

THE FATE OF ORGANIC MATTER DURING PLANETARY ACCRETION: PRELIMINARY STUDIES OF THE ORGANIC CHEMISTRY OF EXPERIMENTALLY SHOCKED MURCHISON METEORITE

TRACY N. TINGLE^{1,2*}, JAMES A. TYBURCZY³, THOMAS J. AHRENS⁴,
and CHRISTOPHER H. BECKER²

¹ Department of Geology, Stanford University, Stanford, CA 94305, U.S.A.

² Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025, U.S.A.

³ Department of Geology, Arizona State University, Tempe, AZ 85287-1404, U.S.A.

⁴ Lindhurst Laboratory of Experimental Geophysics, Seismological Laboratory 252-21, California Institute of Technology, Pasadena, CA 91125, U.S.A.

(Received December 17, 1991)

Abstract. It is possible that Earth's biologic precursors were delivered by late-impacting asteroids or comets, and it is possible that these objects were a source of Earth's volatile inventory. To understand the behavior of organic matter in carbonaceous meteorites during hypervelocity impact (1–2 km s⁻¹), three samples of the Murchison (CM2) carbonaceous chondrite were shocked to 19, 20 and 36 GPa and analyzed by very sensitive thermal-desorption photoionization mass spectrometry (SALI). Thermal-desorption (25–800 °C) SALI mass spectra of unshocked Murchison reveal indigenous aliphatic, aromatic, sulfur and organosulfur compounds. Samples shocked to ≈20 GPa exhibit little or no loss of organic matter relative to the unshocked material. This is consistent with the earlier work of Tyburczy *et al.* (1986) which showed that incipient devolatilization of Murchison occurs at peak shock pressures near 20 GPa. The small amount of organic matter lost appears to have occurred by volatilization of elemental sulfur, amines and aliphatic compounds. In the sample shocked to 36 GPa, approximately 70% of the organic matter was volatilized as a result of impact. The residual organic matter desorbed at somewhat higher temperatures and displayed a different chemical signature. In particular, the shocked material has a lower alkene/alkane ratio than that of the starting material. The preliminary data suggest that it is unlikely that the indigenous organic matter in carbonaceous chondrite-like planetesimals could have survived impact on the Earth in the later stages of Earth's accretion. However, chemical reactions that produce organic compounds with greater thermal stabilities may occur during impact or subsequent to impact by condensation of the impact-produced vapor plume.

Introduction

There is a growing body of evidence to suggest that at least some of Earth's biologic precursors were delivered by late-impacting comets or carbonaceous meteorites. The principal observations supporting this hypothesis are: (1) The lunar cratering record provides strong evidence that the Earth was subjected to an intense bombardment by asteroids and comets between 3.5 and 4.5 Ga (Chyba, 1990 and references therein), and such objects are known to contain relatively abundant organic matter produced abiotically in the early solar system and the interstellar medium (e.g. Hayatsu and Anders, 1981; Kissel and Krueger, 1987; Cronin *et al.*, 1988).

* now at Department of Geology, University of California, Davis, CA 95616, U.S.A.

More importantly, these objects contain carboxylic and amino acids needed to make sugars and proteins, the energy sources and enzymes for life as we know it. (2) Self-replicating biologic systems were operating on Earth by 3.5 Ga (Walter *et al.*, 1980; Schopf, 1983) and may have been present as early as 3.8 Ga (Schidlowski, 1987). (3) It has been suggested that homochirality of Earth's biologic systems requires an extraterrestrial source of prebiotic organic matter (e.g. Bonner, 1991). (4) Aqueous alteration of the carbonaceous matter in Murchison and other carbonaceous meteorites has produced bilayer membranes that functionally and morphologically resemble cell membranes (Deamer, 1986).

If we accept the hypothesis that Earth's biologic precursors were delivered by late-impacting comets or carbonaceous meteorites (Chyba *et al.*, 1990), then it becomes important to know how they were delivered. Dynamical simulations of the planetary accretion process (e.g. Safronov, 1969; Wetherill, 1990) suggest that as the planets grew via gravitational accretion, so did the planetesimals which impacted their surfaces. Initially, these bodies were approximately 1 km in diameter, whereas late in the accretion process, much of the mass delivered to the planets was in planetesimals with diameters in the 10^2 to 10^3 km range. These larger objects may have been shock-heated to high temperatures (10^3 – 10^4 K). Smaller planetesimals (10^0 – 10^2 km diameter) may have broken up in the planets' atmospheres.

It is currently hypothesized that the Earth was extensively melted by the intense late bombardment (e.g. Wetherill, 1990). If true, the surface of the early Earth may have been characterized by volcanism and intense hydrothermal activity, and it becomes difficult to imagine how life could have established itself so quickly and in such hostile conditions. However, recent evidence for high-temperature stability of organic matter (Tingle *et al.*, 1990; Shock, 1990; Engel *et al.*, 1991) and, in particular, the presence of thermophilic organisms along the flanks of mid-oceanic ridges (Deming, 1991; Baross, 1991) indicate that the conditions of the early Earth need not be an obstacle to the origin of life.

