TSR may have occurred in group 2 experiments but reactions between elemental S and hydrocarbons with no CaSO$_4$·2H$_2$O involved. Firstly, the maximum value of the H$_2$S/S$^0$ molar ratio in Group 2 is around 0.9 at the first EasyRo = 1.13 and then slightly decreases from 0.93 to 0.65 with EasyRo from 1.13% to 1.69%. Secondly, the $\delta^{34}$S of H$_2$S generated in Group 2 ranged from −5.79% to −6.79%, within ±1% of elemental S (-6.3‰). Finally, Group 2 produced a very high amount of CO$_2$ (1.71 mmol/g at 1.13% EasyRo) at the first desired time compared to the meager yields produced by Group 1 above 360 °C (Table 2). This indicates H$_2$S was generated via the classical aqueous reaction of elemental S and hydrocarbon shown in Eq. (9).

Therefore, it can be concluded that TSR has occurred in the group 1 experiments as reflected by the positive shift in $\delta^{34}$S value of H$_2$S due to reactant MgSO$_4$ as the most $^{34}$S-enriched sulfur species in this study; the increase of CO$_2$ and H$_2$S/S$^0$ molar ratio, and shows higher degrees with increasing temperatures. In contrast, the non-TSR reactions between hydrocarbons and H$_2$S or elemental sulfur as shown by group 2 experiments have produced H$_2$S/S$^0$ molar ratio of 0.75 and $\delta^{34}$S value of H$_2$S close to the elemental sulfur.

**Generation of diamondoids during TSR.** Group 1 experiments show the presence of TSR reaction significantly accelerates the generation and increases the yield of diamantanes relative to the blank non-TSR experiments (TCA; Fig. 5). Here, diamantanes are shown to be dominantly generated during TSR in the EasyRo range of 0.57–1.81% with maximum yields of 240 μg/g at 1.81% EasyRo. However, peak generation of diamantanes of 184.9 μg/g from TCA on ZS1-L oil occurs at 2.62% EasyRo (Fig. 5d), which is significantly lower than TSR (Fig. 5d). In addition, diamantanes remain stable at up to 528 °C during TCA while the temperature is 480 °C during TSR at the same heating rates of 20 °C/h (Fig. 5f). This result may be due to the catalysis of S radical (i.e., from H$_2$S), which can accelerate the decomposition of HC or OM.

Moreover, TSR significantly increases the yield of diamantanes compared with the thermal chemical alteration (TCA; Fig. 5a–e). From 0.57% EasyRo to 1.81% EasyRo, the yield of diamantanes detected in the TSR was higher than that of TCA, indicating that diamantanes must have been newly generated during TSR (Fig. 5d). Elemental S can substantially lower the onset temperature of thermal chemical alteration and appears to reduce the activation energy of low-sulfur oil thermal chemical alteration by approximately 92 kJ mol$^{-1}$. Therefore, the observed acceleration of diamantanes generation is possibly due to sulfur-derived radical species or H$_2$S formed via TSR or disproportionation reaction that enhances the formation of diamantanes.

The mechanism for generating diamondoids during TSR may be through free radical reactions, a mechanism similar to their generation from high temperature cracking of alkanes during the experiment simulation. Consequently, we considered that the sulfur-derived radical species or H$_2$S during TSR have a facilitative effect on the cleavage of high molecular-mass fractions, resulting in the new generation of diamondoids from TSR experiments in the present study. Meanwhile, hydrogen exchange between water and organic matter also proceeds via sulfur-derived radical species (i.e., from H$_2$S), leading to demethylation and isomerization of hydrocarbon to form diamondoids. Briefly, TSR can lead to the generation of diamondoids through free radical reactions.

Notably, TSR resulted in the new generation of diamondoids (Fig. 5), and thus had a significant effect on the distribution and concentration of diamondoids. Thus, in TSR-altered oils, diamondoid-related maturity proxies have been altered significantly (Table 3), and thus cannot be used to indicate EOC.

