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## Behavior of polycyclic aromatic hydrocarbons at impact shock: Its implication for survival of organic materials delivered to the early Earth

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**Abstract**—Polycyclic aromatic hydrocarbons (PAHs) with a hydrous or an anhydrous mineral matrix were impacted and analyzed, to study the behavior of PAHs against shock. Results of the shock experiments suggested that volatiles discharged from the hydrous mineral did not influence the behavior of PAHs against shock. The shocked samples contained unreacted starting PAHs, soot-like materials insoluble in dichloromethane, and secondarily formed PAHs with molecular weights ranging from 128 to 404. Approximately 95% of starting PAHs decomposed at ~30 GPa and the dominant product was the soot-like materials. Formation mechanisms of the shock products were explained by reaction processes under static high pressure-temperature conditions (e.g., carbonization, radical addition reaction, ring cross linking, and methylation).

We applied these results to estimate the survival degree of organic matter delivered by carbonaceous asteroids against their impact pressures at the accretion stage of early Earth. If we use a simplified homogeneous accretion model without atmosphere to represent the stage, the radius of Earth causing 30 GPa, the pressure at which PAHs almost decompose, was calculated as 2270 km ( $4.0 \text{ km s}^{-1}$  of impact velocity) for the impact of carbonaceous asteroids. In the case of impactors striking not land but oceans on the early Earth, the impact velocity for the decomposition of PAHs was estimated to be  $6.0 \text{ km s}^{-1}$ . These impact velocities should have been commonly realized on the early Earth, due to the airburst and the aerobreak of impactors in the dense atmosphere. The early Earth should have been a favorable environment for obtaining and maintaining a large quantity of prebiotic organic materials leading to life. Copyright © 2005 Elsevier Ltd

### 1. INTRODUCTION

How did life start and evolve on the Earth? The origin of life has been an attractive subject for many scientists. The first question to be answered is how the precursor of essential biogenic compounds (e.g., organic materials) was produced on the Earth and what conditions were needed to prevent the precursor from decomposing. In some models, the organic materials were synthesized on the early Earth by electric discharge in the terrestrial atmosphere (Miller, 1955), by catalysis of active minerals in volcanic gases (Mathez, 1987), and by hydrothermal system (Shock 1990a, 1990b). In other models, extraterrestrial organic materials have been pointed to as the source of prebiological organic materials on the early Earth. Anders (1989), Chyba et al. (1990), Chyba and Sagan (1992), and Maurette et al. (2000) emphasized that a significant fraction of the precursor may have been delivered by carbonaceous asteroids, comets, and interplanetary dust particles (IDPs) during the period of heavy bombardment of the inner solar system 4.5 to 3.8 Ga ago.

We focus on carbonaceous asteroids for the delivery of organic materials to the early Earth. Carbonaceous asteroids are characterized by their high concentration of volatile materials, especially organic materials (Cronin and Chang, 1993). When asteroids impacted on the Earth, the organic materials in these bodies should have experienced high temperature and pressure conditions by the passage of the shock wave generated at impact. In general, organic materials are very sensitive to temperature and pressure, and they easily decompose to form

graphite and CO under high temperature conditions. Graphite and CO are not especially useful materials as the precursor of biogenic compounds, so it is necessary to determine the impact condition on the Earth under which organic materials can survive. Tingle et al. (1992) shocked the Murchison meteorite and analyzed the shocked samples by thermal-desorption photoionization mass spectrometry (SALI). They did not, however, quantitatively examine the behavior of organic materials against shock, because of the low concentration of organic materials in the meteorite. Peterson et al. (1997) impacted amino acids both within and without meteoritic mineral matrices and showed the survival pressure range of amino acids and the composition of products from amino acids by shock reaction. Blank et al. (2001) conducted a series of shock experiments to assess the feasibility of the delivery of organic materials to the Earth by comet impacts and showed that significant concentrations of organic materials could survive a natural impact process.

In the present study, we impacted a mixture of polycyclic aromatic hydrocarbons (PAHs) and silicate minerals and examined the behavior of the PAHs against shock. We report the behavior of PAHs against shock, the composition of shock products from PAHs, the possible formation mechanism of the major products, and the condition on the Earth that PAHs in impactors can survive.

### 2. EXPERIMENT

#### 2.1. Shock Recovery Experiment

The experimental apparatus and techniques employed in this study have been described in Mimura et al. (2003). The outline of the experiment is as follows: A target assembly for a shock recovery experiment consists of three components: a capsule, a capsule holder,

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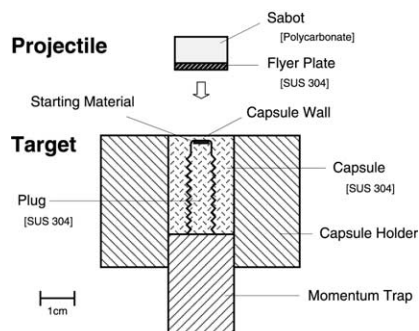


Fig. 1. Cross-section of equipment for shock-recovery experiment.

and a momentum trap (Fig. 1). The capsule is composed of a cap and a plug that has a pit 4 mm in diameter and 0.8 mm deep. The assembly was made of stainless steel (SUS 304). The starting material was placed into the pit of the plug and pressed at  $1000 \text{ kg cm}^{-2}$ . After the plug was driven into the cap, the capsule was impacted with a flyer plate.