The present study focuses on the behavior of organic matter in carbonaceous meteorites during hypervelocity impact and is an extension of the earlier work of Tyburczy *et al.* (1986) on impact-induced devolatilization of Murchison meteorite. They found that incipient devolatilization of Murchison occurred at peak shock pressures near 20 GPa, and complete devolatilization occurred at shock pressures above 50 GPa. The extent of devolatilization of samples recovered from the shock experiments relative to the starting material was determined by two methods, thermogravimetric analysis (total volatile loss) and H_2O loss using a moisture analyzer. No difference in the fraction of volatile loss as a function of shock pressure was observed between the two methods, and they concluded that volatile loss during impact was chemically non-specific (i.e. isochemical with respect to the volatile elements C-H-O-N-S). However, later work by Tyburczy *et al.* (1990) showed that there is a D-H fractionation during the impact-induced devolatilization of serpentine (D is preferentially retained in the solid residue and H is enriched in the escaping gas), suggesting that impact-induced devolatilization may not be strictly isochemical.

One of the goals of the present work was to look specifically at the organic matter of Murchison for chemical fractionation during impact-induced devolatilization.

The sample mass recovered from shock experiments is generally of the order of a few mg. To analyze the organic molecular species in these samples, we have utilized thermal-desorption photoionization mass spectrometry (surface analysis by laser ionization or SALI technique) using 118 nm light (Becker and Gillen, 1984; Schühle *et al.*, 1988; Tingle *et al.*, 1990; 1991b). SALI analyses of unshocked Murchison reveal indigenous aliphatic, aromatic, sulfur and organosulfur compounds, and the detection limit for most compounds is of the order of 1 picomole (Tingle *et al.*, 1991b).

In our preliminary study, the Murchison starting materials and samples recovered from three shock experiments were analyzed. The samples were shocked to peak pressures of 19, 20 and 36 GPa. For samples shocked to 20 GPa, little or no change in the analyzable organic constituents was observed; the small amount of organic matter lost from one sample appears to have occurred primarily by volatilization of aliphatic compounds, elemental sulfur, and amines. Material shocked to 36 GPa suffered 70% loss of organic matter. The residual organic matter desorbed at a higher temperature and displayed a different chemical signature than the unshocked material, indicating that the shock process has modified the indigenous organic matter.

Experimental Methods

STARTING MATERIAL

A sample of the Murchison meteorite (courtesy of Dr. Edward Olson, Field Museum, University of Chicago) was cored (dry) for the shock recovery experiments. Samples were polished to final dimensions using alumina and carbide papers. Direct human contact with the samples was avoided at all stages of sample preparation.

SHOCK RECOVERY EXPERIMENTS

Two different types of solid recovery fixture were employed. Shot 40-818 was performed in the 40 mm solid propellant gun at Caltech using a fixture and methods similar to those described by Tyburczy and Ahrens (1988). The sample assembly utilizes a relatively large sample, 1.0 cm diameter \times 0.5 cm thick (\approx 500 mg). However, this assembly does not allow complete escape of gases generated during impact (referred to hereafter as 'partially vented'). Studies of the kinetics of devolatilization of serpentine using these large-volume, partially vented assemblies show quite regular behavior (Tyburczy and Ahrens, 1988), although some materials yield inconsistent results for devolatilization as a function of shock pressure (Lange *et al.*, 1985). Shots 20-1043 and 20-1044 were performed on the 20 mm solid propellant gun at Caltech, using sample assemblies that permitted rapid escape of shock-induced gases (Lange *et al.*, 1985; Tyburczy *et al.*, 1986; 1990). In the vented assembly,

TABLE I
Shock recovery experiments

Shot number	Projectile Velocity (km/s)	Peak Shock Pressure (GPa)
20-1044 ^b	0.92	19.0
40-818 ^a	1.03	20.0
20-1043 ^b	1.57	35.7

^a Murchison starting material I.

^b Murchison starting material II.

samples were approximately 4 mm diameter by 0.5–1.0 mm thick (≈ 25 mg). Assemblies of this type yield reproducible results for the shock-pressure dependence of impact-induced devolatilization (Lange *et al.*, 1985; Tyburczy *et al.*; 1986; 1990). Peak shock pressures were calculated using impedance-match methods and the shock-wave equation of state for steel as outlined in these earlier works. Shot numbers, projectile velocities, and peak shock pressures are listed in Table I.

After the shock experiment, the sample was recovered by machining away the steel sample assembly. Effort was made to avoid contamination of the sample at this stage of preparation by preventing the stainless steel sample containers from becoming hot to the touch during machining, and by avoiding any contact with human hands or solvents.

THERMAL-DESORPTION SALI USING 118 NM LIGHT

After recovery, the samples were placed in precleaned glass vials and sent to the Molecular Physics Laboratory at SRI International, Menlo Park, CA for the thermal-desorption SALI analyses. The analysis of trace quantities of organic matter in meteorites has been described in detail by Tingle *et al.* (1991b), and is only briefly described here. A small fragment of the shock-recovered material weighing 1–5 mg was attached to a Ta strip heater using Ta wire. All tools used for handling the samples were precleaned with successive rinses of high-purity acetone, and then methanol to remove organic contamination.

