CARBON ISOTOPE ANALYSES OF INDIVIDUAL HYDROCARBON MOLECULES IN BITUMINOUS COAL, OIL SHALE, AND MURCHISON METEORITE

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ABSTRACT

To study the origin of organic matter in meteorite, terrestrial rocks which contain organic compounds similar to the ones found in carbonaceous chondrites are studied and compared with Murchison meteorite. Hydrocarbon molecules were extracted by benzene and methanol from bituminous coal and oil shale and the extracts were partitioned into aliphatic, aromatic, and polar fractions by silica gel column chromatography. Carbon isotopic ratios in each fractions were analysed by GC-C-IRMS. Molecular compound identifications were carried by GC-MS Engine. Bituminous coal and oil shale show the organic compound composition similar to that of meteorite. Oil shale has a wide range of $\delta^{13}C$, -20.1‰ ~ -54.4‰ compared to bituminous coal, -25.2‰~-34.3‰. Delta values of several molecular compounds in two terrestrial samples are different. They show several distinct distributions in isotopic ratios compared to those of meteorite; Murchison meteorite has a range of $\delta^{13}C$ from -13‰ to +30‰. These results provide interpretation for the source and the formation condition of each rock, in particular alteration and migration processes of organic matter. Especially, they show an important clue whether some hydrocarbon molecules observed in meteorite are indigenous or not.

1. INTRODUCTION

The study of the origin of organic matter in extraterrestrial materials has played an important role in our understanding of life in the solar system over forty years. Two exciting ideas have emerged concerning possible relationships between meteorite and life on the Earth. One is that the primitive form of life was already present at the place where carbonaceous chondrites formed and these meteorites brought the precursor to our planet. The other is that impacts by huge meteoroids in early stage of the Earth led the course of biological evolution (Dodd 1986).

The chemical composition of organic compounds in a rock depends on source input, maturation, mineral catalysis, migration, and biodegradation (Tissot & Welte 1984). Carbon isotope analyses have been found useful to investigate the biological and nonbiological processes which occur in the geosphere, origin and evolution of petroleum and natural gases, coal-forming process and environments, and maturity of ancient sediments (Silverman & Epstein 1958, Eckelmann *et al.* 1962, Kvennolden & Squires 1967, Sackett & Menendez 1971, Stahl & Carey 1975, Tissot & Welte 1984, Lichtfouse *et al.* 1994a, 1994b, 1995). Especially, the study of organic matter in meteorite synthesized abiotically in the early stage of solar system history provides an important clue that more than one process occurred and several different environments were needed; dense interstellar clouds, the solar nebula, the surface regions of planetesimals, etc. (Cronin *et al.* 1988). Two laboratory models, the Fischer-Tropsch type process (Studier *et al.* 1972) and the Miller-Urey synthesis (Miller 1955) have been studied. A process that has become of interest in the context of prebiotic synthesis is an ion-molecule reaction in dense interstellar clouds (Watson 1976, Herbst 1985).

Organic matter can be classified into two kinds; (1) soluble matter which is extractable in organic solvents (amino acids, hydrocarbons, pigment, etc.) and (2) insoluble matter known as kerogen. Ideally, the extractable material can provide important information about the processes that produced it. But, this is also very likely from geologic or human contamination (Brownlow 1979). For the study of organic matter, contamination has been the most problematic. One should determine whether or not the observed organic matter is indigenous to the sample. Movement of organic compounds such as hydrocarbons can and does occur during geologic time. Varying ratios of $^{13}C/^{12}C$ for different fractions of a sample would suggest possible seepage of some material into the sample. It is called natural contamination. The other problem is laboratory contamination during sampling and laboratory analysis, which is due to the small amounts of some organic molecules (Sohn 1995, Sohn & Yang 1996).

Until very recently, the studies on organic matter were based on the isotopic ratio of total organic matter in a sample instead of each individual molecular compound. This method obviously has a limitation to investigate the origin and the synthetic processes of organic matter. Moreover, it is not easy to quantitatively sort out the contamination from the indigenous isotopic ratio of the sample. In this work, we study the chemical compositions and the carbon isotope ratios ($^{13}C/^{12}C$) of individual hydrocarbon molecules in extractable organic matter for bituminous coal and oil shale. And we compare these results of terrestrial materials with the Murchison meteorite (CM2) data in literature. This meteorite has been studied extensively by many workers, because of its relatively enriched abundance of primordial organic matter.

