



Review Paper

Crude oil cracking in deep reservoirs: A review of the controlling factors and estimation methods

Yu Qi ^{a, *}, Chun-Fang Cai ^{b, c, **}, Peng Sun ^d, Dao-Wei Wang ^e, Hong-Jian Zhu ^a^a Department of Petroleum Engineering, School of Vehicle and Energy, Yanshan University, Qinhuangdao, 066004, Hebei, China^b Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, 100029, China^c College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing, 100049, China^d Key Lab of Exploration Technologies for Oil and Gas Resources of Ministry of Education, Yangtze University, Wuhan, 430100, Hubei, China^e School of Energy Resource, China University of Geosciences (Beijing), Beijing, 100083, China

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ABSTRACT

The natural cracking of crude oils in deep reservoirs has gained great interest due to continuously increasing depth of petroleum exploration and exploitation. Complex oil compositions and surroundings as well as complicated geological evolutions make oil cracking in nature much more complex than industrial pyrolysis. So far, numerous studies, focused on this topic, have made considerable progress although there still exist some drawbacks. However, a comprehensive review on crude oil cracking is yet to be conducted. This article systematically reviews the controlling factors of oil cracking from six aspects, namely, oil compositions, temperature and time, pressure, water, minerals and solid organic matter. We compare previous experimental and modelling results and present new field cases. In the following, we evaluate the prevailing estimation methods for the extent of oil cracking, and elucidate other factors that may interfere with the application of these estimation methods. This review will be helpful for further investigations of crude oil cracking and provides a guide for estimation of the cracking extent of crude oils.

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1. Introduction

With the depletion of shallow petroleum reserves, petroleum exploration and development are rapidly entering deeper and deeper reservoirs (Fig. 1) (EIA, U.S., 2022). More than 40 giant petroleum fields have been found at depths >4500 m all over the world and the majority produce both oil and gas (Kutcherov and Krayushkin, 2010). The deepest offshore oil field, the BP's Tiber field in the Gulf of Mexico, reached a true vertical depth of 10,685 m as well as an underwater depth of 9426 m (Quillen, 2009). In the Tarim Basin, China, the vertical depths of 41 wells have exceeded 8000 m (Li, 2022). The Well Luntan-1 in the Tarim Basin, the deepest oil well in Asia, has a total vertical depth of 8882 m (Zhu

et al., 2021a). These ultradeep oil wells and fields challenge the traditional viewpoint that oil was only stable to 150–160 °C, and only gas can be found at higher temperatures (McNab et al., 1952; Barker, 1990).

The thermal stability of crude oils determines the so-called “oil deadline”, which has an important impact on the strategies of exploration and development. In nature, the complex components of oils and surroundings, varying temperature and time, and complicated geological evolution histories make it challenging to analyze the controls on oil cracking and to evaluate the extent of oil cracking. The extents of oil cracking commonly have a poor correlation with reservoir temperature due to the multiple controlling factors. Previous studies have involved the following factors: oil compositions, heating rates, overpressure, system closeness, water, clay minerals, thermochemical sulfate reduction (TSR), pyrobitumen and kerogen (Pepper and Dodd, 1995; Schenk et al., 1997; Zhang et al., 2008; Pan et al., 2010; Chen et al., 2014; Uguna et al., 2016a; Cai et al., 2019; He et al., 2022). Considerable progress has been made in the field of crude oil cracking although there exist controversial conclusions and unsolved problems. Nevertheless, a

* Corresponding author. Department of Petroleum Engineering, School of Vehicle and Energy, Yanshan University, Qinhuangdao, 066004, China.

** Corresponding author. Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, 100029, China.

E-mail addresses: yu.qi@ysu.edu.cn (Y. Qi), cai_cf@mail.iggcas.ac.cn (C.-F. Cai).

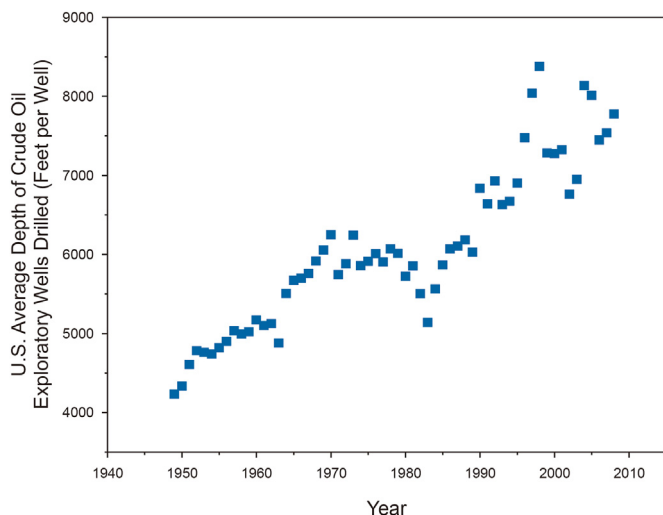


Fig. 1. U.S. average depth of crude oil exploratory wells drilled. Data from EIA, U.S. (2022).

comprehensive review on crude oil cracking is yet to be conducted.

Another important issue is how to estimate the cracking extent of a crude oil. The extent of oil cracking in pyrolysis experiments can be accurately calculated by comparing many parameters before and after pyrolysis (e.g., the yields of gaseous hydrocarbons or pyrobitumen, the residual of liquid oil, the dryness of the gaseous hydrocarbons). However, it is much harder to assess the extent of oil cracking in nature due to the unknown of original oil compositions before cracking. At relatively low thermal evolution conditions, biomarker maturity proxies (e.g., $T_s/(T_s + T_m)$, $C_{29}T_s/(C_{29}T_s + C_{29}H)$, methyl phenanthrene ratios, where $T_s = 18\alpha(H)$ -trisorhopane ratio, $T_m = 17\alpha(H)$ -trisorhopane ratio, $C_{29}T_s = 18\alpha(H)$ -norneohopane, $C_{29}H = C_{29} 17\alpha(H)$ -hopane) can indicate the extent of oil cracking (Hao, 2022). While, most biomarkers are not applicable for highly cracked hydrocarbons, due to being severely degraded (Dahl et al., 1999) and some may be inverted at high maturity stages (Farrimond et al., 1998; Chen et al., 2016).

The two prevailing estimators for the extent of oil cracking are on the basis of GOR and diamondoids. GORs represent the relative quantity of product to reactant, hence reflecting the extent of oil cracking. While, they can be altered by secondary processes, such as the leakage or additional charge of gas, and biodegradation, making the GOR-based cracking proxy inconvincible. An alternative estimator based on diamondoids was then proposed by Dahl et al. (1999). With consideration of the extraordinary thermal stability, diamondoids should be enriched in cracked oils. The larger the diamondoid concentrations, the higher the extent of oil-cracking should be. The diamondoid-based cracking proxy has been applied in worldwide basins, like the Gulf of Mexico, the North Slope of Alaska, the Siberian Basin, the Barents Sea Basin and the Tarim Basin (Zhang et al., 2011; He et al., 2012; Wang et al., 2014; Liu et al., 2016; Yurchenko et al., 2018). However, recent studies show that diamondoid abundance can also be altered by other geological processes, for instance, evaporative fractionation, phase separation, TSR and biodegradation (Moldowan et al., 2015; Chakhmakhchev et al., 2017; Zhang et al., 2019; Zhu et al., 2019b; Forkner et al., 2021; Jiang et al., 2021; Qi et al., 2022).

In this review, we synthesize the research conducted over the past decades in the fields of oil cracking. The controlling factors of oil cracking are reviewed in six aspects: oil compositions, temperature and time, pressure, water, minerals and solid organic matter.

The details of the six aspects, as well as corresponding geological processes and parameters, are summarized in Fig. 2. In the following, we evaluate the main estimation methods of oil-cracking extents, and elucidate the interference factors to the estimators. This review work tries to a) systemically introduce all the influence mechanisms of oil-cracking and presents new field cases; b) point out controversial and poorly understood issues related to oil-cracking; c) provide a guide to the estimation of the cracking extent of crude oils.

2. Controlling factors

2.1. Oil compositions

2.1.1. Saturates and aromatics

Crude oils are naturally occurring mixtures of predominantly hydrocarbons and subordinately nonhydrocarbons. The thermal stability of crude oil highly depends on the compositions. Saturate and aromatic hydrocarbons are the main components of crude oils. Kinetic modelling and pyrolysis experiments have proved that paraffinic oils are more stable than aromatic oils (Pepper and Dodd, 1995; Schenk et al., 1997). With consideration of the relative stability between saturates and aromatics, the saturate/aromatic ratio of crude oils has been used as a maturity indicator (Peters et al., 2005; Kotarba et al., 2020a, 2020b; Hackley et al., 2021). Connan et al. (1975) pyrolyzed an Aquitaine Basin oil for 12 months at 300 °C which is a very low pyrolysis temperature. The saturate/aromatic ratios of their pyrolyzed oil increased from the original 0.28 to 1.0. Hubred (2006) investigated the thermal effects of basaltic sill emplacement in source rocks. They found that the saturate/aromatic ratios increase when approaching the basaltic sill, indicating higher thermal stability of saturates to aromatics. The relative stabilities between saturates and aromatics control the distribution of saturate/aromatic ratios in deep reservoirs. Fig. 3 shows the profiles of the saturate/aromatic ratios of the Ordovician oils in the northern Tarim Basin. The envelopes show that the saturate/aromatic ratios roughly increase with increasing depth, which is consistent with the downward increase of biomarker maturity parameters as indicated by Qi et al. (2022). The increase of saturates relative to aromatics reflects the breakdown of the side chain of alkyl aromatics and the cracking of long chain alkyl saturates (Tissot and Welte, 1984). The breakdown of the side chain of alkyl aromatics converts long chain alkyl aromatics into short chain alkyl aromatics and saturates, raising the saturate/aromatic ratios.

The relative stability of saturates and aromatics intrinsically depends on their bond energies. The carbon-carbon bonds of saturates have larger bond energies than alkyl sidechains at the β position to aromatics (Schenk et al., 1997; Zhao et al., 2017). The thermal cracking of saturated and aromatic hydrocarbons involves two distinct pathways. The cracking of saturates forms free radicals through breaking the carbon-carbon bonds. Whereas, the decomposition of alkyl aromatics is much more complex. It starts with a cleavage of the sidechain at the β position, followed by hydrogen transfer, through which a saturated hydrocarbon and a methylated aromatic hydrocarbon are generated (Freund and Olmstead, 1989; Poutsma, 1990; Savage and Korotney, 1990; McNeil and BeMent, 1996; Behar et al., 2002). The methylated compound then undergoes polycondensation reactions through a very complex reaction network (Smith and Savage, 1993; Leininger et al., 2006; Fusetti et al., 2010).

