



Original research paper

Recent progress on the research of Re–Os geochronology and Re–Os elemental and isotopic systematics in petroleum systems[☆]

Yanming Sai ^a, Keyu Jin ^{b,*}, Mingzhuang Luo ^c, Hui Tian ^d, Jie Li ^e, Junjie Liu ^e

^a Southwest Petroleum Branch, SINOPEC, Chengdu, 610041, China

^b Northwest Oilfield Branch, SINOPEC, Luntai, 841604, China

^c Henan Oilfield Branch, SINOPEC, Nanyang, 473132, China

^d State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China

^e State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China

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Abstract

Re–Os geochronometer has been used in the dating of generation-accumulation, thermal cracking, and thermochemical sulfate reduction of crude oil and the oil-source correlation of petroleum systems in recent years. Re and Os concentrations are higher in the asphaltene fraction of crude oil and the earlier precipitated fractions of asphaltene. The correlations of the Re–Os isotopic systematics between asphaltene and maltene and among the fractions of asphaltenes are complex. It is shown by experiments that Re and Os can transfer from water to oil rapidly in a significant amount. However, Re–Os dating with multiple crude oil samples is suffering from great uncertainties while single oil dating methodology does not always work. A bright future for the application of Re–Os geochronometer on the dating of crude oil generation and accumulation requests further research on the homogenization mechanism of ¹⁸⁷Os/¹⁸⁸Os, the closed system of Re–Os systematics, and how Re and Os reside in crude oil.

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Keywords: Petroleum system; Re–Os dating; Oil source correlation; Re–Os systematics; Oil-water contact

1. Introduction

Rhenium (Re) and osmium (Os) are organophilic elements and can be enriched in the organic-rich sedimentary rock deposited under anoxic environments and the crude oil and asphaltenes generated from such rocks. The half-life of the β decay from ¹⁸⁷Re to ¹⁸⁷Os is ca. 41.6 billion years and thus this scheme is suitable for the dating of petroleum systems from the Proterozoic Eon to the Cenozoic Era.

For petroleum basin analysis, it is important yet difficult to constrain the critical timings of petroleum systems, e.g. the deposition of source rock and the generation, migration, accumulation, and alteration. Radioisotope dating has been applied from the dating of hydrocarbon accumulation with mineral, fluid inclusion, kerogen, crude oil, and asphaltene samples using K–Ar, ⁴⁰Ar–³⁹Ar, Rb–Sr, Pb–Pb, and (U–Th)/He [1–6]. Selby et al. [7] and Selby et al. [8] successfully dated the crude oil generation-migration in 2005 through the Re–Os analysis on crude oil and bitumen samples directly. The progress on the application of Re–Os geochronology on constraining the critical timings of petroleum systems has drawn extensive attention in China [9–18].

There is new progress on the Re–Os study on the petroleum systems in the recent few years. This includes new knowledge on the Re–Os elemental and isotopic systematics

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* Corresponding author.

E-mail address: 852415414@qq.com (K. Jin).

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of crude oils [19–21], oil-water contact experiments [22–25], and the exploration and application of the single oil Re–Os dating method [26]. The purpose of this paper is to introduce these progresses to the researchers with a brief introduction of the relevant literature to facilitate the understanding and evaluation of this methodology during petroleum exploration and exploitation.

2. Characteristics and development of the petroleum Re–Os analysis

Crude oil and asphaltenes consist mainly of hydrocarbons of different molecular weights and their derivatives. Their Re and Os contents are usually from ppt (parts per trillion) to ppb (parts per billion) level. Re and Os present in crude oil and asphaltenes in complex forms; however, they are relatively easy to be digested and with little impurities compared to sulfides and organic-rich rocks [27,28]. The commonly used inversed *aqua regia* can easily digest such samples under 200 °C or higher temperatures. The addition of H_2O_2 can improve the efficiency and signal on a mass spectrometer [29]. The purification of Re is easy and the acetone–NaOH extraction can be skipped to lower the blank [30]. Hurtig et al. [31] employed two steps of acetone–NaOH extraction and resin bead to reduce the influence of the matrix. The generally low Re and Os contents of crude oils lead to the difficulty of their accurate and precise measurements, which further imposed difficulty on the Re–Os geochronology and the study on the Re and Os geochemical behavior in petroleum systems. Besides the optimization of procedures, enhanced precision can also be achieved by increasing the sample amount for analysis. However, the CO_2 generated during the digestion of organics puts a limit on the commonly used digestion vessel Carius tube to be ca. 150 mg [32]. If a high-pressure asher (HPA-S) is employed, the sample amount can be up to 450 mg [26].

The first attempt to establish a crude oil matrix-matched Re–Os analysis reference material was conducted on the Research Material 8505 from the National Institute of Standards and Technology (NIST) of the US with HPA-S and multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) where the Os content and $^{187}Os/^{188}Os$ data were presented [33]. This method saves a lot of time compared to the negative thermal ionization mass spectrometry (NTIMS) method and can be used for the screening of samples.

Liu et al. [30] conducted repeated Re–Os tests on NIST 8505 crude oil using the Carius tubes-isotope dilution-NTIMS method and obtained Re–Os elemental abundance and isotopic ratio data with a distribution close to the normal distribution and a smaller relative standard deviation. Meanwhile, Re–Os data with an even smaller relative standard deviation and close to normal distribution were obtained from the asphaltene isolated from 8505 crude oil which was crushed into powder (<212 μm) and mixed thoroughly. The authors recommended that NIST 8505 and the asphaltene powder can be a petroleum matrix-matched Re–Os analysis reference material.

Hurtig et al. [31] believe that the heterogeneity of crude oil can be reduced in many ways and that NIST 8505 is suitable as reference material for Re–Os isotopic ratios rather than elemental abundances. Meanwhile, Hurtig et al. [31] presented the reference Re–Os elemental abundance and isotopic ratio values for NIST 8505 and two other oils with HPA-S digestion coupling with isotope dilution-NTIMS.