2. EXPERIMENTAL PROCEDURES

2.1 Sample Preparation

Bituminous coal was obtained from the Korea Coal Cooperation. Volatile material is 37.04%. 652mg sample was used for this work. Oil shale was obtained from the Korea Institute of Geology, Mining and Materials. It was collected at the Mahogany zone of the Green river (Miocene). 635mg of interior fragment of oil shale was used for this work. Each sample was crushed in a steel press and was ground to a fine powder in an agate mortar.

2.2 Extraction

The sample was placed in a pyrex container (inner diameter 17mm) with 30ml of benzene (HPLC grade, 99.94%; EM Science) - methanol (HPLC grade, 99.8%; EM Science) 9:1 solution. The container was connected to a vacuum line with a ground joint for evacuation of air. Our vacuum line consists of a mercury diffusion pump and a rotary pump which gives the vacuum pressure of better than 10^{-5}mbar. After the evacuation, the container was sealed off by a glass blowing. Then the container was placed in a furnace at 110°C for 24 hours.

2.3 Centrifugation and Desulfurization

The insoluble residue was removed by centrifugation at 15,000rpm for 10 minutes. If it was needed, centrifugation was done several times. The extract was concentrated to less than 10ml in a water bath at 80°C with a nitrogen stream. The nitrogen stream was obtained from a nitrogen tank (purity 99.999%) with a pipette ending.

Sulfur was removed from the concentrated extract by passing through a 3cm H×0.5cm ID column of Cu powder soaked with benzene. The packing materials of this column were 0.5cm height of sea sand (20~30 mesh, 99.8% SiO_2, 0.05% Al_2O_3, 0.05% Fe_2O_3; Showa Chemicals Inc.), 3cm height of Cu powder (200 mesh, chemical pure; Junsei Chemical Co. Ltd.), and 0.5cm height of sea sand. When sulfur passes the Cu powder, Cu is oxidized to CuS or CuS_2 (Cronin & Pizzarello 1990). The concentrated extract was pushed by a nitrogen stream to maintain a flow rate of one drop per 14~16 seconds. If the rate is too fast, sulfur is not completely removed. Column ending and collecting flask must be sealed from air with a rubber cap to prevent a quick evaporation.

2.4 Silica Gel Chromatography

The combined elution and column rinses were collected in a 50ml flask. The solution was evaporated to dryness on a 80°C water bath with a nitrogen stream and was redissolved with 5ml of distilled hexane (HPLC grade, 97.4%; EM Science) in an ultrasonicator. Then the hexane solution was concentrated to 1ml.

We used a 21cm H×1cm ID column packed with 1cm height of sea sand, 21cm height of silica gel (230~400 mesh; Merk), and 1cm height of sea sand. The silica gel was previously dried at 200°C over 12 hours to remove moisture which can affect the dropping rate. The hexane solution was applied to the column and eluted successively with 25ml each of hexane, benzene, and methanol. Because of the different polarity, each solvent gives aliphatic, aromatic, and polar hydrocarbon fractions (Sohn 1995). Each fraction was concentrated to $< 500\mu$l on a water bath with a nitrogen stream and then analysed by the following two methods.

2.5 Compound Identification

Individual hydrocarbon molecules in each fraction were identified by a GC-MS (Gas Chromatography - Quadrupole Mass spectrometer; Hewlett-Packard 5989B MS Engine) operated at 70eV with an interface temperature of 280°C. Organic compounds were separated by OV-1 capillary column (25m L×0.32mm ID, 0.4μm methyl polysiloxane cross-linked bonded phase). GC oven temperatures were programmed to provide the best separation. Oven temperature programs for three fractions are following: 40°C (2min) - 3°C/min (70min) - 250°C (30min) for hexane fraction, 40°C (4min) - 3°C/min (70min) - 250°C (30min) for benzene fraction, and 60°C (2min) - 3°C/min (63min) - 250°C (40min) for methanol fraction.

Each organic molecule separated by its molecular weight was injected into the quadrupole mass spectrometer and was fragmented by the electron bombardment. These ionized fragments provide electron impact (EI) spectra that show the mass of each molecule. Since each organic compound has its characteristic spectral cracking pattern, library search of EI spectra gives the compound identification (Mclafferty 1963, Mclafferty 1980, Message 1984).