We recovered the shocked sample from the capsule according to the steps reported by Peterson et al. (1997). The recovered sample was dissolved in dichloromethane using an ultrasonic bath. After adding an internal standard, the solution was filtered. The filtrate was analyzed by a gas chromatograph with a flame ionization detector (FID-GC), and a GC mass spectrometer (GCMS). Products in the filtrate were identified by comparison with retention times and fragment patterns of authentic standards. These quantities were estimated from peak areas on the chromatogram by comparison with those of authentic and internal standards.

Peak shock pressure and shock temperature in a sample are achieved by shock - wave reverberation between the stainless steel walls of the capsule. Peak shock pressures in samples were calculated using shock Hugoniot data (Marsh, 1980) of study materials (the shock wave equation of state in the Appendix) and the projectile velocity. This shock loading is quasi isentropic and produces much lower bulk temperatures than a single shock at the same shock pressure. The sample remains at peak shock pressure until the pressure-release wave from the back of the flyer, and quenches the pressure and temperature isentropically. The duration of shock condition was calculated as  $\sim 1 \mu\text{s}$  in the present experiment. Residual temperature results from an increase of internal energy that is caused by the difference between shock compression (irreversible adiabatic process) and pressure release (isentropic process). The residual temperature is quenched by thermal dif-

fusion within the order of 10 ms. Both shock temperature and residual temperature were calculated based on Meyers (1994) and Mimura et al. (2003).

## 2.2. Starting Materials

We used two types of mixtures (MixS and MixO), consisting of PAHs and silicate minerals, as starting materials. MixS was made of phenanthrene (Phe), fluoranthene (Flu), pyrene (Pyr), and serpentine with a mixing ratio of Phe/Flu/Pyr/serpentine = 1/2/2/24 (by weight). MixO was a mixture of Phe, Flu, Pyr, and olivine with a mixing ratio of Phe/Flu/Pyr/olivine = 1/2/2/24 (by weight). Both mixtures were dry-blended and homogenized with an agate ball mill. We used commercial reagents with high purity as starting PAHs. Phe (>97.0%, Tokyo Kasei), Flu (>99.0%, Aldrich), and Pyr (>99.0%, Fluka) were used without further purification. The starting serpentine and olivine were pulverized to  $< 100 \mu\text{m}$  from serpentinite (mainly antigorite) and dunite (mainly forsterite), respectively.

PAHs are thought to be ubiquitous compounds in the universe (Puget and Léger, 1989) and have been identified in IDPs (Allamandola et al., 1987; Clemett et al., 1993), in carbonaceous chondrites (Basile et al., 1984; Cronin and Chang, 1993), and in comets (Moreels et al., 1994). Moreover, Shock and Schulte (1990) proposed that amino acids in carbonaceous chondrites could be produced by hydrothermal alteration of PAHs on the parent bodies. Thus, PAH is one of the most noticeable species in the field of cosmochemistry. Serpentine and olivine are major components of carbonaceous chondrites. Matrices of the Murchison meteorite and the Allende meteorite mainly consisted of serpentine and olivine, respectively (McSween, 1977, 1979).

The composition of PAHs used in this study was adjusted to be the same as that of the PAHs in the Murchison meteorite (Krishnamurthy et al., 1992), and PAHs and silicate minerals are mixed with a ratio in which the volume of PAHs is smaller than that of silicate minerals.

## 3. RESULTS

Peak shock pressure ranged from 12.1 to 33.4 GPa for MixS and from 13.6 to 32.9 GPa for MixO (Table 1). The shocked samples contained black soot-like materials and silicate minerals as an insoluble fraction in dichloromethane. The soluble fraction of the shocked samples contained unreacted starting PAHs and secondarily formed PAHs with molecular weights ranging from 128 (naphthalene) to 404 (fluoranthene dimer and pyrene dimer; Fig. 2 and Table 2). We present some representative gas chromatograms of soluble fractions for the two types of starting materials at various shock pressures in Figure 2. GC

Table 1. Summary of shock recovery experiments on MixS and MixO.

Sample	Initial density of starting material ( $\text{g cm}^{-3}$ )	Velocity of projectile ( $\text{m s}^{-1}$ )	Flyer plate <sup>a</sup>	Peak shock pressure (GPa)
MixS -us <sup>b</sup>	2.23 <sup>c</sup>			
MixS -01	$2.16 \pm 0.02$	$610 \pm 10$	SUS 304	$12.1 \pm 0.2$
MixS -02	$2.17 \pm 0.02$	$1010 \pm 10$	SUS 304	$21.1 \pm 0.3$
MixS -03	$2.16 \pm 0.02$	$1270 \pm 10$	SUS 304	$27.7 \pm 0.3$
MixS -04	$2.16 \pm 0.02$	$1350 \pm 10$	SUS 304	$29.7 \pm 0.3$
MixS -05	$2.19 \pm 0.02$	$1490 \pm 10$	SUS 304	$33.4 \pm 0.3$
MixO -us <sup>b</sup>	2.57 <sup>c</sup>			
MixO -01	$2.40 \pm 0.02$	$680 \pm 10$	SUS 304	$13.6 \pm 0.2$
MixO -02	$2.41 \pm 0.02$	$1000 \pm 10$	SUS 304	$21.0 \pm 0.2$
MixO -03	$2.41 \pm 0.02$	$1130 \pm 10$	SUS 304	$24.2 \pm 0.2$
MixO -04	$2.39 \pm 0.02$	$1350 \pm 10$	SUS 304	$29.7 \pm 0.3$
MixO -05	$2.38 \pm 0.02$	$1470 \pm 10$	SUS 304	$32.9 \pm 0.3$