**Generation of thiaadmantoids during TSR.** Thiaadmantane and methyl thiaadmantanes isomers were detected at 1.81% EasyRo when the yields of diamantanes reached a maximum value during the hydrothermal pyrolysis of ZS1-L oil under TSR condition (Fig. 1). To our knowledge, this is the first successful laboratory synthesis of thiaadmantanes from a petroleum sample via TSR. Although previous laboratory experiments have successfully synthesized thiaadmantanes, thiaadmantanes were only detected from reactions of reduced S or CaSO$_4$ with pure diamondoids. Based on these laboratory experiments, Wei et al. proposed that diamondoids appear to be the only precursors of thiaadmantanes during TSR (Fig. 11a). Our results indicate that diamondoids are formed earlier than thiaadmantanes, thus, thiaadmantanes may have been generated from reactions of diamondoids with sulfur species. However, diamondoids can be formed from alkanes and it is hard to break C–C bonds in cage structure of diamondoids. These facts indicate that thiaadmantoids and diamondoids may have been generated simultaneously, likely not via reactions with diamondoids based on the following aspects (Fig. 11). Firstly, during TSR experiments at EasyRo of 1.81%, both diamantanes and corresponding thiaadmantanes were formed, and thiaadmantanes show positive correlations with the corresponding diamantanes (2-TA vs D; M-2-TA vs MD; DM-2-TA vs DMD; TM-2-TA vs TMD) from (Fig. 12a,b) with a higher yield of diamantanes during TSR compared with hydrothermal pyrolysis (TCA; Fig. 12a). The experimental results indicate that diamondoids and thiaadmantanes may have been formed simultaneously, which is consistent with case studies showing the positive relationships between diamondoids and thiaadmantoids concentrations from oils and condensates from the Tarim Basin and Gulf of Mexico Basin. In contrast, if diamondoids are the only precursor of thiaadmantane, conversion of significant amounts of diamondoids to thiaadmantanes may lead to a...
negative correlation between the yields of diamondoids and thiaadamantanes. Secondly, C–C bonds in the cage structure of diamondoids have been proposed to be hard to break up due to their thermal stability\cite{30-32}, it is more energy-favorable to form thiaadamantanes from other non-diamondoids compounds. Thus, it is reasonable for thiaadamantanes to have been generated during the formation of diamondoids. Considering that diamondoids can be generated from pyrolysis of all four fractions\cite{13-16}, a non-diamondoid source of thiaadamantanes is proposed here as shown in Fig. 11b.

However, thiaadamantanes were only detected at 1.81% EasyRo (480 °C) not at other TSR experiments at temperatures from 336 °C to 600 °C. It is possible for thiaadamantanes to have been formed in relatively high-temperature conditions and are expected to decompose at higher EasyRo. Xiao et al.\cite{67} proposed that thiaadamantanes
show slight to moderate cracking at EasyRo of 1.81%. In contrast, Wei et al. proposed that diamantane is stable up to 550 °C in the laboratory, which is consistent with the stability of adamantane reported by Oya et al., thus are thiadamantanes are far less thermally stable than diamondoids. Similarly, thiadamantanes were found to be thermally degraded at temperatures > 180 °C in TSR-altered oils from the Smackover and Norphlet formations of the US Gulf of Mexico. The temperature of 180 °C can correspond to the equivalent vitrinite reflectance values of about 1.9% based on the thermal history of the Norphlet Sandstone in Mobile Bay, northern Gulf of Mexico. Our TSR experimental results are generally consistent with this field observation. Considering that thiadamantanes may be decomposed, their occurrence at the experiment at 480 °C suggests that the condition may be favorable for thiadamantanes to be generated without being significantly decomposed. More simulation experiments are needed to verify this proposal.

Conclusions
Based on our experiments, we can conclude that:

1. Hydrothermal pyrolysis experiments indicate that water can enhance the yields of diamondoids. Diamondoids may have mainly generated in 0.48% ~ 2.1% EasyRo and decomposed at > 2.1% EasyRo. Especially, diamantanes show decomposition at > 3.0% EasyRo.
2. MDI, EAI, DMAI-1, DMDI-2 are shown to be reliable maturity proxies at maturity over ca.1.0% EasyRo, and TMAI-1, TMAI-2 and DMAI-2 can only be used to reflect the higher maturity at EasyRo > 2.0%.
3. The extents of oil cracking (EOC) calculated from Dahl’s (3- + 4- ) MD method are higher than the actual values, especially for highly mature samples due to their new generation, but can be obtained using our correction formula (EOC2 = 1.2402 × EOC1−28.952) at EasyRo < 3.0%.
4. EAI, DMDI-2, As/DS, MAs/MDs, DMAs/DMDs, and DMAs/MDs can serve as molecular proxies to estimate the extent of oil cracking at EasyRo mainly < 2.1%.
5. TSR is found to newly generate diamantanes at < 1.81% EasyRo followed by their decomposition, while the decomposition of diamantanes by TCA occurs at > 2.62% EasyRo, and thus any diamondoid-related proxy cannot be used to reflect maturity and EOC.
6. Thiadamantanes were generated from an experiment of TSR by oil at 1.81% EasyRo for the first time, likely via pyrolysis of non-diamondoid structure hydrocarbons.

