Formation of meteorite hydrocarbons from thermal decomposition of siderite (FeCO$_3$)

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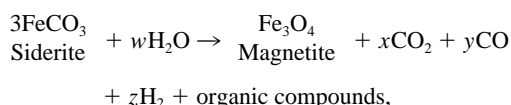
Abstract—Thermal decomposition of siderite has been proposed as a source of magnetite in martian meteorites. Laboratory experiments were conducted to evaluate the possibility that this process might also result in abiotic synthesis of organic compounds. Siderite decomposition in the presence of water vapor at 300°C generated a variety of organic products dominated by alkylated and hydroxylated aromatic compounds. The results suggest that formation of magnetite by thermal decomposition of siderite on the precursor rock of the martian meteorite ALH84001 would have been accompanied by formation of organic compounds and may represent a source of extraterrestrial organic matter in the meteorite and on Mars. The results also suggest that thermal decomposition of siderite during metamorphism could account for some of the reduced carbon observed in metasedimentary rocks from the early Earth. *Copyright © 2003 Elsevier Science Ltd*

1. INTRODUCTION

Two of the features of the martian meteorite ALH84001 that have been cited as evidence of extraterrestrial biologic activity are the presence of the mineral magnetite (Fe$_3$O$_4$) with properties resembling those produced by magnetotactic microbes on Earth and polycyclic aromatic hydrocarbons (PAH) such as phenanthrene (McKay et al., 1996; Clemett et al., 1998; Thomas-Keprta et al., 2000; Friedmann et al., 2001; Gibson et al., 2001). Recent experimental and petrologic observations, however, suggest that the magnetites in ALH84001 may have formed abiotically from decomposition of Fe-rich carbonate minerals during a transient heating event (Brearley, 1998; Scott, 1999; Golden et al., 2001; Treiman, 2001 Here, the possibility that thermal decomposition of the carbonate mineral siderite (FeCO$_3$) could also provide a source for extraterrestrial organic compounds in ALH84001 is investigated.

Synthesis of hydrocarbons from siderite decomposition would be consistent with the overall reaction

$$\begin{array}{c} 3FeCO_3 \\ Siderite \end{array} + wH_2O \rightarrow \begin{array}{c} Fe_3O_4 \\ Magnetite \end{array} + xCO_2 + yCO$$

$$+ zH_2 + \text{organic compounds,}$$

where w, x, y, and z are undetermined stoichiometric coefficients. Water is required in the reaction to provide a source of H for formation of organic compounds. The reduction of oxidized carbon to organic matter is coupled to conversion of ferrous iron [Fe(II)] from siderite to ferric iron [Fe(III)] in magnetite. On the bases of theoretical arguments, Zolotov and Shock (2000) argued that formation of PAH would be thermodynamically favored during decomposition of siderite, and production of complex organic compounds has been observed during laboratory synthesis of magnetite and siderite from thermal decomposition of iron oxalate dihydrate (IOD; FeC$_2$O$_4$·2H$_2$O) (French, 1971; McCollom and Simoneit, 1999). Thermal decomposition of siderite has also been proposed as a

source of reduced carbon, particularly graphite, in metamorphic rocks on Earth (Perry and Ahmad, 1977; Van Zuilen et al., 2001; Ueno et al., 2002). However, the synthesis of organic compounds during siderite decomposition has not previously been reported from laboratory experiments.

2. METHODS

Formation of organic compounds during thermal decomposition of siderite was observed by heating synthetic siderite crystals in the presence of water vapor at 300°C for 48 h and analyzing the organic products. Synthetic siderite was used in the experiments. The siderite was synthesized by dissolving ~5 g FeCl$_2$ in 35 mL Milli-Q H$_2$O in a Teflon beaker under a continuous stream of argon, and then adding ~5 g Na$_2$CO$_3$. The beaker was capped, placed inside a stainless steel containment vessel, and heated at 95°C for 24 h, resulting in a fine, grayish-brown powder. To remove any Fe(III) present in the reaction products and to recrystallize the carbonates, the powder was dried, placed in a gold-titanium reaction vessel with an aqueous solution of 250 mmol formic acid (HCOOH), and heated for 14 d at 250°C and 350 bars. Formic acid decomposes rapidly under these conditions to dissolved H$_2$ and CO$_2$ (McCollom and Seewald, 2001), creating strongly reducing conditions and high CO$_2$ activity within the reaction vessel. These conditions favor the stability of siderite relative to magnetite and other ferric oxides (French, 1971) and thus prevented the siderite from decomposing. After 2 weeks of heating, the solids were filtered and air dried, resulting in a fine gray-white powder (<50 μm diameter) that was predominantly crystalline siderite but also included a small fraction of magnetite.