2.6 Carbon Isotope Analyses

The eluted compounds were also analysed by GC-C-IRMS (Gas Chromatography - Combustion - Stable Isotope Ratio Mass Spectrometer; PRISM Series II VG Isotech) (Matthews & Hayes 1978, Hayes *et al.* 1990). Less than $1\mu l$ of sample was injected into the GC, which was operated by the same temperature program as GC-MS. Organic compounds were separated by OV-1 capillary column ($25m\,L\times0.25mm\,ID$, $0.3\mu m$ methyl polysiloxane cross-linked bonded phase). The separated compounds were completely combusted by passing through a CuO furnace at 850°C. The resulting combustion products were passed through a cryogenic trap maintained at -100°C for removal of water and then were injected into the source of the IRMS which was adapted for the operation at high He (purity 99.999%) pressure. The carbon isotopic ratios were determined for each compound. The isotope ratio was expressed in the usual delta (δ) notation as follows:

$$\delta^{13}C\ (\permil) = (\frac{^{13}C/^{12}C_{sample}}{^{13}C/^{12}C_{standard}} - 1) \times 1000 \qquad (1)$$

The standard for carbon is the Belemnite Americana from the Cretaceous Peedee Formation, South Carolina (PDB).

3. RESULT AND DISCUSSION

3.1 Chemical Compositions of Bituminous Coal and Oil Shale

Figure 1 shows the total ion chromatogram of the hexane fraction extracted from bituminous coal, which is expected to contain predominantly aliphatic hydrocarbons. The distribution is dominated by oleanene isomers, isoprenoid hydrocarbons, normal alkanes, and others. A common biochemical precursor for the oleanene and ursene isomers ($C_{30}H_{50}$) is squalene ($C_{30}H_{50}$) which is frequently occurring in higher plant and animal tissue (Tissot & Welte 1984). $C_{13}\sim C_{31}$ normal alkanes do not show any strong predominance of odd (or even) carbon-number homologues and are more abundant than adjacent isoprenoid hydrocarbons ($_iC_{18}\sim_iC_{20}$). This feature is typical for the hydrocarbons in mature samples; ancient sedimentary organic matter such as fossil fuels (Tissot *et al.* 1971, Tissot & Welte 1984, Lichtfouse *et al.* 1994a). This is due to the stability of normal alkanes. Isoprenoid hydrocarbons are thermally more labile than normal alkanes (Sassen & Moore 1988, Price 1993). The pristane ($_iC_{19}$)/phytane ($_iC_{20}$) ratio is 5 (greater than 1), which suggests that bituminous coal was synthesized at less reducing paleo-conditions (Tissot & Welte 1984).

Figures 2 and 3 show the total ion chromatograms of benzene and methanol fractions of bituminous coal. These fractions are aromatic and polar hydrocarbons. Benzene fraction shows ursenol (peak number 1 in Figure 2), dichlorobenzene (peak number 2 in Figure 2), diethoxy-dinitro-m-quaterphenyl (peak number 5 in Figure 2), alkylbenzenes (marked $\bar{a}$ in Figure 2), several alkyl
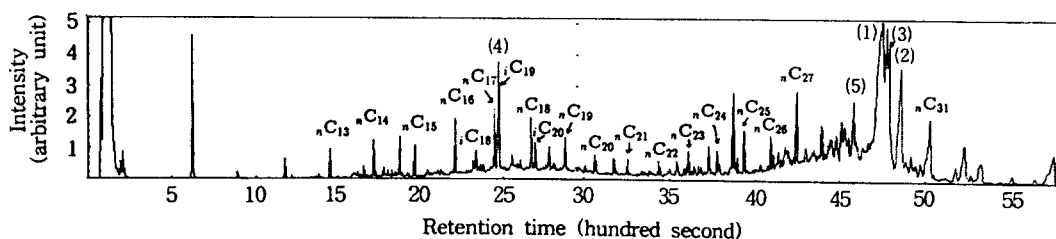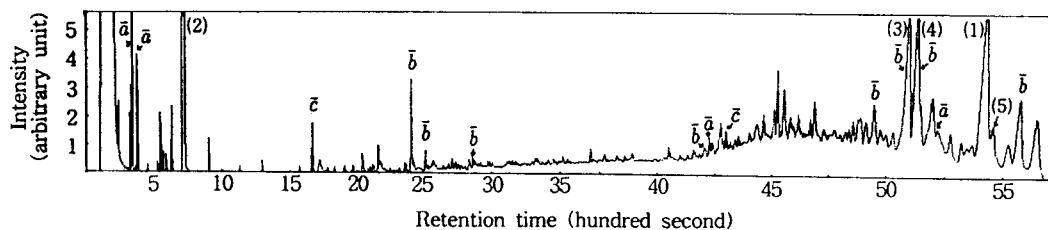
Figure 1. The total ion chromatogram of hexane fraction extracted from bituminous coal. Oven temperature program is 40°C (2min) & 3°C/min (70min) & 250°C (30min). Most abundant five peaks are identified as follows: (1) olean-13(18)-ene; (2) olean-12-ene; (3) olean-18-ene; (4) 2,6,10,14-tetramethylpentadecane ($_iC_{19}$); (5) urs-12-ene. $_nC_{13\sim31}$ indicate normal alkanes. $_iC_{18\sim20}$ indicate isoprenoid hydrocarbons.