Our results provide crucial experimental evidence for understanding the evolution of diamondoids during thermal maturity and TSR under natural conditions.

Received: 4 September 2021; Accepted: 20 December 2021
Published online: 07 January 2022

References
1. Landa, S. Adamantane and its derivatives. *Rapa a Ullie* 1, 5–7 (1959).
2. Petrov, A., Arefjev, O. A. & Yakubson, Z. V. Hydrocarbons of adamantane series as indices of petroleum catagenesis process. In *Advances in Organic Geochemistry 1973* (eds. B. Tissot and F. Biennert). Editions Technip, Paris pp. 517–522. (1974).
3. McKervey, M. A. Synthetic approaches to large diamondoid hydrocarbons. *Tetrahedron* 36, 971–992 (1980).
4. Wingert, W. S. GC-MS analysis of diamondoid hydrocarbons in Smackover petroleums. *Fuel* 71, 37–43 (1992).
5. Dahl, J. E. et al. Diamondoid hydrocarbons as indicators of oil cracking. *Nature* 399, 54–56 (1999).
6. Dahl, J. E., Liu, S. G. & Carlson, R. M. K. Isolation and structure of higher diamondoids, nanometer-sized diamond molecules. *Science* 299, 96–99 (2003).
7. Wei, Z. B., Moldowkan, J. M., Jarvie, D. M. & Hill, R. The fate of diamondoids in coals and sedimentary rocks. *Geology* 34, 1013–1016 (2006).
8. Wei, Z. B., Moldowkan, J. M. & Paytan, A. Diamondoids and molecular biomarkers generated from modern sediments in the absence and presence of minerals during hydrous pyrolysis. *Org. Geochem.* 37, 891–911 (2006).
9. Schulz, L. K., Wilhelms, A., Rein, E. & Steen, A. S. Application of diamondoids to distinguish source rock facies. *Org. Geochem.* 32, 365–375 (2001).
10. Wei, Z. B. et al. Diamondoid hydrocarbons as a molecular proxy for thermal maturity and oil cracking: Geochemical models from hydrous pyrolysis. *Org. Geochem.* 38, 227–249 (2007).
11. Fort, R. C. & Schleyer, P. R. Adamantane: consequences of the diamondoid structure. *Org. Geochem.* 32, 1–8 (2012).
12. Giruts, M. V., Rusinova, G. V. & Gordadze, G. N. Generation of adamantanes and diamantanes by thermal cracking of high-molecular-mass saturated fractions of crude oils of different genotypes. *Pet. Chem.* 46, 225–236 (2006).
13. Giruts, M. V. & Gordadze, G. N. Generation of adamantanes and diamantanes by thermal cracking of polyaromatic hydrocarbons in crude oils of different genotypes. *Pet. Chem.* 47, 12–22 (2007).
14. Fang, C. C. et al. The origin and evolution of adamantanes and diamantanes in petroleum. *Geochim. Cosmochim. Acta* 120, 109–120 (2013).
15. Goldhaber, M. B. & Orr, W. L. Kinetic controls on thermochemical sulfate reduction as a source of sedimentary H2S, in: M.A. Vainramurth, M.A.A. Schoonen (Eds.), Geochemical Transformations of Sedimentary Sulfur, ACS Symposium Series vol. 612, pp. 412–625. (1995).
16. Berwick, L., Alexander, R. & Pierce, K. Formation and reactions of alkyl adamantanes in sediments: Carbon surface reactions. *Org. Geochem.* 42(7), 752–761 (2012).
17. Siskin, M., Bron, G., Katritzky, A. R. & Balasubramanian, M. Aqueous organic chemistry. 1. Aquathermolysis: Comparison with thermolysis in the reactivity of aliphatic compounds. *Energy Fuels* 4, 475–482 (1990).
20. Price, L. C. Thermal stability of hydrocarbons in nature: limits, evidence, characteristics, and possible controls. Geochim. Cosmochim. Acta 57, 3261–3280 (1993).

