

Gamma ^{60}Co -irradiation of organic matter in the Phosphoria Retort Shale

M. D. LEWAN,^{1,*} G. F. ULMISHEK,^{2,*} W. HARRISON,² and F. SCHREINER²

¹Amoco Production Company, Research Center, PO Box 3385, Tulsa, OK 74102, USA

²Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA

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Abstract—Irradiation experiments were conducted on a thermally immature rock sample of the Phosphoria Retort Shale and its isolated kerogen. A ^{60}Co -source for gamma radiation was employed at dosages ranging from 81 to 885 Mrads, which are attainable by Paleozoic and Precambrian black shales with syngenetic uranium enrichments. Kerogen elemental, isotopic, and pyrolysate compositions are not affected at these dosages, but the bitumens extracted from the irradiated rock are affected. The major effects are reductions in the amounts of bitumen, acyclic isoprenoids, and high-molecular weight acyclic carboxylic acids. Natural differences in the amounts of bitumen and acyclic isoprenoid due to regional and stratigraphic variations in organic source input and depositional conditions make the radiation-induced reductions in these parameters difficult to use as indicators of natural radiation damage in black shales. However, the preferential reduction in the high-molecular weight acyclic carboxylic acids, which are ubiquitous in the living precursory organic matter, is diagnostic of experimental γ -irradiation but may not be diagnostic of natural irradiation. The overall process associated with radiation damage is polymerization by cross-linking through a free radical mechanism. As a result, irradiation of organic matter in black shales is more likely to retard rather than enhance petroleum generation.

INTRODUCTION

STUDIES ON NATURAL associations of uranium with organic matter in sedimentary rocks have shown various types of alteration to organic matter as a result of radiation from decaying uranium (TEICHMÜLLER and TEICHMÜLLER, 1958; HATCHER et al., 1986; LEVENTHAL and THRELKELD, 1978; DAHL et al., 1988a,b). Although the effects of radiation damage to organic matter are demonstrated in these studies, the critical dosages needed to initiate detectable degrees of damage are difficult to assess. Factors needed to determine the dosage include size and form of the uranium domain, spatial distribution of uranium domains relative to organic matter, and geological age at which the uranium-organic matter association occurred. Characterizing the uranium domains in natural associations is usually not difficult, but determining their spatial distribution and age of occurrence with the organic matter is difficult. Relative spatial distribution of uranium domains may be readily determined in associations involving epigenetic uranium minerals in direct contact with coals or coalfield logs, but the age of these associations is usually questionable. Conversely, the age of syngenetic uranium enrichment in black shales is known, but because of the sub-micron size of the uranium domains and their occurrence in organic matter and minerals, the spatial distribution is usually difficult to assess.

In an attempt to circumvent this problem in evaluating the radiation dosage experienced by organic matter in the uranium-enriched Alum Shale, LEWAN and BUCHARDT (1989) determined the maximum possible dosage for this syngenetic uranium-organic matter association. This calculated value assumes that all the radiation emitted from the

decay of uranium is absorbed by the organic matter. Using this approach it was determined that obvious radiation damage resulting from cross-linking of high-molecular weight *n*-alkanes occurred at maximum possible dosages of 10^5 Mrads. As noted by LEWAN and BUCHARDT (1989), approximately 90% of this dosage may not be totally effective because of the low penetrating potential of α -radiation. However, even if all the uranium was sequestered in minerals, the effective dosage would be 10^4 Mrads, which is one-order of magnitude higher than critical dosages required to alter *n*-alkanes (CHARLESBY, 1960, p. 260), crude oils (CARROLL and BOLT, 1963), and natural rubber (SISMAN et al., 1963) in laboratory radiation experiments. Unfortunately, no laboratory radiation experiments have been conducted to directly verify the dosage required to damage organic matter in sedimentary rocks. The objective of this study is to provide the needed data on this subject by experimentally determining the dosages required to cause radiation damage to sedimentary organic matter using a ^{60}Co -source.

METHODS

Description of Samples

The irradiation experiments were carried out on five aliquots of a sample of Phosphoria Retort Shale and five aliquots of kerogen isolated from the same rock sample. This sample was chosen because it was available in sufficient quantities and because its organic matter experienced a low radiation dosage through its geological history prior to the experiments. Locality and sampling information are described by LEWAN (1985). The shale is an argillaceous claystone (LEWAN, 1978) with quartz, kaolinite, illite, and pyrite being the major mineral constituents. X-ray fluorescence spectrometry of a fused lithium-tetraborate glass pellet of the shale gave a chemical composition on a weight basis of 50.1% SiO_2 , 9.75% Al_2O_3 , 0.15% CaO , 0.74% MgO , 0.11% Na_2O , 2.16% K_2O , 2.71% total iron as FeO , 0.59% TiO_2 , 0.44% P_2O_5 , and 33.5% loss on ignition. The sample was crushed to a uniform size ranging from 1 to 5 mm.

As documented by LEWAN (1985), the organic matter within this sample consists predominantly of oil-prone, amorphous Type-II ker-

* Present address: USGS, Box 25046, MS 977, Denver Federal Center, Denver, CO 80225, USA.

ogen. The kerogen is thermally immature in the pre-oil generation stage of petroleum formation. Isolation of the kerogen from the rock was accomplished by a series of acid treatments involving HCl and HF, and followed by a heavy liquid separation with a zinc-bromide solution. Specifics on the procedure are described by LEWAN (1986). The isolated kerogen contains less than 10 wt% mineral contaminants, which consist primarily of pyrite, rutile, and anatase. After a final Soxhlet extraction with an azeotropic benzene/methanol mixture, the kerogen is lightly ground to a powder ranging in size from 10 to 50 μm .

Radiation Experiment

The rock and kerogen aliquots were sealed in evacuated 316-stainless steel cylinders closed at one end with a pipe plug and fitted at the other end with a street tee connected to a pressure gage and a bellows valve (Fig. 1a, b). The entire assemblage including the internal portion of the pressure gage is composed of 316-stainless steel. All threaded portions of the fittings were coated with Kester 40/60 solid core solder to insure vacuum and pressure tight seals. The 10-cm³ cylinder assemblages (Fig. 1a) were loaded with 3.5 g of powdered kerogen, and the 30-cm³ cylinder assemblages (Fig. 1b) were loaded with 30 g of crushed shale. Each cylinder assemblage was then evacuated with a belt-drive vacuum pump for 72 h. The resulting vacuum pressures were less than 1 kPa.

The evacuated cylinders were irradiated at room temperature with a ⁶⁰Co-source at the Argonne National Laboratory. This source has been described in detail by HARVEY et al. (1965) and consists of four radioactive cobalt rods that can be lowered below a shielded floor to allow access to the experimental area. At the time these experiments were undertaken, four rods were in place and the total amount of activity in the source was on the order of 5000 to 6000 Curies. The vertical rods were equidistant from one another on a 76.2-mm radius circle (Fig. 1c). In order to achieve the desired dose rate, the five shale- and five kerogen-bearing cylinders were arranged at three different distances from the center of the radiation source (Fig. 1c). Three shale-bearing cylinders, labeled 1, 2, and 3, and three kerogen-bearing cylinders, labeled 6, 7, and 8, were placed at a distance of 16.5 cm from the center of the source. One pair of shale- and kerogen-bearing cylinders, respectively labeled 4 and 9, were placed at a distance of 35.6 cm from the center of the source. Another pair of shale- and kerogen-bearing cylinders, respectively labeled 5 and 10, were placed at a distance of 55.9 cm from the center of the source. This experimental array was designed to study potential differences arising from variations in the dosage rate, as well as dosage.

