Selective release of D and ^{13}C from insoluble organic matter
of the Murchison meteorite by impact shock

Koichi MIMURA[1]*, Michioki OKAMOTO[1], Kenichiro SUGITANI[2], and Shigemasa HASHIMOTO[3]

[1]Department of Earth and Environmental Sciences, Nagoya University, Nagoya, 464-8602, Japan
[2]Department of Environmental Engineering and Architecture, Nagoya University, Nagoya, 464-8601, Japan
[3]Hydrospheric Atmospheric Research Center, Nagoya University, Nagoya, 464-8601, Japan
*Corresponding author. E-mail address: mimura@eps.nagoya-u.ac.jp

Abstract–We performed shock-recovery experiments on insoluble organic matter (IOM) purified from the Murchison meteorite, and determined the abundances and isotope ratios of hydrogen and carbon in the shocked IOM sample. We also performed shock experiments on type III kerogen and compared the results of these experiments with the experimental results regarding IOM.

The shock selectively released D and ^{13}C from the IOM, while it preferably released H and ^{12}C from the kerogen. The release of these elements from IOM cannot be explained in terms of the isotope effect, whereas their release from kerogen can be explained by this effect. The selective release of heavier isotopes from IOM would be due to its structure, in which D and ^{13}C-enriched parts are present as an inhomogeneity and are weakly attached to the main network. Shock gave rise to a high release of D even at a lower degree of dehydrogenation compared with the stepwise heating of IOM. This effective release of D is probably an inherent result of shock, in which a dynamic high-pressure and high-temperature condition prevails. Thus, shock would effectively control the hydrogen isotope behavior of extraterrestrial organic matter during the evolution of the solar nebula.

INTRODUCTION

Insoluble organic matter (IOM) is a major component of organic materials in carbonaceous meteorites (Cronin and Chang 1993). IOM of CM2 chondrites amounts to 54% of their total carbon content (Smith and Kaplan 1970). IOM is obtained by HF-HCl acid digestion methods and is characterized by complicated structures containing polycyclic aromatic hydrocarbon ring systems cross-linked by short methylene chains, ethers, sulfides, and biphenyl groups (Hayatsu et al. 1977, 1980; Murae 1995; Sephton et al. 2004a). Recently, the structure of IOM has been researched by new methods (Gardinier et al. 2000; Derenne et al. 2005; Remusat et al. 2005a; Remusat et al. 2005b).

It is thought that IOM is genetically related to organic materials originating in interstellar medium (ISM), because the IOM shows extremely high δD (+410‰ to +2500‰) (e.g., Robert and Epstein 1982; Kerridge 1983; Yang and Epstein 1984). In fact, Wdowiak et al. (1988) reported that the IOM of the Orgueil meteorite exhibits a spectral signature similar to that observed in the infrared emission spectrum from the Orion Nebula. However, the δD of IOM in meteorites is quite different from those of organic materials in ISM (+12,000‰ to +380,000‰) (Robert 2002), thus indicating that IOM was not formed directly from pristine ISM. The IOM in meteorites must have experienced a variety of events during their evolution. A ubiquitous event in space is impact shock, which generates high-temperature and high-pressure conditions; such a shock should influence the isotope ratios as well as the chemical compositions in precursors of IOM, because organic materials are very sensitive to changes in temperature-pressure conditions.

Shock experiments regarding extraterrestrial organics would allow us to gain useful information concerning the chemical composition and isotope ratio in the evolutionary process of ISM to carbonaceous chondrites. Shock experiments on organic materials have been reported in several studies (e.g., Tingle et al. 1992; Mimura 1995; Peterson et al. 1997; Tyburczy et al. 2001; Mimura et al. 2005a, 2005b, 2005c), but no study has impacted extraterrestrial organics and determined their chemical compositions and isotope ratios.

In the present study, we performed shock-recovery experiments using IOM of the Murchison meteorite and determined the abundances and isotope ratios of hydrogen and carbon in the shocked sample. We also conducted shock

experiments on type III kerogen of a semianthracite in order to compare the results of these experiments with the experimental results regarding IOM. In the present paper, we report the fluctuation of chemical composition and isotope ratio following various shock pressures for the two starting materials, and discuss the importance of shock in the isotope evolution of extraterrestrial organic materials.

EXPERIMENTAL PROCEDURE

Shock-Recovery Experiment

Shock-recovery experiments were carried out according to a procedure previously reported (Mimura et al. 2004, 2005a, 2005b). A sample of starting material was pressed into a shock apparatus (made of SUS 304), and the apparatus was then impacted with a flyer plate (SUS 304) attached to a projectile (polycarbonate). After the shocked sample was recovered, the abundances and isotope ratios of hydrogen and carbon in the sample were determined (see Mimura et al. 2005c). For each shocked sample, the peak shock pressure, initial shock pressure, shock temperature, and residual temperature (Table 1) were estimated using methods similar to those described by Mimura et al. (2004, 2005b).

Starting Materials

IOM

IOM was purified from 16 g of the Murchison meteorite referring to the procedure reported by Kerridge et al. (1987). The purification procedure is outlined in Fig. 1. A fresh inner part of the Murchison meteorite was pulverized finer than 100 μm using an agate ball mill. The pulverized sample was extracted using a Soxhlet apparatus employing a mixture of dichloromethane and methanol (7/1: v/v) to remove soluble organic materials and elemental sulfur. After the extracted sample was treated with HCl to dissolve carbonate minerals, the sample was digested by a mixture of HF-HCl to eliminate silicate minerals. The digested sample was extracted using the Soxhlet apparatus again and was sequentially treated with HCl to leach Fe and Ni from FeS and NiS, respectively. The leached sample was extracted using the Soxhlet apparatus to remove soluble organic materials and elemental sulfur. The two sequential steps of the HCl leaching and the Soxhlet extraction were repeated three times. The purified IOM occupied 1.6 wt% of the Murchison meteorite and contained H: 3.0 wt%, C: 54.9 wt%, N: 1.6 wt%, and S: 4.3 wt%. Because floating black materials were lost during the purification process, the amount of IOM (1.6 wt%) would be the minimum value.