<sup>a</sup> SUS 304: stainless steel 304.

<sup>b</sup> MixS-us: unshocked MixS; MixO-us: unshocked MixO.

<sup>c</sup> These values are estimated from densities of Phe ( $1.212 \text{ g cm}^{-3}$ ), Flu ( $1.252 \text{ g cm}^{-3}$ ), Pyr ( $1.275 \text{ g cm}^{-3}$ ), serpentine ( $2.66 \text{ g cm}^{-3}$ ), and peridotite ( $3.30 \text{ g cm}^{-3}$ ), and the mixing ratios.

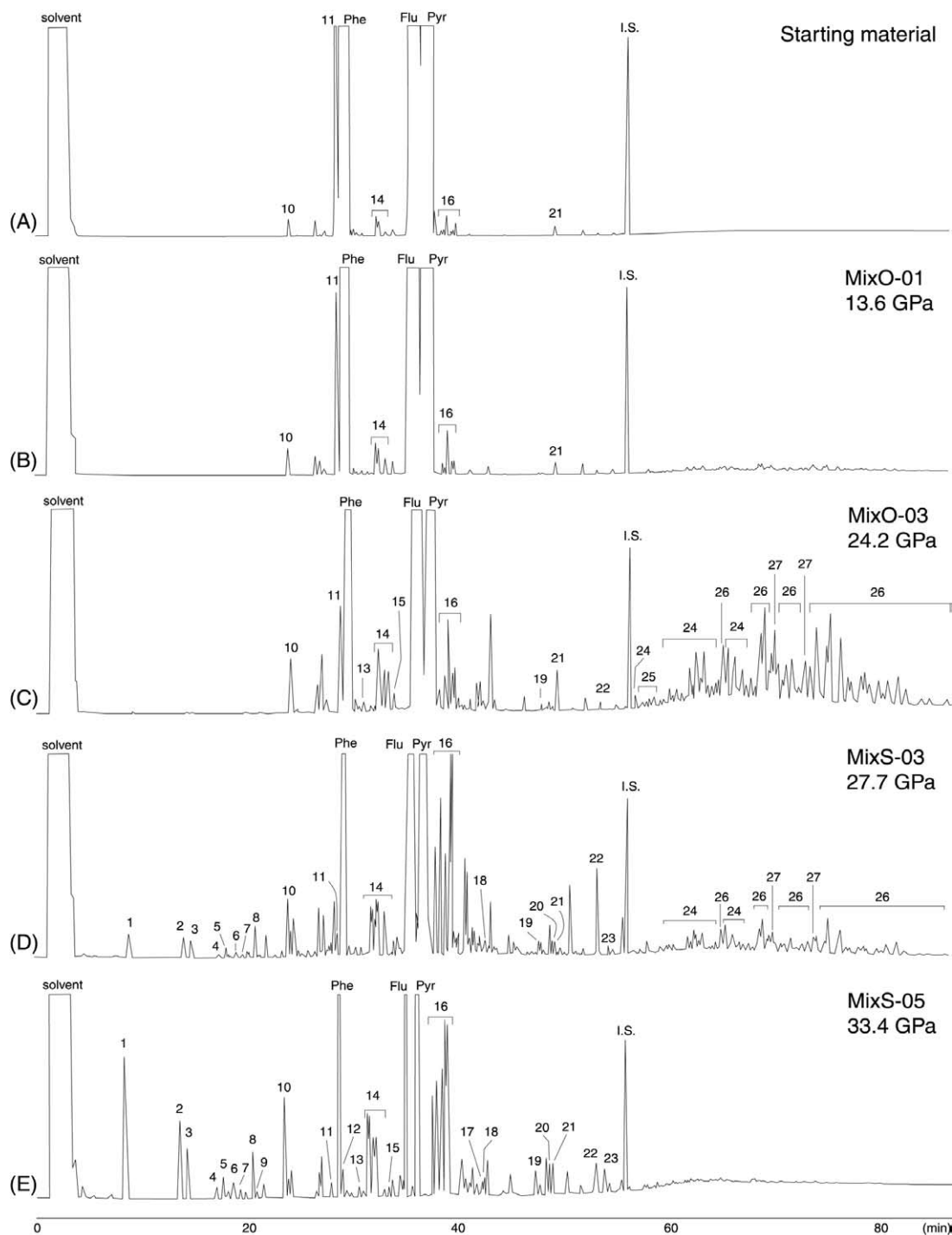


Fig. 2. Gas chromatograms of (A) starting material, (B) sample MixO-01, (C) sample MixO-03, (D) sample MixS-03, and (E) sample MixS-05. Peak numbers correspond to those in Table 2. Phe, Flu, and Pyr are abbreviations of phenanthrene, fluoranthene, and pyrene, respectively.

analyses indicated that shocked samples at similar pressures show similar gas chromatogram patterns regardless of the type of starting material.

