Irradiation caused gas generation from organic matter: evidence from the neutron irradiation experiment

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Abstract. The effects of U natural decay on the oil and gas generation are still controversial. We implemented a simulation experiment of neutron irradiation on immature organic matter, confirmed its benefit on oil generation. Here we report the generated gases and their composition and isotope characteristics. H\textsubscript{2} was the most abundant gas, with a maximum yield of 1145.3 ml/g TOC, followed by N\textsubscript{2}, CO\textsubscript{2}, then CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6}. All of the gases were depleted in D or 13C, indicating their organic source. H\textsubscript{2} was suggested to be directly from kerogen, through a dehydrogenation and abstraction pathway. However, the specific generation mechanisms of N\textsubscript{2}, CO\textsubscript{2}, and CH\textsubscript{4} were still unclear. Gas generation from kerogen will increase the gas-to-oil ratio of the hydrocarbon products, and make the oil much easier to discharge. It is of great importance to consider the artificial irradiation or U natural decay caused gas generation in the exploration and development of low-mature and immature shale oil.

1. Introduction

Organic-rich shale often enriched in uranium (U), for their simultaneous deposition under anoxic or euxinic bottom water [1,2]. Under such conditions, dissolved U(VI) is reduced to insoluble U(IV), which is prone to be absorbed by organic matter [1-3]. Organic-rich sediment is considered to be the largest sink for U in the global budget [4,5]. However, unlike most of other elements, U is radioactive and releases both particles and energy during its natural decay [6]. The decay of the $^{238}$U nuclide, the most common natural isotope with an abundance of 99.27%, involves eight $\alpha$-decay steps and six $\beta$-decay steps, and releases $\sim$7.79$\times$10$^{-12}$ J energy, then eventually becomes $^{206}$Pb [6]. This natural decay is independent of temperature and pressure [6]. Thermal stress from the released energy is considered to be conducive to the organic matter maturation and petroleum generation [7]. However, for the released particles and their bombardment effects, current considerarions are still controversial.

Rings of more mature or carbonized organic matter surrounding U-rich minerals such as thucholite [8], coffinite [9], and uraninite [10] have been found to be radioactive, indicating conducive effects of U natural decay on petroleum production. However, experiment verification still lacks. The main reason is that the half-life of $^{238}$U is up to 4.5 billion years [6]. It is impossible to monitor the effect of U natural decay in the laboratory. Irradiation experiment using $\gamma$ and $\beta$ rays on the organic matter had proposed a progressive amorphization and polymerization of kerogen coupled with hydrogen (H) loss [11,12]. It was considered that $\gamma$-radiation can damage organic matter but does not increase (even may decrease) the amount of petroleum, because there were more aromatic and polymeric hydrocarbons in the products [12]. However, this consideration did not agree with the studies of naturally irradiated samples [13,14]. Such as the U-rich Alum shale (ca. 500 million years) was suggested to be more...
aliphatic and oil-prone after deposition than that after extensive exposure to radiation [13]. Therefore, natural decay of U should have an important effect on organic matter maturation and kerogen structure reconstruction, then affect the generation of oil and gas. So Jaraula et al. proposed a radiolytic cracking pathway of hydrogen generation, in addition to the thermal and microbial pathway [14].

Our previous study implemented a simulation experiment of neutron irradiation on the immature organic matter [15, 16]. The result confirmed that artificial neutron irradiation can cause oil generation, with a maximum yield of 19.5 mg/g TOC [15]. The produced oils were rich in asphaltene, aromatic compounds, high-molecular-weight compounds, and had certain amounts of low-maturity and intermediate products (e.g., alkenes, prist-1-ene, C27-hop-17(21)-ene, and moretanes) in the saturated fractions [15], indicating a possible hydrocarbon generation process through radiolytic cracking pathway, same with that proposed by Jaraula et al. [14].

Here we report the generated gases and their composition and isotope characteristics from the neutron irradiation experiment and talk about the gases generation mechanism. This part is rarely reported in previous geological case studies because it is almost impossible to obtain the gas product in the relatively open system of rock bodies. Our enclosed simulation experiment provides the possibility for the gas study.

2. Materials and methods

2.1. Samples

Kerogen from the organic-rich Chang 7 shale was used in this study. High precise zircon U-Pb dating constrained the top and bottom age of the Chang 7 shale to be 241.06 ± 0.12 Ma and 241.558 ± 0.093 Ma, respectively [17]. Shale samples from well ZK808 in Shaanxi Province were surface-cleaned, crushed to powder, and then prepared into kerogen. The total organic carbon (TOC) of the kerogen was 47%. The Rock-Eval T_{max} of the kerogen was 435 °C, and the vitrinite reflectance (R_o) of it was around 0.6%, suggesting an early oil “window” stage or immature [18]. Natural U ore with a U content of 8748 μg/g and a TOC content of 0.01% was used to enhance neutron-induced irradiation.