The intensity of the radiation field was determined by dosimetry with special radiation-sensitive glass. This glass had been calibrated previously to relate darkening during a 10-min exposure to the dose rate in water. Duplicate measurements at the three different distances from the center of the source gave dose rates of $6.0 \pm 1.0 \times 10^5$ rads/h at 16.5 cm, $1.88 \pm 0.5 \times 10^5$ rads/h at 36.6 cm, and $0.56 \pm 0.25 \times 10^5$ rads/h at 55.9 cm. A correction was applied for attenuation of radiation during passage through the stainless steel walls of the cylinders. This correction was established by placing dosimeters inside and outside a cylinder and measuring the difference in dose rates. It was found that the walls caused approximately 5% reduction in dose rate. Table 1 shows the dose rate, exposure time, and dosage for each sample.

Gas Analyses

After the samples were irradiated, the bellows valves of the cylinder assemblages were connected to the gas inlet system of a CEC 103 mass spectrometer. The inlet system was equipped with a pressure transducer for accurate measurement of the resulting gas pressures. Once the pressures were measured, the gases were analyzed by the mass spectrometer. Mole percentages determined by this analysis for the different gases were converted to moles assuming ideal gas behavior at room temperatures.

Whole-Rock Analyses

Total carbon and organic carbon in the irradiated rocks were determined on a Leco carbon determinator (IR-212), with the latter

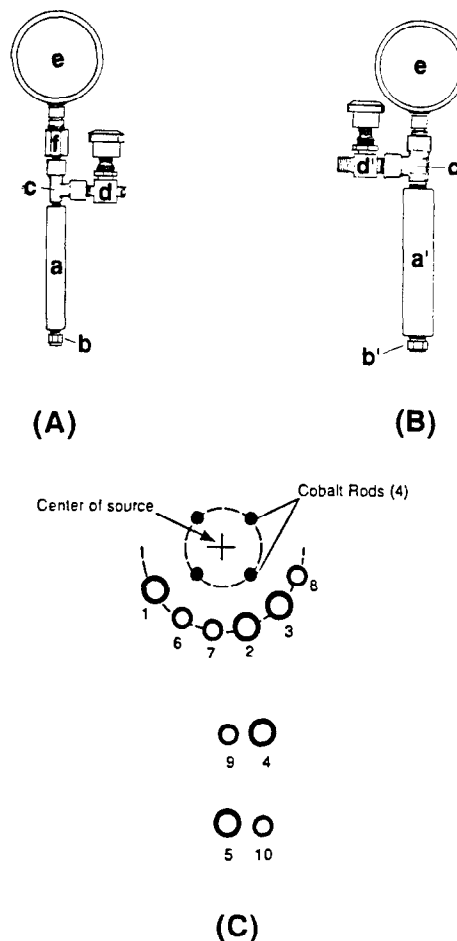


FIG. 1. Drawings of the experimental setup: (A) Drawing of 10-cm³ cylinder assemblage used to irradiate the isolated kerogen. All parts of the assemblages are made of 316-stainless steel; a = 10-cm³ cylinder with an 0.083 inch wall thickness (Hoke No. 2HDY10), b = 1/8 inch plug (Hoke No. 2PP316), c = 1/8 inch street tee (Cajon No. -2ST), d = bellows valve (Nupro "H" series, No. SS-2H2), e = pressure gauge from 30 inch Hg vacuum to 100 psi (Ashcroft No. 25-1009SW-100VAC-02L), and f = reducing adaptor (Cajon No. -4RA2). (B) Drawing of 30-cm³ cylinder assemblage used to irradiate the crushed rock. All parts are made of 316-stainless steel; a' = 30-cm³ cylinder with a 0.065 inch wall thickness (Hoke No. 4HDY30), b' = 1/4 inch plug (Hoke No. 4PP316), c' = 1/4 inch street tee (Cajon No. -4ST), d' = bellows valve (Nupro "H" series, No. SS-4H2), and e' = the same as e. (C) Aerial cross-sectional view showing arrangement of cylinder assemblages relative to the four cobalt reactor rods (not to scale). Numbers refer to experiment numbers in Table 1.

being determined after the rock samples were subjected to 6 N HCl. Bitumen was extracted from pulverized portions of the irradiated rocks in a Soxhlet apparatus for 72 h with a mixture of benzene and methanol (60:40 wt%). Following the extraction, the resulting solution was filtered through a 0.45 μm fluoropore filter. The bitumen was concentrated by rotary vacuum evaporation.

Kerogen Analyses

Kerogen was isolated from the irradiated rocks by a series of HCl and HF treatments, followed by a heavy-liquid separation. Details on this procedure are given elsewhere by LEWAN (1986). Elemental analyses on the isolated kerogens were conducted on a Carlo Erba elemental analyzer (Model 1106) with acetanilide as the standard for carbon, hydrogen, and nitrogen, and benzoic acid as the standard

Table 1. Gamma-radiation dosages received by shale and kerogen from the Phosphoria Retort Shale

Experiment Number	Material	Distance (cm)	Dose Rate ¹ (Mrad/hour)	Time (hours)	Dosage ² (Mrad)
1	Shale	16.5	0.60	142.3	82
2	Shale	16.5	0.60	497.3	285
3	Shale	16.5	0.60	1542.7	885
4	Shale	35.6	0.188	1542.7	277
5	Shale	55.9	0.056	1542.7	83
6	Kerogen	16.5	0.60	142.3	81
7	Kerogen	16.5	0.60	497.3	282
8	Kerogen	16.5	0.60	1542.7	874
9	Kerogen	35.6	0.188	1542.7	274
10	Kerogen	55.9	0.056	1542.7	82

¹ The dose rate was determined with glass dosimeters which had previously been calibrated by $^{59}\text{Fe}^{2+}/^{59}\text{Fe}^{3+}$ actinometry (Fricke dosimeter).

² In calculating the dose received by each sample allowance was made for attenuation of the radiation by the stainless steel wall of the container, amounting to a dose reduction of 4.4% for the shale samples, and of 5.6% for the kerogen samples.

for oxygen. Determinations of $\delta^{13}\text{C}$ on the isolated kerogens were conducted by Coastal Science Laboratory as described by LEWAN (1983).

Pyrolysis/Gas Chromatography

The samples were pyrolyzed in a modified oven injector in two stages: (1) 350°C for 15 min for pre-existing volatile hydrocarbons and (2) 550°C for 15 min for pyrolysate generation. Fractions from both stages were separately analyzed by gas chromatography in the split mode on a Hewlett-Packard 5890 instrument with a 50 meter Quadrex bonded phase, fused silica, 007 methyl silicone column. Initial column temperature for both runs is -80°C with an average programmed heating rate of 8°C/min to a final column temperature of 350°C. H_2 is the carrier gas with a column head pressure of 30 psi.

Gas Chromatography/Mass Spectrometry (GC/MS)

Bitumens extracted from the original and irradiated rocks were analyzed on a Hewlett-Packard 5996A GC/MS. The mass spectrometer was run in the selected-ion-monitoring mode with emphasis being placed on m/z 57 for alkanes, m/z 60 for acyclic carboxylic acids, m/z 191 for terpanes, m/z 217 for steranes, m/z 231 for triaromatic steroids, and m/z 253 for monoaromatic steroids. Compounds were identified in their diagnostic ion chromatograms on the basis of retention times established with laboratory standards. Specific instrument conditions are given elsewhere by LEWAN et al. (1986).