Dichloromethane and methanol were distilled once before use; hydrochloric acid and hydrofluoric acid of high-purity grade reagents were used without further purification. Most of the apparatus was baked at 450 °C for 4 h before use to avoid surrounding contamination. Any apparatus that was unstable in heat was rinsed with distilled dichloromethane.

To examine the evolution of interstellar organics, starting materials should be prepared in a condition similar to that of ISM. Interstellar dust particles are thought to be refractory organic materials containing silicate minerals, and the volume ratio of organic mantles to the silicate core is highly valuable, $V_{or}/V_{sil} = 0.23$–2 (Greenberg and Li 1996; Tielens et al. 1996; Greenberg 1998). We used mixtures of the IOM and olivine at a mixing ratio of 120.3 mg/600.4 mg ($V_{or}/V_{sil} = 0.52$) as a starting material. The olivine sample was composed mainly of forsterite and was pulverized finer than 100 μm.

Type III Kerogen

Type III kerogen was prepared from a semianthracite of the Yubari coal mine, Japan, using the same process as the purification of IOM from the Murchison meteorite. The kerogen sample contained H: 4.5 wt%, C: 75.2 wt%, N: 2.0 wt%, and S: 1.5 wt%. The kerogen and the olivine powder were mixed at a ratio of 200.5 mg/800.9 mg ($V_{or}/V_{sil} = 0.65$) as a starting material. Type III kerogen shows C/H molar ratio and ^{13}C-NMR spectrum similar to those of IOM in the Murchison meteorite (Miknis et al. 1984; Cronin et al. 1987). Kerogen of low volatile bituminous coal may, however, be more suitable for an analogue of IOM in the Murchison meteorite compared with the type III kerogen of semianthracite (Sephton et al. 2004a).

RESULTS AND DISCUSSION

Dehydrogenation and Decarbonization

The abundances of hydrogen and carbon in shocked IOM samples decrease with increasing shock pressure (Tables 1 and 2), indicating that the shock promotes dehydrogenation and decarbonization from the IOM. The dehydrogenation and the decarbonization from IOM similarly occur in a lower pressure range (5.1–21.5 GPa in peak shock pressure), while in a higher pressure range (22.5–37.0 GPa), dehydrogenation occurs more dominantly than does decarbonization (Figs. 2a and 2b). This degassing feature is also indicated from the data regarding the C/H molar ratio in shocked IOM samples; that is, the C/H ratio rapidly increased in the higher pressure range (Tables 1 and 2). The difference between dehydrogenation and decarbonization would be caused by the volatility of shock products. The shock products containing hydrogen are mainly H_2, H_2O, and low molecular weight hydrocarbons (Mimura et al. 1995, 1998), which tend to be lost from the shocked samples. Whereas some of the carbon-bearing products are of CO, CO_2, and low molecular weight hydrocarbons, which are entirely degassed, most of the carbon-bearing products comprising refractory materials such as amorphous carbon would remain in the shocked samples and inevitably increase the samples' C/H ratio.

Table 1. Summary of shock experiments for IOM and type III kerogen.

Sample	Initial density (g cm^{-3})	Projectile velocity (km s^{-1})	Peak shock pressure[a] (GPa)	Initial shock pressure[b] (GPa)	Shock temperature[c] (K)	Residual temperature[c] (K)
Mixture of olivine and IOM with mixing ratio of olivine/IOM = 600.4 mg/120.3 mg						
I00001[d]	2.61[e]	–	–	–	–	–
I01001	2.33 ± 0.05	0.27 ± 0.01	5.1 ± 0.2	1.0 ± 0.1	410	310
I01002	2.38 ± 0.05	0.49 ± 0.01	9.6 ± 0.2	2.0 ± 0.1	500	340
I01005	2.33 ± 0.05	0.53 ± 0.01	10.4 ± 0.2	2.2 ± 0.1	520	340
I01003	2.35 ± 0.05	0.76 ± 0.01	15.4 ± 0.2	3.4 ± 0.1	630	380
I01007	2.37 ± 0.05	0.89 ± 0.01	18.4 ± 0.2	4.2 ± 0.1	700	400
I01004	2.36 ± 0.05	1.02 ± 0.01	21.5 ± 0.2	4.9 ± 0.1	780	430
I01011	2.19 ± 0.05	1.06 ± 0.01	22.5 ± 0.2	5.2 ± 0.1	800	440
I01006	2.37 ± 0.05	1.18 ± 0.02	25.4 ± 0.3	5.9 ± 0.1	880	460
I01012	2.15 ± 0.05	1.39 ± 0.02	30.8 ± 0.3	7.3 ± 0.1	1030	520
I01014	2.37 ± 0.05	1.62 ± 0.02	37.0 ± 0.3	9.0 ± 0.1	1210	580
Mixture of olivine and type III kerogen with mixing ratio of olivine/type III kerogen = 800.9 mg/200.5 mg						
F00001[d]	2.51[f]	–	–	–	–	–
F01002	2.05 ± 0.05	0.31 ± 0.01	5.9 ± 0.2	1.2 ± 0.1	430	310
F01003	2.14 ± 0.05	0.48 ± 0.01	9.3 ± 0.2	2.0 ± 0.1	500	330
F01004	2.02 ± 0.05	0.66 ± 0.01	13.2 ± 0.2	2.9 ± 0.1	580	360
F01008	2.12 ± 0.05	0.89 ± 0.01	18.4 ± 0.2	4.2 ± 0.1	700	400
F01005	2.08 ± 0.05	1.01 ± 0.01	21.2 ± 0.2	4.9 ± 0.1	770	430
F01006	2.06 ± 0.05	1.17 ± 0.02	25.2 ± 0.3	5.9 ± 0.1	880	460
F01013	2.01 ± 0.05	1.42 ± 0.02	31.6 ± 0.3	7.5 ± 0.1	1050	520
F01011	2.09 ± 0.05	1.47 ± 0.02	32.9 ± 0.3	7.9 ± 0.1	1090	540
F01014	2.00 ± 0.05	1.62 ± 0.02	37.0 ± 0.3	9.0 ± 0.1	1210	580

[a]Peak shock pressure was calculated using a one-dimension-impedance-match solution. Equation of state parameters for stainless steel (SUS 304) was taken from Marsh (1980).