For the decomposition experiment, ~1 g of synthetic siderite/magnetite powder and 15 μL H$_2$O were heated for 48 h at 300°C. The experiment was conducted in a 10.6-mL titanium tube reactor equipped with a sampling valve connected to the tube with a Ti capillary. Before the experiment, the titanium parts were heated in air at 330°C for 24 h to remove any organic contaminants and to form an inert TiO$_2$ layer on the reactor walls. Before heating, the reactor headspace was evacuated through the valve with a syringe and then flushed with Ar to remove any residual O$_2$ from air. After reaction, the headspace gases were removed through the valve. Aliquots of the gas were taken into gas-tight syringes and analyzed as described previously (McCollom et al., 2001). Approximately 2 mL of dichloromethane (DCM) was then injected into the reaction vessel through the valve to extract organic products, and after opening, the vessel was rinsed with additional aliquots of DCM to a total extract volume of ~4 mL. Mineral products consisted of very fine grained magnetite.

Organic products in the DCM extract were analyzed by gas chromatography–mass spectrometry (GCMS) with a Hewlett-Packard 5890 gas chromatograph interfaced to an HP 5973 mass spectrometer oper-

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ated in full scan mode. Analyses were performed with a 60-m DB-5 column with a temperature program of 25°C for 10 min, 5°C/min to 300°C, and 300°C for 15 min. The DCM extract was initially concentrated to ~20 μL under a stream of N_2 for analysis of semivolatile compounds. After analysis for semivolatile compounds, the remaining extract was further concentrated to dryness and redissolved in 2 μL DCM to detect higher molecular weight compounds that occurred in abundances that were too low to be positively identified in the initial analysis. Identification of PAH was facilitated by comparing the retention times and mass spectra of experimental products with NIST Standard Reference Material 2260 (http://srmcatalog.nist.gov/srmcatalog/certificates/srm-2260.htm). The experiment was repeated in triplicate, with essentially identical results for each replicate.

To trace the source of carbon in the organic reaction products, an additional experiment was conducted with ^{13}C-labeled siderite. A small amount of labeled siderite was synthesized by means of procedures similar to those described above but with 99% $Na_2^{13}CO_3$ used as the carbon source. The labeled siderite ($Fe^{13}CO_3$) was then mixed with additional unlabeled minerals ($Fe^{12}CO_3$), and the combined minerals were then heated with H_2O for 48 h at 300°C as in the previous experiments. Because the products of both the labeled and unlabeled mineral syntheses included a small but undetermined fraction of magnetite, the exact proportions of labeled and unlabeled siderite in the final experiment was not known; however, the proportion of labeled siderite in the experiment was approximately 15% $Fe^{13}CO_3$. The presence of the ^{13}C label in organic products was detected by comparing the mass spectra of compounds produced in the labeled experiments with spectra for analogous compounds from the unlabeled experiment.

3. RESULTS

The siderite decomposition experiment produced a large variety of organic compounds that were dominated by alkylated aromatic compounds, including alkylbenzenes, alkylphenols, and alkylnapthalenes (Fig. 1a). Within each family of homologous aromatic compounds with the same degree of alkylation, it appeared that all possible isomers were produced, indicating a randomized alkylation process. For instance, all nine possible isomers of C_3-alklybenzene were present (Fig. 2). Also identified among the products were several tri- and tetracyclic aromatic hydrocarbons along with their alkylated analogs, including phenanthrene, fluoranthene, pyrene, benz[a]anthracene, and chrysene (Fig. 3). The relative abundances of alkylbenzenes and alkylphenols generally decreased with increasing degree of alkylation (Fig. 2), but this trend was less apparent in higher order PAH (Fig. 3). Also, the relative abundance of compounds decreased with increasing number of aromatic rings (benzenes > naphthalenes > phenanthrenes, etc.). Although these organic products were not quantified, they appear to represent only a small fraction (≪1%) of the carbon initially present as $FeCO_3$.