RESULTS

The gases generated by the irradiation of shale and kerogen are given in Table 2. Despite the reduction in radiation due to mineral matter enclosing the organic matter of the shale samples, the irradiated rocks generated more gas than the irradiated kerogen. CO_2 and H_2 are the most abundant gases generated from both rock and kerogen, with concentrations respectively being 2.9 and 1.6 times greater for the irradiated rock. Although the gases were analyzed for methane through C_7 -hydrocarbons, methane and ethane were the only detectable hydrocarbons. These two hydrocarbons account for less than 2 mol% of the gases generated in both the irradiated shale and kerogen. The presence of N_2 in the rock experiments

is attributed to degassing of trapped air in the original rock. Minor amounts of CO occur in the irradiated rock and kerogen experiments, but are twice as abundant in the latter.

Different dosage rates for the shale and kerogen experiments at intermediate dosages generated various amounts of gas with no consistent trends. Shale experiments 1 and 5 received similar dosages (82 and 83 Mrads) at different dosage rates (0.600 and 0.056 Mrad/h) and generated similar amounts of hydrocarbon gases but generated greater amounts of nonhydrocarbon gases at the slower rate. Conversely, shale experiments 2 and 4 received similar dosages (285 and 277 Mrads) at different dosage rates (0.600 and 0.188 Mrad/h) and generated greater amounts of hydrocarbon and nonhydrocarbon gases at the faster rate. Amounts of gas generated in the kerogen experiments have similar relations with dosage rate, except for experiments 6 and 10. These experiments generated greater amounts of hydrocarbon gases and H_2 at the faster dosage rate for dosages of 81 and 82 Mrads.

Kerogens isolated from the irradiated shales and isolated kerogens directly irradiated showed no significant change in elemental analyses or stable carbon isotopes (Table 3). Atomic H/C and O/C ratios are indicative of thermally immature Type-II kerogens (TISSOT et al., 1974). The $\delta^{13}\text{C}$ values are depleted in ^{13}C relative to organic matter in modern open-marine systems, which is typical of Phanerozoic amorphous kerogens (LEWAN, 1986). The small variations in these values are attributed to analytical error, and show no relation to dosage or dosage rate.

Gas chromatograms of the volatile hydrocarbons and generated pyrolysates from pyrolysis of the irradiated kerogens and shales show no significant differences with the original non-irradiated samples. As shown in Fig. 2, the amounts and proportionality of alkanes and alkenes in the generated pyrolysates are not affected by radiation at these dosages. The minor differences that do occur are not consistent with intermediate dosages and are attributed to instrument variability. Rock-Eval pyrolysis of the irradiated shales shows a minor decrease in the S_1 - and S_2 -hydrocarbon yields with

Table 2: Gases generated from irradiated rocks and kerogens.* Amounts are given as $\mu\text{mol/g}$ organic carbon. The mass of organic carbon is 6.69 grams in the shale and 2.30 grams in the kerogen.

EXPERIMENT NUMBER	DOSAGE (Mrad)	PRESSURE (KPa)	CH ₄	C ₂ H ₆	CO ₂	CO	H ₂	N ₂	TOTAL
SHALE									
1	82	11.71	0.3	0.0	6.2	0.1	11.4	5.8	23.8
2	285	42.72	2.2	0.2	34.1	1.2	59.2	7.6	104.5
3	885	227.59	4.7	0.5	44.5	1.1	340.6	4.1	395.5
4	277	30.99	1.0	0.1	17.0	0.5	46.3	6.7	71.6
5	83	17.95	0.6	0.0	9.9	0.3	23.6	5.6	40.0
KEROGEN									
6	81	7.24	0.8	0.3	0.3	0.0	35.4	0.2	37.0
7	282	20.81	3.0	0.6	11.2	1.6	94.0	0.0	110.4
8	874	44.79	4.0	0.3	15.4	2.2	215.5	0.0	237.4
9	274	8.48	1.0	0.1	6.0	0.5	37.9	0.0	45.5
10	82	2.71	0.4	0.0	3.2	0.3	10.6	0.0	14.5

* Other gases analyzed for but not detected ($<0.1\mu\text{mol/g}$ of org.C) include propane, isobutane, n-butane, pentanes, hexanes, C₇ and heavier hydrocarbons, benzene, toluene, ethene, propene, butenes, pentenes, hexenes, cyclohexanes, butadienes, hydrogen sulfide, and ammonia.

increasing dosage, but as footnoted in Table 4, this decrease is within the standard deviation of the analyses. The maximum S₂ temperature (i.e., T-max) shows no significant change with dosage.

The total carbon and organic carbon contents of the original rock and its irradiated equivalents show no change with increasing dosage, but as footnoted in Table 4 this decrease tracted bitumen show an 0.7 wt% decrease at the highest dosage. This is also demonstrated in the bitumen/organic

carbon ratio, which decreases by a value of 0.03 at the highest dosage (Table 4). Although the bitumen contents of the irradiated rocks were reduced, this reduction is not reflected in the ion chromatograms of the n-alkanes (Fig. 3), tricyclic terpanes (Fig. 4), pentacyclic triterpanes (Fig. 5), steranes (Fig. 6), monoaromatic steroid hydrocarbons (Fig. 7), or triaromatic steroid hydrocarbons (Fig. 8). The few sporadic variations in these distributions showed no corresponding change in the shale samples irradiated at intermediate dosages and,

Table 3: Elemental analyses of irradiated kerogen and of kerogen isolated from irradiated rock.

EXPERIMENT NUMBER	DOSAGE (Mrad)	C (WT.%)	H (WT.%)	N (WT.%)	O (WT.%)	TOTAL (WT.%)	ATOMIC H/C	ATOMIC O/C	$\delta^{13}\text{C}$ (‰ PDB)
SHALE									
0*	0	68.3	6.9	2.3	7.0	84.5	1.21	0.08	-30.1
1	82	68.1	7.0	2.3	6.3	82.7	1.23	0.07	-30.0
2	285	68.5	6.7	2.4	6.9	84.5	1.17	0.08	-29.9
3	885	67.8	7.0	2.4	6.5	83.7	1.24	0.07	-29.9
4	277	67.3	7.0	2.4	6.8	83.5	1.25	0.08	-29.8
5	83	68.1	7.0	2.4	6.4	83.9	1.23	0.07	-29.8
KEROGEN									
0**	0	65.7	6.5	2.2	7.4	81.8	1.19	0.08	-30.0
6	81	66.3	6.6	2.2	7.7	82.8	1.19	0.09	-29.8
7	282	67.5	6.7	2.3	7.7	84.2	1.19	0.09	-29.8
8	874	67.7	6.8	2.3	7.7	84.5	1.20	0.09	-29.9
9	274	67.0	7.0	2.3	7.4	83.7	1.25	0.08	-30.0
10	82	66.7	6.9	2.3	7.2	83.1	1.24	0.08	-30.1

* Original shale not subjected to radiation.