Figure 2. The total ion chromatogram of benzene fraction extracted from bituminous coal. Oven temperature program is 40°C (4min) & 3°C/min (70min) & 250°C (30min). Most abundant five peaks are identified as follows: (1) 16β,18α,19α-urs-20-en-16-ol; (2) 1,4-dichlorobenzene; (3) 2,2,3a,9-tetramethyl-1,2,3,4,5,6-hexahydro-picene; (4) 2,3-di(p-methylphenyl)-1H-inden-1-one; (5) 2′,4″-diethoxy-2″,6′-dinitro-m-quaterphenyl. Alphabetic symbols represent: $\bar{a}$ alkylbenzene; $\bar{b}$ alkyl substituted polycyclic hydrocarbon; $\bar{c}$ alkylphenol.
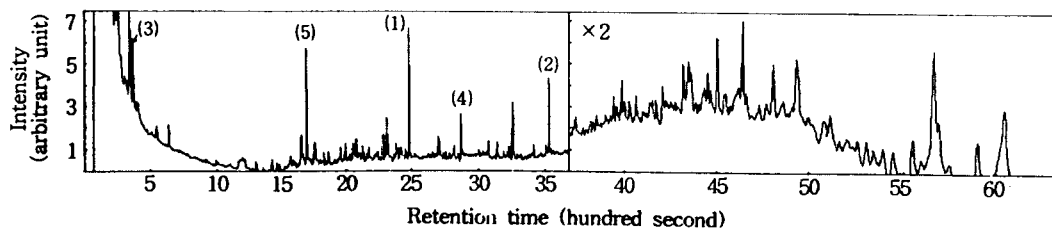

Figure 3. The total ion chromatogram of methanol fraction extracted from bituminous coal. Oven temperature program is 60°C (2min) & 3°C/min (63min) & 250°C (40min). Most abundant five peaks are identified as follows: (1) 1,2-benzenedicarboxylic acid, dibutyl ester; (2) 1,2-benzenedica- rboxylic acid, diisooctyl ester; (3) phenol; (4) octadecanoic acid, methyl ester; (5) 1,2-benzenedicar- boxylic acid, diethyl ester.

substituted polycylcic hydrocarbons (marked $\bar{b}$ in Figure 2), alkylphenol (marked $\bar{c}$ in Figure 2), etc. Methanol fraction shows mainly benzenedicarboxylic acid driven esters and phenol. According to Gallegos (1978), the relative concentration of polycyclic hydrocarbons increases with the age of the coal. This indicates that our coal is not young.

Figure 4 shows the total ion chromatogram of hexane fraction extracted from oil shale. In contrast to bituminous coal, hexane fraction shows that odd carbon-number normal alkanes are more abundant than even homologues and isoprenoid hydrocarbons are more abundant than their adjacent normal alkanes. The pristane ($_iC_{19}$)/phytane ($_iC_{20}$) ratio is 1/3 and norlupane series (carbon number $= 29$; peak number 1, 3, and $\bar{a}$ in Figure 4) are major components. These reflect that this oil shale is immature sedimentary rock (Dunton & Hunt 1962, Han *et al.* 1968, Tissot & Welte 1978, Lichtfouse *et al.* 1994a) and agree with the reports for this sample (Johns *et al.* 1966, Tissot *et al.* 1978). This hexane fraction also shows various contribution of source organisms. For example normal C_{17} alkane was probably derived from algae (Oró & Nooner 1966, Johns *et al.* 1966, Clark & Blumer 1967, Oró *et al.* 1967). Higher weight molecular weight odd carbon number normal alkane ($_nC_{27}$) may be derived from cuticular waxes of higher plants (Martin *et al.* 1963). Sterane (cholestane; peak $\bar{b}$ in Figure 4) and pentacyclic triterpanes (norlupane isomers) have been reported to be deriven also from higher plants. They occur frequently in ancient sediments buried to shallow depths (Tissot & Welte 1984) and were identified in Green River shales (Hills *et al.* 1966, Anderson *et al.* 1969).