21. Seewald, J. S., Benitez-Nelson, B. C. & Whelan, J. K. Laboratory and theoretical constraints on the generation and composition of natural gas. Geochim. Cosmochim. Acta 62, 1599–1617 (1998).

22. Schimmelmann, A., Lewan, M. D. & Wintsch, R. P. D/H isotope ratios of kerogen, bitumen, oil, and water in hydrous pyrolysis of source rocks containing kerogen types I, II, and III. Geochim. Cosmochim. Acta 63, 3751–3766 (1999).

23. Lewan, M. D. Experiments on the role of water in petroleum formation. Geochim. Cosmochim. Acta 61, 3961–3732 (1997).

24. Lewan, M. D. & Roy, S. Role of water in hydrocarbon generation from Type-I kerogen in Mahogany oil shale of the Green River Formation. Org. Geochem. 42, 31–41 (2011).

25. Cai, C. F. et al. 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. Org. Geochem. 101, 49–62 (2016).

26. Orr, W. L. Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation-study of Big Horn Basin Paleozoic Oils. Am. Assoc. Pet. Geol. Bull. 58, 2295–2318 (1974).

27. Krouse, H. R., Viau, C. A., Eliuk, L. S., Ueda, A. & Halas, S. Chemical and isotopic evidence of thermochemical sulphate reduction by light hydrocarbon gases in deep carbonate reservoirs. Nature 333, 415–419 (1988).

28. Cai, C. F., Worden, R. H., Bottrell, S. H., Wang, L. S. & Yang, C. C. Thermochemical sulphate reduction and the generation of hydrogen sulphide and thiols (mercaptans) in Triassic carbonate reservoirs from the Sichuan Basin, China. Chem. Geol. 202, 39–57 (2003).

29. Cai, C. F. et al. Sulfur isotopic compositions of individual organosulfur compounds and their genetic links in the Lower Paleozoic petroleum pools of the Tarim Basin, NW China. Geochim. Cosmochim. Acta 182, 88–108 (2016).

30. Chen, J. H., Fu, J. M., Sheng, G. Y., Liu, D. H. & Zhang, J. J. Diamondoid hydrocarbon ratios: novel maturity indices for highly mature crude oils. Org. Geochem. 25, 179–190 (1996).

31. Li, J. G., Philp, P. & Cai, M. Z. Methyl diamantane index (MDI) as a maturity parameter for Lower Paleozoic carbonate rocks at high maturity and overmaturity. Org. Geochem. 31, 267–272 (2000).

32. Zhang, S. C., Huang, H. P., Xiao, Z. Y. & Liang, D. G. Geochemistry of Palaeozoic marine petroleum from the Tarim Basin, NW China: Part 2. Maturity assessment. Org. Geochem. 36, 1215–1225 (2005).

33. Clark, T., Knox, T. M., McKervey, M. A., Mackie, H. & Rooney, J. J. Thermochemistry of bridgehead-ring substances. Enthalpy, formation and isomerization of some diamondoid hydrocarbons and perhydroquinacene. Comparisons with data from empirical force field calculations. J. Am. Chem. Soc. 101, 2404–2410 (1979).

34. Grice, K., Alexander, R. & Kagi, R. I. Diamondoid hydrocarbon ratios as indicators of biodegradation in Australian crude oils. Org. Geochem. 31, 67–73 (2000).

35. Hanin, S. et al. Bridgehead alkylated 2-thiaadamantanes: novel markers for sulphurisation processes occurring under high thermal stress in deep petroleum reservoirs. Chem. Commun. 16, 1750–1751 (2002).

36. Wei, Z. B. et al. Thiadiamondoids as proxies for the extent of thermochemical sulfate reduction. Org. Geochem. 44, 53–70 (2012).