** Kerogen isolated from original rock for kerogen-irradiation experiments.

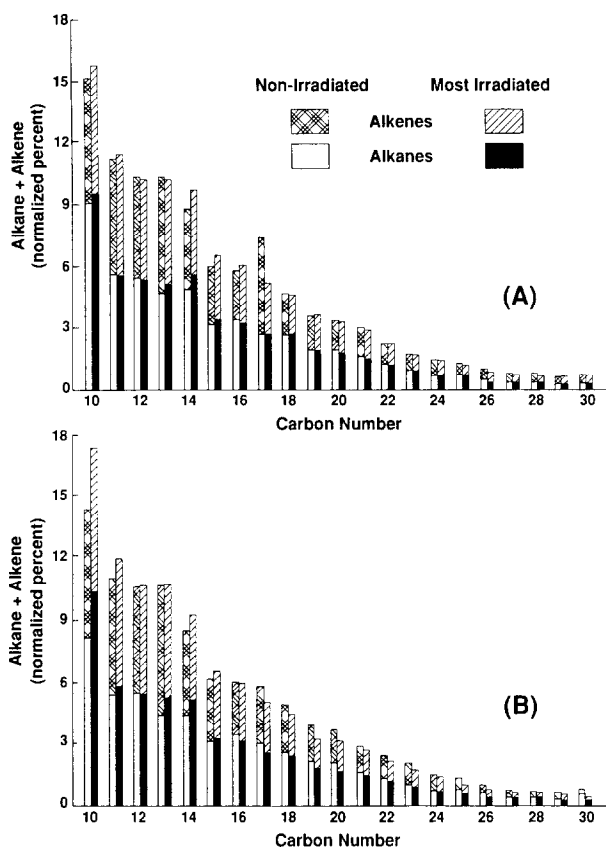


FIG. 2. Histograms showing the relative concentrations of *n*-alkanes and alkenes from gas chromatograms of pyrolysates generated from the non-irradiated and most irradiated (Experiment Nos. 3 and 8) kerogen (A) and rock (B). Alkanes and alkenes from non-irradiated samples are respectively denoted as open and cross hatched bars, and those from the most irradiated samples are respectively denoted as solid and hatched bars.

therefore, are attributed to analytical error. Changes in concentration of these compound classes were evaluated relative to the triaromatic steroid hydrocarbons. This compound class was used as a reference because of the highly resistant nature of aromatic hydrocarbons to radiation (CHARLESBY, 1960, p. 192; CARROLL and BOLT, 1963). Results from this calculation indicate that no significant concentration changes of these compound classes occurred in the irradiated rocks (Table 5).

The only significant molecular changes that may be attributed to radiation damage in these experiments are the relative reductions in the high-molecular weight acyclic carboxylic acids and acyclic isoprenoids. Figure 9 shows the preferential loss of C_{14} , C_{15} , and C_{16} acyclic carboxylic acids at the highest dosage. As shown in Table 6, the lower dosages show only preferential loss of C_{15} and C_{16} acyclic carboxylic acids. These data suggest that the greater the chain length of a carboxylic acid, the greater its susceptibility to radiation damage. This reduction also results in an obvious decrease in the even-carbon predominance of the higher-molecular weight acids. Comparison of experiments 4 and 5 with experiments 1 and 2 suggest the reduction of high-molecular weight acids is more complete at slower dosage rates (Table 6).

The other molecular change attributed to radiation damage is the reduction in acyclic isoprenoid alkanes. Figure 10 shows the relative reduction in phytane, pristane, and norpristane with increasing dosages relative to n - C_{18} , n - C_{17} , and n - C_{16} , respectively. The overall reductions are higher for phytane than for norpristane, with an intermediate overall reduction for pristane. This reduction in isoprenoids at the slower dosage rate is greater than the faster dosage rate at 83 and 82 Mrads and is lesser than the faster dosage rate at 277 and 285 Mrads. The increase of some isoprenoids at the lowest dosages to values greater than those in the original shale suggests the variations in isoprenoid reduction with dosage rates are within the analytical error and are not significant.

DISCUSSION

Results from these experiments indicate that radiation dosages of 81 to 885 Mrads are insufficient to cause detectable damage to kerogen, but are sufficient to cause some damage to bitumen. Radiation dosages within this range have been shown to make n - C_{12} infusible (CHARLESBY, 1960, p. 209), crude oils heavier and more viscous (COLOMBO et al., 1964; CARROLL and BOLT, 1963), polyethylene insoluble (CHARLESBY, 1960, p. 210), and natural rubber brittle (SISMAN et al., 1963). Considerably higher dosages in excess of 10^5 Mrads were found by LEWAN and BUCHARDT (1989) to cause detectable damage to naturally irradiated organic matter in the Alum Shale by uranium decay. This natural irradiation damaged the kerogen and bitumen within the rocks, which resulted in generation of peculiar condensate-like oil when subjected to hydrous pyrolysis. Lack of this type of pyrolysate from the most irradiated shale and kerogen by the pyrolysis/gas-chromatography method (Fig. 2) suggests that the experimental dosages in this study are not as high as the natural dosages experienced by the Alum Shale.

Bitumen Reduction

A result of radiation damage common to both the higher dosages in the Alum Shale and the lower dosages in the ^{60}Co experiments is the decrease in bitumen content of the rock. This decrease is attributed to radiation-induced cross-linking by a free-radical mechanism in which dehydrogenation occurs. Based on cross-linking mechanisms proposed for irradiated hydrocarbon polymers (O'DONNELL and SANGSTER, 1970), the ingressive radiation is envisaged cleaving a C-H bond on an aliphatic chain, which yields a hydrogen atom and a free-radical carbon. The free-radical site may abstract a hydrogen atom from an adjacent aliphatic chain or may migrate along the aliphatic chain until a hydrogen on an adjacent aliphatic chain is close enough (<0.41 nm; UNGAR, 1981) for abstraction. The originally cleaved and subsequently abstracted hydrogen atoms combine to form molecular hydrogen, and the two adjacent free-radical sites form a cross-linking C-C bond. As the amount of cross-linking increases with increasing dosage, portions of the bitumen become insoluble (LEWAN and BUCHARDT, 1989). The lack of any major changes in the different compound classes presented in Table 5 indicates the cross-linking occurs predominantly in the portion of bitumen that is not amenable to gas chromatography. This susceptible portion of bitumen most likely

Table 4: Whole rock analyses of original and irradiated shale samples

EXPERIMENT NUMBER	0*	1	2	3	4	5
DOSAGE (Mrad)	0	8.2	285	885	277	83
ROCK EVAL**						
S ₁ -Hydrocarbons (mg/g rock)	1.47	1.63	1.56	1.22	1.47	1.49
S ₂ -Hydrocarbons (mg/g rock)	105.66	105.29	103.59	98.99	101.76	106.19
T-Max (°C)	417	417	417	417	416	416
TOTAL CARBON (wt.% of rock)	22.7	22.7	22.7	22.6	22.9	23.0
ORGANIC CARBON (wt.% of rock)	22.3	21.5	22.3	21.9	22.2	21.7
EXTRACTED BITUMEN (wt.% of rock)	3.06	3.19	2.66	2.36	2.72	2.73
BITUMEN/ORG. C RATIO	0.137	0.148	0.119	0.108	0.123	0.126

* Original shale not subjected to radiation.