Samples were heated from room temperature to 800 °C at 20 °C min⁻¹ in 10⁻⁸–10⁻⁹ Torr vacuum. Photoionization of the thermally desorbed neutral molecules was accomplished by a beam of 118 nm light passing 1 mm above and parallel to the sample surface. The 118 nm light was generated by frequency tripling the third harmonic of a pulsed (10 Hz) Nd:YAG laser in Ar-Xe (Schühle *et al.*, 1988). Light of this particular wavelength is ideally suited for analysis of organic compounds, because most compounds have ionization potentials less than the 10.5 eV of the beam and relatively large photoionization cross-sections (10⁻¹⁶ to 10⁻¹⁷ cm²) at this wavelength (Berkowitz, 1979; Arps *et al.*, 1989). However, some important compounds with ionization potentials greater than 10.5 eV (and hence not detectable by this method) include C, CO, CO₂, CH₄, C₂H₄, C₂H₂, C₂H₆, OH, H₂O and SO₂

(CRC Handbook of Chemistry and Physics). Photoions were analyzed by time-of-flight mass spectrometry. Mass spectra composed of photoions analyzed during 1500 pulses of the laser were acquired continuously during heating; each spectrum represents a 50 °C heating interval.

The principal classes of compounds detected by SALI using 118 nm in the Murchison meteorite (Figure 1, Table II) are aliphatic compounds (C_3 – C_9 alkenes and alkanes), aromatic compounds (benzene, naphthalene, phenanthrene/anthracene, pyrene/fluoranthene and their alkyl derivatives, acenaphthene, and biphenyl), elemental sulfur (which sublimates to yield S_2 – S_9 cluster species), inorganic sulfides such as troilite (which decompose to yield S_2), amines (which presumably decompose to yield NH_3), and organosulfur compounds (CH_3SH , H_2S , C_4H_4S and alkyl derivatives, COS , and CS_2). Although carboxylic acids are prominent constituents of the Murchison meteorite, as discussed in detail by Tingle *et al.* (1991b), they cannot be unambiguously identified in the thermal-desorption SALI mass spectra. However, C_{14} – C_{18} fatty acids (prominent constituents of fingerprints) are readily identifiable by this method (Tingle *et al.*, 1991b). The absence of such peaks in our spectra indicates that we have been successful in recovering and handling the shocked samples without contaminating them.

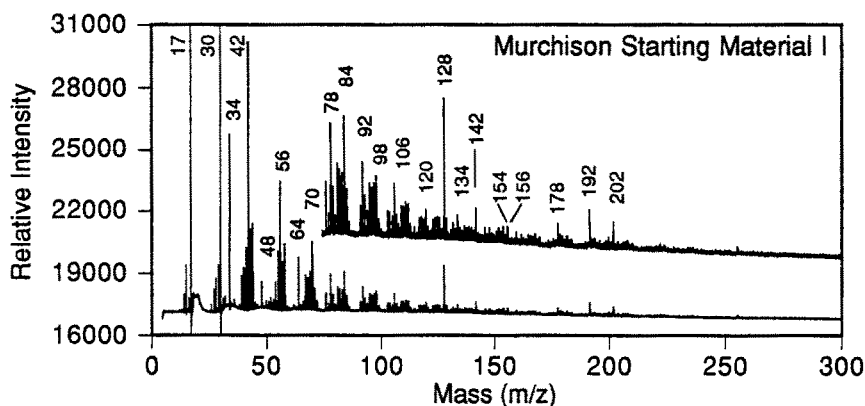


Fig. 1(a).

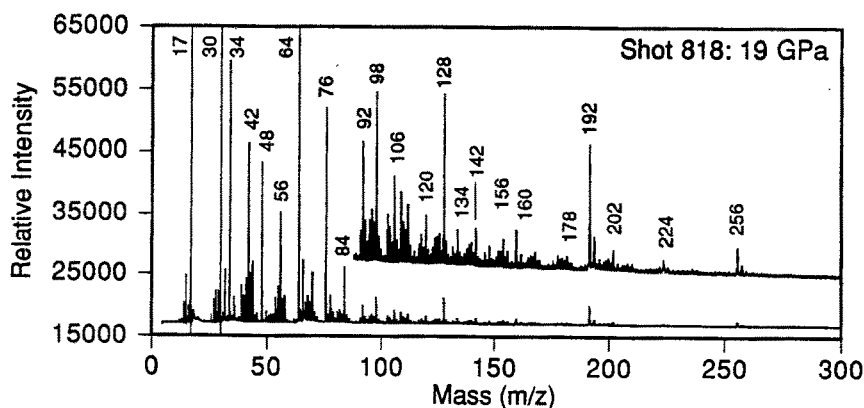


Fig. 1(b).

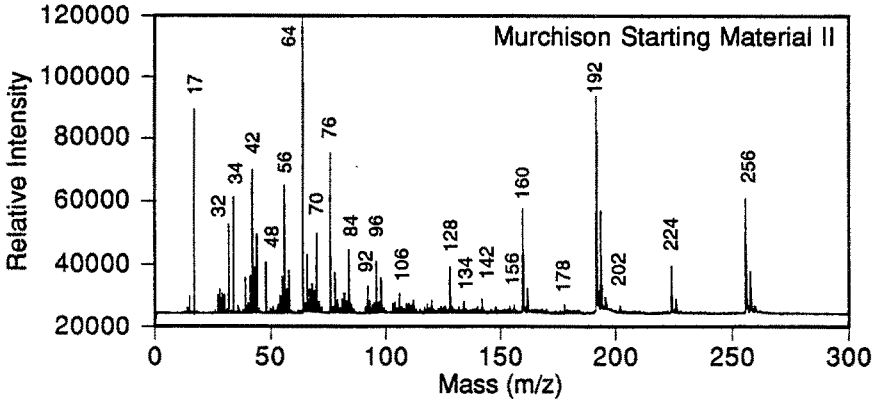


Fig. 1(c).