2.2. Radiation experiment

The experiment was performed in a swimming pool nuclear reactor at the China Institute of Atomic Energy. Samples of pure kerogen, and kerogen plus U ore powder mixed thoroughly, were prepared. After extraction treatment with CHCl_3 to remove possible soluble hydrocarbon, each sample was loaded in a single Aluminum (Al) pot, which was about 10 cm in high and 5 cm in diameter. Then the open end of each Al pot was sealed by welding. The pots were separately placed in different channels of the swimming pool nuclear reactor and irradiated with thermal neutrons. To avoid the potential effects of radiogenic heating, the pots emerged in the circulating water with a maximum temperature of 48 °C. At equilibrium, a sample with a U content of 100 μg/g exposed to a neutron flux of 2.25 × 10^{10} n/(cm^2 s) can emit 570 α/(cm^2 d) [19]. Thus, U content, neutron flux, and irradiation time were reasonably selected to form different doses of neutron irradiation, which were calculated using a previously published Monte Carlo method [20]. Detailed information of the irradiated samples and calculated irradiation doses were presented in Table 1.

Table 1. Composition and calculated irradiation doses of each sample.

| Sample No. | K1  | K2  | K3  | KU1 | KU2 | KU3 |
|------------|-----|-----|-----|-----|-----|-----|
| Kerogen weight (g) | 2   | 2   | 2   | 2   | 2   | 2   |
| U ore weight (g) | 0   | 0   | 0   | 2   | 2   | 2   |
| Radiated time (h) | 1   | 3   | 6   | 1   | 3   | 6   |
| Exposure doses (Mrad) | 216.3 | 565.4 | 1161.7 | 281.6 | 682.1 | 1459.1 |
2.3. Gas analysis

The gas yield of each sample was calculated from the gas pressure in the Al pot before and after irradiation. The gas pressure in the pot before irradiation (P₁) was the normal atmospheric pressure (101.3 kPa). The gas pressure in the pot after irradiation (P₂) was determined using a specially designed device that consisted of a pot puncturing unit and a vacuum pump and was calculated using the equation (1)

\[ P₂ = \frac{(P'' \times V_t) - (P' \times V_D)}{V_i} \]  

where P' and P'' was the gas pressure in the designed device before and after puncturing the pot, respectively. V_D, V_i, and V_t was the dead volume of the device containing the pot (about 194 ml), the internal volume of the pot (about 187 ml), and the sum of V_D and V_i (about 381 ml), respectively. Then the gas yields were calculated using the equation (2)

\[ V = V_i \times \frac{(P_2 - P_1)}{P_0} \]

where P₀ was atmospheric pressure (101.3 kPa).

Gas composition was determined using a two-channel Agilent 7890 Series gas chromatograph (Agilent Technologies Inc., USA) with an auxiliary oven custom-made by Wasson-ECE instrumentation (Fort Collins, USA). The instrument was fitted with two capillary columns and six packed columns, a flame ionization detector, and two thermal conductivity detectors. The carrier gas for the flame ionization detector and the first thermal conductivity detector (for CO₂ analysis) was high-purity He (99.999%), and the carrier gas for the second thermal conductivity detector (for H₂ and H₂S analysis) was high-purity N₂ (99.999%). The measurement precision was better than 5%.

Carbon isotopic composition (δ¹³C) of CH₄ and CO₂ were determined using a Delta Plus isotope mass spectrometer (Thermo Finnigan, USA) equipped with an Agilent 6890N gas chromatograph (Agilent Technologies Inc., USA). Each gas sample was first separated using a Trace GC Ultra gas chromatograph (Thermo Fisher Scientific, USA) fitted with a 60-m J&W fused silica DB-1MS capillary column (100% methylsilicone; 30 m long, 0.25 mm i.d., 0.25 µm film thickness; Agilent Technologies Inc., USA). Hydrogen isotopic composition (δD) for H₂ was determined using a Finnigan gas chromatograph thermal conversion isotope ratio mass spectrometer (Thermo Finnigan, USA). The δ¹³C and δD values were referenced to Pee Dee Belemnite (VPDB) and standard mean ocean water standards (SMOW), respectively. An external pure methane reference standard with a known isotope ratio was analyzed to calibrate the instrument, to improve the precision and reliability of the results. The measurement precision was ±0.3‰ for δ¹³C and ±10.0‰ for δD.