It is noteworthy that the thermal stability of alkyl aromatics declines with increasing length of the sidechains (Smith and Savage, 1991). Pyrolysis experiments have shown that aromatics with no or short sidechains are more stable than saturates (Smith and Savage, 1992; Behar et al., 2002, 2008; Dartiguelongue et al.,

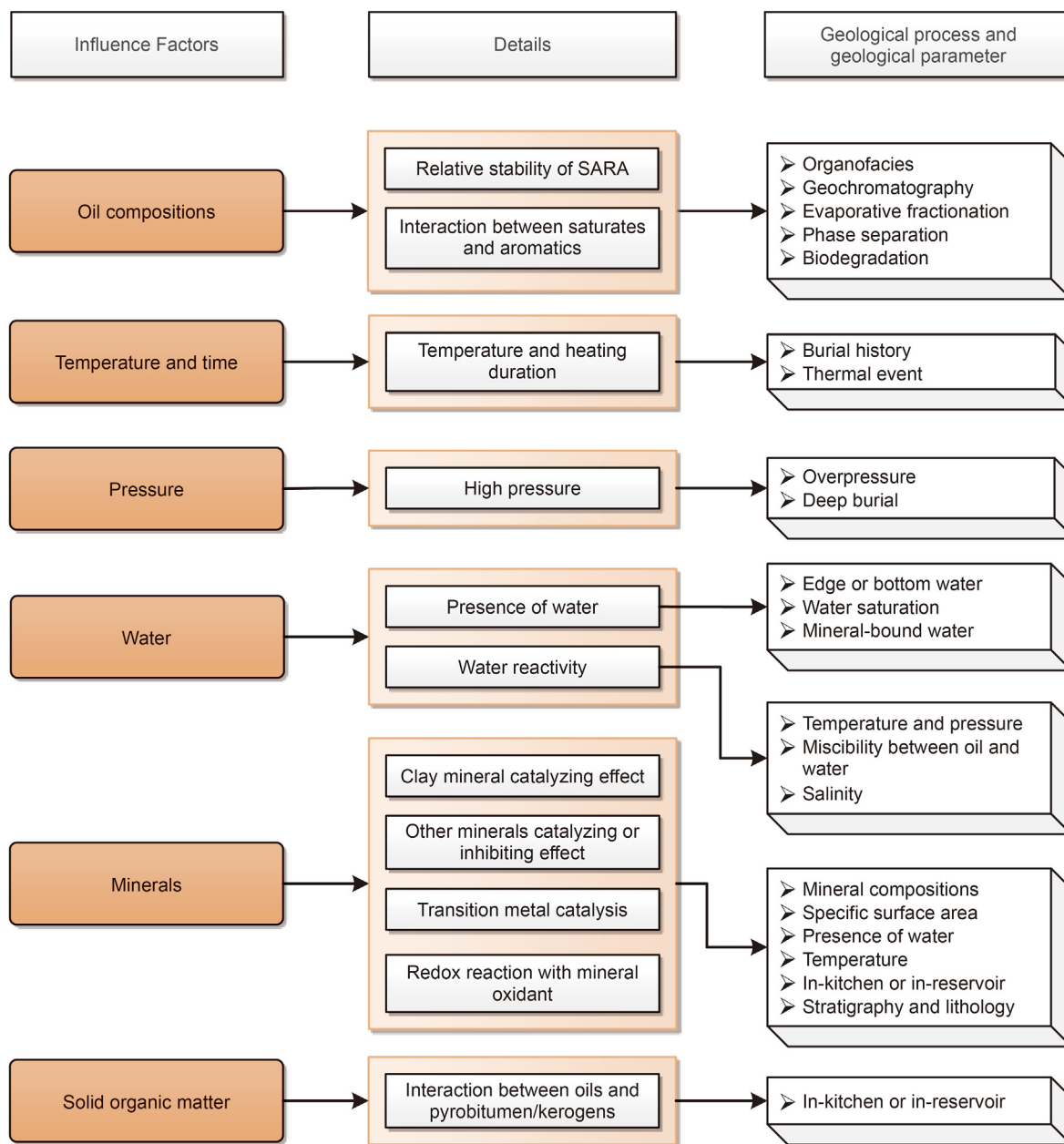


Fig. 2. Summary of the controlling factors of crude oil cracking as well as the corresponding geological processes and parameters.

2006; Zhao et al., 2017). It is because (1) the activation energy for the breakage of carbon-carbon bond on aromatic nucleus (117 kcal/mol) is much larger than those of the carbon-carbon bond breakage of saturates (average 82.6 kcal/mol) (Price, 1993); (2) methylated compounds are more stable than other alkylated ones, including aromatics (Rakotoalimanana et al., 2016a). Leguizamon Guerra et al. (2018) showed that, in geological conditions (100 °C, 70 MPa), the stability of *n*-butylbenzene is close to that of alkanes but is lower than that of toluene. Thus, it seems to be a reasonable inference that *n*-propylbenzene, ethylbenzene, and methylbenzene are more stable than alkanes considering the increase of reactivity with increasing length of the sidechains of the aromatics.

Behar et al. (2002) investigated the temperature effect on the stability of 9-methylphenanthrene (9-MPh) and *n*-C₂₅ and found that the extrapolation of the pyrolytic results to geological low-temperature lead to a reversal of the relative stability between

pyrolysis temperature and geological low-temperature. In other words, 9-MPh is more stable than *n*-C₂₅ in pyrolysis experiments but is less stable than *n*-C₂₅ in geological conditions. It is because both the activation energy and frequency factor of 9-MPh are lower than those of *n*-C₂₅, leading to their Arrhenius plots crossing each other at around 300 °C and the reversal of thermal decomposition rates between high-temperature (>~300 °C) and low-temperature ranges (<~300 °C) (Fig. 4) (Behar et al., 2002, 2008; Dartiguelongue et al., 2006). In fact, most aromatics have lower activation energies and lower frequency factors than saturates (47–54 kcal/mol and 10¹⁰–10¹³ s⁻¹ for the C₁₄₊ aromatics, respectively, and 64–68 kcal/mol and 10¹⁶ s⁻¹ for the C₁₄₊ saturates). It explains why some pyrolysis outcomes (e.g., Willette, 2010) showed that pyrolytic products had lower saturate/aromatic ratios and higher aromaticity as compared to the original crude oils.

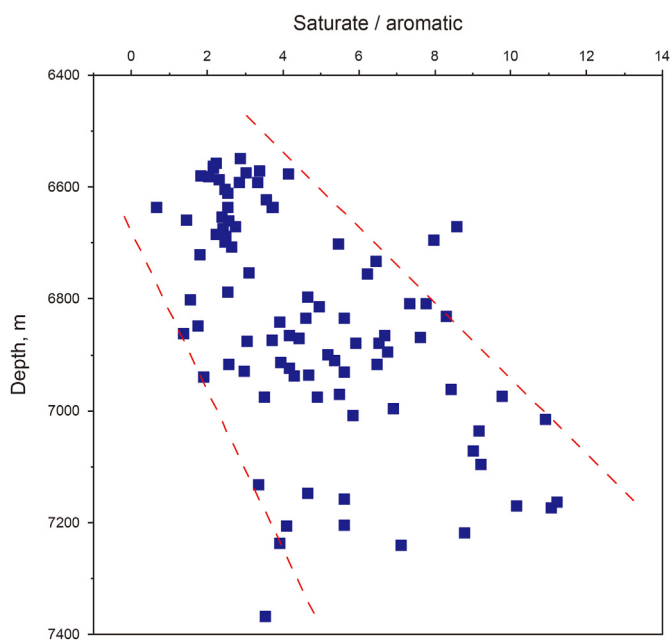


Fig. 3. Profiles of saturate/aromatic ratios in the Halahatang oil field. Data from Li et al. (2018a).

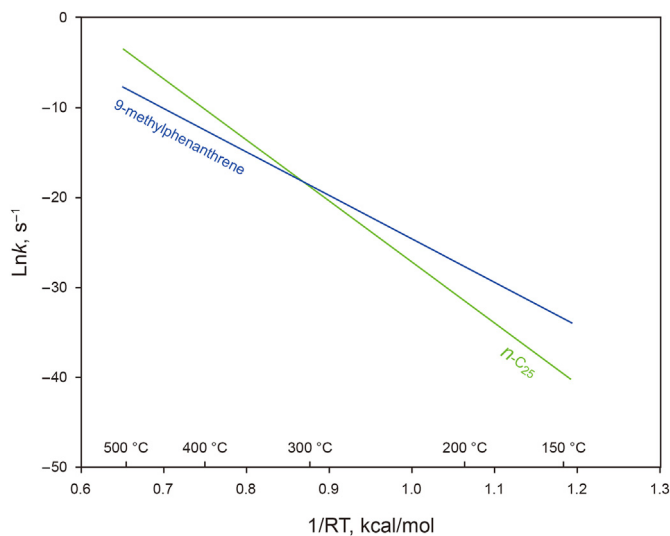


Fig. 4. Arrhenius diagram obtained on 9-methylphenanthrene and n -C₂₅. Modified from Behar et al. (2002).

2.1.2. Asphaltene and resins

Previous studies have not reached an agreement on the thermal stability of asphaltene and resins. The pyrolysis experiments by Karacan and Kok (1997) showed that the activation energy of asphaltene is higher than any other fractions, and is the most stable fraction. The authors also found that resin is more stable than aromatics up to 200 °C but is of lower thermal stability than aromatics above 200 °C. Similarly, Kök and Karacan (1998) concluded that the cracking activation energies of crude oils increase with increasing asphaltene contents, and hence heavier oils have larger activation energies. Both anhydrous and hydrous pyrolysis of crude oils resulted in the increase of asphaltene contents (Uguna et al., 2016a), supporting the higher stability of asphaltenes relative to other fractions. On the contrary, some researchers concluded that asphaltene and resin are less stable than saturates and aromatics.

Boytsova et al. (2017) indicated that asphaltenes have slightly lower activation energies, frequency factors, conversion degree and bond strength than the total oils. The compositional kinetic models in the literature (Vandenbroucke et al., 1999; Zhao et al., 2017) also assign relatively low activation energies to NSO components. Moreover, Hill et al. (2003) observed a decrease in total NSO yields at high maturity ($R_o > 1\%$). The disagreement on the stability of asphaltene and resins is perhaps because of the difference in oil maturity, elemental compositions, and the structures of asphaltenes and resins, and needs further elucidation.

Any geological factors or processes that change oil compositions will have an impact on the thermal stability of oils. Oil compositions are initially determined by organofacies and the thermal maturity of source rocks when the oils were generated. Subsequently, the oil compositions are altered by hydrocarbon expulsions, primary and secondary migrations as well as other secondary alterations. Lacustrine oils are commonly more stable than marine oils. Dahl et al. (1999) showed that the actual cracking extent (c.a. 18%) of a marine aromatic oil after being heated at 400 °C for 6 h is greater than that (c.a. 12%) of a lacustrine oil being heated at 402 °C for 17.4 h. Well Niudong-1 in the Jizhong Depression of Bohai Bay Basin, China has produced a lacustrine condensate with a GOR of 871 m³/m³ from a hot carbonate reservoir (205 °C) (Zhao et al., 2015). The high thermal stability of lacustrine oil is because their bio-precursors, dominated by lacustrine algae, enrich hydrogen compounds compared to marine plankton. The hydrogen-rich components tend to generate more aliphatic hydrocarbons, therefore enhancing the thermal stability of lacustrine oils. Schenk et al. (1997) also concluded that oils derived from marine source rocks are commonly enriched in aromatics and tend to be less stable than terrestrial, high wax oils.

Fractionation during expulsion enriches saturates to aromatics and NSO compounds, and concentrates lighter hydrocarbons (Dzou and Hughes, 1993; Pepper and Dodd, 1995), enhancing the thermal stability of oils. Geochromatography leads to the enrichment of compounds with lower polarity (Larter et al., 1996; Horstad and Larter, 1997; Wang et al., 2004; Li et al., 2018a, 2018b).

Evaporative fractionation lowers the paraffinicity of fractionated oils and raises the paraffinicity of gas condensates (Thompson, 1988, 2010; Losh and Cathles, 2010). Gas invasion precipitates asphaltene (Karlsen and Skeie, 2006), may lower the thermal stability of the oil (Kök and Karacan, 1998). Biodegradation preferentially removes hydrogen-rich components, leading to produce more pyrobitumen and less gas. Kinetic modelling indicated that biodegradation lowers the thermal stability of oils (Liu et al., 2022). All the above mentioned factors and processes have an influence on oil compositions and therefore the thermal stability of the whole oils.

2.1.3. Interaction among hydrocarbons

There exist interactions between saturates and aromatics in oil-cracking reactions. The decomposition of aromatics, such as 9-MPh, was slightly accelerated by oil matrix (Burnham et al., 1995, 1997; McKinney et al., 1998). On the contrary, aromatics can inhibit the thermal deposition of saturates, because they act as a supplier of hydrogen, promoting the saturation of alkenes and inhibiting adding side chains to alkenes. The extra hydrogen suppresses the formation of hydrocarbon radicals, therefore reducing the cracking rate of n -alkenes (Burnham et al., 1997). For example, the thermal cracking of n -hexadecane is retarded by the addition of alkyl aromatics (e.g., toluene, ethylbenzene, decylbenzene) because the rapid abstraction of benzylic hydrogens generates benzyl radical, inhibiting the formation of alkyl radicals (Khorasheh and Gray, 1993; Burklé-Vitzthum et al., 2004). The inhibiting effects of other hydrocarbons (e.g., hydronaphthalenics and tetralin) were also proven (Bounaceur et al., 2002; Burklé-Vitzthum et al., 2005).