** Values are averages of two runs with standard deviations of ± 0.57 mg/g rock for S₁-hydrocarbons, ± 7.24 mg/g rock for S₂-hydrocarbons and $\pm 0.6^{\circ}\text{C}$ for T-Max.

consists of branched alkanes (GOUGH and ROWLAND, 1990), which are more susceptible to radiation-induced cross-linking than straight-chain alkanes (CHARLESBY, 1960, p. 210) and aromatics (CHARLESBY, 1960, p. 192; CARROLL and BOLT, 1963). This higher susceptibility of branched alkanes to radiation damage is supported by the decrease in acyclic isoprenoids relative to normal alkanes with increasing dosage in the experiments (Fig. 10). Although this relative change is notable in the experiments, its detection in naturally irradiated shales would be difficult to evaluate because of comparable variations in the original proportionalities of samples

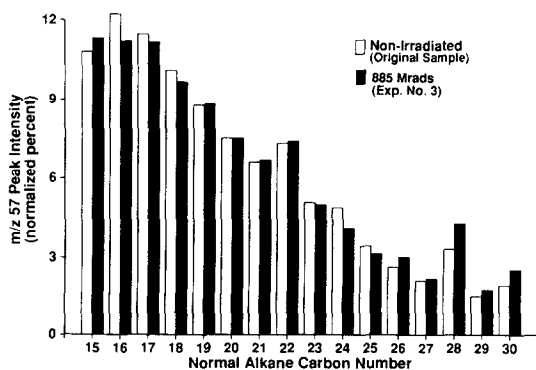


FIG. 3. Distribution of *n*-alkanes in the *m/z* 57 ion chromatograms of bitumens extracted from the non-irradiated rock (open bars) and the most irradiated rock (solid bars, Experiment No. 3).

from the same rock unit (e.g., Alum Shale samples AS-40 and BB-8681, Table 6; LEWAN and BUCHARDT, 1989).

Radiation-induced polymerization through a free-radical cross-linking mechanism results in the generation of molecular hydrogen. As shown in Table 2, H₂ is a major component of the gas recovered at the conclusion of the experiments and may be attributed in part to cross-linking polymerization. The amount of H₂ is significantly greater in the experiments with shales than with kerogens (Table 2). This observation is explained by the presence of bitumen in the rock, which appears to be more susceptible to radiation damage than the

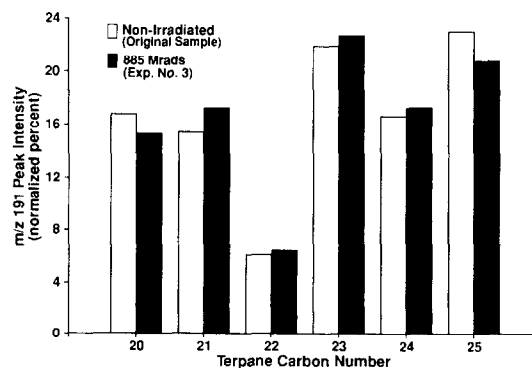


FIG. 4. Distribution of C₂₀ through C₂₅ tricyclic terpanes in the *m/z* 191 ion chromatograms of bitumens extracted from the non-irradiated rock (open bars, original sample) and the most irradiated rock (solid bars, Experiment No. 3).

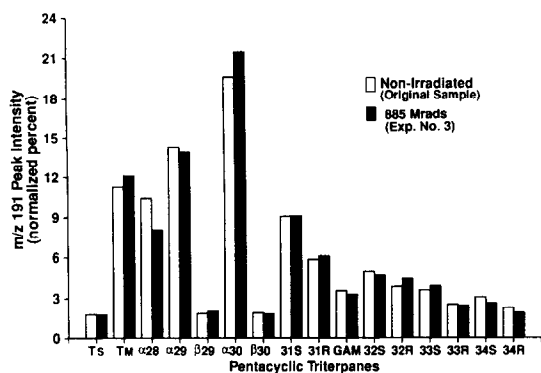


FIG. 5. Distribution of pentacyclic triterpanes in the m/z 191 ion chromatograms of bitumens extracted from the non-irradiated rock (open bars, original sample) and the most irradiated rock (solid bars, Experiment No. 3). Specific compound names are denoted as follows: Ts = $18\alpha(\text{H})$ -trisorneohopane; Tm = $17\alpha(\text{H})$ -trisorhopane; $\alpha 28$ = $17\alpha(\text{H})$ -bisnorhopane; $\alpha 29$ = $17\alpha(\text{H})$, $21\beta(\text{H})$ -norhopane; $\beta 29$ = $17\beta(\text{H})$, $21\alpha(\text{H})$ -norhopane; $\alpha 30$ = $17\alpha(\text{H})$, $21\beta(\text{H})$ -hopane; $\beta 30$ = $17\beta(\text{H})$, $21\alpha(\text{H})$ -hopane; 31S and 31R = $17\alpha(\text{H})$, $21\beta(\text{H})$ -homohopanes (22S and 22R, respectively); GAM = gammacerane; 32S and 32R = $17\alpha(\text{H})$, $21\beta(\text{H})$ -bishomohopanes (22S and 22R, respectively); 33S and 33R = $17\alpha(\text{H})$, $21\beta(\text{H})$ -trishomohopanes (22S and 22R, respectively); and 34S and 34R = $17\alpha(\text{H})$, $21\beta(\text{H})$ -tetrakisomohopanes (22S and 22R, respectively).

kerogen. Cross-linking is likely to have occurred in the kerogen, but, due to its greater concentration and more rigid structure, the effects of radiation at the experimental dosages are not detectable (Table 3). LEWAN and BUCHARDT (1989) noted that dosages in excess of 10^5 Mrads were necessary to detect changes in the kerogen of the naturally irradiated Alum Shale.

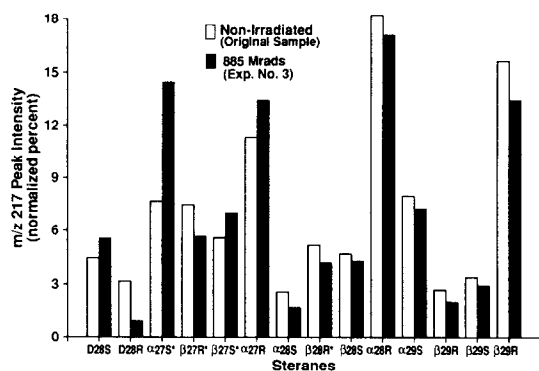


FIG. 6. Distribution of steranes in the m/z 217 ion chromatograms of bitumens extracted from the non-irradiated rock (open bars, original sample) and the most irradiated rock (solid bars, Experiment No. 3). Specific compound names are denoted as follows: D28S and D28R = $13\beta(\text{H})$, $17\alpha(\text{H})$ -diacholestane (20S and 20R, respectively); $\alpha 27\text{S}^*$ and $\alpha 27\text{R}^*$ = $14\alpha(\text{H})$, $17\alpha(\text{H})$ -cholestane (20S and 20R, respectively); $\beta 27\text{R}^*$ and $\beta 27\text{S}^*$ = $14\beta(\text{H})$, $17\beta(\text{H})$ -cholestane (20R and 20S, respectively); $\alpha 28\text{S}$ and $\alpha 28\text{R}$ = 24-methyl- $14\alpha(\text{H})$, $17\alpha(\text{H})$ -cholestane (20S and 20R, respectively); $\beta 28\text{R}^*$ and $\beta 28\text{S}$ = 24-methyl- $14\beta(\text{H})$, $17\beta(\text{H})$ -cholestane (20R and 20S, respectively); $\alpha 29\text{S}$ and $\alpha 29\text{R}$ = 24-ethyl- $14\alpha(\text{H})$, $17\alpha(\text{H})$ -cholestane (20S and 20R, respectively); and $\beta 29\text{R}$ and $\beta 29\text{S}$ = 24-ethyl- $14\beta(\text{H})$, $17\beta(\text{H})$ -cholestane (20R and 20S, respectively). Notations followed by an asterisk indicate peak intensity may be exaggerated due to coelution of diasteranes.