2.4. Kerogen analysis

The δ¹³C and δD of each irradiated kerogen were analyzed after the extraction of bitumen [15], using a Delta V Advantage mass spectrometer (Thermo Finnigan, USA). The samples were combusted to give CO₂ and H₂O using a Flash EA 1112 HT O/H–N/C instrument (Thermo Fisher Scientific, USA). The mass spectrometer was calibrated using NBS-18 (δ¹³C of −5.0‰) and LSVEC (δ¹³C of −46.4‰) standards and an external pure CH₄ reference standard. Replicate analyses were performed, and the measurement precision was ±0.5‰ for δ¹³C and ±10.0‰ for δD, respectively.

3. Results

3.1. Gas yields

Samples were not vacuum-treated before being irradiated, so the initial gas pressure before irradiation (P₁) was the normal atmospheric pressure (101.3 kPa). All of the 6 samples showed increased pressure (P₂) after irradiation (Table 2), indicating gas yield. According to equation (2), the gas yield of each sample was calculated and shown in Table 2 (with the unit of ml) and Table 3 (with the unit of ml/g TOC). It was confirmed that neutron irradiation and the initiated uranium decay can cause gas generation from kerogen, the same as the previous experiment using γ radiation [12]. However, it seemed no relationship between the irradiation doses and gas yields (Figure 1a), also the same as the previous study [12]. Since all the Al pots after irradiation were overpressure, there was no possibility...
of gas leakage. The uncertainty of gas yield might be related to bitumen generation. Actually, certain amounts of bitumen were generated together with the gas, and the bitumen yield has a good positive relationship with the irradiation doses [15,16] (Figure 1b). In general, the radioactivity was beneficial to the generation of oil and gas.

Table 2. Determined gas pressures and calculated gas yields of the irradiated Chang 7 kerogens.

| Sample No. | K1     | K2     | K3     | KU1    | KU2    | KU3    |
|------------|--------|--------|--------|--------|--------|--------|
| Exposure doses (Mrad) | 216.3  | 565.4  | 1161.7 | 281.6  | 682.1  | 1459.1 |
| P' (kPa)   | 60.0   | 60.0   | 1.3    | 3.2    | 60.0   | 1.7    |
| P'' (kPa)  | 370.0  | 105.0  | 188.0  | 74.6   | 231.0  | 83.6   |
| P2 (kPa)   | 691.6  | 151.7  | 381.7  | 148.7  | 408.4  | 168.2  |
| V (ml)     | 1089.7 | 93.0   | 517.6  | 87.5   | 566.9  | 124.2  |

Note: P' and P'' is the gas pressure in the designed device before and after puncturing the pot, respectively. P2 is the calculated gas pressure in the pot after irradiation, using equation (1). V is the calculated gas yield with the unit of ml, using the equation (2).

3.2. Gas composition and isotopic characteristics

In 3 of the 4 samples, H2 was the most abundant gas, with a maximum yield of 1145.3 ml/g TOC, followed by N2, CO2, then CH4 and C2H6. All of the generated H2 was D-depleted. The δD of H2 ranged from −709.7‰ to −449.7‰, great lighter than that of kerogen (−169.9‰) (Table 3). However, the δD of kerogen became heavier with increased H2 yields and showed good positive relationships with the H2 yields (r=0.980, Figure 1c) and exposure doses (r=0.934, Figure 1d).

Figure 1. Relationships between neutron exposure doses and gas yields (a), bitumen yields (b) and δD of kerogen (d), and the relationship between the H2 yields and δD of kerogens (c). Data of sample K1 in (d) was not included in the linear regression analysis. Data of the bitumen yields were cited from our previous studies [15,16].
Table 3. Gases yields, $\delta^{13}$C and $\delta^D$ data of the generated gases and irradiated kerogens.