[b]Initial shock pressure was calculated, assuming that starting materials consist of nonporous pyrene. Equation of state parameters for pyrene was taken from Marsh (1980).

[c]Shock and residual temperatures are mean temperatures of calculated initial shock and peak shock pressures, using physical properties of pyrene.

[d]Unshocked starting materials.

[e]This value is estimated from densities of olivine (3.30 g cm^{-3}) and IOM (1.28 g cm^{-3}: the density of pyrene), and the mixing ratio of them.

[f]This value is estimated from densities of olivine (3.30 g cm^{-3}) and type III kerogen (1.28 g cm^{-3}: the density of pyrene), and the mixing ratio of them.

For kerogen samples, dehydrogenation occurs easily in comparison with the decarbonization in the high pressure range, as observed in the experiments involving the IOM samples. The degassing process increased the C/H ratio in the shocked kerogen samples (Table 2). When we compare the case of kerogen with that of IOM, we notice that, in a high shock pressure range, kerogen samples release less hydrogen than do the IOM samples (Fig. 2). On the other hand, we observed no difference in the decarbonization feature between kerogen and IOM (Fig. 2). The difference of dehydrogenation between the two starting materials indicates that the chemical structure of kerogen is dissimilar to that of IOM, although they are generally acknowledged to be similar to each other. Moreover, our experimental results suggest that some of the hydrogen contained in the IOM combined less firmly with the IOM's main network.

Behavior of Hydrogen Isotopes

The shock process changed the δD of IOM samples. The change ranged from +854‰ of the starting material to +235‰ of the I01014 sample (Table 2). The behavior of hydrogen isotopes versus dehydrogenation is shown in Fig. 3. The D/H factor ([D/H ratio of sample]/[D/H ratio of starting material]) simply decreases from 1 of the starting material to 0.67 of I01014 as dehydrogenation proceeds, indicating that D is emitted preferentially over H from the IOM. In contrast, the D/H factor of kerogen barely increased to 1.04 of the F010014 sample. This result shows that the shock easily releases H compared with D from the kerogen.

The dehydrogenation of organic materials is caused mainly by the dissociation of C-H, C-D, O-H, and O-D bonds, and the energy of dissociation (ED) varies for each bond. Because $ED_{C-H} < ED_{C-D}$ and $ED_{O-H} < ED_{O-D}$, D should remain in the degassed samples. Therefore, the D/H factor of shocked samples is expected to be larger than that of the starting materials. This feature can be ascribed to the mass difference of isotopes (isotope effect). This expectation is consistent with the shock-induced results of kerogen. However, the isotope behavior of the IOM samples cannot be explained by the isotope effect; the effects of the chemical structure of the IOM have to be taken account when analyzing
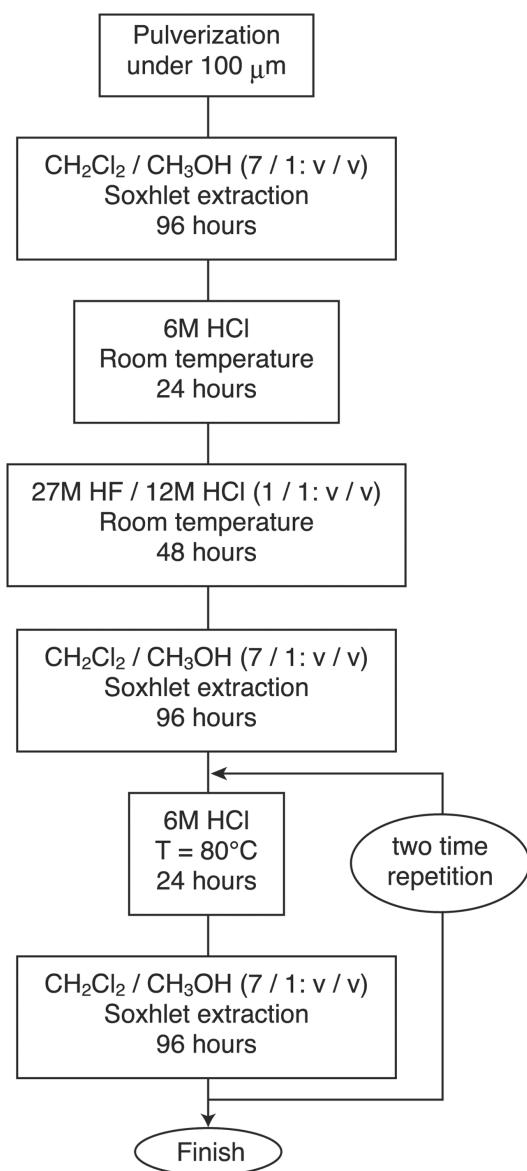
```
┌─────────────────────────┐
│    Pulverization        │
│    under 100 μm         │
└─────────────────────────┘
              │
┌─────────────────────────┐
│ CH₂Cl₂ / CH₃OH (7 / 1: v / v) │
│   Soxhlet extraction    │
│        96 hours         │
└─────────────────────────┘
              │
┌─────────────────────────┐
│       6M HCl            │
│   Room temperature      │
│        24 hours         │
└─────────────────────────┘
              │
┌─────────────────────────┐
│ 27M HF / 12M HCl (1 / 1: v / v) │
│   Room temperature      │
│        48 hours         │
└─────────────────────────┘
              │
┌─────────────────────────┐
│ CH₂Cl₂ / CH₃OH (7 / 1: v / v) │
│   Soxhlet extraction    │
│        96 hours         │
└─────────────────────────┘
              │
┌─────────────────────────┐      ╭──────────╮
│       6M HCl            │      │ two time │
│      T = 80°C          │      │repetition│
│        24 hours         │      ╰──────────╯
└─────────────────────────┘
              │
┌─────────────────────────┐
│ CH₂Cl₂ / CH₃OH (7 / 1: v / v) │
│   Soxhlet extraction    │
│        96 hours         │
└─────────────────────────┘
              │
          ╭────────╮
          │ Finish │
          ╰────────╯
```