37. Wei, Z. B. et al. Origins of thiadiamondoids and diamondoidthiols in petroleum. Energy Fuels 21(6), 3431–3436 (2007).

38. Gvirtzman, Z. et al. Compound-specific sulfur isotope analysis of thiadiamondoids of oils from the Smackover Formation, USA. Geochim. Cosmochim. Acta 167, 144–161 (2015).

39. Sweeney, J. J. & Burnham, A. K. Evaluation of a simple model of vitrinite reflectance based on chemical-kinetics. Am. Assoc. Pet. Geol. Bull. 74, 1559–1570 (1990).

40. Zhang, T. W., Amrani, A., Ellis, G. S., Ma, Q. S. & Tang, Y. C. Experimental investigation on thermochemical sulfate reduction by H2S initiation. Geochim. Cosmochim. Acta 72(14), 3518–3530 (2008).

41. Saccocia, P. J., Seyfried, W. E., Talc–quartz equilibria and the stability of magnesium–chloride complexes in NaCl–MgCl2 solutions at 300 °C and 350 °C, and 400 °C, 500 bars. Geochim. Cosmochim. Acta 54(12), 3283–3294 (1990).

42. Seewald, J. S., Eglintone, B. L. & Ong, Y. L. An experimental study of organic-inorganic interactions during vitrinite maturation. Geochim. Cosmochim. Acta 64(9), 1577–1591 (2000).

43. Zhang, T. W., Ellis, G. S., Ma, Q., Amrani, A. & Tang, Y. Kinetics of uncatalyzed thermochemical sulfate reduction by sulfur-free paraffin. Geochim. Cosmochim. Acta 96, 1–17 (2012).

44. Heydari, E. & Moore, C. H. Burial diagenesis and thermochemical sulfate reduction, Smackover Formation, southeast Mississippi salt basin. Geol. 17, 1080–1084 (1989).

45. Machel, H. G. Saddle dolomite as a by-product of chemical compaction and thermochemical sulfate reduction. Geology 15, 936–940 (1987).

46. Manzano, B. K., Fowler, M. G. & Machel, H. G. The influence of thermochemical sulfate reduction on hydrocarbon composition in Nisku reservoirs, Brazeau River area, Alberta, Canada. Org. Geochem. 27, 507–521 (1997).

47. Worden, R. H., Smalley, P. C. & Oxtoby, N. H. The effects of thermal sulfate reduction upon formation water salinity and oxygen isotopes in carbonate gas reservoirs. Geochim. Cosmochim. Acta 60, 3925–3931 (1996).

48. Worden, R. H., Smalley, P. C. & Oxtoby, N. H. Sulfur sourcing by thermochemical sulfate reduction at 140 °C. AAPG Bull. 79, 854–863 (1995).

49. Kiyoun, Y. & Krouse, H. R. Thermochemical reduction and sulfur behavior of sulfate by acetic acid in the presence of native sulfur. Geochem. J. 27, 49–57 (1993).

50. Cross, M. M., Manning, D. A. C., Bottrell, S. H. & Worden, R. H. Thermochemical sulphate reduction (TSR): Experimental determination of reaction kinetics and implications of the observed reaction kinetics and implications of the observed reaction rates for petroleum reservoirs. Org. Geochem. 35, 393–404 (2004).

51. Toland, W. G. Oxidation of organic compounds with aqueous sulphate. J. Am. Chem. Soc. 82, 1911–1916 (1960).

52. Liang, Q. Y., Xiong, Y. Q., Fang, C. C. & Li, Y. Quantitative analysis of diamondoids in crude oils using gas chromatography—Triple quadrupole mass spectrometry. Org. Geochem. 43, 83–91 (2012).

53. Leif, R. N. & Simonett, B. R. T. The role of alkene produced during hydrous pyrolysis of a shale. Org. Geochem. 31, 1189–1208 (2000).

54. Jiang, W. M., Li, Y. & Xiong, Y. Q. The effect of organic matter type on formation and evolution of diamondoids. Mar. Pet. Geol. 89, 714–720 (2018).

55. Li, Y. et al. Origin of adamantanes and diamanitanes in marine source rock. Energy Fuels 29, 8188–8194 (2015).

56. Tang, Y., Jenden, P. D., Nigrini, A. & Teeram, S. C. Modeling early methane generation in coal. Energy Fuels 10(3), 659–671 (1996).