Figures 5 and 6 show the total ion chromatograms of benzene and methanol fractions of oil shale. In contrast to bituminous coal, benzene fraction of oil shale hardly shows any major peaks after 5000sec. This may be interpreted as that bituminous coal is more aromatized than oil shale, which agrees with the fact that bituminous coal is more mature. Methanol fraction also shows quite different composition compared to bituminous coal. Only one peak (number 5 in Figure 6) out of five major peaks appears in the spectrum of bituminous coal. This shows that ion chromatograms of benzene and methanol fractions could provide important clues for the formation condition of the sample.

3.2 Check of Contamination Level in This Work

The blank experiment was performed following the identical procedure for the sample to evaluate the level of contamination during the sample preparation and extensive analytic procedures. Hexane fraction shows peaks of normal alkanes ($C_{23} \sim C_{29}$) and benzene fraction shows peak of p-xylene. Compared to the samples these blanks are not significant. We estimate that the blank contamination level of hexane fraction is less than 12%, which comes from the measurement of normal hexacosane. These contaminations are due to sample handling, chemical treatment procedure, and impurities in the solvents. Methanol fraction shows insignificant peaks which are not important peaks for our samples.

3.3 Carbon Isotope Measurements of Bituminous Coal and Oil Shale

Since we handle very small amount of sample and there are various peak sizes of organic compounds, we should determine how the isotopic ratio measurements depend on the size of the organic compound. We used normal dodecane ($\delta^{13}C$ value -28.6‰) of predetermined quantity. The flow rate of reference CO_2 gas which is injected into the mass spectrometer before and after the sample run was adjusted to give the $^{44}CO_2$ beam size of $7.5 \times 10^{-8} \sim 8.8 \times 10^{-8}$ Ampere for all measure
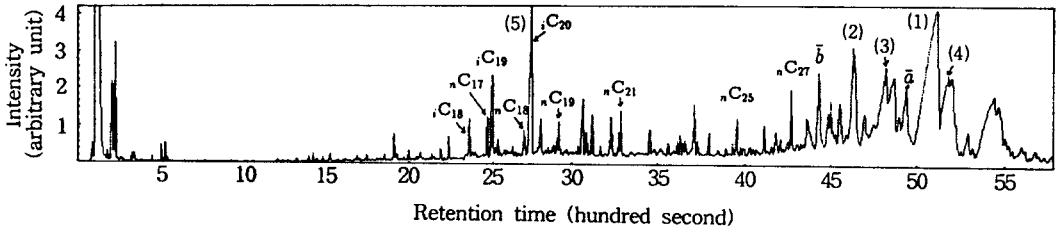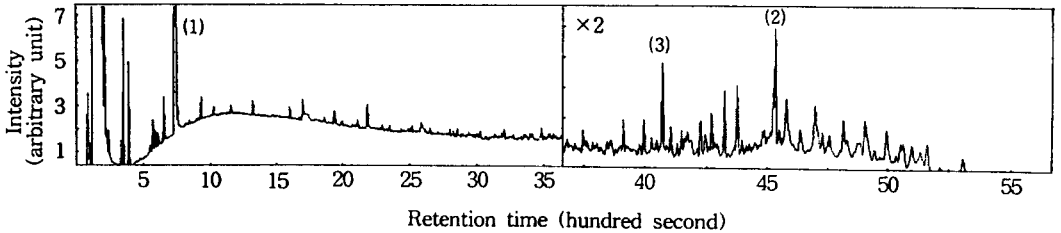
Figure 4. The total ion chromatogram of hexane fraction extracted from oil shale. Oven temperature program is 40°C (2min) & 3°C/min (70min) & 250°C (30min). Most abundant five peaks are identified as follows: (1) 24-nor-lupan-3-one; (2) 3,5-dicyclopentyl-6-methyl-3,4-heptadien-2-one; (3) 17-β(H)-28-norlupane; (4) (22-Z)-dehydrocholesterol-1-ether; (5) 2,6,10,14-tetramethylhexadecane ($_i$C$_{20}$). $_n$C$_{17\sim27}$ indicate normal alkanes. $_i$C$_{18\sim20}$ indicate isoprenoid hydrocarbons. Symbol $\bar{a}$ indicates 17-α(H)-28-norlupane and $\bar{b}$ indicates colestane.