3. The systematics and evolution of Re–Os within petroleum systems

3.1. Hydrous pyrolysis of source rocks

Rooney et al. [34] and Cumming et al. [35] conducted hydrous pyrolysis experiments on source rocks with Type I, II-S, and III kerogens. The Re and Os contents of the oil generated at different maturation stages are all lower than that of natural crude oils. The authors attributed this phenomenon to the much higher temperatures adopted in the experiments than the natural oil generation process which could retain Re and Os through the formation of crosslinks. Most of the Re and Os (>95%) remain in the extracted source rocks leaving the source rock $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ basically intact, demonstrating that maturation will not hamper Re–Os dating of the source rock deposition. The generated bitumen inherits the $^{187}Os/^{188}Os$ of the source rock while their $^{187}Re/^{188}Os$ are different.

The similarity of $^{187}Os/^{188}Os$ provides a chance to trace the source of crude oil through Os isotope composition; however, the oils generated simultaneously can have different initial $^{187}Os/^{188}Os$ on a basinal scale because of the heterogeneous $^{187}Os/^{188}Os$ of the source rock during its maturation and oil generation. The heterogeneous $^{187}Re/^{188}Os$ and decay of ^{187}Re from deposition to maturation has changed the once homogeneous $^{187}Os/^{188}Os$ into a range as the function of $^{187}Re/^{188}Os$ range and deposition-maturation time gap (Fig. 1). This leads to the question of the homogenization mechanism of multiple crude oil samples with Re–Os dating of oil generation [23,36,37].

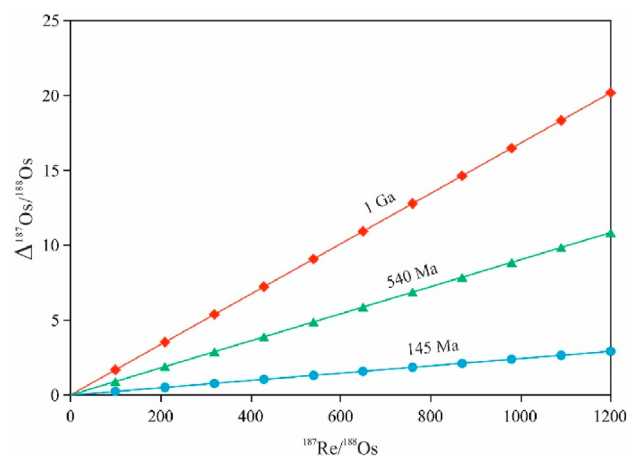


Fig. 1. Simulation of the growth of source rock $^{187}Os/^{188}Os$ over time.

3.2. Re–Os systematics between oils

Crude oil is a complex mixture of thousands of organic compounds occasionally with water and minerals. Crude oil components can be heterogeneous even within a single trap due to gravitational differentiation. The difference in Re–Os systematics was revealed on oils from the same 250 mL bottle of NIST 8505 [30]. Furthermore, subtle differences on Re–Os systematics was detected from repeated tests on the same oil samples from the Duvernay petroleum system of the Western Canada sedimentary basin (WCSB) [37], the Phosphoria petroleum system of the Bighorn basin, USA [36], and the Italian Sicily crude oils [26]. Li et al. [12] saw this as an analog to the repeated tests on the 200 mesh basalt reference material [38] and concluded that no geological meaning should be assigned to isochrons established with repeated tests on the same sample.

3.3. Re–Os systematics of the fractions of crude oil

Crude oil can be separated into multiple fractions and it is commonly separated into asphaltene and maltene by adding 40 times of *n*-heptane. Like many other metals, Re and Os in crude oil are concentrated in the asphaltene fraction. The Re–Os analysis taken on 17 worldwide crude oils by Selby et al. [32] showed that more than 83% Re and 90% Os of crude oil are in asphaltene. Thus, asphaltene determines the Re–Os isotopic composition of crude oil. Asphaltene usually has higher $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ than the corresponding maltene. In the $^{187}\text{Re}/^{188}\text{Os}$ – $^{187}\text{Os}/^{188}\text{Os}$ space, the crude oil should be on the line defined by its asphaltene and maltene and closer to the asphaltene. With more and more studies, maltenes with higher Re and Os proportions have been discovered while the difference in $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ is greater between asphaltene and crude oil [30]. Furthermore, Dimarzio et al. [19] conducted the Re–Os analysis on the saturates, aromatics and resin separated with open column chromatography and believed that both aromaticity and polarity play a role in the chemical binding of Re and Os in crude oil. However, the authors of this paper doubt that the separation method may not be able to support such a discussion although the conclusions are unnecessarily incorrect.

3.4. Re–Os systematics of the fractions of asphaltene

Asphaltene can precipitate from crude oil in many geological processes. During the migration and accumulation of crude oil, asphaltene can be absorbed by rock, i.e., the geochromatographic effect. When pressure and components change, e.g. injection of gases or light hydrocarbons, asphaltene can also precipitate from crude oil. To study the Re–Os elemental and isotopic systematics of crude oil and the influence of asphaltene precipitation on the Re–Os systematics of crude oil, Mahdaoui et al. [21], Dimarzio et al. [19] and Liu et al. [20] conducted the Re–Os analysis on the fractions of asphaltene. The fractionation of asphaltene is realized through the step by step change of the precipitant (*n*-heptane or

acetone) to the solvent (dichloromethane and toluene) ratio, i.e., dissolving the asphaltene into the solvent first and then adding an appropriate precipitant to initiate the precipitation of asphaltene, isolating the precipitated fraction and then adding more precipitant to the supernatant every step. Thus, multiple fractions of asphaltene can be obtained through progressive precipitation.

Mahdaoui et al. [21] and Liu et al. [20] used *n*-heptane (or *n*-pentane) – dichloromethane to fractionate asphaltenes from two and six crude oils, respectively. Dimarzio et al. [19] used two mixtures of solvents to separate two aliquots of an asphaltene sample: *n*-heptane plus dichloromethane (H series), and acetone plus toluene (A series). In general, Re and Os abundances are higher in the fractions precipitated earlier. Dimarzio et al. [19] showed that the changes of the Re and Os abundances are similar to that of Mo and Cd in the progressively precipitated asphaltene fractions.