Free radical modelling performed by Dominé et al. (2002) further suggested that the order of inhibiting effects is tetralin < toluene < alkyl aromatics. The inhibiting effect of alkyl aromatics on oil cracking is greatly enhanced at low geological temperatures (Bounaceur et al., 2002; Burklé-Vitzthum et al., 2004), and is significantly reduced by high pressure (Lannuzel et al., 2010). Accordingly, Dominé et al. (2002) suggested that crude oils can be preserved at up to 240–260 °C depending on their compositions.

2.2. Temperature and time

2.2.1. Temperature and heating duration

Temperature and time are the two most important factors for thermal evolution of organic materials (Lopatin, 1971; Waples, 1980). Temperature may have a control on overall kinetic parameters (Dominé and Enguehard, 1992; Dominé et al., 1998; Waples, 2000). For example, Dominé and Enguehard (1992) indicated that the activation energy of hexane is about 65 kcal/mol at 350–400 °C and increases to about 70 kcal/mol at temperatures below 200 °C. If so, using rate parameters obtained around 350–400 °C to predict oil decomposition at 150–200 °C is incorrect.

Temperature not only controls the cracking reaction rate but also the reaction pathways and products. The high-temperature pyrolysis of crude oils tends to decompose C₁₅₊ hydrocarbons more rapidly and to generate more gaseous hydrocarbons and monoaromatic hydrocarbons than the pyrolysis at a relatively lower temperature (Bjørøy et al., 1988; Schenk et al., 1997; Dieckmann et al., 1998). The pyrolysis of naphthenes at high temperatures (>600 °C) primarily forms isomeric alkenes via ring opening while that at relatively low temperatures (<400 °C) mainly leads to the breaking of alkyl side chains (Rakotoalimanana et al., 2016a, 2016b). Smith and Savage (1993) pyrolyzed 9-methylanthracene at temperatures between 350 and 450 °C. With the temperature increasing from 350 to 450 °C, the major pyrolytic product changed from anthracene to 9, 10-dihydroanthracene (Smith and Savage, 1993).

For a fixed pyrolysis temperature, heating duration controls the conversion of a reactant, as well as the yield of primary and higher order products. pyrolyzed methylanthracenes at 350–450 °C. With respect to the pyrolysis of 1-methylanthracene, the yields of non-primary products (e.g., 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene) were extremely low at conversion less than 20% but were much higher at larger conversions. Besides, long heating duration may lead to the decomposition of some primary and higher order products. With regard to the pyrolysis of 1-methylanthracene, the yield of 1-methyl-9,10-dihydroanthracene, a primary product, decreases with increasing conversion; the yield of 9-methylanthracene, a nonprimary product, reaches the maximum value at the conversion of 55% and then declines with increasing conversion (Smith and Savage, 1993).

Heating rates are a combination of temperature and time. Heating rates change among basins and even within one basin due to different burial histories and thermal regimes, and can vary over one order of magnitude (Vandenbroucke et al., 1999; Waples, 2000). Pyrolysis experiments with different heating rates and kinetic modelling were conducted to elucidate how heating rates influence the thermal cracking of oil or hydrocarbons. It is generally accepted that oils that experienced faster heating rates need higher maximum temperatures to reach a specific degree of cracking. Dieckmann et al. (1998) indicated that at the experimental heating rate of 5.0 K/min oil cracking to gas initiates at ca. 360 °C; while the onset of oil cracking at the geological heating rate of 5.3 K/m.y. occurs at 150 °C. Kinetic modelling and pyrolysis experiments indicated that every tenfold increase in heating rate causes ca. 15 °C

increase in the cracking window (Quigley and Mackenzie, 1988; Pepper and Dodd, 1995). The temperature shift between fast and slow heating rates is reasonable because a faster heating rate leads to a shorter duration at high temperatures and hence a lower extent of oil cracking.

Oils from several basins that involved late, fast burial have been found to survive at extremely high temperatures. One case is the high-pressure and high-temperature Elgin field (1100 bar and 190 °C) in the southern central North Sea (UK), where monophasic paraffinic condensates with almost 50% C₆₊ alkanes were discovered (Lasocki et al., 1999; Vandenbroucke et al., 1999). The reservoir temperature increased from 160 °C to over 180 °C only in the last million years. That C₆₊ hydrocarbons can be preserved at such high temperatures is due to the rapid heating rate and the limited duration under extreme temperatures (Vandenbroucke et al., 1999; Waples, 2000). Another case is the good preservation of oils in the Halahatang oil field in the northern Tarim Basin (Fig. 5a and b). Deep Ordovician reservoirs in the oil field have been found to produce non-cracked or slightly cracked oils. For example, non-cracked oils have recently been developed from extremely hot reservoirs (with temperature >170 °C and depth >7700 m) in the Fuyuan oil field in the Halahatang (Zhu et al., 2018a). The reservoirs in both areas are generally at normal pressure (Zhu et al., 2019c). The most possible explanation for the low extent of oil-cracking in the Halahatang oil field is the rapid heating rate due to the rapid subsidence of more than 2000 m in the last ca. 5 Ma (Fig. 5c) (Zhu et al., 2018a, 2019a).

2.2.2. Discrepancy between pyrolytic and geological temperatures

Kinetic models involving several parallel first-order reactions have been widely used to extrapolate high-temperature pyrolysis outcomes (generally between 250 and 550 °C) to geological conditions (<200 °C) (Quigley and Mackenzie, 1988; Ungerer et al., 1988; Behar et al., 2002, 2008). The geological time is compensated by higher temperatures than reservoir temperatures. The extrapolation remains controversial as pyrolysis temperature is markedly different from reservoir temperature. Pyrolytic products and natural cracked hydrocarbons significantly differ in compositional and isotopic distributions. The gas generated from laboratory pyrolysis contains a lower proportion of methane (~35–40%), compared to natural gas in reservoirs (methane ~60–90+%, where “+” represents “higher than” the value) (Mango, 1997; Snowdon, 2001). The variation of $\delta^{13}\text{C}$ for C₁–C₅ from laboratory pyrolysis does not behave as that of natural gas, which follows a linear trend with 1/n (n = carbon number) (Mango and Elrod, 1999). Moreover, high temperature in pyrolysis experiments induces the rapid cracking of not only initial oils but also secondary products. The latter may not occur or may be insignificant at reservoir temperature. Burklé-Vitzthum et al. (2017) argued that the kinetic parameters of hydrocarbons have a connection with temperature. Apparent kinetic parameters at 400 °C and 200 °C may be slightly or highly different. Extrapolating apparent kinetic parameters obtained at 400 °C–200 °C can induce significant deviations in terms of the rates of oil cracking. They indicated that most hydrocarbons (alkanes, monoaromatics and naphthenes) at 200 °C are more stable than the extrapolated results of the Arrhenius law from 400 °C to 200 °C. Exceptions are tetralin and decylbenzene which is more reactive at low geological temperature (Burklé-Vitzthum et al., 2017).

Computational approaches (e.g., quantum chemistry calculation or reactive molecular dynamics) can bridge the temperature gap between simulation and geological conditions, and can provide insights into the relevant processes at atomic levels (Xiao, 2001). With the development of density functional theory (DFT), *ab initio* method has been practical to simulate cracking reactions at low temperatures. They can calculate reaction energies and barriers, and

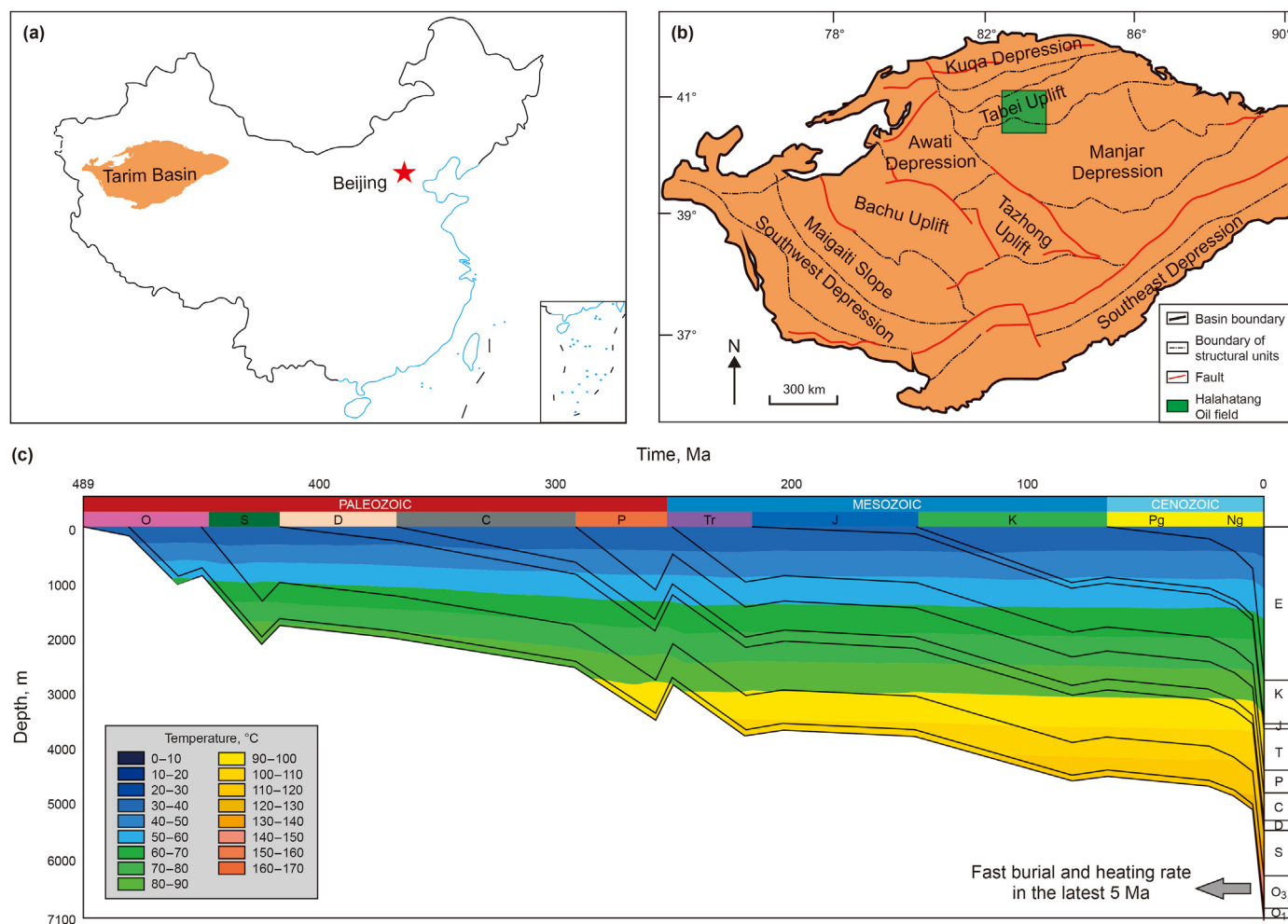


Fig. 5. (a) Location of the Tarim Basin in China. (b) Tectonic sketch map of the Tarim Basin showing the location of Halahatang oil field. (c) Burial and thermal histories of the Halahatang oil field in the Tarim Basin, modified from Zhu et al. (2019a).

activation energies, and are able to explore minimum energy pathways and to analyze transition states (Xiao et al., 1997; Goldstein et al., 1998; Wang and Tao, 2019; Bas et al., 2020). Furthermore, statistical thermodynamics and transition state theory can be used to calculate the frequency factors and activation energies of the cracking reactions (Willems and Froment, 1988a, 1988b). Dartiguelongue et al. (2006) pointed out that kinetic models should be quantitatively tested by *ab initio* calculations. Molecular dynamics simulations based on reactive force field (ReaxFF) for hydrocarbons are another potential method. ReaxFF has been widely applied in industrial problems, which commonly run at very high temperatures (more than 1000 K) (van Duin et al., 2001). Low temperature dramatically slows the computations, which adds a great challenge to the application of ReaxFF in the field of oil cracking in nature. Besides, relevant computational studies on long-chain alkanes are associated with more reactive sites, increasing the complexities of reaction network and the computational expense. With increasing computing power, the ReaxFF may be a realistic method to simulate the cracking reaction of crude oils in the future.