Fig. 1. A flow chart of the purification process used to prepare IOM of the Murchison meteorite and type III kerogen of a semianthracite from the Yubari coal mine.

the isotope behavior. The selective release of D suggests an inhomogeneous distribution of D in IOM. D-enriched parts are weakly bound to the main network of IOM, compared with H-enriched parts. The D-enriched part would be easily cut from the main network and decomposed into hydrogen- and/or carbon-bearing materials with low molecular weights, which are readily lost from the shocked IOM sample. Some scenarios of IOM formation have been provided, by paying attention to the peculiar isotope distribution in IOM. Kerridge et al. (1987) suggested that highly D-enriched materials originated in ISM were mixed together and interacted during a regolith episode on the parent body, consequently formed

IOM showing much lower D/H ratios than ISM. On the other hand, Remusat et al. (2006) proposed that pristine IOM with low D/H ratio formed in the protosolar nebula; then the IOM acquired its high D/H ratio by an exchange with a D-enriched reservoir at the surface of the protosolar disk. We cannot judge which scenario is more appropriate, using our recent data.

The δD values of hydrogen degassed from the IOM during shock are roughly estimated to range from +1200‰ to +2400‰, using the δD values in recovered samples and their dehydrogenation degree. As described above, the degassed hydrogen is closely related to the D-enriched parts. In view of ED values, the C-H and C-C bonds are inferred to become weaker in the following order: olefinic ≈ aromatic > saturated aliphatic > allylic ≈ benzylic carbons (Flynn and Florin 1984). This suggests that the D-enriched parts contain allylic and benzylic bonds and that the main network consists chiefly of olefinic and aromatic bonds. Remusat et al. (2006) performed pyrolyses and ruthenium tetroxide oxidation on IOM of the Orgueil meteorite and reported that δD values of the benzylic, aliphatic, and aromatic hydrogen in the IOM were determined to be +1250‰, +550‰, and +150‰, respectively. This result can provide evidence for our suggestion on the D distribution in IOM of the Murchison meteorite. Kerridge et al. (1987) also carried out stepwise heating of IOM from the Murchison meteorite; their data are modified and plotted in Fig. 3a. The D/H factor remains roughly 1 up to 50% of dehydrogenation and then sharply decreases as dehydrogenation proceeds. The sharp decrease above 50% of dehydrogenation for stepwise heating is very similar to that of shock dehydrogenation for IOM. Kerridge et al. (1987) claimed that the preferential D-loss accompanied by dehydrogenation is caused by release of the labile parts comprising materials with high δD values up to +1800‰. This explanation of Kerridge et al. (1987) supports our inference concerning the δD values of the D-enriched parts in the IOM.

Below 50% dehydrogenation from the IOM samples, the D/H factor regarding shock is very different from that regarding stepwise heating (Fig. 3a). For kerogen, such difference was not observed (Fig. 3b). Dehydrogenation occurs under very different conditions for shock and stepwise heating, namely under the dynamic high-pressure high-temperature condition and at the static low-pressure high-temperature condition, respectively. The experimental result shows that the kerogen sample is not influenced by the difference of reaction condition, while the IOM sample is strongly influenced. This suggests that IOM has a unique structure containing the D-enriched parts and is intensely sensitive to shock. Although at the present stage the structure cannot be uniquely described, the shock more effectively and selectively releases D from the IOM than does the stepwise heating. Because of this effective release of D, the shock dehydrogenates from the IOM sample without major modification in its C/H ratio and, as a result, reduces the D/H

Table 2. Elemental and isotopic data of shocked and unshocked samples.

Sample[a]	Hydrogen content[b] (wt%)	Carbon content[c] (wt%)	C/H molar ratio	δD_{SMOW} (‰)	$\delta^{13}C_{PDB}$ (‰)
Mixture of olivine and IOM					
I00001	0.50 ± 0.01	9.16 ± 0.02	1.5	+854	−15.5
I01001	0.48 ± 0.01	8.41 ± 0.02	1.5	+805	−15.6
I01002	0.51 ± 0.01	8.65 ± 0.02	1.4	+802	−15.5
I01005	0.50 ± 0.01	8.39 ± 0.02	1.4	+819	−15.6
I01003	0.45 ± 0.01	8.13 ± 0.02	1.5	+731	−15.6
I01007	0.47 ± 0.01	8.21 ± 0.02	1.5	+768	−15.5
I01004	0.43 ± 0.01	7.73 ± 0.02	1.5	+596	−15.8
I01011	0.32 ± 0.02	7.59 ± 0.02	2.0	+516	−16.1
I01006	0.30 ± 0.02	6.96 ± 0.02	1.9	+493	−16.1
I01012	0.23 ± 0.02	6.78 ± 0.02	2.5	+318	−16.3
I01014	0.18 ± 0.02	5.23 ± 0.02	2.4	+235	−16.6
Mixture of olivine and type III kerogen					
F00001	0.90 ± 0.01	15.06 ± 0.02	1.4	−125	−23.7
F01002	0.91 ± 0.01	15.11 ± 0.02	1.4	−122	−23.6
F01003	0.87 ± 0.01	14.74 ± 0.02	1.4	−125	−23.6
F01004	0.85 ± 0.01	14.07 ± 0.02	1.4	−125	−23.6
F01008	0.82 ± 0.01	13.54 ± 0.02	1.4	−110	−23.5
F01005	0.73 ± 0.01	12.91 ± 0.02	1.5	−109	n.d.[d]
F01006	0.72 ± 0.01	12.19 ± 0.02	1.4	−115	−23.6
F01013	0.57 ± 0.01	11.04 ± 0.02	1.6	−105	−23.6
F01011	0.67 ± 0.01	12.98 ± 0.02	1.6	−97	−23.6
F01014	0.49 ± 0.01	11.11 ± 0.02	1.9	−90	−23.5

