Irradiation caused petroleum generation: Evidence from simulation experiments at room temperature

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Abstract. Organic-rich shale often receives high doses of radiation from radionuclides, mostly U. Radiogenic heating and particles bombardment can lead to petroleum generation. Artificial irradiation of organic matter with neutrons at room temperature confirms these benefits. Produced bitumen was rich in asphaltene and aromatic compounds. An improved method is used to evaluate the effects of radioactivity on the petroleum generation potential. The maximum oil generation potential increases up to 31% in the artificial irradiation dose range of 280–680 Mrad. Natural irradiation caused by U should be taken into account when evaluating petroleum resources to mitigate the charge risks in both conventional and unconventional hydrocarbons exploration, particularly for Palaeozoic and Proterozoic sediment.

1. Introduction
Organic-rich marine, lacustrine, Proterozoic, and Phanerozoic sediments are often enriched in U [1-4]. Unlike most other elements, U is radioactive and releases both particles and energy when it decays [5]. The decay of the $^{238}\text{U}$ nuclide, the most common natural isotope with a abundance being 99.27%, involves eight α-decay steps and six β-decay steps, and eventually becomes $^{206}\text{Pb}$ [5]. Released energy and particles cause thermal stress and radiation damage, independent of temperature and pressure. The generation of petroleum was assumed to be thermal degradation of organic matter (OM) over time [6]. Geothermal data, particularly thermal conductivity and radiogenic heat production data, are very important when modelling basins and evaluating petroleum production [7], so these data have been estimated in many localities. Rings of more mature or carbonized OM surrounding U-rich minerals such as thucholite [8], coffinite [9], and uraninite [10] have been found to be radioactive. U irradiation was considered to be conducive to petroleum production, while the detail information was not clear. Experiments using γ and β radiation have been performed, and the results indicated that progressive amorphization and polymerization of kerogen coupled with hydrogen loss occurs [11,12]. Lewan et al found that γ-radiation can damage OM but does not increase (and may even decrease) the amount of petroleum produced by increasing the amounts of aromatic and polymeric hydrocarbons produced [12]. However, the results did not agree with those from studies of naturally irradiated samples [13,14]. This may be because of the differences in the radiation sources. Approximately 90% of the natural radiation dose comes from α decay, and the remaining radiation dose comes mostly from β decay [15]. Radiation has been found to have effects in rock and OM within only ~75 μm of the source of the radiation [10], which is similar to range of the penetrating depth of α particle (<100 μm) [12]. Therefore, simulation experiments using different radiation sources, especially α particle, are needed. Neutron-induced α decay of $^{238}\text{U}$ was found to occur several decades ago [16], and this process has been used in non-destructive radiography tests [17]. Herein, OM in kerogen and rock was irradiated...
with artificially energy and particles, including $\alpha$ particle. This study provides new data and evidence for evaluating the effects of irradiation on OM and the production of petroleum in black shale.

2. Materials and methods

2.1. samples
The experiment was performed using black shale and kerogen. The black shale was Chang 7 from the Late Triassic Yanchang Formation in the Ordos Basin, China. The Rock-Eval $T_{\text{max}}$ for the shale was 435 °C, suggesting an early oil “window” stage [18]. Kerogen was isolated from the shale. Natural U ore with a U content of 8748 μg g$^{-1}$ was used to enhance neutron-induced $\alpha$ irradiation. The rock, kerogen, and natural U ore samples were all crushed to 200 mesh. Soluble hydrocarbons were extracted from the kerogen with CHCl$_3$ before exposure to radiation. The degree of soluble hydrocarbon removed was reflected by changes in the Rock-Eval S1 parameter, which represented free hydrocarbon. The Rock-Eval S1 value for the un-extracted kerogen was 22.58 mg/g, which is similar to the reference value (21.86 mg g$^{-1}$, $T_{\text{max}}$ 433 °C) [19]. The Rock-Eval S1 value for the extracted kerogen was 1.39 mg g$^{-1}$, indicating that the extraction procedure reduced the Rock-Eval S1 value by ~93.8%.