In the study of Mahdaoui et al. [21], the earlier precipitated fractions have similar $^{187}\text{Os}/^{188}\text{Os}$ and Re/Os up to 60% of the total asphaltene. The authors believed that when there is only little asphaltene precipitated from the crude oil, the oil Re–Os isotopic ratios and geochronology will not be affected. It is only when massive asphaltene precipitation happens can the oil Re–Os isotopic ratios and geochronology be affected. The variation of the $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ of the fractions of the asphaltenes in the studies of Dimarzio et al. [19] and Liu et al. [20] is complex. To be specific, they can remain similar, increase, decrease, and vary along with the sequential precipitation. Meanwhile, irrelevant, positive, and negative correlations exist between the trends of $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ [20]. The two aliquots of the same asphaltene separated by different solvent mixtures can have different $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ trends as well [19]. Dimarzio et al. [19] reckon that the loss of asphaltene can potentially change the Re–Os systematics of the remaining oil and thus the Re–Os geochronology. Both Dimarzio et al. [19] and Liu et al. [20] discovered the decoupling of ^{187}Re and ^{187}Os along with sequential precipitation.

There is no apparent difference in O and S between the fractions of asphaltene according to Mahdaoui et al. [21]. Dimarzio et al. [19] believe that the polarity and aromaticity of asphaltene molecules control the asphaltene precipitation and thus the Re and Os abundances of the fractions. Liu et al. [20] raised the possibility of asphaltene aggregates as closed systems for Os and Re–Os elemental abundances, and isotopic ratios of the fractions are the joint results of their asphaltene aggregates and the co-precipitated free molecules containing Re and Os.

4. Oil-water contact experiments

According to Mahdaoui et al. [23], the low Re and Os abundances of the source rock hydrous pyrolysis products are unnecessarily the result of the high temperature of the experiment. The Re and Os of some crude oils may come not only from the source rock but also can or even mainly from the basal water.

4.1. The experiments and geological implications of oil-water contact

Mahdaoui et al. [23] and Hurtig et al. [22] conducted an oil-water contact experiment with oils of different asphaltene and S contents. Except for an oil sample with barely any asphaltene, Re and Os can transfer massively from the aqueous solutions to the crude oils on the timescale of hours and with Re and Os as high as 466 $\mu\text{g/g}$ and 90 ng/g , respectively. According to the current limited basinal water Re and Os data [39–41], Mahdaoui et al. [23] calculated that ca. 200–250 times of basinal water will have equivalent Re and Os with that of conventional crude oil from Pechelbronn, France. The water-bearing Re and Os could come from the percolation process of hydrothermal fluid through the organic-rich rocks and crustal sulfide minerals. However, the sulfide minerals could have much more radiogenic Os isotope prints than common crude oils.

In addition to account for the Re and Os contents, the homogenization of Os isotope composition can be easily explained by the theory of water as the main source for oil Re and Os. It can be easier for the basinal water to reach homogenization of $^{187}\text{Os}/^{188}\text{Os}$ than the crude oil and its leach on source rocks can end up with $^{187}\text{Os}/^{188}\text{Os}$ close to crude oil. In the meantime, the Re/Os of the basinal water on the basinal scale is unnecessarily homogeneous as Re and Os can be involved in different geological processes: Os can be absorbed by Fe-hydroxides while Re participates in the formation of pyrites. Thus, formation water of petroleum basins can have homogeneous $^{187}\text{Os}/^{188}\text{Os}$ and heterogeneous Re/Os simultaneously. Mahdaoui et al. [23] concluded that Re–Os defines the age of the closure of the hydraulic trap.

Hurtig et al. [22] conducted the “partial overprint” experiments where the water and oil have Re and Os contents of the same order of magnitude or lower contents in the water. The results showed that after the contact with water and the absorption of different amounts of Re and Os, crude oil and its asphaltene and maltene fractions can define similar Re–Os isochron ages with the original ones. Thus, the authors concluded that age information can be kept after contact with water. The authors of this paper doubt that the distribution of the Re and Os acquired from water in the asphaltene and maltene fractions is complex and understudied. The results of Hurtig et al. [22] are the sum of the oil Re and Os and its acquired water-bearing Re and Os under the special conditions of the study. The range of this phenomenon has not been well-defined, i.e. if this conclusion can be extrapolated to complete overprint situations.

4.2. Comparison of laboratory studies and real geological situations

A potential problem for the oil-water contact experiments to account for the oil Re and Os budget is the source for the basinal water Re and Os. The Re- and Os-rich strata in the crust are normally organic-rich sedimentary rocks under an anoxic environment. Crude oil generated from such source

rocks may have a higher ability to take away the organophilic Re and Os than hydrothermal fluids on the scale of a basin in common scenarios. There is probably no other reservoir in the petroleum basin that can have comparable or higher Re and Os contents than the organic-rich strata. The calculation of Mahdaoui et al. [23] is based on the water to oil ratio of ca. 200–250 times which is not always realistic.

Studies have shown that the influence of basinal water on crude oil Re–Os systematics is limited in some petroleum systems. The Sr isotope composition of the basinal water and carbonate cements of the Leduc and Nisku formation reservoirs in the Western Canada sedimentary basin indicate that the basinal water has been imprinted with the very radiogenic Precambrian strata or the crystalline basement and thus has very radiogenic $^{187}\text{Os}/^{188}\text{Os}$ [37]. For example, the $^{187}\text{Os}/^{188}\text{Os}$ of the Neoproterozoic Old Fort Point Formation shales of Western Canada could have a much higher $^{187}\text{Os}/^{188}\text{Os}$ range than the coeval Duvernay-source oils at both the timing of the Duvernay shales maturation and present. This indicates that the oil has negligible influence from basinal water.

The current seawater has ca. 7 pg/g Re [42] and 10 fg/g Os with $^{187}\text{Os}/^{188}\text{Os}$ of 1.06 [43]. The Re–Os systematics of the asphaltite from the South Australian coastline ($^{187}\text{Os}/^{188}\text{Os}$ of 1.122–1.303) which has long been immersed in seawater has not been severely distorted [44]. There is no apparent difference in the abundances of the organophilic Re and Os between the surface and interior of most asphaltites. There is no evidence of enrichment of Re and Os on the surface of the asphaltites, although it should be attributed to its solid nature at least partially.

Nevertheless, water influence on the oil Re–Os systematics has also been reported. For example, the close Rb–Sr sphalerite date of 366 ± 15 Ma and Re–Os bitumen date of 374 ± 9 Ma in the study on the Polaris MVT deposit in Canada by Selby et al. [7] indicate that the interaction with ore-forming fluids may have reset the Re–Os clock of the bitumen. Meanwhile, the low $^{187}\text{Os}/^{188}\text{Os}$ of some of the oils from the Shetland basin, UK could be the result of the assimilation of the Os of basinal water sourced from the faults coupling with the mantle in the study of Finlay et al. [45].