[a]Sample number corresponds to that in Table 1.
[b]Data were determined manometrically and are given in percentage by weight of bulk samples.
[c]Data were determined by an elemental analyzer and are given in percentage by weight of bulk samples.
[d]n.d. = not determined.

ratio. This suggests that, in the universe, shock significantly decreases the D/H ratio of materials such as IOM without inducing large changes in their chemical compositions.

Behavior of Carbon Isotopes

The $^{13}C/^{12}C$ factor ([$^{13}C/^{12}C$ ratio of sample]/[$^{13}C/^{12}C$ ratio of starting material]) of shocked kerogen samples remains nearly constant or increases slightly with increasing decarbonization degree, while the $^{13}C/^{12}C$ factor of shocked IOM samples decreases (Figs. 4a and 4b). The carbon isotope variation for the kerogen sample can be explained in terms of the isotope effect. In contrast, for the IOM sample, the shock-induced decarbonization selectively released ^{13}C, and hence this carbon isotope behavior cannot be explained by the isotope effect. To explain the case for IOM, it must be assumed that ^{13}C-enriched parts are heterogeneously present in IOM and the parts bind the main network of IOM with weak bonds. These parts produce volatile-carbon-bearing materials which are easily degassed from shocked IOM samples. Rough estimation shows that ^{13}C of the expelled gases range from −15.5‰ to −12.5‰. These ^{13}C values should be related to the carbon isotope ratio of the heterogeneously ^{13}C-enriched parts in the IOM. It was suggested that the labile parts of IOM are enriched in ^{13}C and

that the lability and heterogeneity of the parts control carbon isotope change in the IOM (Kerridge et al. 1987; Sephton et al. 1998, 2004a, 2004b). Moreover, Sephton et al. (2003) narrowed ^{13}C (−13.4‰ to −10.0‰) of the labile parts in the IOM on the basis of stepped-combustion data. These are strongly related to our observation of ^{13}C distribution in the shocked IOM samples.

The $^{13}C/^{12}C$ factor for each starting material similarly changes independently of the type of pyrolysis (the shock and the stepwise heating) (Figs. 4a and 4b). For the IOM sample, little difference in the $^{13}C/^{12}C$ factors between the shock and the stepwise heating was observed, in spite of the significant difference of D/H between the two pyrolysis types. Hence, carbon in the IOM would not make a unique structure sensitive to shock as does hydrogen. Otherwise, signals originating from the structure might not be detected, giving rise to the equivocal difference because of the small variation of the $^{13}C/^{12}C$ factors versus decarbonization.

Role of Shock in Isotope Evolution

It has been accepted that IOM in carbonaceous chondrites inherits the organics of ISM, as indicated by the extremely high δD in the IOM. However, the difference of δD value between ISM (+12,000‰ to +380,000‰) and IOM
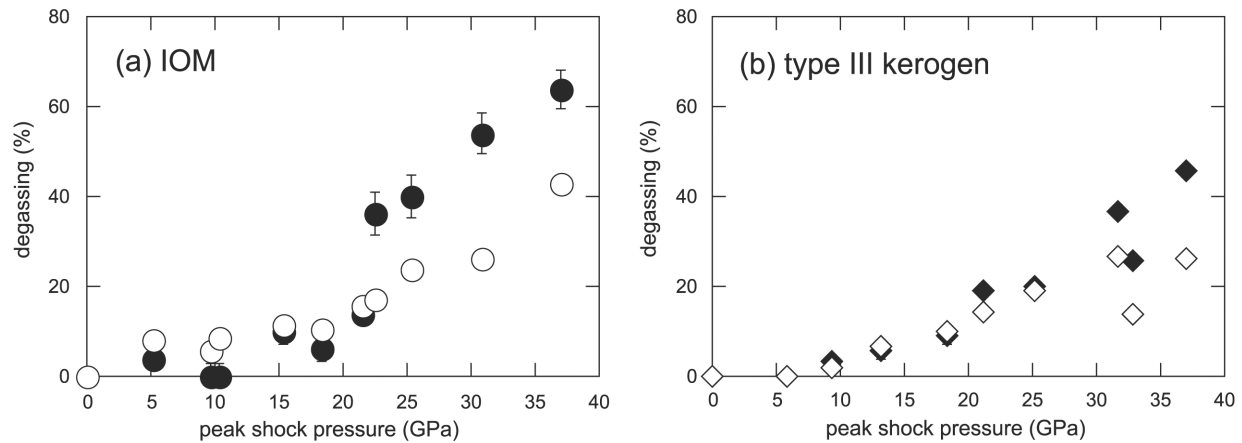
Fig. 2. Shock-induced degassing versus peak shock pressure. a) For IOM samples: solid circles = hydrogen, open circles = carbon. b) For type III kerogen samples: solid diamonds = hydrogen, open diamonds = carbon.
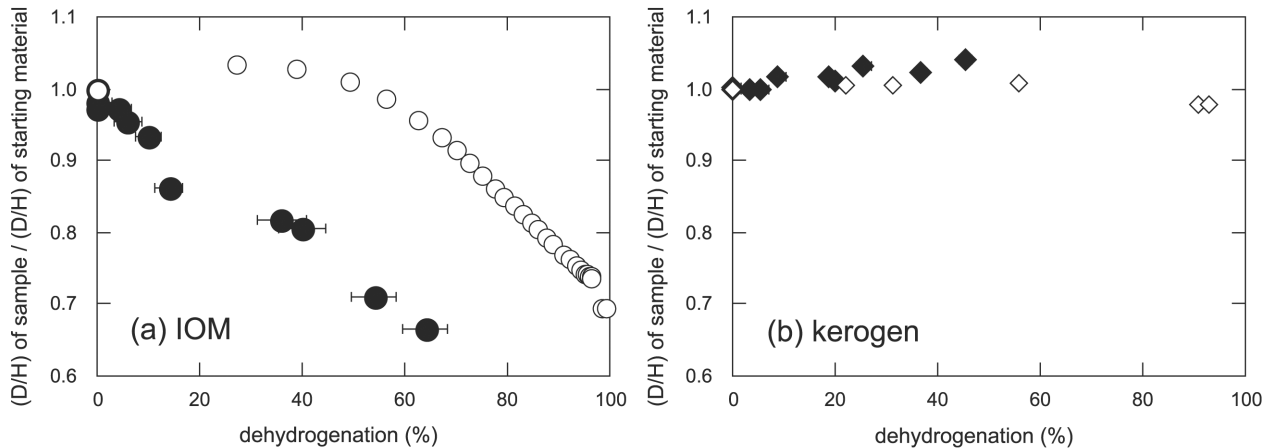