Figure 5. The total ion chromatogram of benzene fraction extracted from oil shale. Oven temperature program is 40°C (4min) & 3°C/min (70min) & 250°C (30min). Most abundant three peaks are identified as follows: (1) 1,3-dichlorobenzene; (2) 2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-tetracosahexaene; (3) 1,2-benzenedicarboxylic acid, diisooctyl ester.
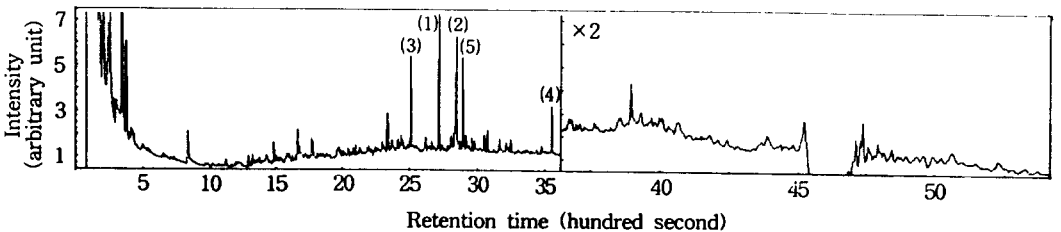

Figure 6. The total ion chromatogram of methanol fractions extracted from oil shale. Oven temperature program is 60°C (2min) & 3°C/min (63min) & 250°C (40min). Most abundant five peaks are identified as follows: (1) 2,4,6-trimethyl-4'-methoxy-diphenyl-amine; (2) .α.-(2-phenylethenyl)-1-piperidineacetonitrile; (3) hexadecanoic acid, methyl ester; (4) di-(2-ethylhexyl)phthalate; (5) octadecanoic acid, methyl ester.
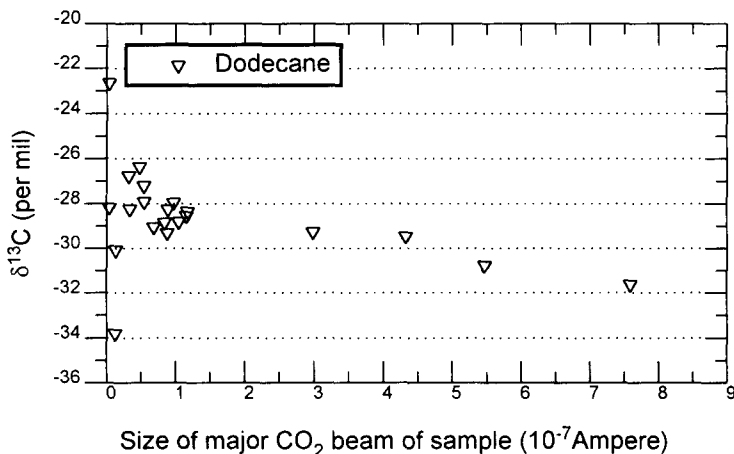
Figure 7. Dependence of $\delta^{13}C$ on the amount of a sample. The size of reference major CO_2 beam was maintained at $7.5 \times 10^{-8} \sim 8.8 \times 10^{-8}$ Ampere. When the size of sample major CO_2 beam is within the range of $5 \times 10^{-8} \sim 4 \times 10^{-7}$ Ampere isotopic value is independent of the beam size with a standard deviation of $0.7\%_0$. If we consider all measured data, the $\delta^{13}C$ of dodecane becomes $-28.7\%_0 \pm 2.2\%_0$.

ments. Figure 7 shows the result. As long as the $^{44}CO_2$ beam size of a sample is between 5×10^{-8} and 4×10^{-7} Ampere, this size effect does not contribute more than $0.7\%_0$ for the $\delta^{13}C$ value of the sample.

The carbon isotope ratios of individual hydrocarbon molecules extracted from bituminous coal and oil shale are shown in Figure 8. Standard mixtures were also shown for comparison. Standard mixtures consist of artificial organic compounds which contain normal alkane ($C_5 \sim C_{18}$) for aliphatic hydrocarbons; naphthalene, biphenyl, and acenaphthene for aromatic hydrocarbons; methyl acetophenone meta, methyl acetophenone para, and benzophenone for polar hydrocarbons.