| Sample No. | Kerogen | K1     | K2     | K3     | KU1    | KU2    | KU3    |
|------------|---------|--------|--------|--------|--------|--------|--------|
| Exposure doses (Mrad) |         | 216.3  | 565.4  | 1161.7 | 281.6  | 682.1  | 1459.1 |
| $\text{H}_2$ (ml/gTOC)   |         | 1145.3 | 149.4  | /      | 43.3   | 527.8  | /      |
| $\text{CO}_2$ (ml/gTOC)  |         | 0.2    | 8.0    | /      | 10.0   | 0.4    | /      |
| $\text{CH}_4$ (ml/gTOC)  |         | 0.5    | 0.3    | /      | 0.1    | 1.0    | /      |
| $\text{C}_2\text{H}_6$ (ml/gTOC) |       | 0.1    | 0.0    | /      | 0.0    | 0.1    | /      |
| $\text{N}_2$ (ml/gTOC)   |         | 59.5   | 2.5    | /      | 70.8   | 110.0  | /      |
| Gas yields (ml/gTOC)     |         | 1159.3 | 98.9   | 550.6  | 93.1   | 603.1  | 132.1  |
| $\delta^{13}$C-kerogen (%o, VPDB) |     | −30.4  | −30.7  | −30.5  | −30.1  | −30.0  | −30.0  |
| $\delta^{13}$C-CH$_4$ (%o, VPDB) |       | −48.0  | −78.2  | /      | −30.1  | −32.3  | −31.7  |
| $\delta^{13}$C-CO$_2$ (%o, VPDB) |       | −19.2  | −28.9  | /      | −35.0  | −27.7  | −35.3  |
| $\delta^D$-$\text{H}_2$ (%o, SMOW) |       | −709.7 | −657.1 | /      | −641.5 | −708.6 | −449.7 |
| $\delta^D$-kerogen (%o, SMOW) |       | −169.9 | −144.8 | −165.3 | −143.0 | −167.0 | −153.2 |

Note: Because the samples were not vacuum-treated before being irradiated, the initial $\text{N}_2$ and $\text{CO}_2$ volumes of enclosed air in each pot were 145.9 and 7.5 ml, respectively. The $\text{N}_2$ and $\text{CO}_2$ data showed here were the amounts that already subtracted the initial amounts.

Both the generated $\text{CH}_4$ and $\text{CO}_2$ were $^{13}$C-depleted, and the $\delta^{13}$C of $\text{CH}_4$ (−78.2‰ to −30.1‰) and $\text{CO}_2$ (−35.3‰ to −19.2‰) were close to or lighter than that of kerogen (−30.4‰). However, the $\delta^{13}$C of kerogen did not show obvious variation during the gas and oil generation, ranged from −30.7‰ to −30.0‰. The slight fluctuations (−0.3‰ to +0.4‰) relative to the initial value (−30.4‰) might be the measurement error.

4. Discussion

4.1. $\text{H}_2$ generation

The radiation experiments were performed under anhydrous conditions, so the only source of $\text{H}_2$ was the organic matter in kerogen. D-depleted $\text{H}_2$ generation and simultaneous heavier $\delta^D$ of kerogens, and the good positive relationship between $\text{H}_2$ yields and $\delta^D$ of kerogens, further confirmed the source of hydrogen to be organic matter in kerogen. The generation of $\text{H}_2$ or $\text{H}$ loss from the organic matter caused by irradiation has been reported in the high U samples [21, 22] and artificially irradiated kerogens with electron [11, 23, 24] or $\gamma$ ray [25]. However, it has not been found or described in the anhydrous and hydrous pyrolysis experiments [26, 27]. So we proposed that the $\text{H}_2$ generation was related to the high-energy particle bombardment or rays produced by radioactivity, but not to the thermal degradation of organic matter. During our experiment process, certain amounts of oil were generated and a $\text{C}_{15}-\text{C}_{30}$ distribution of alkenes was present as pairs with $n$-alkanes in the generated oil [15]. It is unclear whether the H was directly dissociated from kerogen or the dehydrogenation of saturated hydrocarbons. But the former is preferred, because sample K1 has a minimum oil yield [15], but has a maximum $\text{H}_2$ yield (Table 3). For K3 and KU3, although we did not obtain the direct measurement data of $\text{H}_2$ yields, the total gas yield was only 550.6 and 132.1 mg/g TOC, respectively (Table 3), much lower than that of K1. The D-depleted H dissociated from kerogen might be in the form of $\text{H}_2$, fixed in the oil or both. Especially the samples K3 and KU3 had highest $\delta^D$ of kerogens mean greatest lost of D-depleted H, but the $\text{H}_2$ yields of them were low and the $\delta^D$ of $\text{H}_2$ of KU3 was even the heaviest. The mismatch of D-depleted H loss from kerogen and D-depleted $\text{H}_2$ generation indicated that the more D-depleted H should be fixed in the oil, consistent with the highest oil yield (about 19.5 mg/g TOC) of these two samples [15].