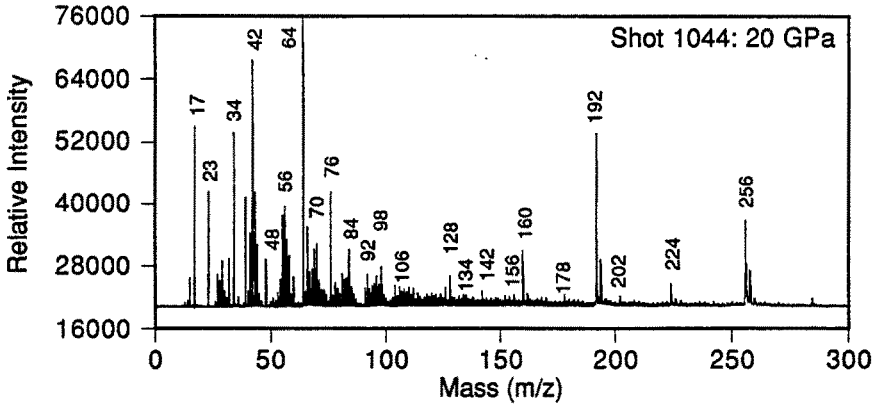


Fig. 1(d).

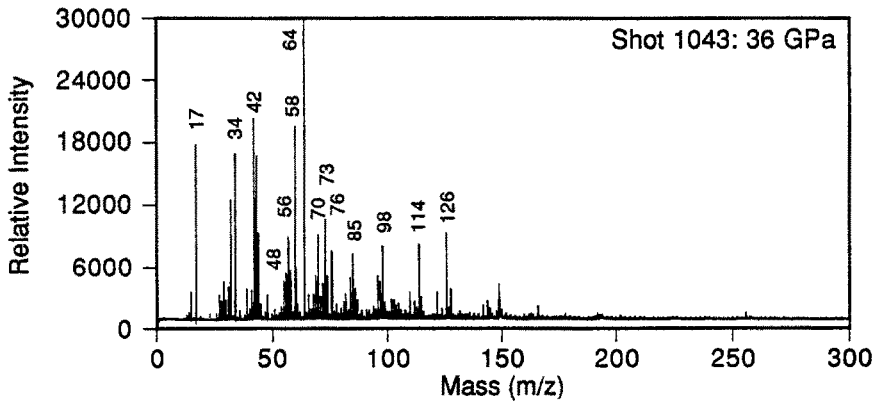


Fig. 1(e).

Fig. 1. Temperature-integrated (25–800 °C) SALI-118 nm mass spectra of (a) Murchison starting material I, (b) sample 40-818, (c) Murchison starting material II, (d) sample 20-1044, and (e) sample 20-1043. Prominent mass peaks are labeled and mass assignments are listed in Table II.

TABLE II
Mass assignments for SALI mass spectra

Mass (m/z)	Formula	Compounds
13	CH	hydrocarbon fragment
14	CH ₂	hydrocarbon fragment
15	CH ₃	hydrocarbon fragment
17	NH ₃	ammonia
23	Na	sodium
30	NO	nitric oxide
	C ₂ HJ ₆	ethane
32	S	sulfur
34	H ₂ S	hydrogen sulfide
42	C ₃ H ₆	propene
44	C ₃ H ₈	propane
48	CH ₃ SH	methyl mercaptan
56	C ₄ H ₈	butene
58	C ₄ H ₁₀	butane
	C ₃ H ₆ O	acetone
60	Ni	nickel
	COS	carbonyl sulfide
64	S ₂	elemental sulfur and sulfides
70	C ₅ H ₁₀	pentene
73	C ₅ H ₁₃	hydrocarbon fragment?
76	CS ₂	carbon disulfide
78	C ₆ H ₆	benzene
84	C ₆ H ₁₂	hexene
	C ₄ H ₄ S	thiophene
92	C ₆ H ₅ CH ₃	toluene
96	S ₃	elemental sulfur
98	C ₇ H ₁₄	heptene
	C ₄ H ₃ SCH ₃	methyl thiophene
106	C ₆ H ₅ C ₂ H ₅	xylene
	C ₆ H ₅ CHO	benzaldehyde
	C ₆ H ₄ (CH ₃) ₂	C ₂ -benzene
112	C ₈ H ₁₆	octene
114	C ₈ H ₁₈	octane
120	C ₆ H ₃ (CH ₃) ₃	C ₃ -alkyl benzene
126	C ₉ H ₁₈	nonene
128	C ₁₀ H ₈	naphthalene
	S ₄	elemental sulfur
134	C ₆ H ₂ (CH ₃) ₄	C ₄ -alkyl benzene
	C ₈ H ₆ S	benzothiophene
142	C ₁₀ H ₇ CH ₃	methyl naphthalene
154	C ₁₂ H ₁₀	biphenyl
156	C ₁₀ H ₆ (CH ₃) ₂	C ₂ -naphthalene
	C ₁₂ H ₁₂	acenaphthalene
160	S ₅	elemental sulfur
178	C ₁₄ H ₁₀	phenanthrene/anthracene
192	S ₆	elemental sulfur
	C ₁₄ H ₉ CH ₃	methyl phenanthrene/ anthracene
202	C ₁₆ H ₁₀	pyrene/fluoranthene
224	S ₇	elemental sulfur
256	S ₈	elemental sulfur