2.2. Radiation experiments
The experiments were performed in a swimming pool nuclear reactor at the China Institute of Atomic Energy. Each sample was wrapped in Al foil and placed in an Al pot. The foil and pots had been washed with CHCl$_3$ before use to remove organic contaminants. Each pot was placed in a different channel of the swimming pool nuclear reactor and irradiated with thermal neutrons. To avoid the potential effects of radiogenic heat on petroleum generation, the pots were emerged in circulating water, and kept the maximum temperature to be lower than 48 °C during the radiation experiments. Three samples of each of rock, kerogen, and mixture of kerogen and U ore were prepared for use. One of each set of triplicate samples was irradiated with thermal neutrons for 1 h, another for 3 h, and the third for 6 h. Detailed information of the samples and exposure doses was presented in Table 1.

| OM status | R1 | R2 | R3 | K1 | K2 | K3 | KU1 | KU2 | KU3 |
|-----------|----|----|----|----|----|----|-----|-----|-----|
| Sample weight (g) | 10 | 10 | 10 | 2  | 2  | 2  | 2   | 2   | 2   |
| TOC(wt%)  | 12 | 12 | 12 | 47 | 47 | 47 | 47  | 47  | 47  |
| U ore weight (g) | 0  | 0  | 0  | 0  | 0  | 0  | 2   | 2   | 2   |
| Radiated time (h) | 1  | 3  | 6  | 1  | 3  | 6  | 1   | 3   | 6   |
| Neutron flux (J g$^{-1}$) | 1625 | 3623 | 7947 | 2163 | 5654 | 11617 | 2816 | 6821 | 14591 |
| Exposure dosage(Mrad) | 162.5 | 362.3 | 794.7 | 216.3 | 565.4 | 1161.7 | 2816 | 682.1 | 1459.1 |

After absorbing one neutron, $^{238}$U will become activated and start-up the $\gamma$, $\beta$ and $\alpha$ decays in turn.

$^{238}$U + n $\rightarrow^{239}$U + gamma  \hspace{1cm} (1)

$^{239}$U $\rightarrow^{239}$Np + beta  \hspace{1cm} (2)

$^{239}$Np $\rightarrow^{239}$Pu + beta  \hspace{1cm} (3)

$^{239}$Pu $\rightarrow^{235}$U + alpha  \hspace{1cm} (4)

The half-life of $^{239}$U and $^{239}$Np is 23.5 min and 2.3d, respectively, while the half-life of $^{239}$Pu is about 24,400 years. Through it is still of a long time, it has already accelerated nearly 18,4400 times, when compared to the natural half-life of $^{238}$U, which is 4.5 billion years.

2.3. Products analysis
Soluble bitumen was extracted from the radiated samples. The glass vessels used to extract bitumen from the samples were first heated to 700 °C in a muffle furnace and then washed with purified water and ultra-sonicated. An aliquot of a powder sample was weighed accurately and then extracted with CHCl₃ for 8 h. The bitumen was dissolved in n-hexane and then subjected to silica gel (100–200 mesh, activated at 200 °C for 4 h) column chromatography. The saturated, aromatic, and resin fractions were eluted sequentially with n-hexane, a 2:1 v/v mixture of dichloromethane and n-hexane, and methyl alcohol (1 dead volume), respectively, and the non-eluted fraction was defined as asphaltene. TOC and Rock-Eval pyrolysis analyses of the radiated samples were performed after the extraction. Each rock sample was treated with 1.5 M HCl for 2 h and then dried at 45 °C before TOC analysis to remove carbonates, whereas each kerogen sample was analysed without pre-treatment. TOC analyses were performed using a LECO CS-230HC carbon–sulphur analyser (LECO, Saint Joseph, MI, USA). Rock-Eval pyrolysis analyses were performed using a programmed heating method using a Rock-Eval 6 workstation (Vinci Technologies, Nanterre, France) with an inert N₂ atmosphere. The initial and final pyrolysis temperatures were 300 and 650 °C, respectively, and the heating rate was 25 °C min⁻¹.

### 3. Results and discussion

#### 3.1. Soluble bitumen yields and compositions

Soluble bitumen was detected in 6 of the 9 irradiated samples (Table 2). The bitumen yields of sample K3 and KU3 were 19.4 and 19.5 mg g⁻¹ TOC, respectively, and the bitumen yield of sample R3 was about half as high, 9.3 mg/g TOC (Table 2). However, very small amounts of bitumen were produced by samples K2, KU1, and KU2, the yields being 0.95, 0.7, and 0.75 mg g⁻¹ TOC, respectively (Table 2). The radiation doses positively correlated with the bitumen yields ($r = 0.931$) (Figure 1a).