Major components of the secondarily formed PAHs were biphenanthrene, bifluoranthene, and bipyrene (we call these species 2M-2H in this paper); phenanthrene dimer, fluoran-

thene dimer, and pyrene dimer (2M); methylphenanthrene (MePhe); methylfluoranthene (MeFlu); methylpyrene (MePyr); naphthalene (Nap); and methyl-naphthalene (MeNap). Except for the starting PAHs, we designated the secondary PAHs determined by GC and GCMS as 'product-GCMS.' Although organic materials with molecular weights < 128 and > 404

Table 2. Identified PAHs in starting materials and shocked samples<sup>a</sup>.

[1] <sup>b</sup> Naphthalene (128) <sup>c</sup>	[2] 1-Methylnaphthalene (142)	[3] 2-Methylnaphthalene (142)	[4] Biphenyl (154)
[5] 2-Methylbiphenyl (168)	[6] Diphenylmethane (168)	[7] Acenaphthylene (152)	[8] Acenaphthene (154)
[9] 3-Methylbiphenyl (168)	[10] Fluorene (166)	[11] Dibenzothiophene (168)	[12] Anthracene (178)
[13] 1-Phenylnaphthalene (204)	[14] Methylphenanthrene (192)	[15] 2-Phenylnaphthalene (204)	[16] Methylfluoranthene (216)
[16] Methylpyrene (216)	[17] Benzo(a)anthracene (228)	[18] Chrysene (228)	[19] Benzo(b)fluoranthene (252)
[20] Benzo(a)pyrene (252)	[21] Perylene (252)	[22] Indeno(1,2,3-cd)pyrene (276)	[23] Benzo(ghi)perylene (276)
[24] Biphenanthrene (354)	[25] Phenanthrene dimer (356)	[26] Bifluoranthene (402)	[26] Bipyrene (402)
[27] Fluoranthene dimer (404)	[27] Pyrene dimer (404)		

<sup>a</sup> Phenanthrene, fluoranthene, and pyrene are not included in this table.

<sup>b</sup> Numbers in brackets [] correspond to peak numbers in Fig. 1.

<sup>c</sup> Numbers in parentheses of () are molecular weights.

were probably present, they cannot be detected by the present analytical method. Figure 2A shows that the starting materials originally contained fluorene, dibenzothiophene, MePhe, MeFlu, MePyr, and perylene as well as Phe, Flu, and Pyr (starting PAHs). Fluorene, MePhe, MeFlu, MePyr, and perylene can be thought of as product-GCMS, because almost all samples showed higher concentrations of those compounds than the starting materials do (Fig. 2). Dibenzothiophene, however, was recognized not as a product-GCMS but as an impurity in the starting materials, because the concentration decreased with increasing shock pressure.

The experimental results for MixS were similar to those for MixO in the survival ratio of starting PAHs, the yield of product-GCMS, and the chemical composition of product-GCMS. Figures 3A and 3B are plots of survival ratios for three starting PAHs in each shocked sample, showing that the survival ratios decrease with increasing shock pressure and that they drastically decrease at ~25 GPa. The survival ratios are < 5% above 30 GPa, suggesting that the starting PAHs almost decompose above 30 GPa. Moreover, each of the three components in the starting PAHs shows a different survival ratio in the same shocked sample, and the relationship is survival ratio<sub>Pyr</sub> > survival ratio<sub>Flu</sub> > survival ratio<sub>Phe</sub>. This feature is remarkable in the samples from 10 to 25 GPa. The yield of product-GCMS increased with increasing pressure up to 25 GPa and decreased above 25 GPa (Fig. 4). The yield reached a maximum (2.61%) at 24.2 GPa (MixO-03). The composition of product-GCMS depends on the shock pressure and shows that the molecular weights of product-GCMS become smaller with

increasing shock pressure. Although the major components in the product-GCMS are 2M-2H and 2M below 25 GPa, and are changed to methylated compounds (MePhe, MeFlu, and MePyr) with increasing shock pressure, Nap and MeNap become the major components above 30 GPa (Figs. 2 and 5).