The data are grouped into two sets: (1) Murchison starting material I and sample 40–818, and (2) Murchison starting material II, samples 20–1043 and 20–1044. The two groups of data should be viewed separately for two reasons. First, sample 40–818 (partially vented) and samples 20–1043 and 20–1044 (vented) were shocked in different shock-recovery assemblies as discussed earlier, and it is important to determine whether they provide similar results. Second, the Murchison meteorite is not chemically homogeneous at the scale of samples utilized for the shock experiments or the SALI analyses. The samples for the two groups of measurements were cored from different regions of the starting material, and these two regions displayed minor variations in the abundance of specific compounds.

Results and Discussion

The abundance of analyzable organic matter in shocked Murchison decreases with increasing shock pressure consistent with the earlier work of Tyburczy *et al.* (1986). The extent of devolatilization was judged by comparing the total ion intensities in the organic mass spectra of the shocked samples to those of their respective starting materials (Figures 1, 2). The starting materials show a broad or bimodal thermal release pattern (Figure 2), which has been observed by several investigators (Hayes, 1967; Studier *et al.*, 1972; Robert and Epstein, 1982; Halbout *et al.*, 1986; Grady *et al.*, 1988). The low-temperature release (50–300 °C) is generally thought to represent loss of the indigenous (but see Cronin and Pizzarello, 1990) aliphatic component and elemental sulfur (Tingle *et al.*, 1991a, b). The higher-temperature release (>300 °C) is associated with pyrolysis of the kerogen-like material in Murchison. Sample 20–1043 (36 GPa) contained only 30% as much organic matter

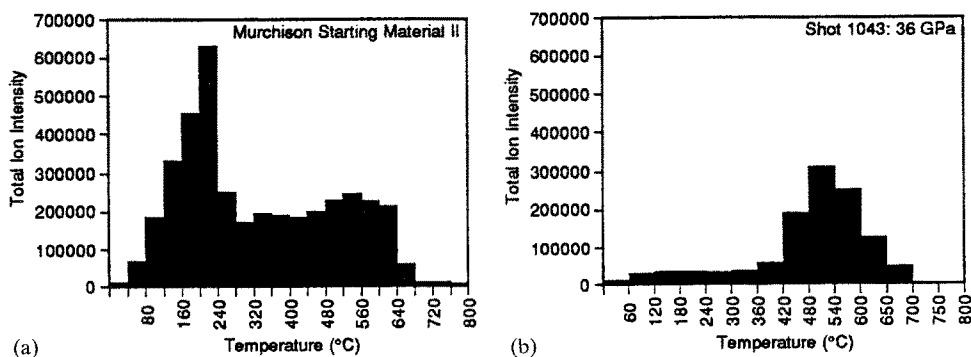


Fig. 2. Total ion intensity versus temperature for (a) Murchison starting material II, (b) sample 20-1043 (36 GPa). The starting material generally shows a bimodal or very broad release pattern; the release at <300 °C corresponds most likely to indigenous aliphatic hydrocarbons and elemental S, whereas the higher-temperature release is associated with the pyrolysis of the kerogen-like matter in Murchison. The low-temperature release is absent in the shocked sample. The abundance of analyzable organic matter decreases with increasing shock pressure, and the residual organic matter desorbs at relatively higher temperatures.

as the starting material. The low-temperature release, characteristic of the starting material, is conspicuously absent, and most of the analyzed organic matter was released above 360 °C (Figure 2). In contrast, the organic mass spectra for samples 40–818 and 20–1044 (20 and 19 GPa, respectively) were very similar to those of their respective starting materials (Figure 1), suggesting that little or no organic material was lost during impact, and that at least to 20 GPa shock pressure, results from the two different shock recovery assemblies are consistent.

More detailed examination of the organic mass spectra (Figure 1) indicates that impact-induced devolatilization is not an isochemical process. Figure 3 compares thermal-desorption spectra for specific masses analyzed in unshocked Murchison and the most highly shocked specimen. Sample 20–1043 (36 GPa) showed a significant decrease (relative to the starting material) in the abundance of elemental sulfur ($m/z = 64$, $T < 400$ °C), amines ($m/z = 17$), C_3 – C_6 aliphatic compounds, and aromatic ($m/z = 178$) compounds (Figure 3). However, the abundance of sulfides