2.3. Pressure

2.3.1. Reservoir pressure

Reservoir pressure increases with increasing depth and is affected by non-equilibrium compaction, fluid expansion, mineral

diagenesis, seal integrity, and tectonic compression. Overpressure retarding the thermal maturation of kerogens has been proven by pyrolysis experiments and geological cases (Hao et al., 1995, 2007; Le Bayon et al., 2011; Uguna et al., 2016b). Modified vitrinite reflectance models (e.g., T-P- R_0 and basin% R_0) for kerogen evolution were proposed to take the retarding effect into account (Zou and Peng, 2001; Nielsen et al., 2017). However, the effect of pressure on oil cracking has not reached an agreement (see Table 1 for details). Some pyrolysis experiments observed constant retarding effects with increasing pressure (Dominé, 1989; Jacksón et al., 1995; Chen et al., 2014; Uguna et al., 2016a; Xie et al., 2016, 2019), while other researchers found that pressure promoted oil cracking at relatively low pressures and inhibited cracking reactions at relatively high pressures (Fabuss et al., 1964; Behar and Vandenbroucke, 1996; Hill et al., 1996; Bounaceur et al., 2016).

Dominé (1989) performed the pyrolysis experiments of hexane at various pressures, showing that the response of pyrolytic products to pressure strongly depends on their molecular weight. The yields of gaseous hydrocarbons constantly decreased with increasing pressure; the yields of some median weight hydrocarbons (e.g., 4-methyloctane and total C_9 hydrocarbons) firstly increased and then decreased with increasing pressure; the yields of heavier products (e.g., total C_{11} hydrocarbons and total C_{12} hydrocarbons) constantly increased with increasing pressure. Based on the observations, the author claimed that high pressure favours

Table 1
Summary of pyrolysis experiments relevant to the effect of pressure on oil cracking.

References	Pyrolytic samples	Temperature	Pressure	Effect of pressure	Relevant findings
Dominé (1989, 1991)	Hexane	290–365 °C	21–1560 MPa	Continuous retarding effect	Gaseous hydrocarbons constantly decreased with increasing pressure; some median weight hydrocarbons firstly increased and then decreased with increasing pressure; heavier products constantly increased with increasing pressure.
Jackson et al. (1995)	Hexadecane	300–370 °C	15–60 MPa	Continuous retarding effect	The retarding effect is significant at geological temperatures.
Al Darouich et al. (2006)	C ₆ –C ₁₄ aromatic fraction of a crude oil	375 °C	10–120 MPa	Continuous retarding effect Continuous inhibiting effect	Significant retarding effect at 10–40 MPa; insignificant retarding effect at pressure >40 MPa.
Chen et al. (2014)	A low-mature non-marine oil	300–650 °C	0.1–20 MPa	Continuous retarding effect	Increasing water pressure retards both primary and secondary cracking.
Uguna et al. (2016a)	A North Sea oil and <i>n</i> -hexadecane	350 °C	2–90 MPa	Continuous retarding effect	Increasing water pressure reduces the yields of light hydrocarbons but increases the yields of heavier <i>n</i> -alkanes, asphaltene and unresolved complex material (UCM)
Xie et al. (2016, 2019)	C ₉₊ fraction of saturate-rich oil	350–425 °C	17.5–90 MPa	Continuous retarding effect, significant between 20 and 47 MPa	This work also focuses on the effect of water pressure.
Fabuss et al. (1964)	Individual alkanes (C ₃ –C ₁₆)		0.1–100 MPa	Promoting and then retarding effects	The pressure at the turning point between promoting and inhibiting effects depends on components.
Behar and Vandembroucke (1996)	<i>n</i> -C ₂₅	325–425 °C	12–80 MPa	Promoting (12–40 MPa) and then retarding (40–80 MPa) effects	
Hill et al. (1996)	The C ₉₊ fraction of a saturate-rich oil	350–400 °C	9–200 MPa	Promoting (9–39 MPa) and then retarding (39–200 MPa) effects	The effect of pressure is larger at geological temperatures.
Bounaceur et al. (2016)	<i>n</i> -Octane	330–450 °C	1–70 MPa	Promoting and then retarding effects	The pressure at the turning point between promoting and inhibiting effect depends on temperature. (1 MPa at 250 °C; 30 MPa at 350 °C).

bimolecular reactions and hinders unimolecular decomposition (Dominé, 1989). In other words, the increase of pressure inhibits the cracking of unstable compounds, and is conducive to the formation of heavier compounds (Al Darouich et al., 2006; Bounaceur et al., 2016). The retarding effect of pressure on oil cracking is greater at lower temperatures (Jackson et al., 1995). The consistent retarding effects were also reported by other studies (Chen et al., 2014; Xie et al., 2016, 2019). According to the calculations of Al Darouich et al. (2006), the increase of pressure from 10 MPa to 40 MPa leads to a difference in apparent activation energies of 0.6–1.0 kcal/mol. Moreover, Uguna et al. (2016a) showed that increasing pressure in the presence of water also inhibited oil cracking and enhanced the generation of heavier hydrocarbons. The effect of pressure is significant in the near-critical regions (Yu and Eser, 1997).

Fabuss et al. (1964) performed pyrolysis experiments for individual alkanes (C₃–C₁₆) and showed that increasing pressure accelerated the thermal cracking of the alkanes at pressures <40 MPa but inhibited the cracking reactions at higher pressures. Similarly, Behar and Vandembroucke (1996) performed the pyrolysis experiment for *n*-C₂₅ and found that increasing pressure accelerated the cracking in the pressure range of 12–40 MPa and suppressed the cracking at higher pressures (40–80 MPa). Hill et al. (1996) conducted the pyrolysis of the C₉₊ fractions of a saturate-rich crude oil. They found that the yields of alkanes and pyrobitumen were enhanced at pressures up to 69 MPa as compared to 9 MPa; whilst the yields of all products were reduced at higher pressures (69–200 MPa). Bounaceur et al. (2016) pyrolyzed *n*-octane at 1–70 MPa in experiments and conducted a free-radical reaction modelling. Their results indicated that increasing pressure firstly promoted and secondly inhibited the cracking reaction. Besides, the pressure at which the reaction reached the maximum conversion increased with temperature (Fig. 6). Similarly, Mallinson et al. (1991) concluded that pressure accelerates thermal cracking of *n*-butane at high temperatures (e.g., 600 °C) but retards the *n*-butane cracking at low temperatures (e.g., 200 °C).

The inconsistent conclusions on the effect of pressure are not clear and may be due to the difference in hydrocarbon component and pyrolysis temperature as well as the evaluation method of oil-cracking extend. Nevertheless, both sides accept that pressure inhibits oil cracking at least in high-pressure geological conditions. High reservoir pressure is present in two scenarios, namely overpressure and deep burial. The preservation of oils in high-temperature overpressure reservoirs has been widely reported

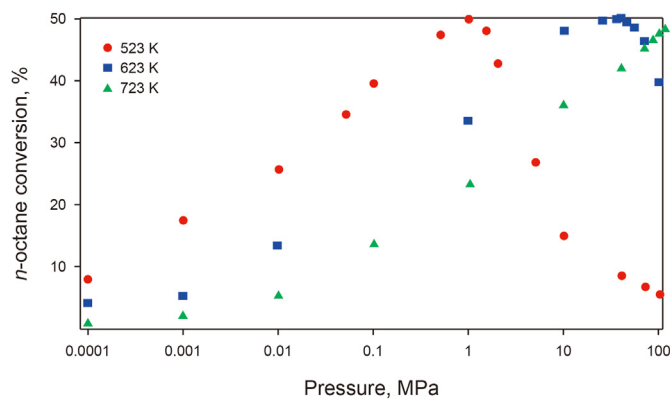


Fig. 6. Simulated *n*-octane conversion as a function of pressure at identical reaction times (1200 years at 523 K, 650 h at 623 K and 42 min at 723 K). Reproduced from Bounaceur et al. (2016) with permission from Elsevier.

(Isaksen, 2004; Nadeau et al., 2005; Hao et al., 2007; Mankiewicz et al., 2009; Olsvik et al., 2013). Whereas, high pressure created by deep burial in cold basins was rarely noticed. With respect to a cold basin, a larger depth is needed to reach the same temperature in a hot basin. High reservoir pressure will be created by the large depth, even without overpressure. For example, the reservoirs in the Halahatang oil field are characterized by normal pressure (Zhu et al., 2019c, 2021a). Due to the low geothermal gradient (19 °C/km), the high-temperature reservoirs in the Halahatang oil field have been buried to deeper positions as compared to hot basins, and thus have high reservoir pressure even without overpressure. For example, the trend between reservoir temperature and the high pressure induced by deep burial in the Halahatang oil field in the Tarim Basin approximates the trend between reservoir temperature and high pressure caused by overpressure in North Sea Basin (Fig. 7).

Besides, oil cracking is also controlled by the closeness of petroleum systems, which has a connection with overpressure. The higher the system closeness, the less the leakage of cracked products. High concentrations of products can suppress cracking reactions due to chemical equilibria. Therefore, high pressures and close systems together contribute to the preservation of high-molecular-weight hydrocarbons at extremely high temperatures (Karlsen et al., 1993; Price, 1993; Karlsen and Skeie, 2006; George et al., 2008).

2.3.2. Extreme pressure in earth's interior

The theory of the abyssal abiogenic origin of petroleum is a part of modern scientific theories for petroleum formation (Kenney et al., 2002; Kutcherov et al., 2020). The relevant studies consider the pressure and temperature conditions compatible with Earth's upper mantle (Spanu et al., 2011). Serovaiskii et al. (2020) investigated the stability of synthesized condensates utilizing diamond anvil cells, and found that the hydrocarbons remained unchanged

even under conditions corresponding to the earth depth of 50 km. The extreme thermal stability of the hydrocarbons is because Gibbs energy increases with increasing pressure and the sequence of Gibbs energy of different hydrocarbons reverses at ~3.5 GPa (Fig. 8) (Kenney et al., 2002). *Ab initio* molecular dynamic simulations indicated that higher hydrocarbons are energetically favoured at temperatures ≥ 2000 K and pressures ≥ 4 GPa, and can be formed from methane (Spanu et al., 2011). Relevant high-pressure and high-temperature (HP-HT) experiments demonstrated that petroleum hydrocarbons can be formed from inorganic materials (iron oxide, FeO, marble, CaCO₃ and water) at 50 kbar and 1500 °C (Kenney et al., 2002). Under extreme pressure (>2.5 GPa), heavier alkanes do not necessarily decompose to light components at elevated temperature but, contrarily, elevated temperature induces methane to transform into heavier alkanes. For example, C₇₊ hydrocarbons can be formed from methane at 2.5 GPa and 850–1000 K (Serovaiskii and Kutcherov, 2020). Although the above mentioned pressure and temperature are far over those of petroleum reservoirs, these studies shed light on the stability of hydrocarbons in a much wider range of pressure and temperature.

2.4. Water

2.4.1. The presence of water

Water is ubiquitous in rock pores, fractures and hydrated minerals. It occurs as edge or bottom water, irreducible water, or mineral-bound water. Although the effect of water on the thermal decomposition of kerogen to oil and gas has been fully investigated (Hoering, 1984; Michels et al., 1995; Lewan, 1997; Tsuzuki et al., 1999; Behar et al., 2003; Pan et al., 2008; Lewan and Roy, 2011), the influence of water on thermal cracking of oils is still in dispute

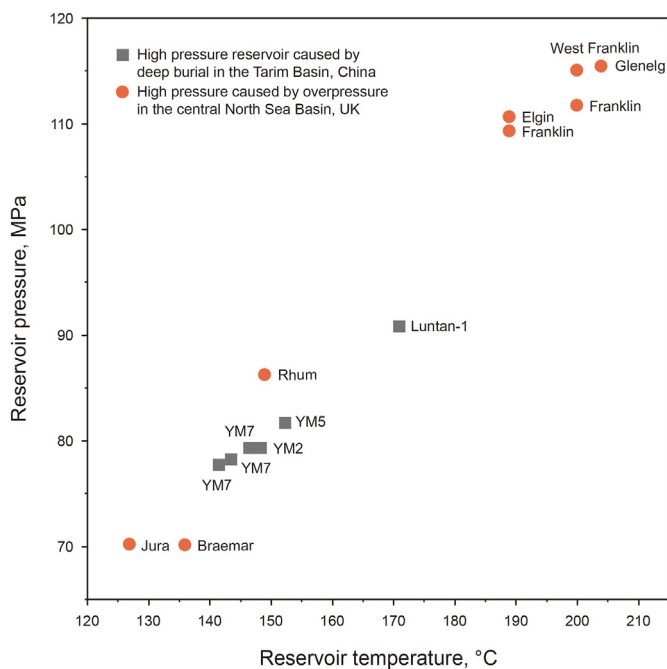


Fig. 7. The relationship between reservoir pressure and temperature of high-pressure reservoirs in the Halahatang oil field, Tarim Basin (data from Zhu et al., 2018b, 2021a) and central North Sea Basin, UK (data from Lasocki et al., 1999; Olsvik et al., 2013). The high reservoir pressure in the Halahatang oil field, Tarim Basin and central North Sea Basin were created by deep burial and overpressure, respectively. The labels next to the data points are the corresponding well name or field name.