Most of the carbon from $FeCO_3$ appears to have accumulated in the headspace gas. The analyzed components of the gas were dominated by CO_2 and H_2 with traces amounts of methane and low-molecular-weight hydrocarbons (Table 1). However, CO and residual H_2O were not analyzed. The H/C ratio of the initial reactants (~0.2) was much lower than that of the analyzed compounds in the headspace gas (~0.8), indicating the presence of an unidentified product (or products) with a low H/C ratio. This consideration suggests that CO may have been a major component of the gas phase, or that insoluble high-molecular-weight C-rich compounds were produced.

To eliminate the possibility that the observed organic compounds were derived from background sources, an additional experiment was performed in which approximately 15% of the siderite was replaced with isotopically labeled $Fe^{13}CO_3$. Anal-

yses of the products of this experiment by GCMS indicated that the organic compounds were proportionally labeled with ^{13}C (Fig. 4). Furthermore, analysis of the siderite used in the unlabeled experiments revealed trace amounts of a complex mixture of high-molecular-weight organic compounds, but at levels lower than the products of the decomposition experiments. These results confirm that the organic compounds identified here were synthesized by reduction of carbon from siderite within the reaction vessel during the experiments.

4. DISCUSSION

The experimental results indicate that synthesis of organic compounds during thermal decomposition of siderite is a potential source of extraterrestrial organic matter in ALH84001 and other carbonate-bearing martian meteorites. Indeed, the results suggest that if the magnetite observed in ALH84001 did result from thermal decomposition of siderite, in situ formation of organic matter may have been an inevitable consequence of the process. Furthermore, the results suggest a source of indigenous organic compounds for Mars that may have implications for interpreting the organic content of samples obtained from future spacecraft missions to that planet.

Previously, the most frequently invoked process for endogenous formation of organic compounds within meteorites has been the Fischer-Tropsch synthesis (Studier et al., 1972; Hayatsu and Anders, 1981; Cronin et al., 1988). In contrast to the aromatic-dominated suite of compounds observed in the siderite experiments, the products of typical Fischer-Tropsch-type syntheses are predominantly saturated, straight-chain aliphatic compounds including alkanes, alkanols, and alkanoic acids (Fig. 1c) (Dry, 1981; Anderson, 1984; McCollom et al., 1999). In this respect, the products of the siderite decomposition experiment more closely resemble the aromatic-dominated organic compounds identified in ALH84001 and other martian meteorites (McKay et al., 1996; Becker et al., 1997, 1999; Clemett et al., 1998). The products also resemble the predominant organic compounds found in nonmartian meteorites (Fig. 1b). A mechanism for the formation of organic compounds during siderite decomposition cannot be determined from the present experiments. However, possible pathways include: (1) formation of a CO_2+CO+H_2-rich gas phase during decomposition followed by a surface-catalyzed reduction and polymerization of carbon similar to the Fischer-Tropsch synthesis, but with hydrogen-limited conditions allowing for a greater predominance of aromatic compounds; or (2) polymerization of C on the mineral surface concurrent with the decomposition of siderite.

Several tri- and tetracyclic PAH, including those identified among the products of siderite decomposition (Fig. 3), have been observed in ALH84001 and have been inferred to be derived from an extraterrestrial source (McKay et al., 1996; Clemett et al., 1998; Gibson et al., 2001). Analyses of ^{14}C in the martian meteorites, however, suggest that a large fraction of the organic matter in the mass range of the PAH may be terrestrial contaminants (Jull et al., 1998, 2000). On the other hand, the isotope studies also indicate that a minor fraction of the organic matter appears to be extraterrestrial in origin, suggesting that the terrestrial contaminants overprint an extraterrestrial component. The composition of the organic matter with