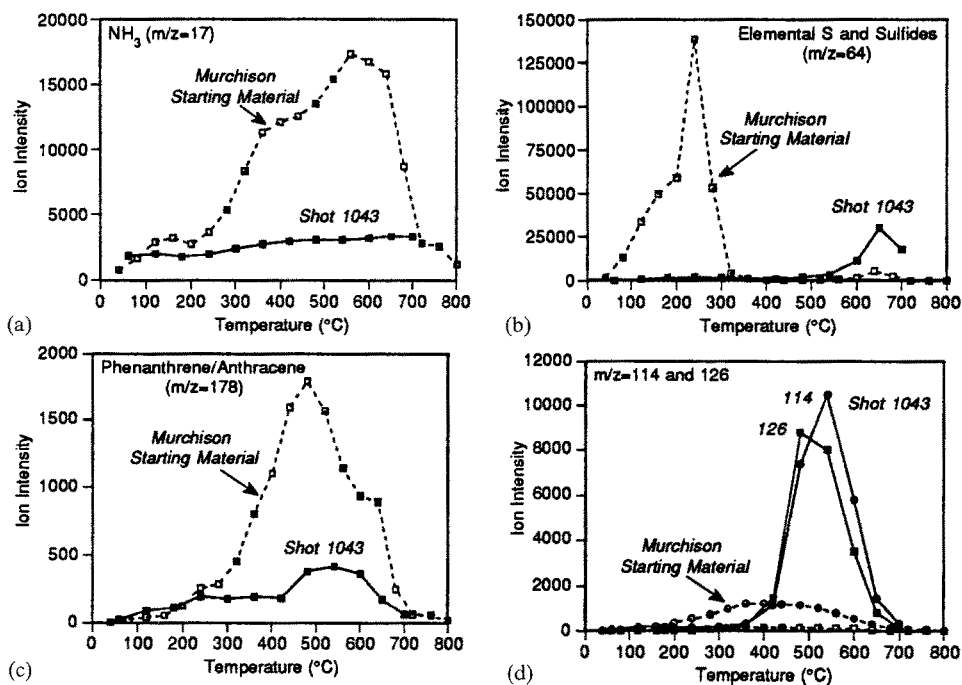


Fig. 3. Thermal-desorption mass spectra for Murchison starting material II and sample 20-1043 (36 GPa): (a) NH_3 ($m/z = 17$) presumably derived from decomposition of amines. (b) Elemental sulfur ($m/z = 64$, $T < 400$ °C) and inorganic sulfides ($m/z = 64$, $T > 400$ °C). Elemental S sublimes at low temperatures to produce S_2 – S_9 cluster species; inorganic sulfides (e.g. troilite, pyrite, pentlandite, pyrrhotite) decompose above 400 °C to produce S_2 . (c) Aromatic compounds phenanthrene and anthracene ($m/z = 178$). (d) Masses (m/z) 114 and 126. In the starting material, these peaks most likely represent C_8 and C_9 aliphatic hydrocarbons. However, it seems unlikely that these peaks represent aliphatic hydrocarbons in the shocked material, because their abundance does not conform to the logarithmic decrease in intensity with increasing C number observed in the starting material. These peaks are evidence that the residual organic matter in the shocked material was modified by the shock process.

($m/z = 64$, $T > 550$ °C) was comparable to that of the starting material. We conclude that elemental sulfur and amines are the least-stable compounds during hypervelocity impact, aliphatic and aromatic compounds appear to be somewhat more stable, and the most-stable compounds are organosulfur compounds (Figure 1, $m/z = 34$, 48, 60, and 76) and sulfides.

Significantly in sample 20-1043 (36 GPa), peaks at $m/z = 98$, 114, and 126 were more intense than in the starting material (Figure 1), indicating that some new chemical species were formed during the shock process. These peaks most likely are not heptene, octane, and nonene as identified in the starting material, because these peaks do not conform to the logarithmic decrease in abundance with increasing C number displayed by the starting material (see also Cronin *et al.*, 1988). Similarly, we conclude that the $m/z = 98$ and 126 peaks do not correspond to mono- and trimethyl thiophene because the peak for unsubstituted thiophene at $m/z = 84$ is of low intensity. Furthermore, these peaks evolved above 360 °C where pyrolysis is expected to occur. Most likely, these peaks represent pyrolysis fragments of more complex organic matter, although, an unambiguous identification of the compounds giving rise to these peaks is not possible from the present results. Essentially all of the analyzed organic matter (including $m/z = 98$, 114, and 126) in sample 20-1043 was released above 360 °C (Figure 2), indicating that the organic material surviving impact is also the most thermally stable.

The change in chemistry of the organic matter with increasing shock pressure is further reflected by a change in the ratio of alkenes to alkanes (expressed as the sum of ion intensities for C_3 - C_6) (Figure 4). Above 400 °C, the ratio is significantly lower in the shocked sample than it is in the starting material. Keeping in mind that the higher-temperature release is associated with pyrolysis of the kerogen-like carbonaceous matter, the lower ratio in the shocked sample reflects an impact-induced change in the composition of this kerogen-like material. Specifically, the

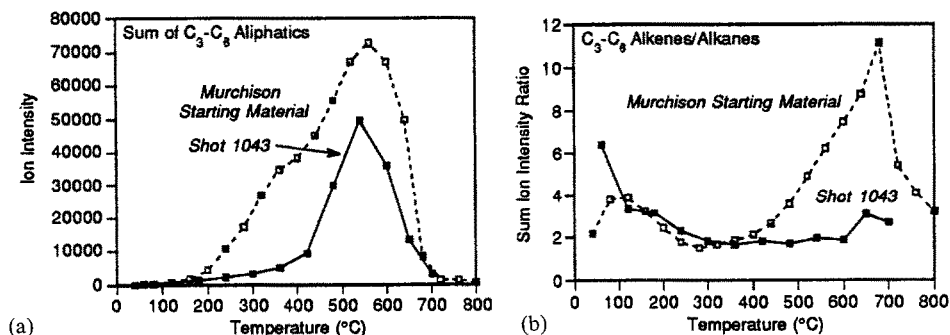


Fig. 4. Thermal-desorption mass spectra for the Murchison starting material II and sample 20-1043 (36 GPa): (a) The sum of ion intensities for peaks corresponding to C_3 - C_6 alkenes and alkanes. (b) The ratio of the summed ion intensities for C_3 - C_6 alkenes to C_3 - C_6 alkanes. The decrease in the alkene/alkane ratio suggests that the C/H ratio of the residual organic matter in the shocked material is lower than that of the starting material.