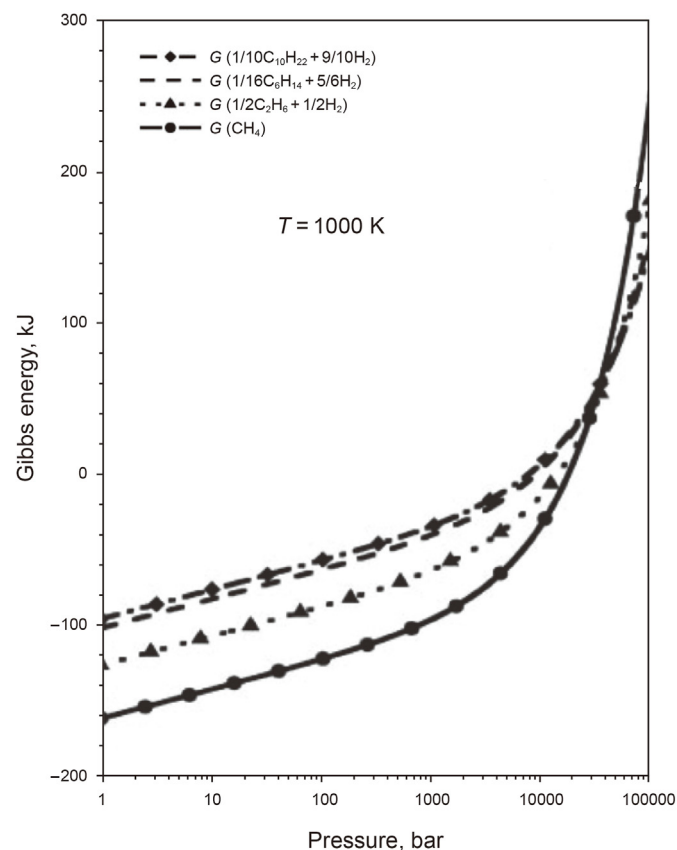


Fig. 8. Gibbs energies of methane and of some hydrocarbon systems. Reproduced from Kenney et al. (2002). Copyright 2002 National Academy of Sciences.

(Jin et al., 2009; Uguna et al., 2016a; He et al., 2018). It has been verified by hydrous pyrolysis involving deuterioxide (D_2O) that water directly participates in the reactions of oil-cracking (He et al., 2018; Yuan et al., 2019). In these experiments, the ratios of deuterium to protium of generated methane were remarkably elevated, demonstrating the hydrogen exchange between water and hydrocarbons.

Previous studies focused on the effect of water have not reach an agreement (Table 2). Some comparative pyrolysis with and without water found that water retarded the destruction of crude oil to gas (Hesp and Rigby, 1973; Price, 1993). The retarding effect is also supported by the prediction model of deep-gas yields (Henry and Lewan, 1999). Willette (2010) showed that the effect of water on oil cracking was negligible at 340 °C. At higher temperatures, the water promoted oil cracking, and increased the yields of methane, but reduced the generation of ethane, propane as well as char. Uguna et al. (2016a) investigated the combined effect of water and pressure, and found that increasing water pressure retarded oil cracking. The retarding effect was interpreted to be due to water quenching or suppressing the formation of free radicals (Price, 1993). By contrast, more recent work indicated that oil-cracking is enhanced by the presence of water (YanHua et al., 2012; Xie et al., 2016; He et al., 2018; Yuan et al., 2019, 2022; Jin et al., 2021). With regard to specific pyrolytic products, water increases the yields of C_1 – C_5 hydrocarbons and reduces the formation of high-molecular-weight hydrocarbons (Burnham et al., 1997; YanHua et al., 2012; Chen et al., 2014; He et al., 2018; Yuan et al., 2019, 2022; Jin et al., 2021); besides, water promotes the generation of CO_2 and H_2 (Burnham et al., 1997; Willette, 2010; YanHua et al., 2012; He et al., 2018; Yuan et al., 2019). The increase of low-molecular-weight hydrocarbon is because water promotes the free-radical thermal-cracking reactions. Water can act as an extra source of hydrogen, promoting the hydrogenation of alkene intermediates to alkanes, and increasing the yields of H_2 (Michels et al., 1996; Burnham et al., 1997; Lewan, 1997; Lewan and Roy, 2011; Uguna et al., 2016a). Because of the large hydrogen budget of water, there is not so much demand for the formation of coke and pyrobitumen to conserve hydrogen balance. Therefore, the formation of higher-molecular-weight hydrocarbons through cross-linking reactions is markedly suppressed (Lewan, 1997; Yuan et al., 2019). The CO_2 is formed by the stepwise oxidation of

alkanes to form O-containing groups and the subsequent decarboxylation reaction of organic acids (Seewald, 2003; Bu et al., 2017). In stepwise oxidation reactions, H_2O serves as an oxidant and supplies extra oxygen (Lewan, 1992, 1997; Seewald, 2003).

It is noteworthy that bound water and the hydroxyl groups in minerals also react with hydrocarbons, analogous to free water (Wu et al., 2012). The anhydrous pyrolysis of oil plus montmorillonite produced a dramatically higher amount of CO_2 and H_2 than the anhydrous pyrolysis of oil alone (Pan et al., 2010). The oxygens in CO_2 should be originated from $-OH$ in montmorillonite or dehydrated H_2O from montmorillonite. CO_2 is formed by oxygenating hydrocarbons and consuming oxygen atoms from montmorillonite; simultaneously, the released hydrogen atoms are reduced to H_2 or incorporated into cracked hydrocarbons (Lewan, 1997; Seewald, 2003; Pan et al., 2010).

2.4.2. Water reactivity

Researchers have paid attention to the influence of water phases on hydrous pyrolysis experiments. Behar et al. (2003) pointed out that it is important to know the amount of water and the phase which occurs in hydrous pyrolysis. Water properties (e.g., density, solvation power, degree of hydrogen bonding, polarity, dielectric strength, molecular diffusivity, and viscosity) change with temperature and pressure (Peterson et al., 2008), especially near the critical point at 374 °C and 22 MPa. Fig. 9a illustrates the variation of water density, static dielectric constant and ion dissociation constant with temperature at 30 MPa, suggesting distinct water properties between geological and pyrolysis temperature. Although pyrolysis temperatures in many experiments were set to be lower than 374 °C to avoid the occurrence of supercritical water, the properties of subcritical water change substantially with temperature (Fig. 9a). The overlay of temperature and pressure changes can induce greater differences of water properties.

Schenk et al. (1997) indicated that hydrous pyrolysis might overemphasize the role played by water because the mutual solubilities of water and oils at geological temperature are much lower than those at experiment temperature (>300 °C). Pressure changes impact the miscibility between hydrocarbons and water, especially in high-temperature conditions (Fig. 9b). Salinity also influences the hydrous pyrolysis of oils because increasing salinity reduces the solubility of most hydrocarbons in water by a factor of two (Sutton

Table 2
Summary of studies relevant to the effect of water on oil cracking.

References	Pyrolytic samples	Temperature	Pressure	Effect of water	Relevant findings
Hesp and Rigby (1973)	A middle oil distillate fraction (mainly C_{10} – C_{26} n -alkanes)	350–375 °C	Varying pressures	Retarding effect	The yields of gas in the absence of water are 5–10 times as much as those with water.
Burnham et al. (1997)	Three crude oils with isotopically labelled n -hexadecane	310–360 °C	35 MPa	Little effect on alkane decomposition	Water inhibits the coking of aromatics and significantly increases the yields of methyl aromatics as well as H_2 and CO_2 .
Willette (2010)	Smackover oil	340–400 °C	Varying pressures depending on the reaction	Negligible effect at 340 °C and promoting effect at higher temperatures	The presence of water promotes the generation of total gas and methane, but reduces yields of ethane, propane as well as char.
YanHua et al. (2012)	Crude oil	350 °C	50 MPa	Promote the yields of gaseous hydrocarbons and H_2 and CO_2	Mg^{2+} promotes hydrous pyrolysis.
Xie et al. (2016, 2019)	A C_{9+} fraction of saturate-rich oil	370–425 °C	Fixed pressures up to 90 MPa	Promoting effect	Water promotes wet gas generation with no significant effects on methane generation.
He et al. (2018)	n -Hexadecane (n - C_{16})	330–420 °C	50 MPa	Promoting effect	Increasing salinity reduces gas yields.
Yuan et al. (2019)	Eicosane ($C_{20}H_{42}$)	360 °C	Varying pressures depending on the reaction	Promoting effect	Dissolved salt ions promote oil-cracking reactions which are good nucleophiles that favour the breakage of carbon-carbon bond.
Jin et al. (2021)	n - $C_{16}H_{34}$	340 °C	Varying pressures depending on the reaction	Promoting effect	Water results in forming more low-molecular-weight hydrocarbons, CO_2 and organic acids but less high-molecular-weight hydrocarbons.

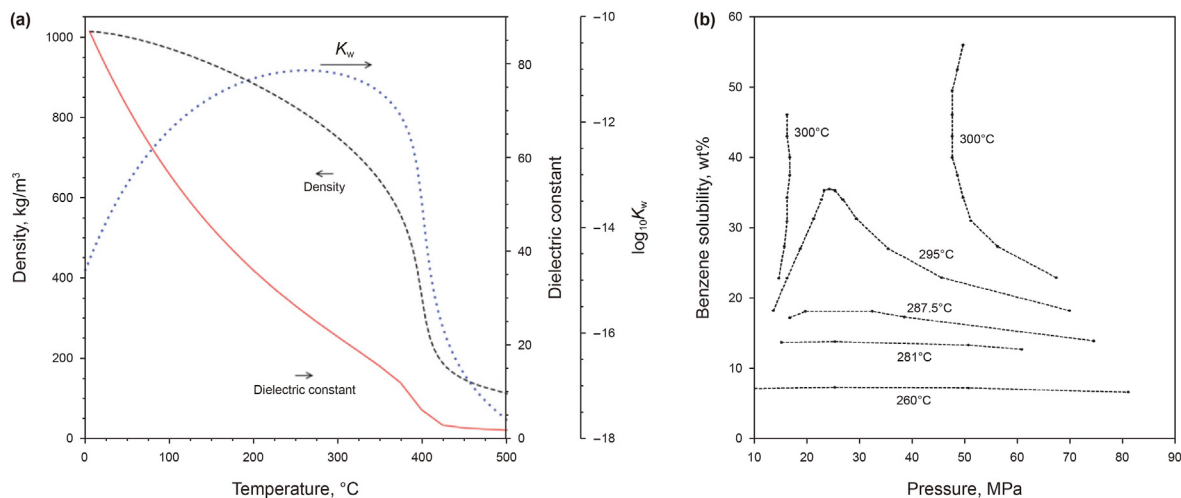


Fig. 9. (a) Density, static dielectric constant and ion dissociation constant (K_w) of water at 30 MPa as a function of temperature; (b) Benzene solubility in high-pressure water. Reproduced from Peterson et al. (2008) with permission from the Royal Society of Chemistry.

and Calder, 1974; Whitehouse, 1984; Lewan, 1997). Besides, dissolved salts have an influence on water structure (Li et al., 2003; Nilsson and Pettersson, 2011) and the self-ionization of water (the concentration of H^+ and OH^-) (Busey and Mesmer, 1978). Therefore, temperature variations may affect the reaction pathways of the hydrous reactions. Water influences pyrolysis via combined ionic-radical type reactions, which are restricted to temperatures lower than 350 °C (Michels et al., 1995, 1996). At higher temperatures, ionic-radical type reactions can not compete with the faster pure radical reactions of hydrocarbons (Behar and Pelet, 1988).