## 4. DISCUSSION

### 4.1. Generalization of Shock Reaction

No difference in the behavior of starting PAHs against shock was observed between MixS and MixO, although the two types of starting materials are composed of different matrix minerals. Serpentine, the matrix mineral of MixS, discharges water and hydrogen gas by shock (Lange et al., 1985; Tyburczy et al., 1990). According to shock recovery experiments by Tyburczy et al. (1990), the incipient devolatilization of porous serpentine occurs at a peak pressure of ~17 GPa and 89% of the volatiles are degassed from the serpentine at 43.8 GPa. In the pressure range of our shock experiments, 0% to 30% of volatiles are inferred to be degassed from the serpentine of MixS, on the basis of data by Tyburczy et al. (1990). The discharged volatiles may cause dynamic decomposition of PAHs. Furthermore, the devolatilized hydrogen may influence the formation mechanism of product-GCMS because of the hydrogen activity. In contrast, olivine does not cause shock-induced devolatilization as serpentine does, because of its anhydrous character. Regardless of the difference in matrix minerals under consideration, the shock experiments of MixS and MixO showed similar

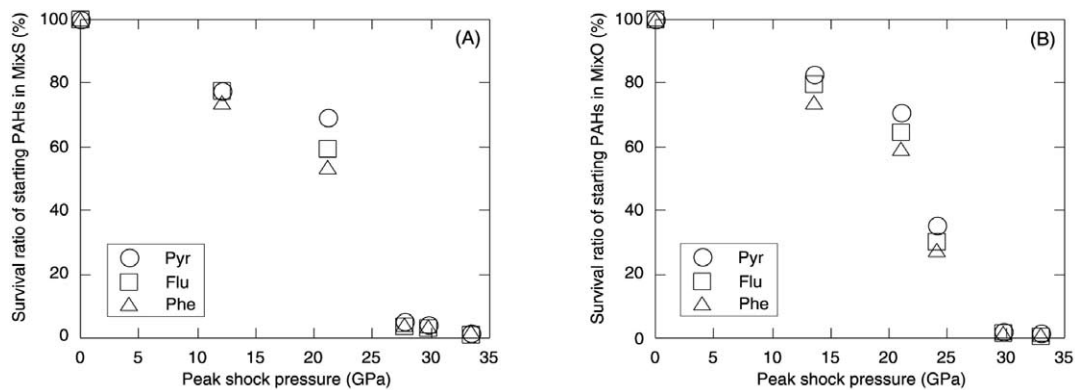


Fig. 3. Survival ratio of starting PAHs in (A) MixS samples, and (B) MixO samples vs. peak shock pressure. Open circles, Pyr; open squares, Flu; open triangles, Phe.

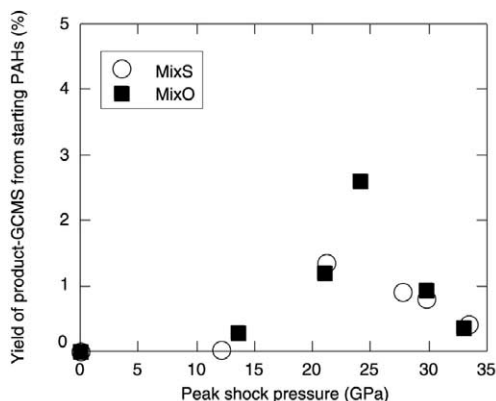


Fig. 4. Yield of product-GCMS from starting PAHs vs. peak shock pressure. Open circles, MixS samples; filled squares, MixO samples.

results in the behavior of starting PAHs. It seems likely that the devolatilization from the mineral matrix does not influence the behavior of PAHs against shock. We cannot exclude the effect of water abundance on chemical reactions and their products. In the present experimental condition, the relative abundance of water to PAHs may be not high enough to observe the effect of water from the mineral matrix.

The composition of product-GCMS changes with the range of shock pressure. The major components of product-GCMS are 2M-2H and 2M below 25 GPa, methylated compounds at  $\sim 27$  GPa, and Nap and MeNap above 30 GPa. This indicates that the molecular weight of major products decreases with increasing shock pressure. In general, the higher the shock pressure, the higher the shock temperature. The high-temperature condition should preferably produce low molecular weight compounds for the effect of the kinetic stability against the thermal decomposition. We may also account for the feature of survival ratios,  $\text{survival ratio}_{\text{Pyr}} > \text{survival ratio}_{\text{Flu}} > \text{survival ratio}_{\text{Phe}}$ , by the kinetic stability. In the higher-pressure range, the starting PAHs will turn into much lower molecular weight compounds (e.g.,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{H}_2$ ) and will become ultimately carbon and hydrogen. The history of temperatures associated with shock waves is one of important factors

for reaction of organic materials. We cannot exactly estimate the shock temperatures and the residual temperatures of our experiments, because the shock wave Hugoniot data of the starting materials are not available. However, if we assume that the starting material is composed of only Phe and the shock-wave structure is a single shock, we can calculate the shock temperature of 1250 and 1480 K and the residual temperature of 600 and 680 K at 25 GPa and 30 GPa, respectively. This calculation includes some errors derived from the obscurity in the composition of starting materials, the shock-wave structure, and others, and hence the calculation temperatures should be treated as representing the upper limit.

Shocked materials have experienced the remarkable condition in which pressure and temperature are drastically changed for an extremely short period (on the order of a microsecond). Therefore, shock-induced chemical reactions may include unique mechanisms, in particular there may be a dynamic process. The formation mechanisms of major products in our experiments can be analogically explained by reaction processes under static high pressure-temperature conditions. This explanation is correlated with the conclusion of Davis (1996), who applied shock experiments to the measurement of reaction rates of various organic compounds including the decomposition of explosives and concluded that “all reaction rates are consistent with known activation parameters and reaction conditions, and there is no indication of unique chemical processes connected with the subnanosecond rise time of the shock front.”