(a) Siderite decomposition
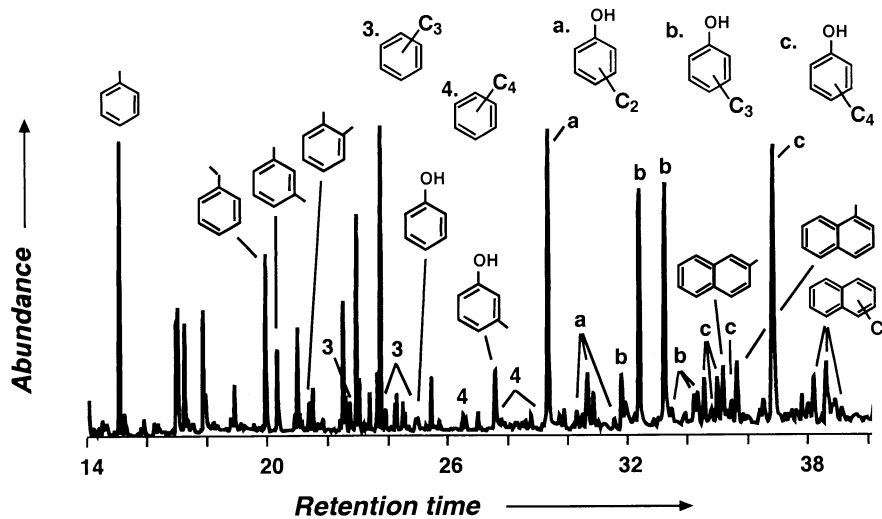
(b) Carbonaceous chondrite
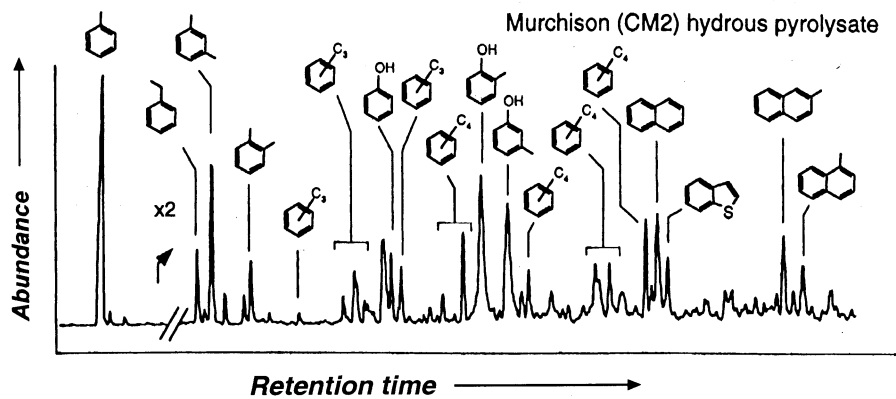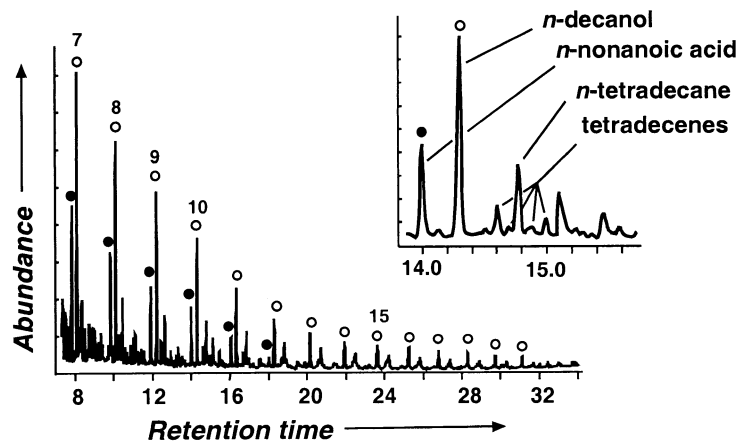