Fig. 3. D/H factor [(D/H of sample)/(D/H of starting material)] versus dehydrogenation. a) Solid circles = shocked IOM samples; open circles = stepwise heated IOM samples reported by Kerridge et al. (1987). b) Solid diamonds = shocked type III kerogen samples, open diamonds = stepwise heated kerogen samples by Kerridge (1983). The IOM by Kerridge et al. (1987) was obtained from the Murchison meteorite. Because the D value for the stepwise-heated IOM sample at 380 °C was not available in Kerridge et al. (1987), we took the mean value (+710‰) between +769‰ at 375 °C and +650‰ at 385 °C. The kerogen sample used by Kerridge (1983) was obtained from the Bungle-Bungle dolomite/chert.

(+410‰ to +2500‰) is too large to recognize that the IOM was directly formed from ISM without alteration. During the process of evolution from ISM to IOM, the gain of H and/or the loss of D must have occurred. Kerridge et al. (1987) showed that stepwise heating causes the loss of D from the IOM in carbonaceous chondrites. Our experimental results also showed that the shock effectively expelled D from the IOM of the Murchison meteorite. The shock and the heating should participate in the evolution of the isotopes of extraterrestrial organics, especially hydrogen isotopes. Moreover, these results indicate that the pristine distribution of D/H ratios acquired by IOM at its formation was not entirely erased during the evolution process of the Murchison meteorite.

When interstellar clouds collapsed to form the solar nebula, organic materials of ISM collided with each other and involved surrounding gases to produce more complicated organics. These complicated organics might be included somewhere in the solar system. Meteorites, interplanetary dust particles (IDPs), and comets contain complicated organics. Of those extraterrestrial materials, meteorites collected on Earth might be most strongly influenced by shock and heating, due to the formation of their parent bodies, the hydrothermal process in the bodies, the meteorites' entrance into Earth's atmosphere, and impact against Earth's surface. Although IDPs entering the atmosphere are collected by aircraft in the stratosphere at an altitude of 20–25 km, the influence of shock and heating on IDPs is extremely low compared with those on meteorites because of the smallness of IDPs' size (1–50 μm) (Bradley 2003). In contrast to meteorites and IDPs, comets are though to be influenced less by shock and heat, and are regarded as the best-preserved
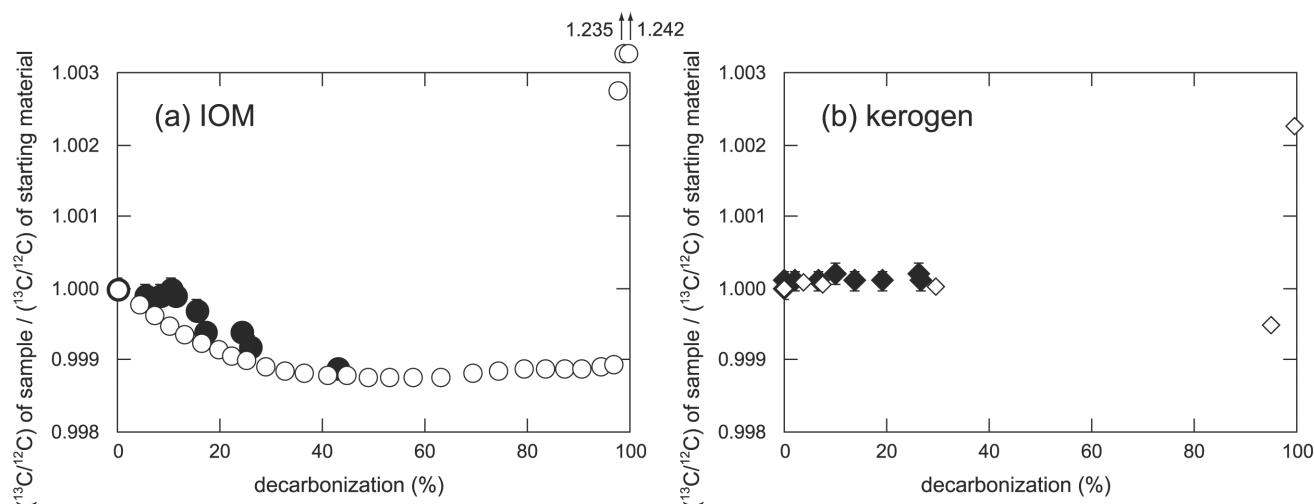
Fig. 4. ^{13}C/^{12}C factor [(^{13}C/^{12}C of sample)/(^{13}C/^{12}C of starting material)] versus decarbonization. a) Solid circles = shocked IOM samples, open circles = stepwise-heated IOM samples reported by Kerridge et al. (1987). b) Solid diamonds = shocked type III kerogen samples, open diamonds = stepwise-heated kerogen samples by Kerridge (1983).

materials in the solar system on the basis of their orbits and their chemical compositions (Brownlee 2003).