Possible mechanisms of shock reactions are presented by the composition of major products. The starting PAHs react to form the mixture of unreacted starting PAHs, product-GCMS, and soot-like materials by shock. The total amount of the unreacted PAHs and product-GCMS does not reach the amount of unshocked starting PAHs for each sample (Figs. 3 and 4). The shortage should be ascribed to the production of the soot-like materials, which are estimated as  $> 95\%$  on the basis of the consumed PAHs. Although the yield of the soot-like materials may be overestimated owing to the presence of undetected soluble products in dichloromethane, the soot-like materials are evidently the dominant product in shocked samples. This is supported by Mimura et al. (2003), who impacted

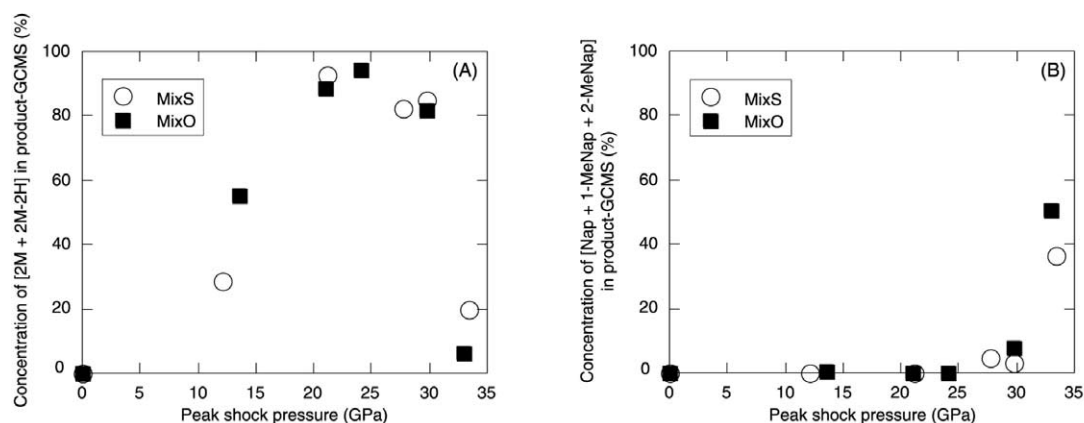


Fig. 5. Concentration of some products in product-GCMS vs. peak shock pressure. (A) Total concentration of 2M-2H and 2M, (B) total concentration of Nap, 1-MeNap, and 2MeNap. Open circles, MixS samples; filled squares, MixO samples.

pure phenanthrene without silicate minerals and showed that the yield of the soot-like materials was > 90% of the consumed phenanthrene. They identified the materials as amorphous carbon. Therefore, the soot-like materials in our experiments should be amorphous carbon, although the materials were not determined owing to the difficulty of isolating them from silicate minerals. The soot-like materials are probably produced by carbonization, which forms carbonaceous materials lacking in hydrogen. The carbonization is easily promoted under high temperature conditions (Lewis, 1980; Greinke and Lewis, 1984).

2M-2H is formed from two molecules of the starting PAHs by eliminating one hydrogen molecule and was the major component in product-GCMS. The possible mechanism for the formation of 2M-2H is a radical addition reaction. In this reaction, a cleavage of the carbon-hydrogen bond occurs to produce highly reactive radicals of starting PAHs, which polymerize and form 2M-2H. This reaction tends to occur at high temperature conditions (Lewis, 1980).

2M is formed from two molecules of the starting PAHs without mass loss and was one of the major products in product-GCMS. 2M should be a face-to-face double cross bond compound attached to a four-carbon rectangular structure. The possible mechanism is a ring-cross linking in which intraring  $\pi$  bonds are converted to interring  $\sigma$  bonds. This reaction tends to occur at high pressure conditions, because the density of the product is greater than that of the starting material (Murphy and Libby, 1977). It is noticeable that many isomers of 2M-2H were produced, while 2M has only 2 isomers (Figs. 2C and 2D). This result suggests that the position of ring-cross linking is strongly controlled in the formation mechanism of 2M.

Major constituents of methylated products were MePhe, MeFlu, and MePyr. These methylated products were probably produced from the starting PAH and the methyl radical, which was generated by the ring cleavage of the starting PAH and subsequent thermal hydrogen transfer. The ring cleavage of PAHs seems to easily form acetylene but rarely form a methyl radical. However, Mimura et al. (1995) compressed benzene by shock and determined methane and acetylene as major products. The above mechanism is not inappropriate for the formation of methylated compounds, although the formation process of methyl radicals is not clear at present.