(c) Fischer-Tropsch

Fig. 1. Total ion chromatogram from GCMS analysis of organic compounds formed during siderite decomposition (a). Also shown, for comparison, are (b) hydrous pyrolysate of macromolecular organic matter from the Murchison carbonaceous chondrite (from Sephton et al., 2000) and (c) typical hydrocarbon products of the Fischer-Tropsch synthesis (modified after McCollom et al., 1999). (b) Chromatogram shows individual compounds that presumably were linked together to form macromolecular material structurally similar to terrestrial kerogen. The individual moieties in this structure were released by hydrous pyrolysis and extracted by supercritical fluid extraction. This macromolecular material represents the largest reservoir of organic carbon (>90%) in the carbonaceous chondrites. (c) Prominent peaks are homologous series of straight-chain n-alkanes, n-alkenes, n-alkanols (open circles), and n-alkanoic acids (solid circles); numbers reflect the number of carbons in alkanols.
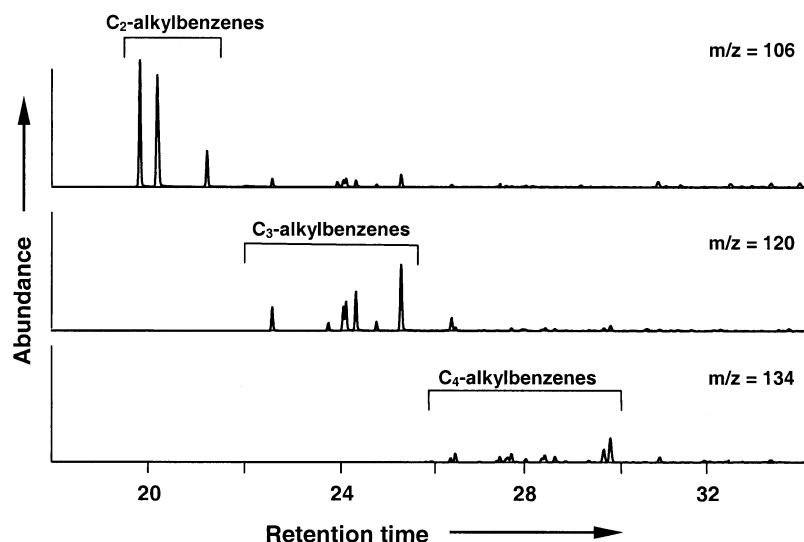
Fig. 2. Ion fragmentograms for mass/charge ratios (m/z) equal to 106, 120, and 134 from GCMS analysis of organic compounds formed during siderite decomposition. The mass/charge ratios shown are characteristic of the molecular ions of C_2-, C_3-, and C_4-alkylbenzenes, respectively. As a result of the lack of chromatographic separation for some compounds, some peaks represent more than one alkylbenzene isomer.

an apparent extraterrestrial origin has not been determined. To date, carbon isotope analyses of martian meteorites have only been reported for bulk fractions, so it is not yet possible to unequivocally evaluate the endogenous nature of individual compounds, including PAH, in the meteorites. Given the available data, it appears reasonable to hypothesize that the small amounts of PAH observed in martian meteorites including ALH84001 may be part of the fraction that is apparently extraterrestrial in origin, and that some or all of the PAH could have originated from decomposition of Fe-rich carbonates.

The PAH in ALH84001 that have been inferred to be extraterrestrial differ in some respects from those identified here as products of siderite decomposition. For instance, the compounds produced by siderite decomposition appear to be more extensively alkylated than the PAH in ALH84001 (McKay et al., 1996; Clemett et al., 1998). Also, although naphthalene and its alkylated analogs have been identified in some samples (Becker et al., 1999), the PAH from ALH84001 primarily have three or more aromatic rings. These discrepancies, however, do not necessarily preclude the possibility that the PAH observed

in ALH84001 could have formed by decomposition of siderite. Although the products of the decomposition experiments were extensively alkylated, under different conditions than those used in the present study the decomposition of siderite may generate a larger fraction of nonalkylated PAH (for instance, higher temperature, lower fugacities of H_2O and H_2, or longer reaction times). Furthermore, thermal maturation of alkylated PAH results in the continuous loss of methyl and alkyl side chains (e.g., Savage and Klein, 1987; Garrigues et al., 1990; Smith and Savage, 1991), so continued heating of the products of siderite decomposition would result in an increasing proportion of nonalkylated PAH. The paucity of lower molecular weight aromatic compounds in ALH84001 could be explained by volatilization of these compounds subsequent to siderite decomposition, leaving a residual of the larger aromatic compounds.