Three kinds of extraterrestrial objects (meteorites, IDPs, and comets) in the solar system may have been formed in various environments in which temperatures, pressures, and accretion conditions undergo noticeable change. Therefore, these three objects may have initially contained organics with different δD and δ^{13}C values from those observed at present. However, these three objects must have originated in the gases and dusts of presolar materials. If the organics initially had common δD and δ^{13}C values when they were formed, their isotope ratios would have been modified by the events that they had experienced after their formation. Studies of extraterrestrial organics using shock (this study), stepwise heating (e.g., Kerridge et al. 1987), and thermal-aqueous processing (e.g., Sephton et al. 2004b) show that their isotope ratios become lower as the influence of shock, heating, and aqueous processing is enhanced, and that the trend toward variation in isotope ratios is especially remarkable for hydrogen isotope. As described above, the three extraterrestrial objects have each experienced different degrees of shock and heating. The specific δD range of each kind of extraterrestrial object is expected to be higher in the following order: meteorites < IDPs < comets. Robert (2002) compiled δD data concerning organics in extraterrestrial materials: +410‰ to +2500‰ (carbonaceous chondrites), +1500‰ to +6000‰ (IDPs), and +14,000‰ (comets). This tendency is consistent with our expectation, as based on our assumption and experimental results which suggest that shock and heating control isotope behavior in the solar nebula. Moreover, our results show that shock more effectively releases D from organic materials than does heating. This suggests that shock events play an important role in the hydrogen isotope differentiation of organic

materials during the evolution of the solar nebula. The selective and effective release of D by shock may be a mechanism to mediate between the δD of ISM and that of IOM.

SUMMARY

1. Shock waves expel hydrogen and carbon from the IOM of the Murchison meteorite.
2. IOM preferentially releases D and ^{13}C due to shock. This provides the following information regarding the structure of IOM: 1) D and ^{13}C are inhomogeneously distributed in IOM; 2) the parts enriched in D and ^{13}C are weakly attached to the main network of IOM; and 3) due to shock, the enriched parts of the sample would be easily cut from the network and decomposed into the low-molecular-weight materials, which are expelled readily.
3. Shock more effectively releases D from IOM than does heating. This may be attributed to the different pyrolysis condition between shock (a dynamic high-pressure, high-temperature condition) and heating (a static low-pressure, high-temperature condition).
4. Shock and heating should control the isotope behavior of organic materials during the evolution of the solar nebula. In particular, shock plays an important role in the evolution of hydrogen isotope because of the highly effective release of D.

*Editorial Handling—*Dr. Scott Sandford

REFERENCES

Bradley J. P. 2003. Interplanetary dust particles. In *Meteorites, comets, and planets,* edited by Davis A. M. Treatise on geochemistry, vol. 1. Amsterdam: Elsevier. pp. 689–711.

Brownlee D. E. 2003. Comets. In *Meteorites, comets, and planets,* edited by Davis A. M. Treatise on geochemistry, vol. 1. Amsterdam: Elsevier. pp. 663–688.

Cronin J. R. and Chang S. 1993. Organic matter in meteorites: Molecular and isotopic analyses of the Murchison meteorite. In *The chemistry of life's origins,* edited by Greenberg J. M., Pirronello V., and Mendóza-Gomez C. X. Dordrecht, The Netherlands: Kluwer Academic Publishers. pp. 209–258.

Cronin J. R., Pizzarello S., and Frye J. 1987. ^{13}C NMR spectroscopy of the insoluble carbon of carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 51:299–303.

Derenne S., Rouzaud J. E., Clinard C., and Robert F. 2005. Size discontinuity between interstellar and chondritic aromatic structures: A high-resolution transmission electron microscopy study. *Geochimica et Cosmochimica Acta* 69:3911–3918.

Flynn J. H. and Florin R. E. 1984. Degradation and pyrolysis mechanisms. In *Pyrolysis and GC in polymer analysis,* edited by Liebman S. A. and Levy E. J. New York: Mercel Dekker. pp. 149–208.

Gardinier A., Derenne S., Robert F., Behar F., Largeau C., and Maquet J. 2000. Solid state CP/MAS ^{13}C NMR of the insoluble organic matter of the Orgueil and Murchison meteorites: Quantitative study. *Earth and Planetary Science Letters* 184:9–21.

Greenberg J. M. and Li A. 1996. What are the true astronomical silicates? *Astronomy and Astrophysics* 309:258–266.

Greenberg J. M. 1998. Making a comet nucleus. *Astronomy and Astrophysics* 330:375–380.

Guillois O., Papoular R., and Reynaud C. 1996. Coal models for the infrared emission spectra of proto-planetary nebulae. *The Astrophysical Journal* 464:810–817.

Hayatsu R., Matsuoka S., Scott R. G., Studier M. H., and Anders E. 1977. Origin of organic matter in the early solar system—VII. The organic polymer in carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 41:1325–1339.

Hayatsu R., Winans R. E., Scott R. G., McBeth R. L., Moore L. P., and Studier M. H. 1980. Phenolic ethers in the organic polymer of the Murchison meteorite. *Science* 207:1202–1204.

Kerridge J. F. 1983. Isotopic composition of carbonaceous-chondrite kerogen: Evidence for an interstellar origin of organic matter in meteorites. *Earth and Planetary Science Letters* 64:186–200.

Kerridge J. F., Chang S., and Shipp R. 1987. Isotopic characterization of kerogen-like material in the Murchison carbonaceous chondrite. *Geochimica et Cosmochimica Acta* 51:2527–2540.