5. Application of Re–Os dating in the oil-mine-coal systems

There are successful applications on the timing constraint of crude oil generation and accumulation, oil-mine coupling, and coal deposition with Re–Os analysis in the past fifteen years. This part introduced the Re–Os dating with multiple crude oil samples. The Re–Os dating of the fractions of single oil will be introduced in Section 5.

5.1. The applicable scope of the Re–Os dating of crude oil generation

The source rock hydrous pyrolysis experiments conducted by Rooney et al. [34] and Cumming et al. [35] lead to the question of heterogeneous initial $^{187}\text{Os}/^{188}\text{Os}$ of crude oils on

a basinal scale. Geological processes like the expulsion, migration, and accumulation of crude oil could mix the crude oil and thus the $^{187}\text{Os}/^{188}\text{Os}$ of crude oil will tend to homogenize. Mahdoui et al. [23] hold that if source rock is the major source for the crude oil Re and Os budget, only when the oil is generated soon after the deposition of the source rock for the initial $^{187}\text{Os}/^{188}\text{Os}$ of crude oils to be small enough and the Re–Os geochronometer to be applicable for the crude oil generation timing constraint.

Liu et al. [37] tested the applicable range of Re–Os dating of crude oil generation with the Duvernay–Leduc/Nisku petroleum system of the Western Canada sedimentary basin for which the time between the Duvernay formation source rock deposition (ca. 378 Ma) and the oil generation (primarily from 80 to 50 Ma) is as long as ca. 300 Ma. The asphaltenes of crude oil samples all over the Leduc and Nisku carbonate reservoirs of the petroleum system define Re–Os isochron age of 66 ± 31 Ma (Model 3; $n = 14$; $\text{Os}_i = 0.77 \pm 0.20$; mean standard weighted deviation (MSWD) = 6.7). Although with high uncertainty, this age is identical to the main oil generation stage defined by basinal modeling. This study demonstrates that Re–Os dating of crude oil generation can be realized when there is a long time between source rock deposition and oil generation. The range of the initial $^{187}\text{Os}/^{188}\text{Os}$ of the crude oils (at 66 Ma) is from 0.55 to 1.06, which is within the range of the coeval source rock, i.e. from 0.46 to 1.48. Thus, the Os isotope composition shows its ability to link the oil from Leduc and Nisku reservoirs to their verified source rock, the Duvernay Formation shales. Meanwhile, it shows that oil generation, expulsion, and accumulation processes can promote the homogenization of the $^{187}\text{Os}/^{188}\text{Os}$ of crude oils.

5.2. Re–Os dating with bitumens

Through the study on the bitumens of Xuefeng Uplift, Ge et al. [1] concluded that Re–Os data of the bitumens of low maturity ($R_o < 1.0$, T_{max} of ca. 450 °C, yellow fluorescence, high H/C) define the age of oil generation while the Re–Os data of the bitumens of high maturity ($R_o > 2.0$, T_{max} of ca. 550 °C, no fluorescence, high adamantane) define the age of the thermal cracking of crude oil and the formation of pyrobitumen and dry gas. In consideration of the similarity between the apatite fission-track (AFT) age and pyrobitumen Re–Os age, the authors proposed that the crude oil Re–Os systematics has similar closure temperature to that of AFT, i.e. 120–60 °C. Ge et al. [46] defined Re–Os age of 239 ± 150 Ma ($n = 11$; MSWD = 398) for the oil thermal cracking with pyrobitumen samples and attributed the high MSWD to the unsatisfactory conditions for precise isochron age, e.g. asynchronous age, unidentical initial $^{187}\text{Os}/^{188}\text{Os}$ and distortion of the Re–Os systematics of the samples. If the thermal cracking process is prolonged, the closure of the Re–Os systematics of the samples can be asynchronous. If the original crude oils being thermally cracked have heterogeneous $^{187}\text{Os}/^{188}\text{Os}$, the corresponding pyrobitumens may also be unidentical in initial $^{187}\text{Os}/^{188}\text{Os}$. Samples close in physical distance can be taken to avoid these uncertainties [47];

however, it may introduce new issues of possible small ranges of $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ which are disadvantages for obtaining the precise age.

In the study on the asphaltite from the South Australian coastline, Corrick et al. [44] define an Re–Os isochron age of 68 ± 15 Ma (Model 1; $n = 9$; $\text{Os}_i = 0.66 \pm 0.12$; MSWD = 0.95) which is believed to indicate oil generation. One of the asphaltites shows subtle differences between the superficial and internal Re–Os systematics: the superficial Re and Os are lower than those of the internal values by ca. 25%. This could be the heterogeneity of the asphaltite or the result of weathering. Scarlett et al. [48] defined Re–Os age of 103 ± 22 Ma (Model 1; $n = 5$; $\text{Os}_i = 0.44 \pm 0.18$; MSWD = 1.2) for asphaltites from different locations of the South Australian coastline. Corrick et al. [49] found that the asphaltic tar samples have similar Re–Os isotopic ratios and thus are unable to define an isochron age.

5.3. Re–Os application on oil coupling with mines

Selby et al. [7] first adopted the Re–Os geochronometer to decipher the relative timing and formation relations between bitumen and ores. Selby et al. [7] believe that the migration of the Pb–Zn ore-forming fluids and oil precursors of bitumen are generally coeval through a similar Re–Os age defined by the coating and pore-filling bitumens and the Rb–Sr sphalerite date.

With the Re–Os age of 155 ± 51 Ma defined by the Jurassic tar sand samples from the northwestern margin of the Junggar basin was interpreted to indicate the age of the devastation of the deep oil reservoir by tectonic activities and remigration of crude oil [50,51]. The authors proposed an “oxidation-reduction-oxidation” model for the superimposed uranium metallogenesis with this Re–Os age.

The Re–Os date of 254.3 ± 2.8 Ma defined by the bitumens from Qinglong paleo-reservoir, Guizhou, China is older than the Sb mineralization age of ca. 142–148 Ma defined by fluorite and calcite Sm–Nd analysis in the Qinglong antimony deposit [52]. This means the paleo-reservoir of oil existed before the Sb mineralization and provided a reducing environment and S element.