Although much of the debate concerning the organic matter in martian meteorites has focused on PAH because of their putative connection to biologic activities, these compounds make up only a minor fraction ($<1\%$) of the total organic carbon in the meteorite when both terrestrial and extraterrestrial components are considered (McKay et al., 1996; Becker et al., 1999). However, if the PAH prove to be extraterrestrial, they may comprise a much larger fraction of the extraterrestrial component. In any case, much of the organic carbon in the martian meteorites that is apparently extraterrestrial in origin appears to reside in the form of a high-molecular-weight, kerogen-like component (Jull et al., 1998, 2000; Becker et al., 1999). The nature of the kerogen-like material in ALH84001 has not been determined, but it may be similar in composition to the macromolecular organic matter found in nonmartian meteorites such as the carbonaceous chondrites. The macromolecular organic matter in carbonaceous chondrites is apparently composed primarily of alkylated and hydroxylated aromatic

Table 1. Relative abundances of gases in headspace of siderite decomposition experiment; CO was not analyzed..

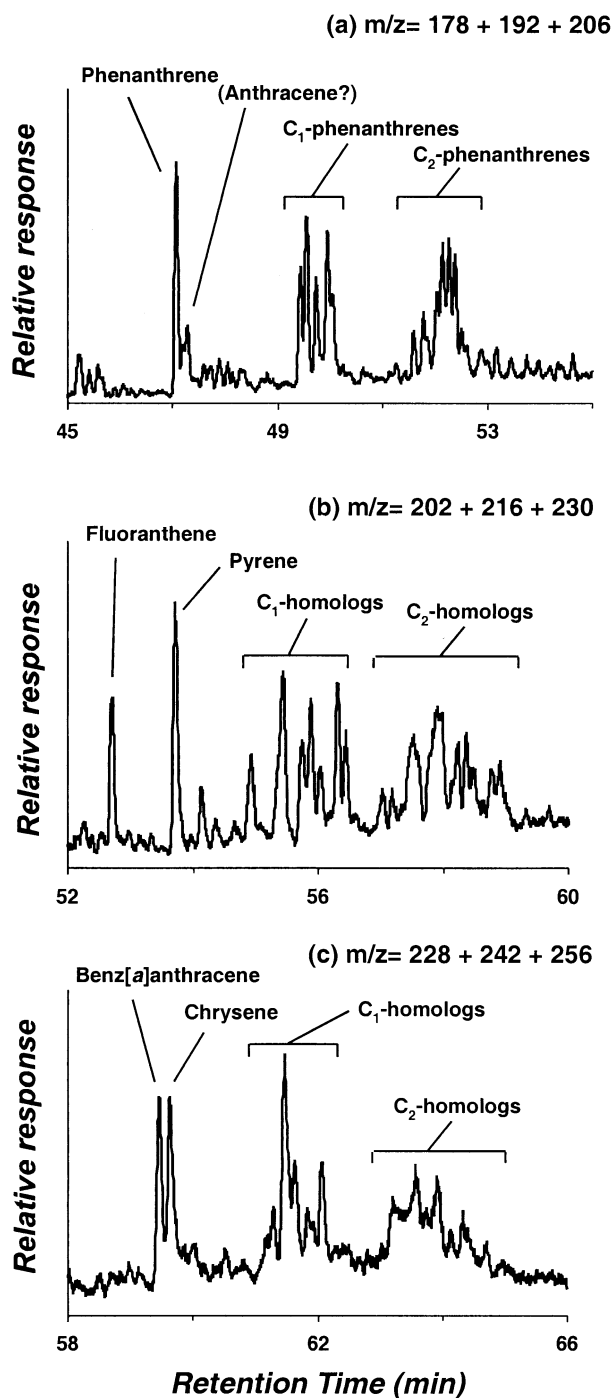| Compound	Relative concentration (mol)
CO_2	1.0
H_2	0.40
CH_4	0.00045
C_2H_4	0.000014
C_2H_6	0.0000085
C_3H_6	0.0000042
C_3H_8	0.0000032
C_4H_8	0.0000037
n-C_4H_{10}	0.0000021
iso-C_4H_{10}	<0.0000002