Marsh S. P. 1980. *LASL shock Hugoniot data.* Berkeley: University of California Press. 658 p.

Miknis F. P., Lindner A. W., Gannon A. J., Davis M. H., and Maciel G. E. 1984. Solid state ^{13}C NMR studies of selected oil shales from Queensland, Australia. *Organic Geochemistry* 7:239–248.

Mimura K. 1995. Synthesis of polycyclic aromatic hydrocarbons from benzene by impact shock: Its reaction mechanism and cosmochemical significance. *Geochimica et Cosmochimica Acta* 59:579–591.

Mimura K., Ohashi M., and Sugisaki R. 1995. Hydrogen gases and aromatic hydrocarbons produced by impact shock from frozen benzene: Cosmochemical significance. *Earth and Planetary Science Letters* 133:265–269.

Mimura K., Kato M., Ohashi M., and Sugisaki R. 1998. Shock reaction of hexane at 77, 193, and 273 K with special reference to shock pressure. *Shock Waves* 8:311–319.

Mimura K., Madono T., Toyama S., Sugitani K., Sugisaki R., Iwamatsu S., and Murata S. 2004. Shock-induced pyrolysis of naphthalene and related polycyclic aromatic hydrocarbons (anthracene, pyrene, and fluoranthene) at pressures of 12–33.7 GPa. *Journal of Analytical and Applied Pyrolysis* 72:273–278.

Mimura K. and Toyama S. 2005a. Behavior of polycyclic aromatic hydrocarbons at impact shock: Its implication for survival of organic materials delivered to the early Earth. *Geochimica et Cosmochimica Acta* 69:201–209.

Mimura K., Toyama S., and Sugitani K. 2005b. Shock-induced dehydrogenation of polycyclic aromatic hydrocarbons with or without serpentine: Implications for planetary accretion. *Earth and Planetary Science Letters* 232:143–156.

Mimura K., Okamoto M., Nakatsuka T., Sugitani K., and Abe O. 2005c. Shock-induced isotope evolution of hydrogen and carbon in meteorites. *Geophysical Research Letters* 32:L11201.

Murae T. 1995. Characterization of extraterrestrial high-molecular-weight organic matter by pyrolysis-gas chromatography/mass spectrometry. *Journal of Analytical and Applied Pyrolysis* 32:65–73.

Peterson E., Hörz R., and Chang S. 1997. Modification of amino acids at shock pressure of 3.5 to 32 GPa. *Geochimica et Cosmochimica Acta* 61:3937–3950.

Remusat L., Derenne S., Robert F., and Knicker H. 2005a. New pyrolytic and spectroscopic data on Orgueil and Murchison insoluble organic matter: A different origin than soluble? *Geochimica et Cosmochimica Acta* 69:3919–3932.

Remusat L., Derenne S., and Robert F. 2005b. New insight on aliphatic linkages in the macromolecular organic fraction of Orgueil and Murchison meteorites through ruthenium tetroxide oxidation. *Geochimica et Cosmochimica Acta* 69:4377–4386.

Remusat L., Palhol F., Robert F., Derenne S., and France-Lanord C. 2006. Enrichment of deuterium in insoluble organic matter from primitive meteorites: A solar system origin? *Earth and Planetary Science Letters* 243:15–25.

Robert F. and Epstein S. 1982. The concentration and isotopic composition of hydrogen, carbon and nitrogen in carbonaceous meteorites. *Geochimica et Cosmochimica Acta* 46:81–95.

Robert F. 2002. Water and organic matter D/H ratios in the solar system: A record of an early irradiation of the nebula? *Planetary and Space Science* 50:1227–1234.

Sephton M. A., Pillinger C. T., and Gilmour I. 1998. ^{13}C of free and macromolecular aromatic structures in the Murchison meteorite. *Geochimica et Cosmochimica Acta* 62:1821–1828.

Sephton M. A., Verchovsky A. B., Bland P. A., Gilmour I., Grady M. M., and Wright I. P. 2003. Investigating the variations in carbon and nitrogen isotopes in carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 67:2093–2108.

Sephton M. A., Love G. D., Watson J. S., Verchovsky A. B., Wright I. P., Snape C. E., and Gilmour I. 2004a. Hydropyrolysis of insoluble carbonaceous matter in the Murchison meteorite: New insights into its macromolecular structure. *Geochimica et Cosmochimica Acta* 68:1385–1393.

Sephton M. A., Verchovsky A. B., and Wright I. P. 2004b. Carbon and nitrogen isotope ratios in meteoritic organic matter: Indicators of alteration processes on the parent asteroid. *International Journal of Astrobiology* 3:221–227.

Smith J. W. and Kaplan I. R. 1970. Endogenous carbon in carbonaceous meteorites. *Science* 167:1367–1370.

Tielens A. G. G. M., Wooden D. H., Allamandola L. J., Bregman J., and Witteborn F. C. 1996. The infrared spectrum of the galactic center and the composition of interstellar dust. *The Astrophysical Journal* 461:210–222.

Tingle T. N., Tyburczy J. A., Ahrens T. J., and Becker C. H. 1992. The fate of organic matter during planetary accretion: Preliminary studies of the organic chemistry of experimentally shocked Murchison meteorite. *Origins of Life and Evolution of the Biosphere* 21:385–397.

Tyburczy J. A., Xu X., Ahrens T. J., and Epstein S. 2001. Shock-induced devolatilization and isotopic fraction of H and C from Murchison meteorite: Some implications for planetary accretion. *Earth and Planetary Science Letters* 192:23–30.

Wdowiak T. J., Flickinger G. C., and Cronin J. R. 1988. Insoluble organic material of the Orgueil carbonaceous chondrite and the unidentified infrared bands. *The Astrophysical Journal* 328:L75–L79.

Yang J. and Epstein S. 1984. Relic interstellar grains in Murchison meteorite. *Nature* 311:544–547.