The isotopic ratios of most organic compounds in bituminous coal and oil shale range from $-20\%_0$ to $-35\%_0$, which agrees the ranges reported in sedimentary organic material and coal. Some of the values less than $-35\%_0$ may be due to co-elution problem. This tends to appear at the latter part of retention spectra. However the low $\delta^{13}C$ values should be better attributed to methanogenic bacteria and their metabolic processes (Strauss 1986). Such extremely ^{13}C depleted organic compound may represent special conditions during the evolution of life forms (Hoefs 1987).

The ranges of $\delta^{13}C$ of three fractions in bituminous coal are quite similar each other; $-26.0\%_0 \sim -34.3\%_0$ for hexane, $-25.2\%_0 \sim -33.2\%_0$ for benzene, and $-28.6\%_0 \sim -32.6\%_0$ for methanol. The intervals of the $\delta^{13}C$ values of these three fractions are $4\%_0 \sim 8\%_0$. Craig (1953, 1957a, 1957b) reported the range of $-21.1\%_0 \sim -26.7\%_0$ for coal. This range shows the influence of different source inputs, synthetic processes, and degree of thermal maturation (Redding *et al.* 1980, Peters *et al.* 1981, Smith *et al.* 1982, Lewan 1983, Arthur *et al.* 1985). On the contrary, oil shale shows a wide distribution
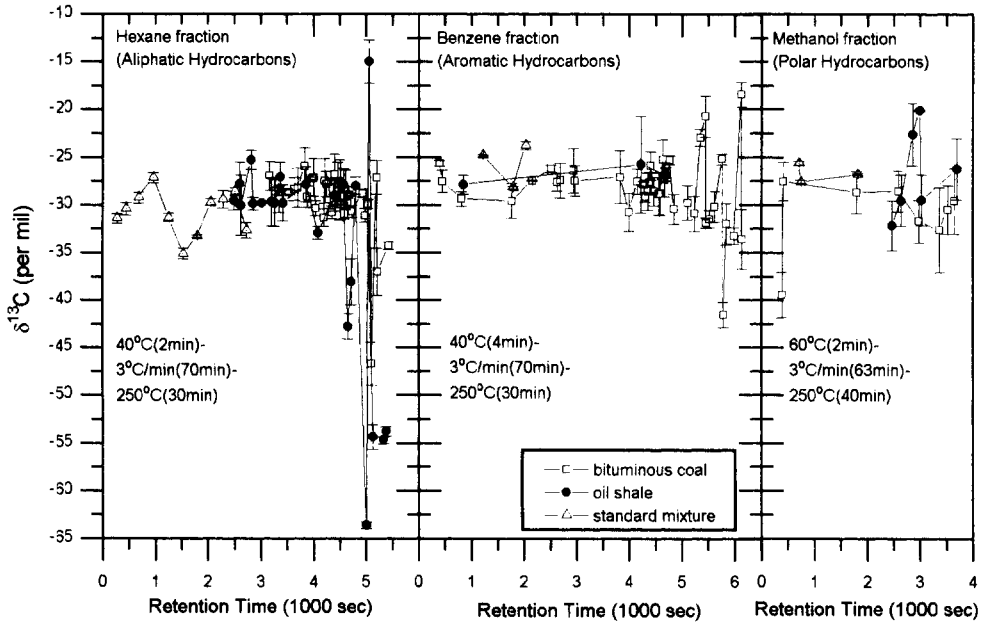
Figure 8. Carbon isotope ratios of organic molecules in bituminous coal, oil shale, and standard mixture. The error bar indicates the standard deviation of each delta value, which was obtained by three repeated measurements.

of isotopic ratio in hexane fraction (-25.3‰~-54.4‰) and methanol fraction (-20.1‰~-32.1‰). The isotopic data of co-eluted peaks are excluded from the range. The range of $\delta^{13}C$ in benzene fraction is -25.7‰~-27.9‰. Oil shale may have been originated from the sources which contain organic carbons of diverse $\delta^{13}C$ values. Silverman & Epstein (1958) reported that the total isotopic ratio of extractable organic matter in Green River shale (Eocene) is -30.5‰, with which our results agree.