Fig. 3. Combined ion fragmentograms for selected mass/charge ratios (m/z) characteristic of the molecular ions of PAH and their C$_1$- and C$_2$-alkyl homologs. Individual plots show the following: (a) m/z = 178 + 192 + 206, representing phenanthrene, anthracene, and their homologs; (b) m/z = 202 + 216 + 230, representing fluoranthene, pyrene, and their homologs; and (c) m/z = 228 + 242 + 256, representing Benz[a]anthracene, chrysene, and their homologs. The peak to the right of phenanthrene corresponds to the retention time of anthracene, but its mass spectrum could not be obtained as a result of coelution with another compound, so the identification is uncertain.

compounds that are cross-linked to one another (Fig. 1b) (Sephton et al., 2000, 2001). The similarity of these materials to terrestrial kerogens formed by maturation of biologically derived organic compounds suggests that the chondrite macromolecular materials may have formed by condensation of individual aromatic compounds during thermal maturation. Although it has been proposed that the high-molecular-weight organic material observed in ALH84001 may have been derived from an exogenous source delivered to the surface of Mars during meteorite or cometary impacts (Becker et al., 1999; Jull et al., 2000), the results presented here suggest that the material could also have been produced endogenously within the meteorite through condensation of alkylated aromatic compounds produced during siderite decomposition.

Petrologic constraints suggest that the following scenario is consistent with the presence of both magnetite and organic matter including PAH in association with carbonates in ALH84001. First, the carbonates precipitated from aqueous solutions at low temperature (Golden et al., 2000; Kent et al., 2001) or within a hydrothermal environment (Treiman et al., 2002). A subsequent transient thermal event, perhaps associated with an impact, heated the meteorite precursor to a temperature sufficient to decompose Fe-carbonates, resulting in the formation of magnetite (Brearley, 1998; Scott, 1999; Golden et al., 2001; Treiman, 2001) and synthesis of organic compounds. Some of the lower molecular weight organic compounds may have been evaporated during this process and migrated out of the rock, and some of the synthesized organic compounds may have subsequently cross-linked to form macromolecular materials during continued heating. The maximum temperature of the heating event would have been high enough to decompose Fe-carbonates, but below the temperature (400 to 600°C) required for decomposition of Mg- and Ca-carbonates, leaving the remaining carbonate minerals enriched in the Mg and Ca end members (Brearley, 1998; Scott, 1999; Golden et al., 2001; Treiman, 2001).

The experiments may have broader implications for understanding the origin of hydrocarbons in other meteorites not associated with Mars, including the carbonaceous chondrites. As noted previously, although the Fischer-Tropsch process has been proposed as a mechanism for the formation of some organic compounds in meteorites, the principal products of this process don't correspond to the type of compounds that predominate in carbonaceous chondrites (cf. Fig. 1b with Fig. 1c). On the other hand, the close resemblance of the products of the siderite decomposition experiments to the individual moieties that comprise the bulk of organic matter in carbonaceous chondrites (cf. Fig. 1a with Fig. 1b) suggests the possibility that the mechanisms forming these compounds may share some common features. This would not necessarily imply that all organic matter in carbonaceous chondrites is derived directly from carbonate decomposition, although such a process cannot be precluded for some organic matter. Rather, this may indicate that the conditions that favored the formation of aromatic compounds during the siderite decomposition experiment (e.g., temperature, gas composition, surface catalysts) were similar to those present wherever the organic matter in the carbonaceous chondrites originally formed. If this proves to be the case, this process could represent a significant source of organic matter in