#### 4.2. Implication for Survival of Organics Delivered to the Early Earth

The Earth has experienced various shock events in its history (e.g., the formation by accreting planetesimals, the last heavy bombardment 4.5 to 3.8 Ga ago, etc.). How did organic matter in the planetesimals and on the Earth behave during these shock events? In this section, we apply our experimental results to the impact events of carbonaceous asteroids on the Earth. As mentioned in the previous section, the water abundance and the thermal history should be important factors in the shock reaction. A molar ratio of PAHs/water in MixS is higher than that in carbonaceous chondrites (Mullie and Reisse, 1987). Moreover, the size of impactors controls the shock duration, which influences the thermal history of shock reaction. Although these effects make differences in the survival behavior of PAHs between experimental system and natural one, to a certain

extent, we could propose an implication for cosmochemistry on the basis of our results.

We examine the relationship between the radius of growing Earth and the impact velocity of impactors on the Earth, using a simplified homogeneous accretion model (Tyburczy et al., 1986, 1990). In this model, we assume that the Earth's surface is composed of serpentine (the shock wave equation of state in the Appendix), that the Earth does not have an atmosphere, and that the density of Earth throughout the growth period is the same as the final average density. Under these conditions, the Earth's radius is a linear function of the minimum impact velocity, as follows:

$$r = Vp(8\pi G\rho/3)^{-1/2},$$

where  $r$  is the Earth's radius,  $Vp$  is the impact velocity,  $G$  is the gravitational constant, and  $\rho$  is the average density of the present-day Earth. This model shows the relationship between the Earth's radius and shock pressure generated by impacts of carbonaceous asteroids with chemical composition like the Murchison meteorite (Fig. 6). Shock wave equation of state for the Murchison meteorite is given in the Appendix.

As shown in Figure 6, the Earth's radius causing 30 GPa at which PAHs almost decompose is calculated as 2270 km ( $Vp = 4.0 \text{ km s}^{-1}$ ) for the impact of carbonaceous asteroids. When the Earth grows larger and reaches its present-day size, the impact velocity is calculated as  $11.2 \text{ km s}^{-1}$  and shock pressure is estimated as 140 GPa. PAHs in the impactors (carbonaceous asteroids) cannot survive these pressure conditions. The above discussion suggests that PAHs in impactors survived only the early stage of Earth formation, when it was < 2270 km in radius. If the surviving organic matter (including PAHs) delivered by the impactors was not released to space, it would have remained on the Earth and been buried by the next layer of accreting material, ultimately residing deep in the interior of Earth. The organic matter delivered to the Earth may be connected with carbon derived from the mantle (Marty and Jambon, 1987; Galimov 1991) and with carbonaceous materials in mantle-derived rocks (Tingle et al., 1991; Sugisaki and Mimura, 1994).

The above discussion suggests that PAHs cannot survive

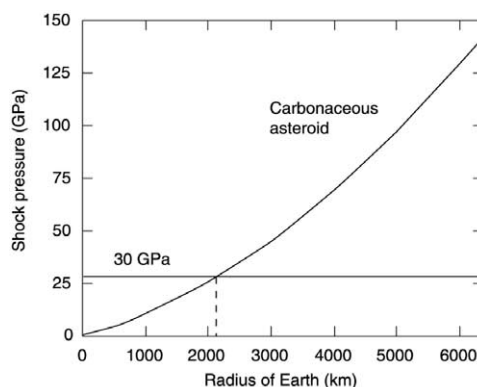


Fig. 6. Shock pressure for a carbonaceous asteroid impacting the solid Earth composed of serpentine. The pressure 30 GPa is the pressure at which PAHs almost decompose.

impacts on the Earth at its present-day size. In the above model, we did not consider the existence of atmosphere and water ocean, which controls shock pressure. When impactors traverse the atmosphere, the impactors are aerobreaked and strike the ground of Earth at a lower velocity than that estimated in the model without the atmosphere. Some models suggest that the Earth may have had a dense, 1-MPa CO<sub>2</sub> atmosphere before 3.8 Ga ago (Walker, 1986; Kasting and Ackerman, 1986). Under these conditions, impactors, especially comets, would be effectively aerobreaked before striking ground (Chyba et al., 1990). Moreover, because carbonaceous asteroids have low compressive strengths, they should break up (airburst) and become smaller fragments during atmospheric passage. Since the fragmentation greatly increases the surface-area-to-volume ratio of the impactor, the airburst enhances aerobreaking and reduces the impact velocity. The atmosphere attenuates the impact velocity by aerobreak and airburst and allows organic matter in the impactor to survive.

We also consider the impact of asteroids not on the solid Earth but on a water ocean. It seems that the early Earth has been a water-covered planet for most of its history, since ~4.4 Ga ago (Kasting and Ackerman, 1986; Abe, 1993; Wilde et al., 2001). Therefore, there is great possibility that impactors struck not land but a water ocean on the early Earth. When an impactor strikes the ocean, the generated shock pressure is lower than when it strikes land, because of the lower impedance of water. Figure 7 shows the relationship between impact velocity and shock pressure for carbonaceous asteroids, when these impactors strike the ocean. On the basis of data for water (Appendix), the impact velocity causing 30 GPa, the PAH survival limit, is estimated to be 6.0 km s<sup>-1</sup>. The range of the impact velocity probably prevailed in the environment of early Earth. Peterson et al. (1997) carried out shock experiments of amino acids and reported that amino acids almost decomposed at 20 GPa. To prevent amino acids from being destroyed by impact on an ocean, the impact velocity should be < 4.7 km s<sup>-1</sup> (Fig. 7). Impactor velocity is effectively decelerated by the airburst and the aerobreak that occur with decreasing radius of the impactors (Chyba et al., 1990). Therefore, the smaller the impactor radius becomes, the greater the chance of amino acids surviving.