5.4. Oil-source correlation with Re–Os isotope compositions

Since Selby et al. [7] and Selby et al. [8], most Re–Os studies on petroleum systems tried to use Os isotope composition as an oil-source tracer. This application is based on the inheritance of source rock $^{187}\text{Os}/^{188}\text{Os}$ by the crude oil and provides a valuable oil-source tool especially when the biomarkers fail, e.g. due to biodegradation, while the major bearer of Re and Os asphaltene is resistant to biodegradation.

For example, Finlay et al. [53] discussed how to use Os isotope composition coupling with Pt/Pd to trace the source rocks for the United Kingdom Atlantic Margin oils and the Western Canadian oil sands. Liu et al. [37] successfully identified the correct source rock for the crude oil of the

Duvernay-Leduc/Nisku petroleum system of the Western Canada sedimentary basin through the comparison of their Os isotope composition. Corrick et al. [44] excluded the A-B segment of the organic-rich strata ($^{187}\text{Os}/^{188}\text{Os}$ at 68 Ma of ca. 0.2) deposited during the early stage of the Ocean Anoxic Event (OAE2) as the source for the Southern Australian coastline asphaltite ($^{187}\text{Os}/^{188}\text{Os}$ at 68 Ma of 0.66 ± 0.12), but suggested that the late stage of OAE2 (B–C segment) and the source rocks deposited before and after OAE2 are possible source rocks for the asphaltite according to their similar $^{187}\text{Os}/^{188}\text{Os}$ at 68 Ma. High-resolution oil-source correlation is thus realized with Os isotope composition. Mahdoui et al. [23] stated that if the oil Re and Os are from basinal water which brings the Re and Os from the source rock, Os isotope composition can still be used for oil-source correlation.

Nevertheless, this is not to say that Os can always work in the identification of the source of crude oil all by itself. In the Western Canada sedimentary basin, for example, the Lower Jurassic Gordondale member, Devonian-Mississippian Exshaw Formation, and the Middle Devonian Keg River Formation have similar $^{187}\text{Os}/^{188}\text{Os}$ ranges at their maturation during their mutual oil generation stage during Laramide orogeny. The crude oils generated from these source rocks can hardly be distinguished through Os isotope composition only (Fig. 2). Os isotope composition as a tool for oil-source correlation will not be disabled by the geological processes which do not disturb the Re–Os systematics and geochronology, e.g. biodegradation and loss of light fractions. However, the geological processes that may disturb the Re–Os systematics of crude oil and bitumen may increase the difficulty of or even invalidate the oil-source correlation with Os isotope composition, e.g. thermal cracking and thermochemical sulfate reduction.

5.5. Re–Os dating of coal

As an important fossil energy source, coal constitutes an important part of the sedimentary, structural, and thermal

evolution history of the sedimentary basins. Tripathy et al. [54] successfully obtained the first Re–Os age for a coalbed affected by marine incursion (Matewan coalbed, West Virginia, USA; 325 ± 14 Ma). This age is consistent with the Re–Os age of the immediately overlying shale interval (317 ± 2 Ma). The Re and Os concentrations of this coalbed are several orders of magnitude higher than the previously published coalbeds and Re and Os should primarily come from the seawater. Meanwhile, the Os isotope equilibrium under the marine environment overrides the terrigenous variation and thus the scatter of the samples on Isoplot is reduced. Subsequently, no geological meaningful Re–Os ages were obtained by Goswami et al. [55] for two terrigenous coalbeds and the Re–Os systematics of the samples close to the tonstein beds were heavily distorted. The key for successful Re–Os dating for coalbeds is the homogenization of isotopes within the Re–Os reservoir after deposition, e.g. the homogenization induced by transgression, while the terrigenous coalbeds are difficult to date with the Re–Os geochronometer.

6. Endeavours on the improvement of Re–Os dating of crude oil generation

6.1. Theoretical and practical challenges of Re–Os dating

Progress has been achieved over the past decade on the Re–Os dating of crude oil and bitumens. However, the whole datasets without data screening often define Re–Os dates with high uncertainties or even fail to define a geologically reasonable Re–Os date. This could be the result of the low precision of Re–Os data due to the low concentrations of the samples, heterogeneous initial Os isotope composition, limited $^{187}\text{Re}/^{188}\text{Os}$ range, prolonged oil generation, and influences from subsequent geological processes. Meanwhile, the interpretation of the geological implications of the Re–Os ages often relies on the support from other dating methods due to the lack of understanding of the Re–Os geochemical

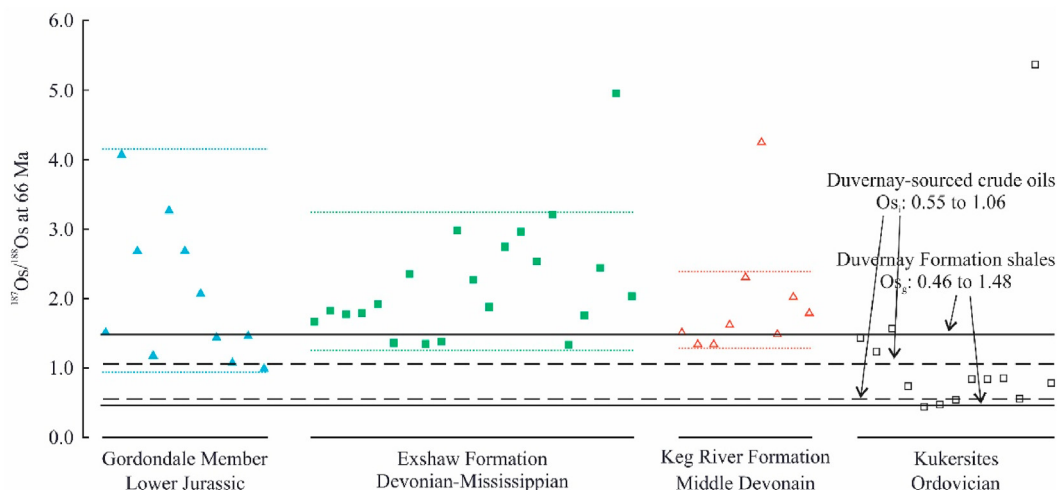


Fig. 2. Comparison of the $^{187}\text{Os}/^{188}\text{Os}$ at 66 Ma of the Duvernay-source crude oils and the source rocks of the Western Canadian Sedimentary Basin [37].

behaviors, especially the mechanism for Os isotope composition homogenization.