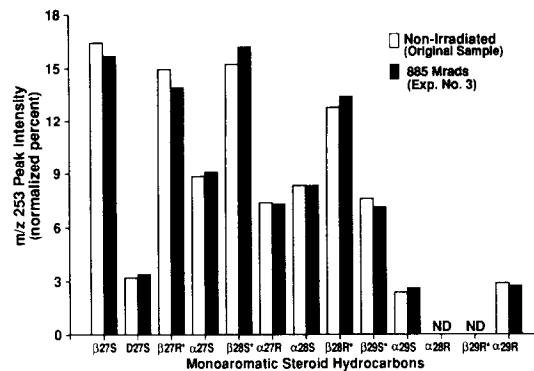


FIG. 7. Distribution of monoaromatic steroid hydrocarbons in the m/z 253 ion chromatograms of bitumens extracted from the non-irradiated rock (open bars, original sample) and the most irradiated rock (solid bars, Experiment No. 3). Specific compounds are denoted as follows: α and β refer to the H orientation at the C-5 chiral carbon, D refers to dia-monoaromatic steroids with a methyl group at the C-5 position; 27, 28, and 29 refer, respectively, to -H, - CH_3 , and - C_2H_5 functional groups at the C-24 position; and R and S refer to the H orientation at the C-20 chiral carbon. Notations followed by an asterisk indicate peak intensity may include a coeluting dia-monoaromatic steroid. The ND notation indicates that the peaks were not detected.

Acyclic Carboxylic Acids

Another class of compounds affected by radiation in these experiments is the carboxylic acids in the bitumen and kerogen. Radiation dosages in the range of 10^2 Mrads cause dehydrogenation or decarboxylation of acyclic carboxylic acids with chain lengths from C_2 through C_{22} (WHITEHEAD et al., 1951). Susceptibility to dehydrogenation increases with increasing chain length, and susceptibility to decarboxylation increases with decreasing chain length. A considerable amount of experimental data on the effects of radiation on acyclic carboxylic acids has been collected (JONES, 1971a,b, 1972; WU and HOWTON, 1974; HAU and NAWAR, 1986), but specific mechanisms for the opposing susceptibility of

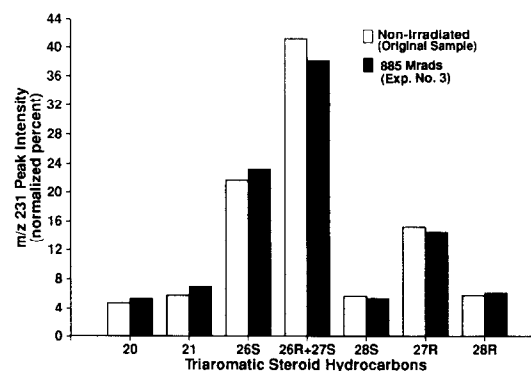


FIG. 8. Distribution of triaromatic steroid hydrocarbons in the m/z 231 ion chromatograms of bitumens extracted from the non-irradiated rock (open bars, original sample) and the most irradiated rock (solid bars, Experiment No. 3). Specific compounds are denoted as follows: The numbers 20 and 21 refer, respectively, to - CH_3 and - C_2H_5 functional groups at the C-17 position; the numbers 26, 27, and 28 refer, respectively, to -H, - CH_3 , and - C_2H_5 functional groups at the C-24 position; and R and S refer to the methyl group orientation at the C-20 chiral position.

Table 5: Peak intensities of compound classes relative to peak intensities of triaromatic steroid hydrocarbons in bitumen extracts from shale subjected to different radiation dosages.

EXPERIMENTAL NUMBER	0*	1	2	3	4	5
DOSAGE (Mrad)	0	82	285	885	277	83
RELATIVE CONCENTRATION OF COMPOUND CLASSES **						
ALKANES						
TA + ALKANES	0.77	0.78	0.78	0.80	0.79	0.78
TRICYCLIC TERPANES						
TA + TRICYCLIC TERPANES	0.16	0.15	0.16	0.17	0.17	0.17
PENTACYCLIC TERPANES						
TA + PENTACYCLIC TERPANES	0.46	0.46	0.45	0.44	0.45	0.47
STERANES						
TA + STERANES	0.01	0.01	0.01	0.01	0.01	0.01
MONO AROMATICS						
TA + MONO AROMATICS	0.83	0.83	0.81	0.80	0.83	0.81

* Original shale not subjected to radiation.

** Relative concentrations of compound classes are given relative to the summation of the C₂₀, C₂₁, C₂₆, C₂₇, and C₂₈ triaromatic steroid (TA) peak intensities on the m/z 231 ion chromatograms. alkanes = summation of C₁₅ through C₃₀ peak intensities on the m/z 57 ion chromatograms. Tricyclic terpanes = summation of C₂₀ through C₂₅ peak intensities on the m/z 191 ion chromatograms. Pentacyclic terpanes = summation of C₂₇ through C₂₉ peak intensities on the m/z 217 ion chromatograms. Monoaromatic steroids = summation of C₂₇ through C₂₉ peak intensities on the m/z 253 ion chromatograms. Peak intensities used for the decimal fractions in this table are not normalized.

acids to decarboxylation and dehydrogenation with increasing chain length remain unclear. A common aspect to most explanations involves where on an acid molecule the incoming energy is absorbed. Energy absorbed by the carboxyl group would have a greater tendency to result in decarboxylation, while energy absorbed by the aliphatic chain would have a greater tendency to result in dehydrogenation. As the acid carbon number increases, the probability of incoming energy

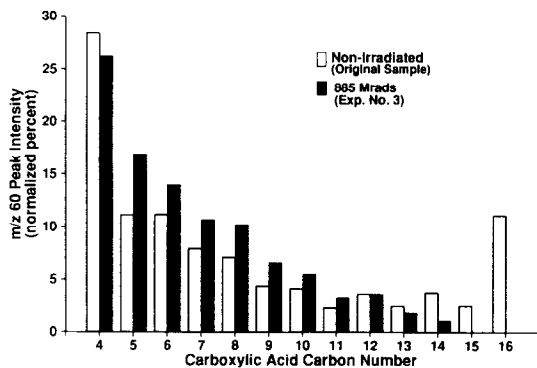


FIG. 9. Distribution of acyclic carboxylic acids in the m/z 60 ion chromatograms of bitumens extracted from the non-irradiated rock (open bars, original sample) and most irradiated rock (solid bars, Experiment No. 3).

making contact with the carboxyl group decreases because of its reduced occurrence through dilution by the increasing aliphatic-chain length. The resulting inverse relation between decarboxylation susceptibility and aliphatic chain length has been well established for C₄ through C₃₀ acyclic carboxylic acids (WU and HOWTON, 1974), but the relation is not maintained for C₁ through C₃ carboxylic acids (JONES, 1971a,b). This deviation is attributed to carboxylic acids below C₄ having an abrupt increase in density, which is suggested to reduce decarboxylation by intermolecular dissipation of the absorbed energy (WU and HOWTON, 1974).

The presence of CO₂ and lesser amounts of CO in the generated gases suggests the occurrence of radiation-induced decarboxylation of acid groups in the bitumen and kerogen (Table 2). Although carboxylic acids with chain lengths less than C₅ are more susceptible to decarboxylation (JONES, 1971a,b), this process is difficult to assess because of evaporative loss of C₁ through C₃ during the concentration of bitumen and the lack of an m/z 60 fragment for C₁ and C₃ acids. The anomalous reduction in the normalized percentage of C₄ in the irradiated samples relative to the original sample (Fig. 9; Table 6) suggests some decarboxylation of the shorter-chain carboxylic acids may have occurred. Lack of detectable propane in the generated gases (Table 2) suggests less than 0.7 μmol of C₄ acid was decarboxylated during the experiments. Similarly, based on the amounts of methane and ethane generated (Table 2), the maximum amounts of C₂

Table 6: Peak intensities of acyclic carboxylic acids in bitumen extracts subjected to different radiation dosages. intensities are given as normalized percentages from m/z 60 ion chromatograms.