2.5. Minerals

2.5.1. Clay minerals

Crude oils are naturally reservoid in porous rocks with varying mineral compositions. The influence of minerals on oil cracking has long been realized from the pyrolysis of oils plus clastic rocks (Phillips et al., 1985; Abu-Khamsin et al., 1988). Among minerals, clay minerals are well-known catalysis for oil-cracking. Clay minerals comprise Brønsted and Lewis acid sites, where the degradation reactions of hydrocarbons can be catalyzed. The catalytic mechanisms between Brønsted and Lewis acid sites are completely different. Brønsted acid sites can donate protons, which is an essential condition of a carbonium ion mechanism (Greensfelder et al., 1949; Thomas, 1949). Catalytic products via carbonium-ion intermediates are commonly enriched in branched alkanes in the C_4 – C_6 range (Sackett, 1978; Tannenbaum and Kaplan, 1985b; Pan et al., 2010; Yuan et al., 2013; Bu et al., 2017). By contrast, Lewis acid sites accept electrons, promoting the formation of free radicals and the cleavage of carbon-carbon bonds, as well as the generation of CO_2 (Solomon and Rosser, 1965; Solomon, 1968).

The Brønsted acid sites of smectite can be formed from (i) the polarization of interlayer water molecules (Johns, 1979); (ii) specific sites (e.g., aluminol groups, silanol groups and some OH groups compensating the broken bonds) at the edge surface (Liu et al., 2013) and (iii) H_3O^+ adsorbed on the basal surface by the net negative charge induced by the isomorphous substitution of one Al^{3+} for a Si^{4+} in the tetrahedron (Du et al., 2021). Lewis acid sites derive from the exposed octahedral Al^{3+} or Mg^{2+} due to the dehydration at the edges of crystallites (Solomon, 1968; Brown and Rhodes, 1997). Compared to montmorillonite, illite has more Al^{3+}/Si^{4+} substitutions in tetrahedral sites, which increase layer charges and exchangeable ions. Hence, illite has higher Brønsted

acidity than montmorillonite (Reynolds and Hower, 1970; Johns and McCallip, 1989), and Brønsted acidity is enhanced by smectite illitization during diagenesis (Cai et al., 2022b). Brønsted acidity is also affected by the presence and the state of interlayer water, as well as the interlayer spaces (Wu et al., 2012; Yuan et al., 2013; Bu et al., 2017). Lewis acid sites can be converted to Brønsted acid sites via chemisorption of water (Galwey, 1970; Brown and Rhodes, 1997). Therefore, Lewis acidity is enhanced by removing water.

Nevertheless, the catalytic activity of clay minerals is commonly considered to be suppressed by the presence of water and seems to be negligible in nature, as evidenced by the absence of catalytic effects in hydrous pyrolysis of hydrocarbons plus clay minerals (McNab et al., 1952; Hayashitani et al., 1978; Goldstein, 1983; Tannenbaum and Kaplan, 1985a), and by the low proportion of branched alkanes in most natural crude oils (Seewald, 2003). The water films on water-wet rocks are suspected to stop the formation of acid conditions (McNeil and BeMent, 1996) and may prevent the clay minerals from contacting oils (Pepper and Dodd, 1995). Xiao et al. (2010) found that clay minerals even retarded oil-cracking in the presence of water.

2.5.2. Other minerals

Some researchers studied the influence of other main minerals, such as calcite, feldspar and quartz. Calcite has been found to slightly inhibit the thermal cracking of hydrocarbons in anhydrous pyrolysis because it prohibits carbonium ion reactions due to its basic nature (Tannenbaum and Kaplan, 1985a, 1985b; Jiang et al., 2009; Pan et al., 2010). It has been shown that the pyrolysis of oil shales after removal of carbonates and silicates yields more gasoline and diesel fractions (Mozhayskaya et al., 2021). The retarding effect in anhydrous pyrolysis is also reported for quartz (Yuan et al., 2022). However, according to the literatures (Zhao et al., 2008; Jin et al., 2021; Yuan et al., 2022), calcite enhances the yields of gas and high-molecular hydrocarbons in anhydrous pyrolysis of n - $C_{16}H_{34}$ by promoting both thermal cracking reactions and the cross-linking reactions of free radicals. The inconsistent results need future investigation.

In the presence of water, it is generally accepted that calcite has a catalytic effect on oil-cracking and reduces the generation of high-molecular-weight hydrocarbons, because it can act as an alkane buffer, facilitating the oxidation of hydrocarbons (Xiao et al., 2010; He et al., 2018; Jin et al., 2021; Yuan et al., 2022). The

influence of quartz in hydrous pyrolysis remains controversial. With regard to quartz, both catalytic (Xiao et al., 2010) and inhibitory effects (Jin et al., 2021; Yuan et al., 2022) have been reported in the hydrous pyrolysis of oil plus quartz. Yuan et al. (2019) showed the alteration of feldspar to boehmite, illite, and muscovite promotes the degradation of oils in oil-water transition zones. Besides, all the above conclusions are based on pyrolysis conditions. There is a need to understand the influences of minerals on oil-cracking in geological conditions, and to quantitatively estimate the influence intensities.

2.5.3. Transition metals

Gas generated from conventional pyrolysis of crude oils contains a lower proportion of methane (~35–40%) compared to secondary gas in reservoirs (methane ~ 60–90+%) (Mango, 1997; Snowdon, 2001). Geological thermal stresses are unlikely to thermally equilibrate the pyrolytic products even over geological time (Mango et al., 1994, 2009). The kinetic Monte-Carlo modelling of thermal cracking also failed to reproduce the wetness of high mature gases, suggesting that the high mature gases were formed or modified via other mechanisms (Xie et al., 2022). Transition metals (e.g., V, Co, Fe, and Ni) were proposed catalysts for the conversion of petroleum to wet gas or dry gas at geological temperature (<200 °C) (Mango, 1992, 1994). The dryness of the catalytic products varies from 60% to 95+%, resembling natural gas in molecular compositions (Mango, 1996; Mango and Hightower, 1997). The variation of $\delta^{13}\text{C}$ for C_1 – C_5 of the catalytic products accords with the typical rule of natural gas which follows a linear trend with $1/n$ (n = carbon number) (Mango and Elrod, 1999).

Catalytic reactions by transition-metal always proceed to reach thermodynamic equilibrium. Hence, the reactions may proceed in the opposite direction of decomposition, depending on the compositions of hydrocarbons (Taran et al., 2007; Cesar et al., 2020, 2021; Gao et al., 2020). It has been found that single iron sites embedded in a silica matrix enable the conversion of methane to ethylene, aromatics and hydrogen, by the catalytic generation of methyl radicals and subsequent gas-phase reactions (Guo et al., 2014). The pyrolysis of the Cretaceous Mowry shale plus additional propylene at 50 °C resulted in the dimerization of propylene to methyl cyclopentane and *n*-hexanes, which is interpreted to be the catalytic effect of low-valent transition metals (Mango et al., 2010).

However, the hypothesis of transition metal catalysis has been doubted. NiO, the transition metal oxide used in the Mango's experiments, is commonly absent in mature sediments and the metals in natural shales are not present in proper forms. The commonly occurring nickelous- and vanadyl-porphyrins do not contribute to the catalytic conversion of hydrocarbons because the metals occurring as cations will strongly bind to large tetrapyrrole molecules (Lewan et al., 2008). The presence of water can invalidate the catalytic effect due to the nucleophilicity of water (McNeil and BeMent, 1996). Polar-rich bitumen may also deactivate the transition metal (Lewan et al., 2008).

Despite the uncertainty, the catalytic cracking hypothesis in geological conditions is receiving more attention in the investigation of clumped isotopes of methane and ethane (Taran et al., 2007; Stolper et al., 2014; Clog et al., 2018; Cesar et al., 2020; Thiagarajan et al., 2020; Xie et al., 2021). The application of clumped isotopologues to assess the formation temperature of methane is on the basis of internal isotopic equilibrium, which requires that the hydrogen exchange of methane precursors is faster than the rate of net methane generation. Transition metal catalysis is a possible mechanism since the internal isotopic equilibrium can be successfully acquired by exposing methane to nickel catalysts (Stolper et al., 2014).

2.5.4. Reactions between mineral and hydrocarbon

Apart from being catalysts and inhibitors, some minerals directly react with hydrocarbons. The most prominent reaction between mineral and hydrocarbon is thermochemical sulfate reduction (TSR). TSR is an abiobiochemical, thermally-driven reaction between hydrocarbons and reservoir sulfates. TSR commonly initiates at temperatures of around 120 °C (Cai et al., 2022a), and thus lowers the temperature threshold of oil-cracking which is generally considered to be over 150–160 °C (Horsfield et al., 1992; Schenk et al., 1997; Dieckmann et al., 1998). According to Cross et al. (2004), the half-life of aqueous sulfate in the presence of aqueous acetate and elemental sulphur is only 372,000 years at 100 °C and 1650 years at 150 °C.

Experiments showed that the gas yields of oil cracking involving TSR were twice that of conventional thermal cracking of oils (Zhang et al., 2008). TSR preferentially destructs branched saturated hydrocarbons relative to *n*-alkanes and enriches monoaromatic hydrocarbons and organosulfur compounds (Wei et al., 2012; Walters et al., 2015; Cai et al., 2019). After the exhaustion of C_{2+} hydrocarbons, even methane can be oxidized (Machel, 2001; Hao et al., 2008, 2015; He et al., 2019). The rates of TSR are controlled by other mineral mediums (Xiao et al., 2018). Montmorillonite accelerates TSR because the exchange cations on the surface of clay generate increase H^+ concentrations and hence HSO_4^- , and because the carbonium-ion mechanism of montmorillonite catalytic reactions favours the formation of iso-alkanes, which are prone to be oxidized by TSR. By contrast, carbonates decelerate TSR because carbonate dissolution reduces the concentrations of H^+ and HSO_4^- , and hence reduces the TSR rates. Moreover, elevated pressure also significantly declines the rate of TSR, similar to the retarding effect of pressure on the thermal cracking of crude oils. Other mineral oxidants, such as haematite, magnetite, pyrite and iron-bearing aluminosilicates, can react with hydrocarbons, which is analogous to TSR (Surdam et al., 1993; Seewald, 2003).

TSR accounts for 10–80% H_2S in high-temperature petroleum accumulations. The generated H_2S may have an antagonistic effect on the thermal cracking of *n*-alkanes and the antagonistic effect increases with increasing pyrolysis temperature (Nguyen et al., 2015; Burkle-Vitzthum et al., 2019). Anyhow, the antagonistic effect of H_2S should be limited relative to the direct destruction of oils by TSR reactions. These redox reactions also generate organic acids by step oxidation reactions, and CO_2 by the thermal decarboxylation of organic acids (Seewald, 2003; Yuan et al., 2019). It has been well documented that organic acids and CO_2 cause the dissolution of acid labile minerals (e.g., carbonate and silicate), generating secondary porosity (Surdam et al., 1984; Surdam and Crossey, 1987; Taylor, 1990; Morad et al., 2000; Worden and Burley, 2003; Taylor et al., 2010; Cai et al., 2022a). Simultaneously, the consumption of organic acids and the mineralization of CO_2 may promote the overall redox reactions, and hence the degradation of oils.

2.6. Solid organic matter

Kerogen and pyrobitumen are the main solid organic matter in petroleum systems. Kerogen is an important component of source rocks and can generate liquid and gaseous hydrocarbons (Ujiié, 1978; Vandenbroucke and Largeau, 2007). Pyrobitumen can occur in reservoirs and source rocks where thermal cracking of crude oils initiates, and is regarded as a sign of secondary cracking (Hill et al., 2003; Hao et al., 2008; Bernard et al., 2012; Xiong et al., 2016; Mastalerz et al., 2018; Meredith et al., 2020). Both kerogen and pyrobitumen can interact with crude oils during cracking reactions. On one hand, carbonaceous surfaces can catalyze hydrogen exchange between liquid hydrocarbons, including alkenes, saturates

and aromatics (Alexander et al., 2009). On the other hand, solid organic matter can donate extra hydrogen, promoting the thermal degradation of crude oils (Serio et al., 1987; Behar and Pelet, 1988; Behar et al., 1991; Hill et al., 2003). Therefore, oil-cracking *in-reservoir* in the absence of pyrobitumen is considered to be slower than that *in-kitchen* (Quigley and Mackenzie, 1988; Pepper and Dodd, 1995). The presence of extra hydrogen may alter the reaction pathways of oil cracking. Pepper and Dodd (1995) assumed that the thermal degradation of oils in source rocks may reach a 100% cracking efficiency without forming coke to conserve hydrogen balance. Comparative pyrolysis of oils with and without solid organic matter has been performed to quantitatively illustrate the problem. Jin et al. (2013) showed that oil-cracking rate in the pyrolysis of oil plus coal can be more than 10 times the pyrolysis of oil alone. Pan et al. (2012) indicated that the pyrolysis of oil plus pyrobitumen increases the yields of methane but reduces the production of wet gas and total gas hydrocarbons, compared to the pyrolysis of oil alone. They concluded that pyrobitumen catalyzes the cracking of wet gas but inhibits the conversion of oils to wet gas.