57. Schimmelmann, A., Sessions, A. L. & Mastalerz, M. Hydrogen isotopic (D/H) composition of organic matter during diagenesis and thermal maturation. Annu. Rev. Earth Planet. Sci. 34, 501–533 (2006).

58. Li, Y. et al. The application of diamondoid indices in the Tarim oils. Am. Assoc. Pet. Geol. Bull. 101, 267–291 (2018).

59. Takach, N. E., Barker, C. & Kemp, M. K. Stability of natural gas in the deep subsurface: thermodynamic calculation of equilibrium compositions. Am. Assoc. Pet. Geol. Bull. 71, 322–333 (1987).

60. Robinson, B. W. Sulphur isotope equilibrium during sulphur hydrolysis at high temperatures. Earth Planet. Sci. Lett. 18, 443–450 (1973).

61. Said-Ahmad, W., Amrani, A. & Aizenstat, Z. The action of elemental sulfur plus water on 1-ocetene at low temperatures. Org. Geochem. 59, 82–86 (2013).
62. Krein, E. B. & Aizenshtat, Z. Proposed thermal pathways for sulfur transformations in organic macromolecules: Laboratory simulation experiments. In Geochemical Transformations of Sedimentary Sulfur (eds Vairavamurthy, M. A. & Schoonen, M. A. A.) 110–137 (American Chemical Society, 1995).
63. Nguyen, V. P., Burkle-Vitzthum, V., Marquaire, P. M. & Michels, R. Thermal reactions between alkanes and H2S or thiols at high pressure. J. Anal. Appl. Pyrol. 103, 307–319 (2013).
64. Ellis, G. S., Zhang, T. W., Kralert, P. G. & Tang, Y. C. Kinetics of elemental sulfur reduction by petroleum hydrocarbons and the implications for hydrocarbon thermal chemical alteration. Geochim. Cosmochim. Acta 251, 192–216 (2019).
65. Gordadze, G. N. & Giruts, M. V. Synthesis of adamantine and diamantine hydrocarbons by high-temperature cracking of higher n-alkanes. Pet. Chem. 48, 414–419 (2008).
66. Dahl, J. E. et al. Synthesis of higher diamondoids and implications for their formation in petroleum. Angew. Chem. Int. Ed. 49, 9881–9885 (2010).
67. Xiao, Q. L., Sun, Y. G., He, S., Liu, J. Z. & Zhu, C. S. Thermal stability of 2-thiadiamondoids determined by pyrolysis experiments in a closed system and its geochemical implications. Org. Geochem. 130, 14–21 (2019).
68. Oya, A., Nakamura, H., Otani, S. & Marsh, H. Carbonization of adamantane to a graphitizable carbon. Fuel 60, 667–669 (1981).
69. Walters, C. C. et al. Petroleum alteration by thermochemical sulfate reduction—A comprehensive molecular study of aromatic hydrocarbons and polar compounds. Geochim. Cosmochim. Acta 153, 37–71 (2015).
70. Mankiewicz, P. J., Pottorf, R. J., Kosar, M. G. & Vrolijket, P. Gas geochemistry of the Mobile Bay Jurassic Norphlet Formation: Thermal controls and implications for reservoir connectivity. Am. Assoc. Pet. Geol. Bull. 93, 1319–1346 (2009).

Acknowledgements
This work has been financially supported by the National Natural Science Foundation of China (Grant Nos. 41730424 and 4181101560). The authors are very grateful to Dr. Yongqiang Xiong for providing the HD23 oil sample and his valuable suggestion in improving work. We also thank Dr. Wennin Jiang and Dr. Yun Li for their help with GC-MS-MS analysis and pyrolysis experiments. Two anonymous reviewers and Editor Yunpeng Wang are thanked for their thorough and critical reviews and suggestions to improve the manuscript.

Author contributions
Y.P.: data curation, writing- original draft preparation, validation; C.C.: Writing- reviewing and editing, validation, supervision; C.F., L.W.: investigation, conceptualization; J.L., P.S., D.L.: methodology, data curation.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary Information The online version contains supplementary material available at https://doi.org/10.1038/s41598-021-04270-z.

Correspondence and requests for materials should be addressed to C.C.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2022