The $\delta^{13}C$ ranges of C3 plants, CAM plants, and eukaryotic algae (Schidlowski *et al.* 1983) are similar to our results of bituminous coal and oil shale, which means that C3 and CAM plants and eukaryatic algae could have been the sources of bituminous coal and oil shale. The $\delta^{13}C$ values of bituminous coal and oil shale are consistent with the values of organic matters of non-marine origin (Craig 1953, Silverman & Epstein 1958). Besides various sources there are several parameters such as thermal alteration and degradation, which affect isotopic ratio. It is consistent with the analyses of chemical compositions.

3.4 Comparison with Murchison (CM2) Meteorite

Murchison meteorite has been studied extensively by many workers, because of its relatively enriched abundance of primordial organic matter. Organic compounds founded in Murchison meteorite (Krishnamurthy *et al.* 1992) such as normal alkanes, isoprenoid hydrocarbons, branched-alkyl-

substituted cycloalkanes, phenanthrene, biphenyl, and $C_{20}H_{12}$ isomers are found in bituminous coal and oil shale. But, the organic carbon extracted from Murchison meteorite is enriched in ^{13}C relative to terrestrial organic carbon. Reported $\delta^{13}C$ values of various fractions for Murchison are following; hexane -13‰~-5‰, benzene -6‰~-5‰, methanol +5‰ ~+6‰, amino acid fraction +23.1‰, carboxylic acid fraction +6.7‰, the individual amino acids +5‰~+30‰ (Epstein *et al.* 1987, Engel *et al.* 1990, Krishnamurthy *et al.* 1992). These values are quite different from those of bituminous coal and oil shale. It is important to note that the exact delta value for each fraction could play a role in interpretation of the formation and the evolution of meteorite.

Gilmour & Pillinger (1994) performed the isotope analyses of individual polycyclic aromatic hydrocarbons using the same method as this work. The isotopic ratios are following: phenanthrene -7.5‰, fluoranthene -5.9‰, pyrene -13.1‰, chrysens -14.5‰, benzo(ghi)fluoranthene -14.2‰, benzo(e)pyrene -22.3‰±4.1‰, and benzo(j)fluoranthene -15.4‰. Compared with bituminous coal, which has phenanthrene -27.5‰, benzo(a)pyrene -28.8‰±2.2‰, and alkyl benzenes -25‰~-30‰, Murchison meteorite has enriched ^{13}C organic compounds. Moreover, the $\delta^{13}C$ of benzopyrene isomer in bituminous coal and the Murchison meteorite are similar, which implies that there might be a contamination problem.

Sohn (1995) and Sohn & Yang (1996) reported the isotopic ratios of individual hydrocarbon molecules in hexane, benzene, and methanol fractions for Murchison meteorite. Each fraction has $\delta^{13}C$ as follows; hexane fraction -13.3‰~-39.7‰, benzene fraction -5.8‰~-39.4‰, and methanol fraction -15.5‰~-58.3‰. Pristane -18.6‰ and phytane -17.1‰ differ from bituminous coal (-30.1‰, -28.4‰) and oil shale (-30.1‰, -29.9‰). Most isotopic ratios are similar to our results of bituminous coal and oil shale, except a few cases in benzene and methanol fractions. This shows that contamination problems in meteorite study can be serious. The nature of aliphatic hydrocarbons of the Murchison meteorite has been a matter of some controversy (Cronin & Pizzarello 1990, Krishnamurthy *et al.* 1992).

4. CONCLUSION

The distribution of n-alkane in bituminous coal does not show any strong predominance of odd (or even) carbon-number homologues, typical pattern occurring in ancient sedimentary organic matter. Oil shale shows predominance of odd carbon-number alkanes, typical pattern occurring in immature organic matter. The $\delta^{13}C$ values of most organic compounds in bituminous coal and oil shale are from -20‰ to -35‰. Several heavy organic compounds of hexane fraction of bituminous coal and oil shale show very negative $\delta^{13}C$ values up to -65‰, which may be due to co-elution effect or bacteria origin. The broad ranges of delta values show various source input and synthetic processes.

Murchison meteorite shows the organic compound compositions similar to those of bituminous coal and oil shale. But a notable difference in $\delta^{13}C$ between terrestrial material and meteorite is important to understand the origin and evolution of organic matter in meteorite. The positive $\delta^{13}C$ shows that the organic matter in meteorite should be synthesized by other processes than terrestrial one and influenced by extraterrestrial sources. Contamination problem must be considered seriously for the study of small samples. Especially aliphatic hydrocarbons are easy to be contaminated by

terrestrial material. The $\delta^{13}C$ values of each compound provide whether its origin is terrestrial or extraterretrial.

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