C/H ratio of the analyzable organic matter appears to be lower in the shocked samples than it is in the starting material.

Conclusions

Our preliminary data allow us to make the following conclusions. (1) The abundance of organic matter in shocked Murchison decreases with increasing shock pressure; incipient devolatilization of organic matter occurred at peak shock pressures of approximately 20 GPa, and approximately 70% of the organic matter was lost at a peak shock pressure of 36 GPa. (2) Impact-induced devolatilization is not an isochemical process; the least-stable compounds are the amines and elemental S, aliphatic and aromatic compounds have intermediate stabilities, and the most stable compounds are organosulfur compounds and inorganic sulfides. (3) The shock process gives rise to chemical reactions which produce compounds with greater thermal stability. (4) The residual organic matter of the shocked samples has a lower C/H ratio than the starting material.

There are several important questions and problems in the present work that deserve further study. First of all, at what shock pressure is all the organic matter in a carbonaceous chondrite (such as Murchison) devolatilized and what is the composition of organic matter that survives to higher shock pressures? It will be necessary to employ more sophisticated methods of analyzing the SALI mass spectra and perhaps other organic analysis techniques to identify the new compounds produced at higher shock pressures. In addition, it would be desirable to perform shock experiments at higher impact velocities to determine quantitatively what fraction of organic matter is lost as a function of shock pressure and to determine if further chemical reactions take place at higher shock pressures. Simple gravitational models suggest that impact velocities of incident bodies during the late bombardment would be greater than 5 km s^{-1} . That the precursors of life on Earth may have an exogenous source is supported by the probable non-reduced nature of Earth's primordial atmosphere, in which endogenous mechanisms such as the Miller-Urey synthesis are inefficient or inoperative (Chyba and Sagan, 1991; 1992). Also, it seems likely that molecular chiral purity preceded self-replication, and enantiomeric excesses (much less chiral purity) cannot be produced readily here on Earth (Bonner, 1991). If organic matter in chondritic and cometary materials cannot survive hypervelocity impacts during the late bombardment, then the mechanism of delivery of organic matter is constrained to have occurred by infall of interplanetary dust or airbursts, or some other relatively 'soft' delivery. Of course, the compounds of greatest relevance to the origin of life are the carboxylic and amino acids. The work of Peterson *et al.* (1991) and our thermal desorption spectra for NH_3 (Figure 3) suggest that amino acids are unstable at relatively low impact velocities ($\leq 1 \text{ km s}^{-1}$). It was not possible in the present study to ascertain the stability of carboxylic acids, although it should be feasible in the future to study the behavior of these constituents during hypervelocity impact.

The mechanisms of impact-induced devolatilization are not known. Can the stability of organic compounds be predicted from thermal decomposition studies conducted at atmospheric conditions, or is the stability of organic matter affected by increasing pressure or the nature and duration of the shock-heating event? Determining the shock-wave equation of state for Murchison would permit better estimation of the peak temperature experienced by the sample during impact.

It would be desirable to measure the abundance and isotopic composition of C, H, N, and S in the shocked materials and the composition of gases evolved during impact. The volatile inventory of the Earth is poorly constrained by cosmic abundances and uncertainties in the accretion and differentiation history of the planet. For example, the decrease in the alkene/alkane ratio of shocked materials suggests that the C/H ratio of the solid residue decreases with increasing shock pressure. This is an important observation, inasmuch as the C geochemistry of some mantle-derived materials seems to require a primordial source of C (Marty and Jambon, 1987; Galimov, 1991; Tingle, manuscript in preparation). Similarly, volatiles released during impact probably constituted a significant portion of Earth's primordial atmosphere (Ahrens *et al.*, 1989), and a knowledge of the composition of the primordial atmosphere is required to evaluate the relative importance of exogenous and endogenous sources of biologic precursors (Chyba and Sagan, 1992).

Acknowledgments

The authors would like to thank J. F. Kerridge and M. H. Engel for thorough and constructive reviews. TNT and CHB acknowledge financial support from Gas Research Institute grant 5087-260-1626 and technical assistance from L. Jusinski, W. Olson, and S. Young at SRI International. E. Gelle and M. Long provided assistance with the shock experiments. TJA acknowledges financial support from NASA grants NAGW-1941 and NAGW-1953. JAT acknowledges financial support from NSF Grant EAR86-09782. Contribution #5094, Division of Geological and Planetary Science, California Institute of Technology.