3. Estimation of cracking extent of oils

The thermal cracking of crude oils induces complex compositional and isotopic changes, both of which are potential estimators of the extent of oil cracking. The oil-cracking extent in pyrolysis experiments can be accurately calculated by comparing parameters of reactants and products before and after pyrolysis (e.g., the yields of gaseous hydrocarbons or pyrobitumen, the residual of liquid oil, the dryness of the gaseous hydrocarbons). While, it is much harder to assess oil-cracking extent in nature due to the unknown of original oil compositions.

At relatively low thermal evolution conditions, traditional biomarker maturity proxies (e.g., $T_s/(T_s + T_m)$, $C_{29}T_s/(C_{29}T_s + C_{29}H)$, methyl phenanthrene ratio ($MPI = 1.5 \times (3-MP + 2-MP)/(P + 9-MP + 1-MP)$, 4-MDBT/1-MDBT (where MDBT = methyl dibenzothiophene)) can assess the extent of oil-cracking (Peters et al., 1990; Hang et al., 2010; Zhang et al., 2016; Hao, 2022), but are of limited use for intensely cracked hydrocarbons due to the absence or extremely low concentrations of the biomarkers, or the reversal of some biomarker maturity indicators (Peters et al., 1990; Farrimond et al., 1998; Dahl et al., 1999; Chen et al., 2016). Besides, biomarker maturity indicators are not dedicated estimators for the extent of oil-cracking. Biomarkers bounding into kerogens and asphaltenes reflect the thermal evolution of kerogens, solid bitumen and asphaltenes, respectively (Stalker et al., 1998; Liao et al., 2015; Liu et al., 2022). Therefore, they may reflect the source rock maturity when oils were expelled (Qi et al., 2020). In other words, the thermal cracking of an oil expelled from a less mature source rock may have approximately the same maturity of an uncracked oil expelled from a high mature source rock. Therefore, using maturity indicators to assess the extent of oil has laminations. The widely applied estimation methods for the extent of oil-cracking are based on GORs and diamondoids, which we will discuss in the following parts.

3.1. GOR-based cracking indicator

Crude oil cracking generates gaseous hydrocarbons and pyrobitumen. GOR, as a ratio of the amounts of product to residual reactant, increases with oil-cracking extent, as verified by pyrolysis experiments (Behar et al., 2008). Claypool and Mancini (1989) assumed that the complete cracking of one oil molecule averagely forms six molecules of gas, and proposed a formula (Eq. (1)) to calculate the extent of oil cracking.

$$EOC = GOR / (GOR + 7.95 \times 10^5 \times \text{density} / \text{mol.wt.}) \quad (1)$$

where EOC is the extent of oil-cracking, namely the fraction of original oil that has been destroyed; GOR is in scf/bbl; density (g/cm³) and mol.wt. (g/mol) are the average values of density and molecular weight of the original oil, respectively.

Unfortunately, crude oils with similar cracking extent may correspond to a wide range of GORs (Claypool and Mancini, 1989; England and Mackenzie, 1989; Karlsen and Skeie, 2006; Ohm et al., 2008), because GORs are readily altered by secondary processes, such as the gas leakage through seal rocks, the addition of gas from deeper reservoirs, and biodegradation.

According to Tian et al. (2008), the thermal cracking of oils is unlikely to lead to the leakage of cracked gas even in an open system, provided that depressurization does not occur. For an open reservoir saturated with 100% oils at hydrostatic pressure gradient, gas spills out until the destructed oils reach ~87% (corresponding to a reservoir temperature of 196 °C). If overpressure occurs, the gas leakage becomes more unlikely. For an open reservoir containing 50% oils, the complete destruction of the oils (corresponding to the temperature of 240 °C) only generates a gas volume of 64–89% system volume which moves the gas–water contact downward and does not cause the spilling out of gas. In view of this, gas leakage is unlikely to occur in a subsiding basin. GORs in a subsiding basin are mainly altered by the additional charges of gas from deeper reservoirs or source rocks. The additional gas will displace the *in-situ* water or even oils, raising the GOR values. The altered GOR values should be greater than or at least equal to the original GOR values.

The alternation of GORs in an elevated basin differs from that in a subsiding basin. With respect to an elevated basin, phase separation will occur when fluid pressure is lower than the saturation pressure of the hydrocarbon mixtures. If the reservoir is not well sealed, the free gas fractions subsequently leak out, lowering the GORs. Otherwise, the volume expansion induced by depressurization will move the gas–oil and oil–water contacts down, may increasing the GORs. Moreover, biodegradation may also alter GORs when the reservoirs are uplifted to shallow, cool reservoirs. It can be seen that GOR variations in elevated basins are more complex than those in subsiding basins.

3.2. Diamondoid-based cracking indicator

3.2.1. 3- + 4-methyldiamantane as a thermal cracking indicator

Diamondoids are a series of aliphatic hydrocarbon cage compounds, and exist in crude oil, natural gas and other natural hydrocarbon-rich sediments. Diamondoids have considerable thermal stability compared to other components in oils. They commonly occur in trace amounts in uncracked crude oils but can be concentrated to up to high abundance in highly cracked oils. They can even compose 90% of a highly cracked condensate (Lin and Wilk, 1995; Mankiewicz et al., 2009). When crude oils are partly decomposed to gas and pyrobitumen, refractory diamondoids will be progressively enriched in residual oils. Based on the mechanism, Dahl et al. (1999) proposed a diamondoid-based oil-cracking proxy:

$$EOC = [1 - (C_o/C_c)] \times 100 \quad (2)$$

where C_o is the “diamondoid baseline”, namely the diamondoid concentration in uncracked, nonbiodegraded and nonfractionated oils, and C_c is the diamondoid concentration in cracked oils.

3- + 4-Methyldiamantanes (3- + 4-MDs) were chosen as representatives by Dahl et al. (1999) because 3- + 4-MDs, C_{15} diamondoids, are not readily lost to evaporation and are easy to be detected by Gas Chromatography–Mass Spectrometry (GC–MS).

Experimental pyrolysis showed good correlations between diamondoid-based cracking degree and actual cracking extent determined by comparing the original to the final weight of the pyrolytic oil (Dahl et al., 1999). The proxy has been applied in worldwide basins, such as the Gulf of Mexico, the North Slope of Alaska, the Siberian Basin, the Barents Sea Basin and the Tarim Basin (Zhang et al., 2011; He et al., 2012; Wang et al., 2014; Liu et al., 2016; Yurchenko et al., 2018).

The proxy bases on the assumption that diamondoids are only formed by carbonium ion rearrangements of suitable organic precursors (such as multi-ringed terpene hydrocarbons) on the Lewis acid sites of clay minerals in source rocks, and are neither generated nor destroyed during *in-reservoir* oil-cracking (Dahl et al., 1999). Later studies showed that diamondoids can be formed from non-catalytic pyrolysis of kerogen (Wei et al., 2006), crude oil (Fang et al., 2012), specific oil fractions (Giruts et al., 2006; Giruts and Gordadze, 2007) and *n*-alkanes (Gordadze and Giruts, 2008). Therefore, Dahl's diamondoid-based cracking proxy should overestimate the cracking extent without considering newly generated diamondoids. To fix the problem, Peng et al. (2022) introduced a revised formula ($1.2402 \times [1 - (C_0/C_c)] - 28.952$).

3.2.2. Other controlling factors

However, caution should be taken when applying the diamondoid-based proxy to crude oils and condensates. Natural petroleum may have experienced complex geological processes, such as oil mixing, biodegradation, phase separation and evaporative fractionation, all of which change the concentrations of diamondoids.

Mixing of uncracked and highly cracked oils can be identified by the plot of biomarker (e.g., stigmastane) concentration versus 3- + 4-MD concentration (Dahl et al., 1999). The mixtures should be enriched in both thermally unstable biomarkers and thermally stable diamondoids (Fig. 10). It should be noted that this method is invalid for identifying the mixture of a slightly cracked and a highly cracked petroleum if both the petroleum contain trace amounts of stigmastane.

The biodegradation resistance of diamondoids is as high as that of polycyclic terpenes and steranes (Williams et al., 1986; Wei et al., 2007b). Many biodegraded oils have been found to contain higher concentrations of diamondoids compared to those unaffected by biodegradation (Cortes et al., 2018; Scarlett et al., 2019; Jiang et al., 2020; Spaak et al., 2020; Chai et al., 2022). However, Wei et al. (2007a) found that increasing intensity of biodegradation slightly reduces the diamondoid abundance of the oils from the San Joaquin Valley. The severely biodegraded oils can have very low concentrations of diamondoids, which approach the diamondoid baseline. Similarly, many biodegraded, heavy oils from the Halahatang oil field have lower concentrations of 3- + 4-MDs compared to non-biodegraded, normal oils (Fig. 11a). Reiser et al. (1996) measured the solubility of diamondoids in alkanes (from pentane to pentadecane) at 25 °C. The solubility of both adamantane and diamantane generally decreases with increasing carbon number of the alkane solvents (Fig. 11b). We believe that the decrease of 3- + 4-MDs concentrations in these biodegraded, heavy oils is due to the low solubility of diamondoids in heavy oils. Overall, individual biodegradation should concentrate diamondoids while diamondoid abundance may be greatly declined by sufficient evaporative loss.

Diamondoid fractionation occurs with hydrocarbon migration. Forkner et al. (2021) reported a marked difference in diamondoid concentrations between source rock extracts and hydrocarbons, suggesting a fractionation effect during hydrocarbon expulsion and migration. Evaporative fractionation indicates the selective removal of components from liquid oils by flushing with excess gas (Thompson, 1987, 1988). Diamondoids, as volatile compounds,

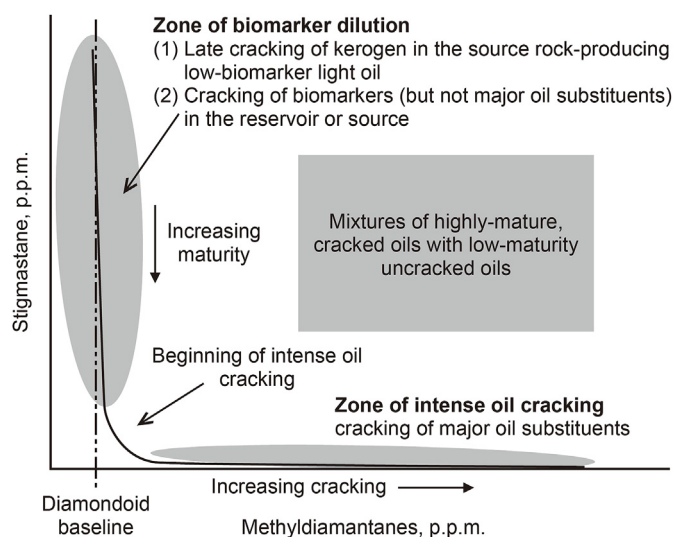


Fig. 10. Schematic diagram of the concentrations between diamondoids (methyladamantanes) and biomarkers (stigmastane) in oils of different thermal maturities, cracked and uncracked crude oils. Reproduced from Dahl et al. (1999) with permission from Nature Publishing Group. The increasing maturity of a crude oil decreases the biomarker concentration. Further thermal cracking of the oil will enrich diamondoids due to their high thermal stability. An oil rich in both stigmastane and methyladamantanes is interpreted to be a mixture of uncracked and highly cracked oils.

should be susceptible to evaporative fractionation (Li et al., 2014; Chakhmakhchev et al., 2017). Through evaporative fractionation, diamondoids, especially adamantanes, are enriched in gas condensates and are impoverished in residual oils (Moldowan et al., 2015; Yurchenko et al., 2018; Zhu et al., 2021b). Thus, evaporative fractionation can be identified by the varying ratios of 1- + 2-methyladamantanes/3- + 4-methyladamantanes ((1- + 2-MAs)/(3- + 4-MDs)) (Moldowan et al., 2015; Yurchenko et al., 2018).