Oil Re and Os are found to be dominantly in the asphaltene fraction and asphaltene and crude oil are found to be similar in Re–Os isotopic ratios [32]. Thus, asphaltene can substitute the whole oil in the Re–Os test for higher precision. However, the geological meaning is unclear for the dates defined by asphaltenes with an apparent difference with the whole oil on Re–Os isotopic ratios. As a result, the substitution of whole oil with asphaltene should be determined by the balance between the geological implications and better precision of the ages.

The heterogeneity of the initial Os isotope composition could be the result of the prolonged oil generation processes, large range of the Re/Os of the source rock, and weak homogenization mechanism. Samples with a large age span are inappropriate for Re–Os dating as the $^{187}\text{Os}/^{188}\text{Os}$ of both the source rock and oil evolve during the long oil generation stage. The initial Os isotope composition of the layers of the source rock can be heterogeneous which is the Os input into the waterbody changes [44]. Ideal homogenization of Os isotope composition is not reached by processes of oil generation, expulsion, and accumulation for the multiple crude oils sampled from large geographical areas in the crude oil Re–Os dating practices so far. Such practices will largely obtain Model 3 Isoplot ages, i.e. the model for the scenario where the scatter of the samples is beyond the analysis uncertainties and there is the heterogeneity of initial $^{187}\text{Os}/^{188}\text{Os}$ as the result of geological processes. The geographical range and extent of the homogenization of Os isotope composition reached during thermal cracking of crude oil are also poorly understood.

Biodegradation is believed to have little influence on the Re–Os systematics of crude oil as the main carrier of Re and Os in crude oil, i.e. the asphaltene fraction, is resistant to biodegradation [36]. Thermal cracking and thermochemical sulfate reduction could distort or even reset the Re–Os systematics of crude oil [1,36]. It is demonstrated that the Re–Os

systematics of the organic-rich rocks can be altered by weathering; the same alteration could also happen to the surface oil seeps and bitumen.

Re–Os dates defined by crude oils may indicate the age of oil migration and accumulation rather than oil generation according to Li et al. [56], as the end of accumulation processes is more likely to be the end of oil $^{187}\text{Os}/^{188}\text{Os}$ homogenization and closure of the system. Unfortunately, the current Re–Os date is not precise enough to distinguish oil generation, migration, and accumulation processes. Oil generation and migration will disturb the Re–Os systematics of the source rock according to Wang et al. [57] thus interfering the Re–Os dating of the source rock deposition, and Li et al. [56] further pointed out the role of absorption of the migrating crude oil by source rock.

For Re–Os age obtained for oil generation, thermal cracking, and thermochemical sulfate reduction with the samples with confirmed same source and age without disturbance on Re–Os systematics, if the uncertainty of age comes primarily from the deficient homogenization of initial Os isotope composition, sample screening can be considered for better age precision.

If the uncertainty comes primarily from the deficient homogenization of initial Os isotope composition for the Re–Os age obtained for oil generation, thermal cracking, and thermochemical sulfate reduction, and the samples are confirmed with the same source and age and Re–Os systematics has not been disturbed, sample screening can be considered for better geochronology precision. Ge et al. [1] divided samples into groups according to apparent clusters of initial Os isotope composition while Ge et al. [46] and Corrick et al. [44] selected only samples within a certain deviation range (e.g. 2%) from a reasonable isochron for the establishment of a new isochron, both ways getting geologically reasonable ages with higher precision. Besides, this paper recommends screening of data by cluster analysis. Samples with close initial $^{187}\text{Os}/^{188}\text{Os}$ of the possible ages can be through hierarchical cluster analysis and then be used

Table 1

The calculated initial $^{187}\text{Os}/^{188}\text{Os}$ (Os_i) at 68 Ma, 74 Ma, 81 Ma, and 104 Ma of the Australian asphaltite samples.

No.	Samples	Os_i @ 68 Ma	Os_i @ 74 Ma	Os_i @ 81 Ma	Os_i @ 104 Ma
1	W13/007477 (interior)	0.72	0.67	0.61	0.42
2	W13/007507 (interior)	0.65	0.60	0.54	0.35
3	W13/007516 (interior)	0.66	0.61	0.54	0.34
4	W13/007668 (interior)	0.68	0.63	0.56	0.37
5	W13/007671 (interior)	0.65	0.60	0.54	0.35
6	W13/007672 (interior)	0.67	0.63	0.58	0.43
7	W13/007742 (interior)	0.71	0.66	0.59	0.40
8	W13/007764 (interior)	0.64	0.59	0.53	0.35
9	W13/007845 (interior)	0.71	0.66	0.60	0.41
10	W13/007976 (interior)	0.64	0.60	0.54	0.37
11	#162	0.74	0.69	0.63	0.44
12	#CL1	0.73	0.68	0.62	0.43
13	#27A	0.74	0.69	0.63	0.44
14	#85	0.73	0.68	0.62	0.44
15	#306	0.72	0.67	0.62	0.44

Note: Samples from 1 to 10 are from Corrick et al. [44]; samples from 11 to 15 are from Scarlett et al. [48].

Table 2
Hierarchical clustering of Australian asphaltite samples according to Os_i at different timings and corresponding Re–Os dates.

Items	Os_i @ 68 Ma	Os_i @ 74 Ma	Os_i @ 81 Ma	Os_i @ 104 Ma
Clusters 1	1,7,9,15	1,7,9,15		
Ages	38 ± 67 (Model 1; $Os_i = 0.52 \pm 0.43$; MSWD = 1.7)			
Clusters 2	11,12,13,14	11,12,13,14	11,12,13,14,15	6,11,12,13,14,15
Ages	94 ± 51 (Model 1; $Os_i = 0.52 \pm 0.43$; MSWD = 1.7)	94 ± 51 (Model 1; $Os_i = 0.52 \pm 0.43$; MSWD = 1.7)	103 ± 22 (Model 1; $Os_i = 0.44 \pm 0.18$; MSWD = 1.2)	104 ± 12 (Model 1; $Os_i = 0.43 \pm 0.10$; MSWD = 0.91)
Clusters 3	2,5,8,10	2,3,5,8,10	2,3,5,8,10	2,3,5,8
Ages	79 ± 45 (Model 1; $Os_i = 0.56 \pm 0.38$; MSWD = 0.08)	84 ± 32 (Model 1; $Os_i = 0.51 \pm 0.28$; MSWD = 0.09)	84 ± 32 (Model 1; $Os_i = 0.97 \pm 0.55$; MSWD = 0.0007)	96 ± 59 (Model 1; $Os_i = 0.40 \pm 0.51$; MSWD = 0.03)

for the establishment of isochron with a higher precision age. The physical distance between the samples should be considered and the consecutiveness of samples is preferred, while isolated sample points which obviously control the isochron should be treated with caution.