References

- Ahrens, T. J., O'Keefe, J. D., and Lange, M. A.: 1989, *Origin and Evolution of Planetary and Satellite Atmospheres*, University of Arizona Press, Tuscon, pp. 328-385.
- Arps, J. H., Chou, C. H., McCann, M. P., and Datskou, I.: 1989, *Appl. Spectr.* **43**, 1211-1214.
- Baross, J. A.: 1991, *Geol. Soc. Amer. Abstr. with Prog.* **23**, 19.
- Becker, C. H. and Gillen, K. T.: 1984, *Anal. Chem.* **56**, 1671-1674.
- Berkowitz, J.: 1979, *Photoabsorption, Photoionization, and Photoelectron Spectroscopy*, Academic Press, New York.
- Bonner, W. B.: 1991, *Origins of Life* **21**, 59-111.
- Chyba, C. F.: 1990, *Nature* **343**, 129-132.
- Chyba, C. F. and Sagan, C.: 1991, *Origins of Life* **21**, 3-17.
- Chyba, C. F. and Sagan, C.: 1992, *Nature* **355**, 125-132.
- Chyba, C. F., Thomas, P. J., Brookshaw, L., and Sagan, C.: 1990, *Science* **249**, 366-373.
- Cronin, J. R. and Pizzarello, S.: 1990, *Geochim. Cosmochim. Acta* **54**, 2859-2868.

- Cronin, J. R., Pizzarello, S., and Cruikshank, D. P.: *Meteorites and the Early Solar System*, University of Arizona Press, pp. 819–857.
- CRC Handbook of Chemistry and Physics*: 1984, CRC Press, Florida, pp. E-80–84.
- Deamer, D. W.: 1986, *Origins of Life* **17**, 3–25.
- Deming, J. W.: 1991, *Geol. Soc. Amer. Abstr. with Prog.* **23**, 19.
- Engel, M. H., Qian, Y., Macko, S. A., and Deming, J.: 1991, *Geol. Soc. Amer. Abstr. with Prog.* **23**, 25.
- Galimov, E. M.: 1991, *Geochim. Cosmochim. Acta* **55**, 1697–1708.
- Grady, M. M., Wright, I. P., Carr, R. H., Poths, J., and Pilinger, C. T.: 1988, *Earth Planet. Sci. Lett.* **87**, 293–302.
- Hayes, J. M.: 1967, *Geochim. Cosmochim. Acta* **31**, 1395–1440.
- Hayatsu, R. and Anders, E.: 1981, *Topics in Current Chemistry* **99**, Springer-Verlag, Berlin, pp. 1–37.
- Halbout, J., Mayeda, T. K., and Clayton, R. N.: 1986, *Earth Planet. Sci. Lett.* **80**, 1–18.
- Kissel, J. and Krueger, F. R.: 1987, *Nature* **326**, 755–760.
- Lange, M. A., Lambert, P., and Ahrens, T. J.: 1985, *Geochim. Cosmochim. Acta* **49**, 1715–1726.
- Marty, B. and Jambon, A.: 1987, *Earth Planet. Sci. Lett.* **83**, 16–26.
- Peterson, E., Horz, F., Haynes, G., and See, T.: 1991, *Comets and the origins and evolution of life*, University of Wisconsin, Eau Claire, Wisconsin.
- Robert, F. and Epstein, S.: 1982, *Geochim. Cosmochim. Acta* **46**, 81–95.
- Safronov, V. S.: 1969, *Formation of the Protoplanetary Cloud and Formation of the Earth and Planets*, Nauka, Moscow. Translated by the Israel Program for Scientific Translation (1972).
- Schidowski, M.: 1987, *Ann. Rev. Earth Planet. Sci.* **15**, 47–72.
- Schopf, J. W.: 1983, *Earth's Earliest Biosphere: Its Origin and Evolution*, Princeton University Press, New Jersey.
- Schühle, U., Pallix, J. B., and Becker, C. H.: 1988, *J. Amer. Chem. Soc.* **110**, 2323–2327.
- Shock, E. L.: 1990, *Origins of Life* **20**, 331–367.
- Studier, M. H., Hayatsu, R., and Anders, E.: 1972, *Geochim. Cosmochim. Acta* **36**, 189–215.
- Tingle, T. N., Hochella, M. F., Jr., Becker, C. H., and Malhotra, R.: 1990, *Geochim. Cosmochim. Acta* **54**, 477–485.
- Tingle, T. N., Mathez, E. A., and Hochella, M. F., Jr.: 1991a, *Geochim. Cosmochim. Acta* **55**, 1345–1352.
- Tingle, T. N., Becker, C. H., and Malhotra, R.: 1991b, *Meteoritics* **26**, 117–127.
- Tyburczy, J. A. and Ahrens, T. J.: 1988, *Proc. 18th Lunar Planet. Sci. Conf.*, Lunar and Planetary Institute, Texas, pp. 435–441.
- Tyburczy, J. A., Frisch, B., and Ahrens, T. J.: 1986, *Earth Planet. Sci. Lett.* **80**, 201–207.
- Tyburczy, J. A., Krishnamurthy, S., Epstein, S., and Ahrens, T. J.: 1990, *Earth Planet. Sci. Lett.* **98**, 245–261.
- Walter, M. R., Buick, R., and Dunlop, J. S. R.: 1980, *Nature* **284**, 443–445.
- Wetherill, G. W.: 1990, *Ann. Rev. Earth Planet. Sci.* **18**, 205–256.