(a) Product from^{13}C-label experiment
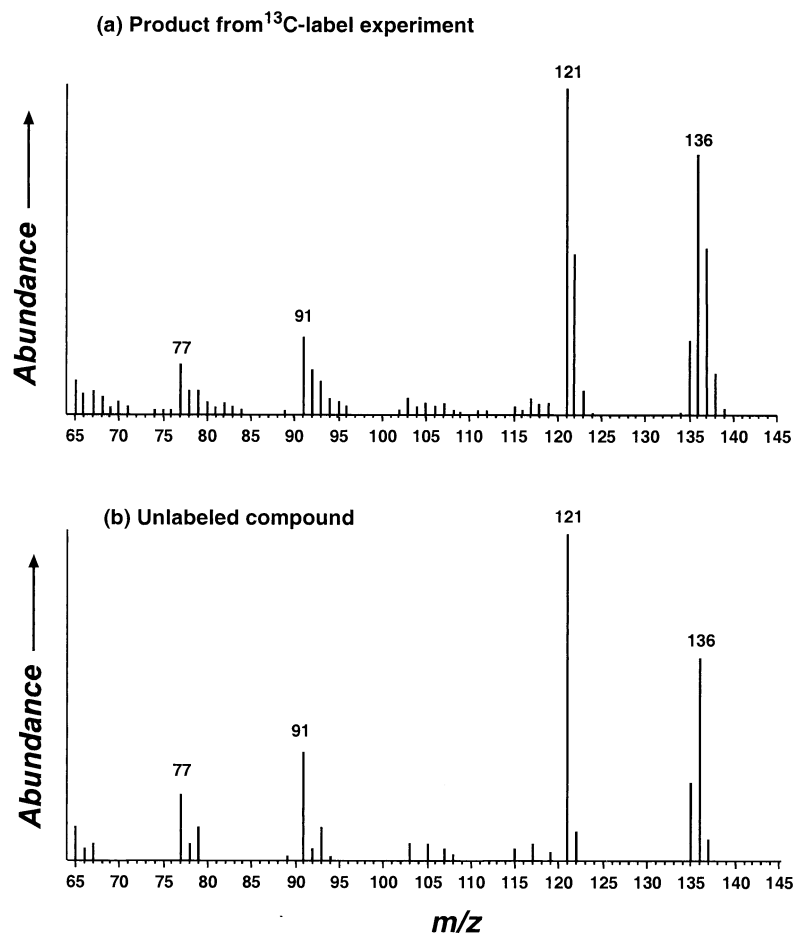

(b) Unlabeled compound

m/z

Fig. 4. Mass spectrum for a trimethylphenol isomer produced during thermal decomposition of siderite in the labeled experiment (a) compared with a spectrum for an unlabeled compound (b). The increased abundances of ions with mass/charge ratios (m/z) of 92, 122, 123, 137, 138, and 139 in (a) are indicative of partial labeling of the trimethylphenol with ^{13}C from Fe^{13}CO$_3$.

the early solar system during the formation of the Earth and the subsequent origin of life.

The experimental results may also have some bearing on the interpretation of reduced carbon in rock samples from the early Earth. Studies that claim life on Earth originated before 3.8 billion years ago rely on isotopic measurements of reduced carbon in graphite and kerogen from Archaean rocks as evidence for biologic processes (Schidlowski, 1988; Mojzsis et al., 1996). Alternatively, it has also been suggested that graphite and other organic matter in these rocks could have formed during thermal decomposition of carbonates during metamorphism (Perry and Ahmad, 1977; Van Zuilen et al., 2001; Ueno et al., 2002). The formation of organic compounds during thermal decomposition of siderite in the present study provides experimental support for the possibility of an abiotic source of reduced carbon in these rocks.

5. FUTURE WORK

Both further experimental work and additional analyses of meteorite samples will be required to determine whether the organic products of siderite decomposition can be definitively correlated with organic matter in martian meteorites. Particularly useful in this regard will be measurement of the fractionation of carbon isotopes associated with the formation of organic compounds during siderite decomposition. Isotopic analyses of the martian meteorites suggest there may be large differences in δ^{13}C compositions between carbonates and apparent extraterrestrial organic matter on the order of 60 to 80% (Wright et al., 1989; Jull et al., 1998, 2000). Explanation of isotopic differences this large with known fractionation processes is problematic. However, it seems feasible that abiotic synthesis of organic compounds during siderite decomposition could produce large fractionations because it may involve two kinetically controlled fractionating steps: mineral decomposition and organic synthesis. Also useful will be experiments investigating the role of factors such as temperature, duration of heating, and initial H/C ratio in controlling the types of organic compounds that are formed, particularly in regard to the extent of alkylation.

One aspect of siderite decomposition that was not explored in this initial study was the possible production of macromolecular organic material. The extraction and analytical methods

used in this study would not have been able to identify and characterize any macromolecular material produced in the experiments. However, given that such macromolecular products may provide the clearest link between siderite decomposition and the organic matter found in meteorites and ancient metamorphic rocks on Earth, future studies should investigate the production of these compounds.

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