Hierarchical cluster analysis is conducted on the initial $^{187}Os/^{188}Os$ datasets calculated at 68 Ma, 74 Ma, 81 Ma, and 103 Ma of the coastal asphaltites of South Australia, five of which are from Scarlett et al. [48] with the interior samples from Corrick et al. [44] (Table 1, Fig. 3). The clusters with four or more samples and their Re–Os isoplot are presented in Table 2, Fig. 4, and Fig. 5. Two ages, 84 ± 32 (Model 1; $n = 5$; $Os_i = 0.51 \pm 0.28$; MSWD = 0.09) and 104 ± 12 (Model 1; $n = 6$; $Os_i = 0.43 \pm 0.10$; MSWD = 0.91), are possibly geologically meaningful and indicative of the oil generation or asphaltite formation.

6.2. Re–Os dating with the fractions of single crude oil

There are drawbacks to sample multiple crude oils on large geographical areas of the petroliferous basin for large

$^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ ranges for Re–Os dating, e.g. the differences in source kitchens and alteration processes of the samples. To avoid such drawbacks, Lillis et al. [36] recommend sampling in a small geographical range while Georgiev et al. [26] proposed to dating with the fractions of a single oil practiced on the Gela oilfield of Italy.

The fractions Georgiev et al. [26] obtained from an oil sample are the asphaltenes and maltenes separated by a series of different alkanes. To be specific, a gram of crude oil is blended first with a 3 mL mixture of dichloromethane and methanol (v:v of 93:7) and then 40 mL of alkane, i.e. $n-C_5$, $n-C_6$, $n-C_7$, or $n-C_{10}$. A Model 1 age of 200.0 ± 5.2 Ma (initial $^{187}Os/^{188}Os = 1.39 \pm 0.11$; MSWD = 0.52; $n = 4$) is defined by the maltenes of crude oil from the Streppenosa Formation which is close to the age of source rock deposition and interpreted by the authors to be the age of rapid oil generation.

Liu et al. [20] adopted the methodology of Georgiev et al. [26] with two more alkanes of $n-C_8$ and $n-C_9$ on six crude oils. The experiments showed that the precipitated asphaltene decreases with the increase of the carbon number of the alkane molecules from $n-C_5$ to $n-C_7$ but remains steady with the further increase of alkane carbon numbers till $n-C_{10}$. This is consistent with some previous studies on the precipitation of asphaltene with different alkanes [58,59]. It is not difficult to imagine the lack of change in the Re and Os concentrations and $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ ratios from the lack of change in the proportions of the asphaltenes and maltenes in response to the change of alkanes. Thus, it is difficult to establish isochrons not to mention the fact that the asphaltenes and maltenes have substances in common.

Nevertheless, the fractions of asphaltene can be different in their $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ [19,20] and the fractions of the asphaltene of the Venezuelan RM8505 crude oil define an Re–Os date of 98.4 ± 9.5 Ma (Model 1; $Os_i = 0.7 \pm 0.1$; MSWD = 2). Most of the Venezuelan crude oils are sourced from the Upper Cretaceous Cenomanian-Turonian-Coniacian La Luna Formation (ca. 100–86 Ma) of which the oil generation started as early as the Eocene (56 Ma) but peaked in the Oligocene and Miocene (34–5 Ma) [60,61]. This Re–Os date is close to the source rock deposition age rather than the oil generation age. Age information could be kept by the fractions

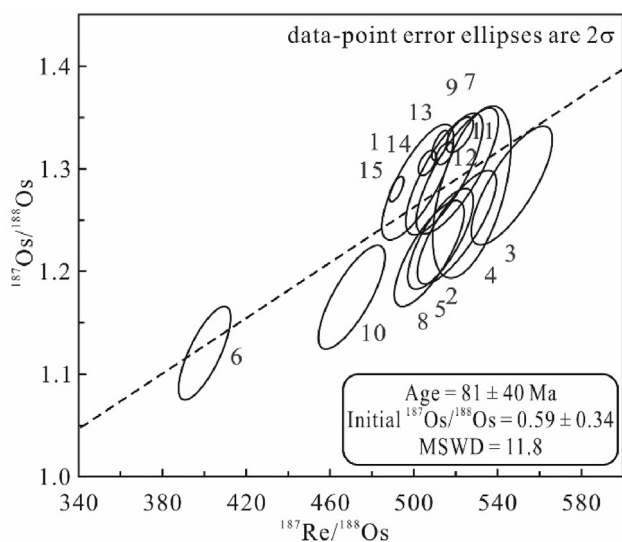


Fig. 3. All Australian asphaltite samples on $^{187}Re/^{188}Os$ – $^{187}Os/^{188}Os$ space [44,48].