The shock pressure by impact calculated above is the max-

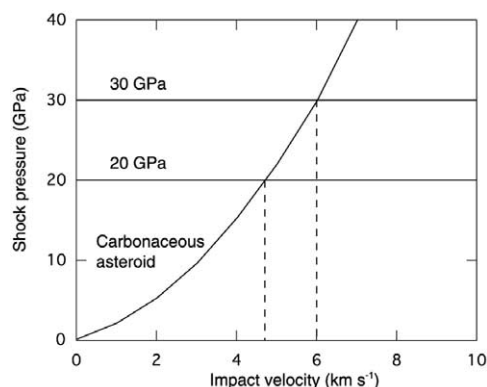


Fig. 7. Shock pressure for a carbonaceous asteroid impacting a water ocean. The pressures of 20 GPa and 30 GPa are the pressures at which amino acids and PAHs almost decompose, respectively.

imum value. In general, the heterogeneity of shock pressure occurs in the body of an impactor (Meyers, 1994). The highest pressure should be observed in the interface region of the impactor, and, in contrast, the lowest pressure should be found in the region opposite the interface. The feature of shock waves causes the difference in the degree of shock modification for organic materials. The higher-pressure part should include abundant soot-like materials and PAHs with low molecular weights, whereas the lower-pressure part should include intact PAHs and PAHs with high molecular weights. The low-pressure part of the impactor is easily ejected into the air. These ejecta are obviously advantageous for the survival of PAHs. Even if an impactor strikes an ocean at > 6.0 km s<sup>-1</sup>, PAHs may not decompose and they may be sustained in these ejecta. Small-sized particles of the ejecta would have settled in the atmosphere. In the dense atmosphere saturated with water vapor, these particles served as condensation nuclei and made raindrops. Aqueous chemistry and evaporation of raindrops containing organic materials should have promoted the formation of more complicated organic materials (Oberbeck et al., 1989). The organic materials in suspended particles in the atmosphere would have been modified and polymerized by the frequent atmospheric passage of impactors (Bar-Nun and Shaviv, 1975; McKay et al., 1988; Mimura, 1995; Mimura et al., 1995, 1998). After the complicated organic materials were deposited in oceans, the materials were further evolved by hydrothermal activity and by catalytic activity of clay minerals, and continued prebiotic evolution leading to life.

## 5. CONCLUSIONS

The results of our shock experiments allow us to draw the following conclusions. The presence of serpentine did not influence the behavior of PAHs against shock. The abundance of starting PAHs in the shocked samples decreased with increasing shock pressure; > 95% of the PAHs decomposed around a peak shock pressure of 30 GPa. The dominant product by shock was soot-like materials, which were estimated to occupy > 95% of the consumed starting PAHs. Other products were the secondarily formed PAHs with molecular weights ranging from 128 to 404. As shock pressure increased, the major components in the secondary PAHs changed and became lower molecular weight compounds. The yields of the secondary PAHs increased with increasing shock pressure up to 25 GPa and decreased above 25 GPa. The possible mechanisms of major products were carbonization, radical addition reaction, ring-cross linking, and methylation.

Assuming a simplified homogeneous accretion model without terrestrial atmosphere, we estimated that the radius of Earth causing PAHs to almost decompose was 2270 km (4.0 km s<sup>-1</sup> of impact velocity) for carbonaceous asteroids. The delivered PAHs on the Earth < 2270 km in radius may have been sustained in the Earth's interior and may have connected with mantle carbon and carbonaceous materials in mantle-derived rocks. In the case of impact on an ocean after the formation of the Earth, the decomposition impact velocity was 6.0 km s<sup>-1</sup>. Because aerobreak and airburst in the dense atmosphere effectively decrease impact velocity, these conditions probably prevailed on the early Earth. Moreover, even if the impact velocity was > 6.0 km s<sup>-1</sup>, PAHs may have survived and been sus-

tained in the ejecta of impactors, because the ejecta generally suffered relatively low shock pressure.

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#### APPENDIX

The shock pressures were calculated by the impedance matching method. The shock wave equations of state parameters are as follows:

Material	$\rho_0$ (g cm <sup>-3</sup> )	$C_0$ (km s <sup>-1</sup> )	S	Reference
Stainless steel 304	7.89	4.58	1.49	Marsh (1980)
Serpentine	2.50	5.30	0.78	Tyburczy et al. (1991)
Murchison meteorite	2.656	1.87	1.48	Anderson and Ahrens (1998)
Water	0.998	1.90	1.57	Marsh (1980)

where  $\rho_0$  is initial density and shock velocity  $U_s$  and particle velocity  $U_p$  are related by  $U_s = Co + SU_p$ .