EXPERIMENT NUMBER	0*	1	2	3	4	5
DOSAGE (Mrad)	0	82	285	885	277	83
CARBOXYLIC ACID (CARBON NO.)						
4	28.39	25.03	24.68	26.22	25.47	24.03
5	11.17	13.41	14.43	16.90	14.48	16.94
6	11.18	13.33	13.85	14.02	15.26	14.99
7	7.93	9.46	9.90	10.70	10.52	11.46
8	7.07	7.56	9.90	10.25	10.70	11.09
9	4.36	6.92	7.42	6.56	8.22	7.53
10	4.13	5.88	5.79	5.54	5.44	4.71
11	2.29	3.96	4.13	3.19	3.18	3.44
12	3.63	4.60	4.25	3.64	3.52	3.25
13	2.45	2.87	3.10	1.86	1.73	1.59
14	3.77	2.76	2.55	1.12	1.46	0.97
15	2.49	1.12	0.00	0.00	0.00	0.00
16	11.14	3.10	0.00	0.00	0.00	0.00

* Original shale not subjected to radiation.

and C₃ acids decarboxylated are, respectively, only 31 and 3 μmol at the highest dosage (i.e., experiment 3). The remaining 263 μmol of generated CO₂ suggest that sources other than free straight-chain carboxylic acids experienced decarboxyl-

ation. Other possible sources include carboxylic acids bound to the kerogen matrix or to high-molecular weight complexes in the bitumen, or free branched, cyclic, or aromatic carboxylic acids in the bitumen.

The more obvious effect of radiation on the acyclic carboxylic acids is the reduction of high-molecular weight acids with more than 12 carbon atoms (Fig. 9; Table 6). Dosages as low as 83 Mrads (Experiment 5, Table 6) result in the reduction of C₁₅ and C₁₆ acids below detection limits. This reduction is attributed to dehydrogenation and subsequent polymerization or cleavage at any carbon on the aliphatic chain (VAJDI et al., 1982). Living organisms have acyclic carboxylic acids typically in the range of C₁₂ through C₃₄ (DOUGLAS et al., 1970), and carbon number distributions within this range have been used to evaluate biological sources for organics in sedimentary rocks (e.g., DES LAS HERAS et al., 1989). It is obvious from Fig. 9 that radiation damage may obscure this type of interpretation due to the preferential loss of the higher carbon-number acids.

Radiation-induced reductions in high-molecular weight carboxylic acids also results in a significant reduction in the even-carbon predominance, which is common in living organisms and in organic matter of recent sediments (PARKER, 1969). This reduction may be explained by the higher probability of emitted radiation striking a more abundant molecule than a less abundant molecule with comparable susceptibility to dehydrogenation. KVENVOLDEN (1970) noted a general decrease in the even-carbon predominance of carboxylic acids in sedimentary rocks with increasing age, but notable exceptions preclude time as the only factor. LEWAN and BUCHARDT (1989) showed that the probability of radiation damage to organic matter in black shales increases with geological age

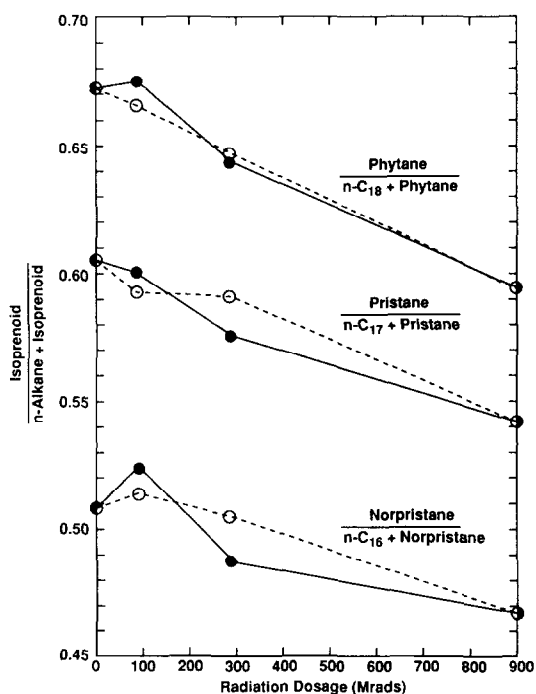


FIG. 10. Reduction in acyclic isoprenoids relative to *n*-alkanes with increasing radiation dosages at a constant rate (solid lines) and for a constant time (dashed lines).

and with increasing proportionality of uranium to organic matter. The implication that variations in the even-carbon predominance of carboxylic acids in Paleozoic or older black shales may be a result of radiation damage due to decaying syngenetic uranium is not supported by the naturally irradiated Alum Shale. Acyclic-carboxylic acid distributions in the m/z 60 ion chromatograms of bitumens extracted from samples of Alum Shale with maximum possible dosages in excess of 10^5 Mrads show no signs of preferential loss of high-molecular weight or even-carbon acyclic acids. This discrepancy brings into question the validity of comparisons between natural and experimental effects of radiation.

Experimental Versus Natural Irradiation

Assessing the comparability of these experiments with naturally irradiated Alum Shale samples is an important consideration that warrants some discussion. Dosages are an obvious difference, with the experiments only approaching 10^3 Mrads and the Alum Shale exceeding 10^5 Mrads (LEWAN and BUCHARDT, 1989). Despite this difference, there are two major radiation-induced changes that may be compared. The first is bitumen reduction in both the experimentally and naturally irradiated organic matter. And the second is reduction of high-molecular weight carboxylic acids in bitumens experimentally irradiated but not in bitumens naturally irradiated. Differences between these experiments and naturally irradiated Alum Shale include radiation type, dose rate, and dose uniformity.

Approximately 90% of the radiation from decaying uranium in black shales is in the form of α -particles, with the remaining 10% consisting of β -particles and γ -rays. Alpha-particles expend their energy over a few tens of micrometers in a rectilinear path, while γ -rays expend their energy over tens of centimeters in a tortuous path. The same dosage of energy may be transferred by α -particles and γ -rays, but their effects on the irradiated substance may be different. This difference is most obvious in biological systems in which α -particles are twenty times more likely to cause tissue damage than γ -rays at a similar dosage (DURRANCE, 1986, p. 69). Conversely, similar dosages of different radiation types usually result in similar changes to irradiated polymers (CHAPIRO, 1962, p. 342). Molecular hydrogen yields from irradiated octane and vacuum-pump oil sorbed on vermiculite showed only minor differences between α - and γ -radiation (BIBLER, 1976). Similarly, α - and γ -irradiation of polycaprolactam (i.e., Nylon 6; $-\text{NH}[\text{CH}_2]_5\text{CO}-$) produced essentially the same yields and steric distributions of stabilized radicals at equivalent dosages (PASAL'SKII et al., 1977).

Radiation-induced cross-linking and polymerization, which is considered responsible for experimental and natural reductions in bitumen, vary in degree with type of radiation depending on the type of polymer. Alpha- and γ -irradiated polyethylene show the same degree of cross-linking and polymerization (LAVRETOVICH et al., 1972). Gamma-radiation more effectively causes cross-linking and polymerization in polypropylene than α -radiation at dosages below 200 Mrads, but above this dosage no significant differences are observed

(STAREN'KII et al., 1970). Copolymers of polyethylene and polypropylene show similar results with differences in degree of cross-linking and polymerization between α - and γ -radiation below 200 Mrads being less for copolymers containing a lesser component of polypropylene (STAREN'KII et al., 1973). Although experimental verification is needed, the available data suggests the degree of cross-linking and polymerization may be greater for γ - than α -irradiated organic matter. However, the resulting difference is likely to be within the same order of magnitude.