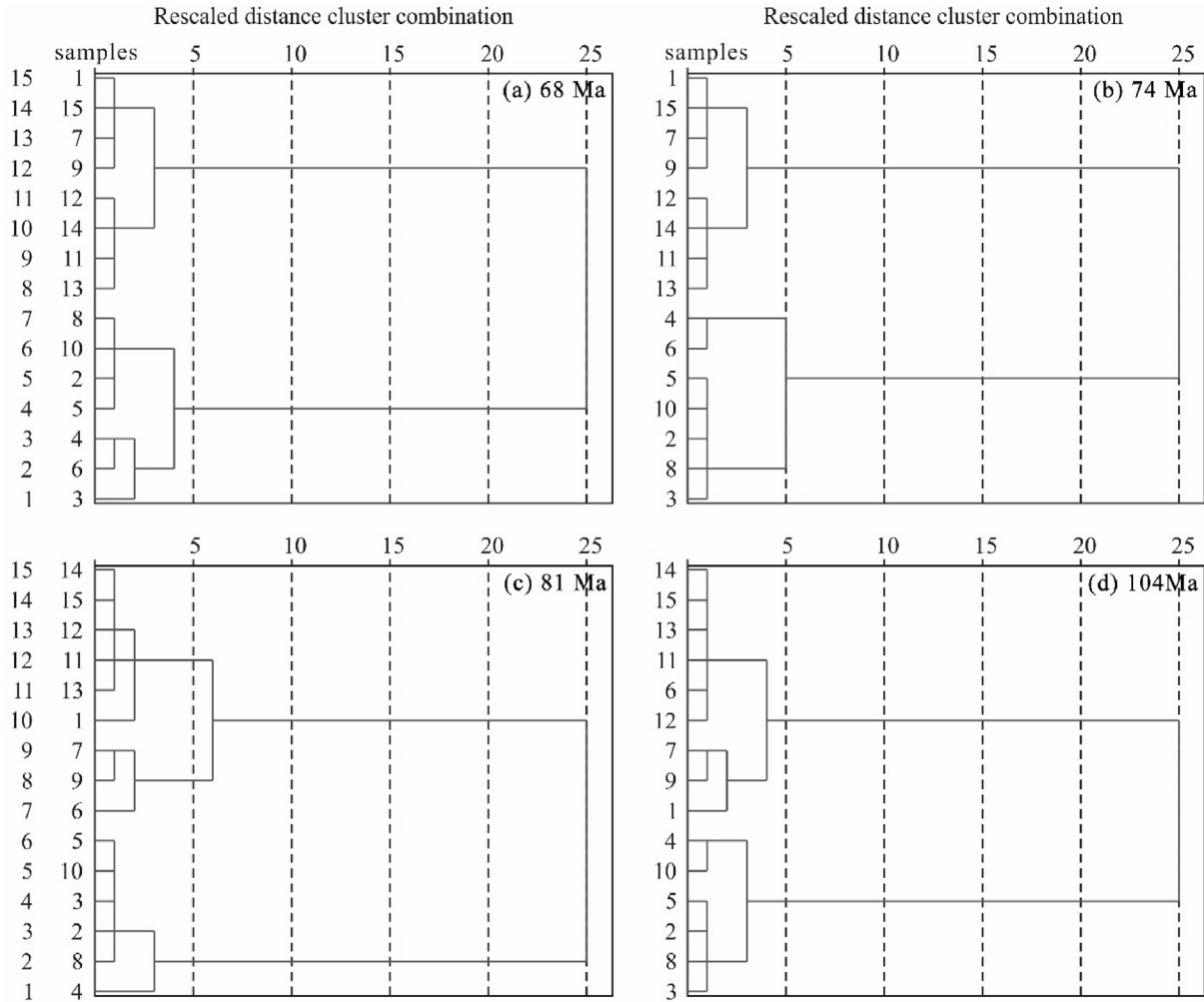


Fig. 4. Hierarchical clustering results of the Australian asphaltite samples according to $^{187}\text{Os}/^{188}\text{Os}$ at 68 Ma, 74 Ma, 81 Ma, and 104 Ma using average linkage (between groups).

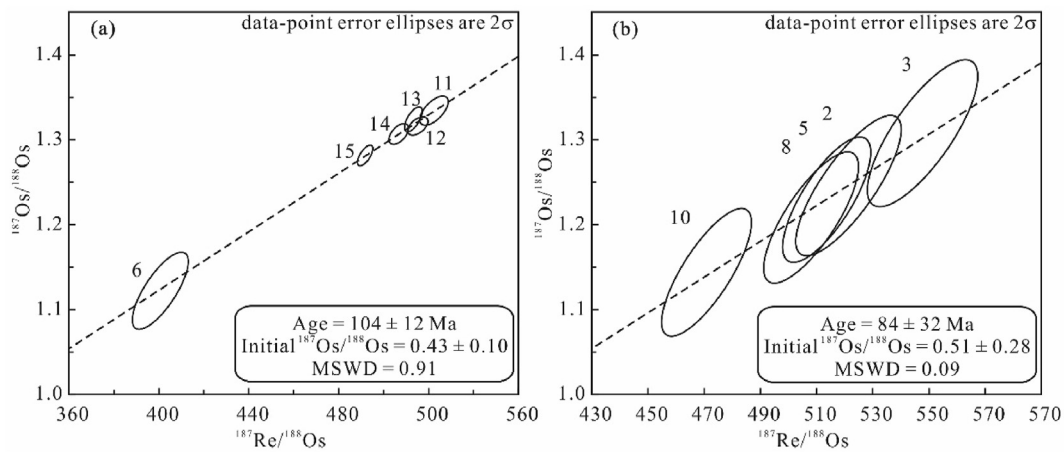


Fig. 5. Re–Os Isochrons of the clustered samples.

of asphaltene considering their heterogeneity in Re–Os elemental abundances and isotopic ratios according to Liu et al. [20]. However, the fractions of asphaltenes of the five other crude oils are unable to define any Re–Os age with

reasonable uncertainty and clear geological implications. The property of the particular oil and the fractionation method could play key roles in Re–Os dating with the fractions of crude oil.

7. Prospects

Re–Os dating with crude oil and bitumen samples has been applied to the timing-constraint of the oil generation, accumulation, thermal cracking, and thermochemical sulfate reduction in petroleum systems over the past decade. Besides, laboratory experiments have been conducted to reveal the Re and Os geochemical behaviours during some of the geological processes of petroleum systems, e.g. oil generation, loss of asphaltene, and oil-water contact. There are also attempts of Re–Os dating with the fractions of a single oil.

There are still issues and challenges for the Re–Os dating with crude oil and bitumen samples. In practice, refinement and improvements on the sampling strategy, age precision, and interpretation are in demand. This requires the cooperation of researchers from both the oil companies and research institutes and the promotion of theory development with practical application. The key theoretical issue that remains addresses the geological processes and mechanism for the homogenization of Os isotope composition while keeping differentiated Re/Os and the closure of the Re–Os systematics of crude oil and bitumen.

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Declaration of competing interest

The authors declare no conflict of interest.

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