The bitumen produced through irradiation had a high aromatic/saturated hydrocarbon ratio (>1.5) and a high asphaltene content (>60%) (Table 2), similar to the results found for samples naturally rich in U [12,13,20,21] but different from the results found for crude oil [22] and un-irradiated extracts (Table 2). Large differences between the asphaltene and saturated hydrocarbon contents before and after irradiation (Table 2), indicate that the kinetics and mechanism of petroleum production induced by irradiation are different from that of petroleum generation through the traditional thermal degradation pathway.

| Sample No. | Primary extract | R3 | K2 | K3 | KU1 | KU2 | KU3 |
|------------|-----------------|----|----|----|-----|-----|-----|
| Exposure dosage (Mrad) | / | 794.7 | 565.4 | 1161.7 | 281.6 | 682.1 | 1459.1 |
| Bitumen (mg) | 10.12 | 11.2 | 1.9 | 18.2 | 1.4 | 1.5 | 18.3 |
| Bitumen yield (mg g⁻¹ TOC) | 0.73 | 9.3 | 0.95 | 19.4 | 0.7 | 0.75 | 19.5 |
| Saturated fractions (%) | 28.7 | 2.7 | / | 2.6 | / | / | 3.0 |
| Aromatic fractions (%) | 24.2 | 5.5 | / | 5.8 | / | / | 4.5 |
| Resin fractions (%) | 41.1 | 33.4 | / | 28.7 | / | / | 30.8 |
| Asphaltene fractions (%) | 6.0 | 58.4 | / | 62.9 | / | / | 61.8 |
| Aromatic/Saturated | 0.84 | 2.04 | / | 2.23 | / | / | 1.50 |

It was unclear why the saturated hydrocarbon yield was low. One possibility is that the saturated hydrocarbon yield was low. The kerogen structure would have been altered and reconstructed because of damage caused by irradiation. Free-radical reactions would have promoted H loss and the oxidation of aliphatic precursors, increasing aromatization and polymerization and the branching ratio of the kerogen [21]. Long-chain saturated hydrocarbon yield would have decreased and the contents of polar hetero- or macro-molecules (called resins and asphaltenes) would have increased.
3.2. TOC and Rock-Eval pyrolysis data
The variations of TOC and \(T_{\text{max}}\) values with increased radiation doses were within the standard deviations for the analytical methods (Table 3), similar with the results in a previous experiment using \(\gamma\) radiation \[12\]. The bitumen yield accounted for <2% of the C in the kerogen, so the effects on the loss of C can be ignored. The stable \(T_{\text{max}}\) values indicate that the production of bitumen caused by irradiation does not affect the maturity of the OM.

![Figure 1](image)

**Figure 1.** The relationship of exposure dosages with bitumen yields (a) and maximum oil generation potential (MOGP) (b).

| Sample No. | R     | K     | R1    | R2    | R3    | K1    | K2    | K3    | KU1   | KU2   | KU3   |
|------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Exposure dosage (Mrad) | 162.5 | 362.3 | 794.7 | 216.3 | 565.4 | 1161.7| 281.6 | 682.1 | 1459.1|
| TOC (wt%)  | 12.0  | 47.0  | 12.1  | 11.9  | 11.8  | 47.5  | 46.6  | 46.0  | 46.0  | 47.0  | 47.7  |
| \(T_{\text{max}}\) (°C) | 435   | 436   | 435   | 435   | 433   | 435   | 435   | 435   | 437   | 435   | 433   |
| S1 (mg g\(^{-1}\)) | 0.45  | 1.39  | 0.22  | 0.23  | 0.17  | 0.83  | 4.64  | 0.91  | 3.36  | 3.58  | 1.26  |
| S2 (mg g\(^{-1}\)) | 52.4  | 178.0 | 52.3  | 51.7  | 39.6  | 154.0 | 208.0 | 154.1 | 226.4 | 206.1 | 162.4 |
| S1+S2 (mg g\(^{-1}\)) | 52.9  | 179.4 | 52.5  | 52.0  | 39.8  | 154.8 | 212.6 | 155.0 | 229.8 | 209.7 | 163.6 |
| HI (mg g\(^{-1}\) TOC) | 437   | 379   | 432   | 435   | 335   | 324   | 446   | 335   | 492   | 438   | 340   |
| Extracted bitumen (mg g\(^{-1}\)) | /     | /     | /     | /     | 1.12  | /     | 0.95  | 9.10  | 0.70  | 0.75  | 9.15  |
| MOGP (mg g\(^{-1}\) TOC) | 441   | 382   | 434   | 437   | 346   | 326   | 460   | 357   | 501   | 448   | 362   |

\[\text{MOGP}=(\text{S1+S2}+\text{Extracted bitumen})/\text{TOC}.\]

The Rock-Eval pyrolysis parameters reflect the effects of radiation on the petroleum generation potentials of the kerogen and rock samples. The S1, S2, and HI values were lower for the irradiated samples R3, K3, and KU3 than for the raw samples (Table 3), consistent with the results of most previous studies [12,13,15]. However, the S1, S2, and HI values were higher for samples K2, KU1, and KU3 than for the raw samples, indicating that irradiation increased the petroleum generation potential of the kerogen. More bitumen could be produced through subsequent thermal degradation or particle bombardment. Overall, our results confirm that irradiation can damage OM and produce bitumen but that the outcome can be rather variable.