It is generally considered that deeper reservoirs at higher temperatures should be enriched in diamondoids due to the increasing intensity of oil cracking. Interestingly, it was recently reported that, in the Halahatang and eastern Lunnan oil fields, Tarim Basin, deeper reservoirs contain fewer 3- + 4-MDs than shallower reservoirs (Qi et al., 2022). The phenomena have been observed in the entire Tarim Basin (Fig. 12) (Zhou et al., 2021). The reversal distribution of diamondoids has been interpreted to be the result of a combination of evaporative fractionation and subsequent phase separation (Qi et al., 2022). The detailed mechanism is like this: late charges of gas firstly extracted diamondoids from deep-buried, highly-cracked oils through the evaporative fractionation effect, reducing the diamondoid in these deep oils. As the diamondoid-rich vapour migrated upward, the decrease of pressure and temperature leads to the condensation of diamondoids in the vapour, raising the diamondoid abundance in oils.

All the above mentioned processes remarkably change the diamondoid abundance, interfering with the application of the diamondoid-based cracking proxy. Before application of the diamondoid-based proxy, the geological processes that may alter the diamondoid abundance should be clear.

4. Summary and future recommendation

Recent progress in the controlling factors of oil cracking is reviewed from six aspects, namely, oil compositions, temperature and time, pressure, water, minerals and solid organic matter. Subsequently, the estimation methods for the extent of oil cracking are reviewed. The following is a summary of the reviewed studies.

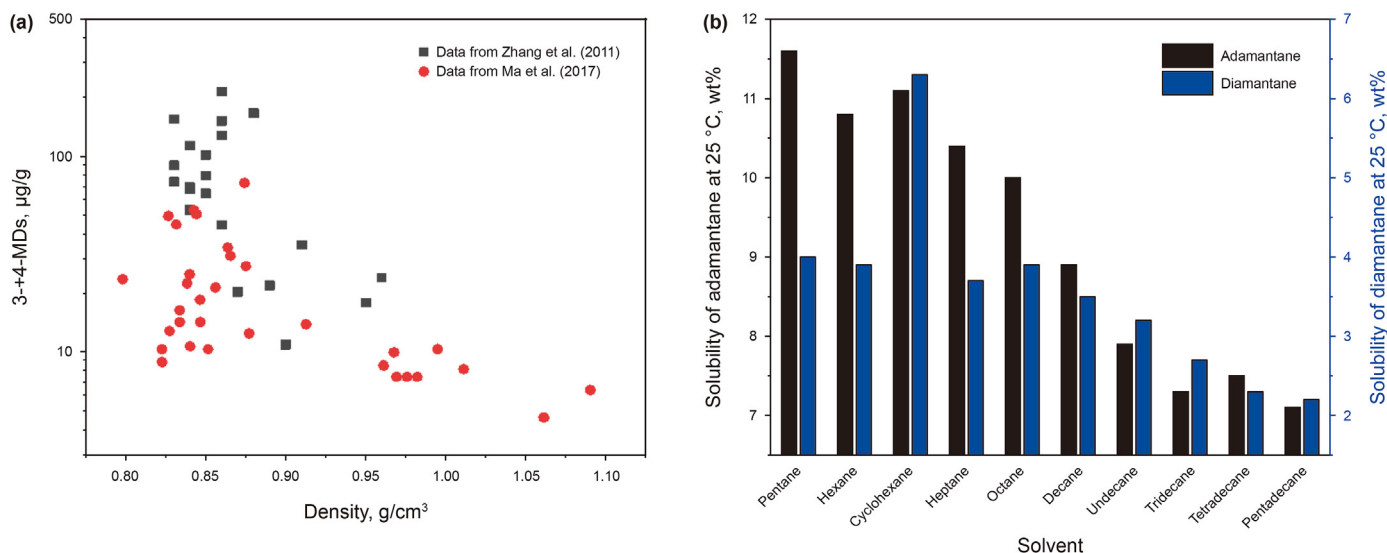


Fig. 11. (a) The plot of 3- + 4-MD concentration versus oil density for Ordovician oils in the Tabei Uplift (data from Zhang et al., 2011; Ma et al., 2017) indicating that heavy oils have a low abundance of 3- + 4-MDs. (b) The solubility of adamantane and diamantanes in different saturates at 25 °C (data from Reiser et al., 1996) indicating that diamondoids are more readily to be dissolved in light oils rather than heavy oils.

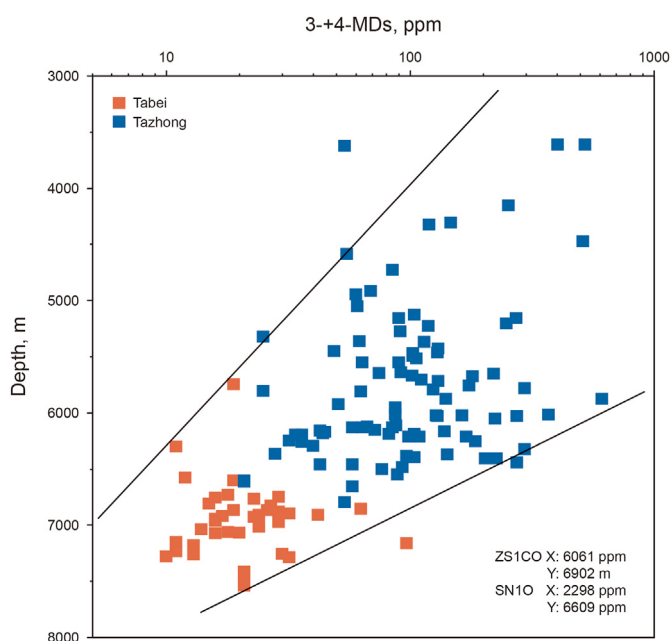


Fig. 12. The plot of 3- + 4-MDs versus depth in the Tarim Basin (data from Zhou et al., 2021) indicating that diamondoids are enriched in shallower reservoirs. Two data points out of range (Wells ZS1CO and SN10) are labelled in the bottom right.

- (1) The carbon-carbon bonds on saturates are more thermally stable than alkyl sidechains at the β position to aromatics. The degradation of long-chain alkyl aromatics is dominated by the breakdown of side chains rather than the break of aromatic rings. The cracking of a long-chain alkyl aromatic generates a saturate and a methyl aromatic, raising saturate/aromatic ratios. The thermal stability of alkyl aromatics declines with increasing length of sidechains. Short-chain alkyl aromatics (e.g., toluene) can be more stable than saturates.
- (2) Alkyl aromatics (e.g., toluene, ethylbenzene, decylbenzene) can suppress the thermal degradation of saturates. The

- inhibiting effects are enhanced at low-temperature geological conditions but are reduced by high pressure.
- (3) Temperature and heating duration have impact on the rate, pathways and products of oil-cracking reactions. Faster heating rate leads to a shorter duration at high temperature and hence less extent of oil cracking. We highlight the effects of heating rates, which could be the key for the survival of oils in many ultra-deep oil reservoirs.
- (4) The effect of pressure on oil cracking remains controversial in low-pressure range. While, it is generally accepted that high pressure inhibits oil cracking. The inhibiting effect of pressure is enhanced at lower temperatures. High reservoir pressure can be developed from overpressure or ultra-deep burial. According to the theory of the abyssal abiogenic origin of petroleum, the sequence of Gibbs energy and the relative stability of different HCs reverse at several GPa. Under extremely high pressure (>2.5 GPa), complex hydrocarbon molecules even can be formed from small hydrocarbon molecules rather than crack into them.
- (5) Water promotes the free-radical thermal-cracking reactions and the formation of low-molecular-weight hydrocarbons, and suppresses the cross-linking reactions and the formation of higher-molecular-weight hydrocarbons. It supplies extra oxygen and hydrogen for oil-cracking reactions. The solubility of oil compounds in water and the reactivity of water change with temperature, pressure and salinity. What's more, bound water and hydroxyl groups can react with hydrocarbons, analogous to free water.
- (6) Clay minerals comprise Brønsted and Lewis acid sites, where oil cracking can be catalyzed. Brønsted acid sites can donate protons, which is an essential condition of a carbonium ion mechanism. Lewis acid sites accept electrons, promoting the formation of free radicals and the cleavage of carbon-carbon bonds. The Brønsted and Lewis acidities vary among different clay minerals, and are affected by the presence and the state of interlayer water. Nevertheless, the catalytic effects of clay minerals are commonly considered negligible because they are remarkably suppressed by water. Besides, it was proven that other minerals (e.g., calcite, quartz and feldspar) also

have an influence on oil cracking, and the influence is different in the presence and absence of water.

- (7) Transition metals are proposed catalysts for the conversion of petroleum to wet gas or dry gas that resemble natural gas in molecular and isotopic compositions. Nevertheless, transition metal catalysis is debatable because (i) transition metals in sediments are not present in proper form or absent in reservoir rocks; (ii) the presence of water and polar-rich bitumen can invalidate the catalytic effect.
- (8) Apart from being catalysts and inhibitors, minerals may directly react with hydrocarbons, promoting the degradation of crude oils. The most prominent reaction is thermochemical sulfate reduction (TSR). TSR initiates at ca. 120 °C and markedly lowers the temperature threshold of thermal cracking of oils. TSR preferentially destructs branched saturated hydrocarbons relative to *n*-alkanes, and enriches monoaromatic hydrocarbons and organosulfur compounds. After the exhaustion of C₂₊ hydrocarbons, even methane can be oxidized.
- (9) Solid organic matter, including kerogen and pyrobitumen, can donate extra hydrogen, promoting the thermal degradation of crude oils. Oil cracking in reservoirs without pyrobitumen should be slower than that in source rocks.
- (10) The extent of oil cracking can be estimated by gas-to-oil ratio (GOR). Whereas, GORs may be altered by secondary processes, such as gas leakage or additional gas charges. GORs in subsiding basins should be greater or at least equal to the original GOR values.
- (11) The concentrations of 3- + 4-methyldiamantanes have been used to calculate the extent of oil cracking in worldwide basins. It is worth noting that diamondoid concentrations may be altered by other geological processes, such as TSR, oil mixing, biodegradation, phase separation and evaporative fractionation. Phase fractionation induced by hydrocarbon migration even completely reverses the diamondoid distribution, leading to the enrichment of diamondoids in shallower reservoirs. Before applying the diamondoid-based proxy, it should be clear whether diamondoid concentrations have been altered by other geological processes apart from thermal cracking.

Despite the broad understanding of crude oil cracking, the following issues should be further addressed to enable an in-depth understanding of oil cracking in nature.

- (1) The controls of some factors on oil cracking remain controversial and need further investigation. The disagreements include the relative stability of asphaltene and resins, the effect of loading low-pressure (e.g., <40 MPa), and the effect of water and some minerals. The reasons for previous controversial results and conclusions should be elucidated.
- (2) Previous investigations focus on the influence of individual factors, and rarely compare the impact strength between different factors. The effect of one factor may be negligible relative to another factor. Considering the complexity of crude oils, surroundings and geological evolution histories, the coupling effect of multiple factors should be figured out, so as to understand the destruction and preservation of liquid hydrocarbons in actual reservoir conditions.
- (3) The huge temperature gap between geological conditions (<200 °C) and pyrolysis temperature (250–400 °C) lowers the credibility of the extrapolation of laboratory pyrolysis results to geological conditions. Computational approaches (e.g., quantum chemistry calculation or reactive molecular dynamics) can reproduce the real geological conditions, and

provide insights into relevant processes at atomic levels. With increasing computing power, computational petroleum geochemistry will play a more important role in the future.

- (4) An in-depth understanding of geological evolution history, source rock facies, hydrocarbon expulsion and migration, as well as other secondary alternation is essential for analyzing the controls on oil cracking and assessing oil-cracking extent. On one hand, these factors have an influence on oil compositions and thus the thermal stability of the oil. On the other hand, the geological processes may alter oil-cracking indicators, leading to inaccurate estimation results.

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