Reduction of low-molecular weight acyclic carboxylic acids by radiation-induced decarboxylation also varies with type of radiation. Irradiation of acetic acid gives higher CO_2 and CH_4 yields with γ -radiation than with α -radiation (AYSCOUGH et al., 1971; DZYUBA et al., 1976). Similarly, CO_2 yields from γ -radiation of C_3 - through C_{22} -acyclic carboxylic acids are approximately two to three times greater than those from α -irradiation (JONES, 1971a). Reduction in high-molecular weight acyclic carboxylic acids through dehydrogenation and subsequent reactions is also likely to occur more effectively under γ -irradiation than under α -irradiation. This presumption is based on the more effective decomposition of other polar compounds like uracil under γ -radiation than under α -radiation (BHATTACHARYYA et al., 1988). All of these differences between γ - and α -radiation are significant, but are within the same order of magnitude. The greater effectiveness of γ -radiation may explain some of the discrepancy in the experimental reduction of carboxylic acids and the lack of their reduction in the Alum Shale. However, the higher dosage by two orders of magnitude in the naturally irradiated Alum Shale suggest additional factors are also responsible for the discrepancy.

Dose rates in these experiments are approximately seven orders of magnitude greater than those calculated for the Alum Shale (0.02 to 0.09 rads/h; LEWAN and BUCHARDT, 1989). The one order of magnitude change in dose rate of the experiments in this study was not sufficient to show unequivocal differences. Although radiation-induced polymerization through combination of styrene, methyl methacrylate, or vinyl acetate monomers is highly dependent on dose rate (CHAPIRO, 1962, Chap. V), radiation-induced polymerization through cross-linking in polyethylene (ATCHISON, 1959; KURIYAMA et al., 1979), asphalt (DOJIRI et al., 1977), and normal-alkanes (FALCONER et al., 1971; ARAI et al., 1981) is essentially independent of dose rate. These latter studies are only based on two to five orders of magnitude of change in dose rate, but suggest that the cross-linking responsible for bitumen reduction and hydrogen generation from kerogen is not significantly influenced by dose rate. Similarly, if the reduction of high-molecular weight acyclic carboxylic acids is also attributed to cross-linking of the aliphatic chain, then presumably the influence of dose rate on this reduction is not likely to be significant.

The other difference between these experiments and the Alum Shale that may account in part for the discrepancy in reduction of high-molecular weight carboxylic acids is dose uniformity. The external source of γ -rays used in the experiments results in uniformly irradiated samples. Conversely, the internal source of natural radiation in black shales consists

of submicron uranium domains that may be heterogeneously distributed, which results in nonuniformly irradiated samples. This nonuniformity of dose in black shales may also be enhanced by variations in the proportion of uranium domains in contact with organic matter relative to those sequestered in minerals (e.g., ROSS, 1952; BATES and STRAHL, 1957; RYNNINGER, 1957). As a result of this dose nonuniformity, it is envisaged that organic matter in some laminae or beds of a sample may have experienced a lower radiation dose than that calculated for the total organic matter in the entire sample (e.g., LEWAN and BUCHARDT, 1989). Bitumen extracted from this type of sample may be dominated by bitumen from less irradiated zones and thereby have molecular distributions not representative of the overall dosage. Although this factor remains to be tested by quantitative GC/MS, its likelihood coupled with the higher efficiency of γ -radiation offers a viable explanation for the discrepancy between high-molecular weight carboxylic acids being present in the naturally irradiated Alum Shale and their reduction in these experiments at lower dosages.

Petroleum Formation

The potential for radiation to enhance petroleum generation as advocated by KHARIN (1982) is not supported by the experimental data from this study nor by the natural data from the study of the Alum Shale (LEWAN and BUCHARDT, 1989). Irradiation of kerogen and bitumen primarily involves polymerization through bond cross-linking rather than fragmentation through bond scission. Radiation-induced cross-linking commonly occurs in vinyl polymers (e.g., polyethylenes, polypropylene, and polystyrene) and bond scission commonly occurs in polymers containing tetra-substituted carbons in the main chain (e.g., polyisobutylene and polymethyl methacrylate; CHAPIRO, 1962, p. 355; O'DONNELL and SANGSTER, 1970, p. 119). Oil-prone kerogens have been considered in part analogous to polymers (SAXBY, 1981; GOTH et al., 1988), and their proposed structures contain an abundance of polymethylene chains with only minor occurrences of tetrasubstituted carbons (BEHAR and VANDENBROUCKE, 1986; SCOUTEN et al., 1987; YEN, 1976). Therefore, radiation is more likely to reduce than enhance petroleum formation as concluded in the study of the Alum Shale (LEWAN and BUCHARDT, 1989).

As shown in Table 2, insignificant amounts of hydrocarbon gases were generated in this study. The observed reduction of acyclic isoprenoids relative to the *n*-alkanes in the radiation experiments (Fig. 10) is characteristic of thermally maturing organic matter (e.g., TISSOT et al., 1974), but the accompanying decrease in the bitumen/organic carbon ratio (Table 4) is not. It may be argued that radiation in conjunction with thermal stress may enhance petroleum formation. Although the collective effects of radiation and thermal stress are not addressed in the experiments of this study, published experimental results on hydrocarbons and polyethylene are available. ETIENNE and DE GAUDEMARIS (1967) address this collective effect on polymerization of C₉ through C₁₄ *n*-alkanes at temperatures as high as 350°C. In addition, CHAPIRO

(1962, p. 418) compared the yields of cross-linking in irradiated polyethylene up to a temperature of 250°C. Results from both of these studies indicate that radiation-induced polymerization is enhanced with increasing thermal stress. It is, therefore, unlikely that the combined effect of radiation and elevated temperatures will enhance petroleum formation.

CONCLUSIONS

Gamma ⁶⁰Co-irradiation of organic matter within and isolated from the Phosphoria Retort Shale has only minor effects at dosages between 81 and 885 Mrads. The observed damage is limited to extractable bitumen in the irradiated shale, with no detectable changes in the stable carbon isotopes, elemental composition (C, H, N, and O), or generated pyrolysates of the kerogen. Damage to the bitumens includes reductions in the bitumen/organic carbon ratios, acyclic isoprenoids relative to *n*-alkanes, and high-molecular weight acyclic carboxylic acids. These reductions are attributed to polymerization through radiation-induced cross-linking by a free-radical mechanism. High-molecular weight branched alkanes and acyclic carboxylic acids are particularly susceptible to radiation-induced dehydrogenation and subsequent cross-linking. Although the reductions in bitumen/organic carbon ratios and acyclic isoprenoids to *n*-alkanes are detectable in these experiments, they are not significant with respect to natural stratigraphic or regional variations to be considered diagnostic of natural radiation damage in black shales. Conversely, the loss of acyclic carboxylic acids with carbon numbers in excess of C₁₄ and loss of their even-carbon predominance may be considered diagnostic of experimental radiation damage, but this reduction has not been observed in the naturally irradiated Alum Shale. This discrepancy is attributed to the greater effectiveness of γ -rays and the more uniform irradiation in the ⁶⁰Co experiments. The overall preferences for radiation to induce polymerization through cross-linking rather than fragmentation through chain scission makes it unlikely that irradiation of organic matter will enhance petroleum formation. Generation of only trace amounts of hydrocarbon gases (i.e., methane and ethane) in these experiments also supports this conclusion.

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