3.3. Implications of irradiation for petroleum generation
Oil fields commonly have relatively high levels of radioactivity, but the contribution of radiation emitted by U to petroleum production is still controversial [12]. One possible reason is that dose accumulation, kerogen degradation, and petroleum production are dynamic processes but most data that have been analysed are static, so only already produced hydrocarbons and potential hydrocarbons are considered. This makes analysing the relationship between irradiation and petroleum production too simplistic and prone to errors, making it difficult to understand the effects of radiation on petroleum production. The ability to produce all petroleum components and variations in this should be taken into account. Adding the soluble bitumen to the S1 and S2 values and then dividing the results by the TOC (to convert the value to units of mg g⁻¹ TOC) gives a value that can be considered the maximum oil generation potential (MOGP).

Irradiation increases the MOGP over a certain range (Figure 1b). Lower or higher doses can be detrimental to the production of oil. For the relatively stable kerogen, low radiation doses will not initiate petroleum production but there will be some loss of H, decreasing the MOGP. Bitumen and soluble hydrocarbons adsorbed to kerogen or rock pores are more susceptible to being damaged by radiation, and this will cause aromatization and cross-linking accompanied by H loss and gas production [12]. These will cause the extractability to decrease. Samples K1, which received radiation doses of 216.3 Mrad, confirmed this. The S1 and S2 values were lower than that of the un-irradiated sample. In the beneficial dose ranges, the kerogen structure was damaged and reconstructed, and the MOGP increased. For example, doses of 281.6–682.1 Mrad increased the S1 and S2 values for samples K2, KU1, and KU2, and small amounts of extractable oil were produced. The MOGPs increased 17%–31% at the radiation doses ranges of 280–680 Mrad. Increasing the radiation dose further increased kerogen damage and reconstruction, and large amounts of oil were produced, although increasing polymerization would decrease the MOGP. The representative samples R3, K3, and KU3 had MOGPs of 9.3 mg g⁻¹ TOC in oil for rock and 19.5 mg g⁻¹ TOC in oil for kerogen, and the S1 and S2 values all decreased. This could also explain the S1 and HI values being much lower for a very U-rich sample (5280 μg g⁻¹) and a U-poor sample (173 μg g⁻¹) than for average U-content samples (642–1700 μg g⁻¹) from the Mulga Rock deposit [14].

The accumulated doses for the average U-content samples were probably just within the effective range, whereas the dose for the very U-rich sample exceeded the effective range and the dose for the U-poor sample was below the effective range. From this point of view, the doses giving the MOGP can be considered to have possible beneficial ranges of 280–680 Mrad. In a previous experiment using γ radiation [12], the oil generation potential did not benefit from doses <285 Mrad and started to decrease at doses >885 Mrad. Therefore, it is not a simple inference that radioactivity is beneficial or avoidable to petroleum generation. Radioactive dose should be fully considered. Within a possible dose range, it may be advantageous. Radioactive dose is a function of many parameters, including uranium content, radiation decay time and material composition. More attention should be paid to the effects of radiation on OM in ancient strata, particularly Palaeozoic and Proterozoic sediments.

4. Conclusions
We performed a simulation experiment in which OM was exposed to artificially irradiation at room temperature. The produced bitumen was rich in asphaltene and had a high aromatic/saturated hydrocarbon ratio. An improved method was used to evaluate the effects of radiation on the petroleum generation potential, and the MOGP increased 17%–31% at effective radiation doses of 280–680 Mrad and an extractable oil yield of 20 mg/g TOC can be achieved without the OM maturing further, confirmed the benefit of radiation emitted by U to petroleum production.

Acknowledgements
This research was financially supported by the National Key Research and Development Program of China (2017YFC0603101), the National Natural Science Foundations of China (41602144 and 41530317), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA14010101), the Technology Major Project of PetroChina (2016ZX05004-001).

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