For the dissociation pathway of H from kerogen, it has been considered as interactions between incoming particles and bonded H atoms on organic matter, resulting in bonds instability and then break [11]. During neutron irradiation, elastic collisions occur with the nuclei leading to atomic displacements or atomic displacement cascades followed by the production of vacancies and...
interstitials. H ions diffuse to vacancies in order to passivity the dangling bonds causing decreases in the total energy of the system[28]. Further diffusion of H into the void is driven by the formation of H2 molecules[29]. These voids grow via Ostwald ripening, i.e. the interchange of the vacancies and H atoms from the smaller void which are dissolved, to the larger ones which are growing and then coalescence between these voids[30]. When the H-induced pressure inside the agglomerated defects (e.g. microcracks) is sufficiently large enough to cause the macroscopic propagation of cracks[31]. However, another cross-linking mechanism for irradiated hydrocarbon polymers was also proposed [12, 21], that C–H bonds are cleaved after absorbing radiation energy, yielding a free H atom and a free radical on the C atom (Figure 2). The free-radical site can abstract another H atom from an adjacent aliphatic chain or migrate along the aliphatic chain until a H atom on an adjacent aliphatic chain is close enough to be abstracted [12] (Figure 2). The originally cleaved H atom and the subsequently abstracted H atom can then combine to give H2. For our experiment, it seems that the latter one is more likely. Because H can leave kerogen more readily than D during the cleavage and abstraction processes, consistent with our result of D-depleted H2 generation. And also, the linear relationship between the H loss (reflected by δD of kerogens) and irradiation doses was different from the former one [11].

Figure 2. Radiation-induced gas generation through radiolytic cracking of C–C bonds and C-H bonds. H2 is the main gas, followed with N2, CO2, and CH4. The gas and bitumen generation might result in the kerogen damage without maturity increase [15,16].

4.2. N2 generation
In our experiment, the N2 yields were high, different from the previous irradiation experiment using γ ray [12]. Sample KU1 even had a higher N2 yield than H2 (Table 3). High N2 contents even up to 100% can be found in the natural gas reservoirs, with organic or/and inorganic sources [32-34]. We had already ruled out the possibility of air residue, and there was no surrounding rock to provide N as an inorganic source. So the only possible source was the organic matter. Organic source N2 had been found in the products of both anhydrous and hydrous pyrolysis experiments of kerogen with a working temperature >300 °C [27,34]. Thermogenic transformation of humic and sapropelic organic matter was preferred to have a great contribution on N2 generation [34,35]. However, the low working temperature (<48 °C) of our experiment, indicated an alternative process of N2 generation, might be through the particles bombarding on nitrogenous groups and then N cleavage from the kerogen.

4.3. Carbon-containing gas generation
Carbon-containing gas, including CO2 and hydrocarbon gases, such as CH4 and C2H6, were detected with low yields in our experiment products. Although there were a little amount of modern atmosphere CO2 (about 0.056 ml) with δ13C of −6.4‰ [36] was sealed in the pot before irradiation, the great 13C-depleted CO2 (−19.2‰ to −35.0‰) detected after irradiation, close to the δ13C of kerogen (−30.4‰)
indicated its organic source. Hydrocarbon gases from CH$_4$ to C$_7$ hydrocarbons were analyzed, but only CH$_4$ and C$_2$H$_6$ were detected, similar to the previous irradiation experiment using $\gamma$ ray [12]. Though the yields of CH$_4$ and C$_2$H$_6$ were both <1% of the total gas yields, our study still confirmed the radioactivity related process of hydrocarbon gases generation, different from the typical thermal degradation process. However, for the low yields and varied $\delta^{13}$C values, it was difficult to draw the generation pathway of CO$_2$ and CH$_4$. Although the radiation-induced decarboxylation of acid groups in bitumen and/or kerogen had been assumed to have a contribution on the generation of CO$_2$ [12], the straight-chain carboxylic acids, particularly with chains <C$_5$, which are more susceptible than other carboxylic acids to decarboxylation [37,38], were below our experiment detection limits. So the straight-chain carboxylic acids might be not the main sources of CO$_2$.

5. Conclusion
The experiment of artificial neutron irradiation with immature kerogen confirmed the gas generation from organic matter. The gas was mainly H$_2$, with a maximum yield of 1145.3 ml/gTOC. D-depleted H$_2$ generation and simultaneous heavier $\delta$D of kerogens, and the good positive relationship between H$_2$ yields and $\delta$D of kerogens, provided sufficient evidence to confirm the source of hydrogen to be organic matter and indicated a direct dehydrogenation and abstraction mechanism from kerogen. Small amounts of N$_2$, CO$_2$, and CH$_4$ were also detected in the products. Although their organic source can be confirmed, the specific generation pathway is still unclear. More simulation experiment and geological case analysis need to be implemented and to provide robust evidence. Gas generation from kerogen will increase the gas-to-oil ratio of the hydrocarbon products, and make the oil much easier to discharge. It is of great importance to consider the artificial irradiation or U natural decay caused gas generation in the exploration and development of low-mature and immature shale oil.

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