An abiotic origin for hydrocarbons in the Allan Hills 84001 martian meteorite through cooling of magmatic and impact-generated gases

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Abstract—Thermodynamic calculations of metastable equilibria were used to evaluate the potential for abiotic synthesis of aliphatic and polycyclic aromatic hydrocarbons (PAHs) in the martian meteorite Allan Hills (ALH) 84001. The calculations show that PAHs and normal alkanes could form metastably from CO, CO2, and H2 below approximately 250–300 °C during rapid cooling of trapped magmatic or impact-generated gases. Depending on temperature, bulk composition, and oxidation-reduction conditions, PAHs and normal alkanes can form simultaneously or separately. Moreover, PAHs can form at lower H/C ratios, higher CO/CO2 ratios, and higher temperatures than normal alkanes. Dry conditions with H/C ratios less than approximately 0.01–0.001 together with high CO/CO2 ratios also favor the formation of alkylated PAHs. The observed abundance of PAHs, their low alkylation, and a variable but high aromatic to aliphatic ratio in ALH 84001 all correspond to low H/C and high CO/CO2 ratios in magmatic and impact gases and can be used to deduce spatial variations of these ratios. Some hydrocarbons could have been formed from entrained magmatic gases, especially if the cooling was fast enough to prevent reevaporation. We propose that subsequent impact heating(s) in ALH 84001 could have led to dissociation of ferrous carbonates to yield fine-grain magnetite, formation of a CO-rich local gas phase, reduction of water vapor to H2, reevaporation of the trapped magmatic gases, aromatization of hydrocarbons formed previously, and overprinting of the synthesis from magmatic gases, if any. Rapid cooling and high-temperature quenching of CO2, H2-rich impact gases could have led to magnetite-catalyzed hydrocarbon synthesis.

INTRODUCTION

The association of polycyclic aromatic hydrocarbons (PAHs) with carbonates in the meteorite Allan Hills (ALH) 84001 has been interpreted as a sign of biological activity on ancient Mars (McKay et al., 1996). Since the original description, no compelling new data have been obtained to prove a biologic source for PAHs or other species originally suggested to be "biomarkers" in that martian meteorite. In contrast, new analytical data on the distribution of PAHs support an abiotic origin of these compounds. Stephenson et al. (1998a,b) and Becker et al. (1999) found a broad heterogeneous distribution of PAHs among magmatic orthopyroxene, impact-generated feldspathic glass, and carbonate. No PAH enrichment in carbonates was observed. Flynn et al. (1999b,c, f) reported the presence of the same type of organic compounds in carbonate globules and the surrounding feldspathic and carbonatic rims. Several types of data also indicate the presence of aliphatic hydrocarbons in ALH 84001 (Flynn et al., 1998a,c; Bishop et al., 1999). Some samples show close spatial association of PAHs with aliphatic hydrocarbons (Flynn et al., 1998a,c), and other samples do not (Flynn et al., 1999).

Aliphatic as well as aromatic hydrocarbons could have formed on Mars from biological sources, through abiotic processes, or be present in martian meteorites as a result of terrestrial contamination. Carbon isotopic data show that organic material in ALH 84001 is predominantly terrestrial (Jull et al., 1996). In particular, amino acids appear to be terrestrial in origin (Bada et al., 1998). Microbial contamination seems to be unavoidable for almost all meteorite samples (Steele et al., 1999). However, PAHs and heavy aliphatic hydrocarbons are much less water-soluble than amino acids and therefore have a lower chance to be contaminated. Indeed, isotopic data indicate that ALH 84001 contains a refractory preterrestrial C component (Jull et al., 1998), which can consist of high molecular weight organic material (Becker et al., 1999).

Polycyclic aromatic hydrocarbons can be among this component and their indigenous character in ALH 84001 is supported by lower PAH abundance in the fusion crust compared to the interior of the samples (McKay et al., 1996; Clemett et al., 1998), and by a low abundance of PAHs in Antarctic ice and the lack of contaminant PAHs in other Allian Hills meteorites that contain no indigenous PAHs (Clemett et al., 1998). An extraterrestrial origin of PAHs in ALH 84001 is also supported indirectly by the resemblance of PAH spectra in ALH 84001 and carbonaceous chondrites (Stephan et al., 1999). Finally, the presence of hydrocarbons in magmatic orthopyroxene and feldspathic glass (Stephan et al., 1998a,b; Flynn et al., 1998b,c; Becker et al., 1999) also argues against terrestrial contamination of PAHs in ALH 84001.

The presence of similar hydrocarbons in minerals, some of which crystallized from magma, could indicate that these substances formed through similar mechanisms in a single process that is independent of martian biological activity. Anders (1996) suggested that PAHs in ALH 84001 could have formed through some kind of abiotic (e.g., Fischer–Tropsch [FT] type) synthesis from simple inorganic molecules. In previous theoretical studies (Zolotov and Shoc, 1999, 2000), we evaluated the thermodynamic potential for PAH and aliphatic hydrocarbon formation from CO, CO2, and H2 in rapidly cooling hydrothermal fluids, as well as in volcanic gases on Mars and Earth. We made the suggestion (Zolotov and Shoc, 1999) on the basis of our theoretical analysis that hydrocarbons in ALH 84001 could have formed abiotically from trapped magmatic or impact-generated gases. The purpose of this paper is to test this suggestion using thermodynamic calculations of metastable equilibria to explore hydrocarbon synthesis mechanisms in this meteorite. Our goals are to explain the observed distribution of hydrocarbons, the variable yet high aromatic to aliphatic ratios, the low degree of alkylation of the PAHs, and the deficiency of light PAHs.
CONCEPT AND MODEL

We suggest that hydrocarbons in ALH 84001 could have formed in cooling magmatic or impact-generated gases via the following net reactions exemplified by the formation of \( n \)-alkanes and a four-ringed PAH pyrene:

\[
\begin{align*}
&n\text{CO} + (2n+1)\text{H}_2 \rightarrow C_{n+2}H_{2n+2} (n\text{-alkanes}) + n\text{H}_2O & (1) \\
&16\text{CO} + 21\text{H}_2 \rightarrow C_{16}\text{H}_{10} \text{ (pyrene)} + 16\text{H}_2O & (2) \\
&n\text{CO}_2 + (3n+1)\text{H}_2 \rightarrow C_{n+2}H_{2n+2} + 2n\text{H}_2O & (3) \\
&16\text{CO}_2 + 37\text{H}_2 \rightarrow C_{16}\text{H}_{10} + 32\text{H}_2O & (4)
\end{align*}
\]

Reactions (1) and (2) illustrate reactions of the FT-type synthesis, which is used to produce synthetic fuels (Anderson, 1984). Reactions (3) and (4) proceed slower than reactions (1) and (2) and require the reduction of CO\(_2\) to CO at an early stage that precedes FT synthesis (Berndt et al., 1996; Hardy and Gillham, 1996). Despite the predominance of CO\(_2\) over CO in magmatic, volcanic, and hydrothermal gases on Mars and Earth, the formation of organic species from CO + H\(_2\) is thermodynamically more favorable than from CO\(_2\) + H\(_2\) (Zolotov and Shock, 1999, 2000). The formation of hydrocarbons from either CO + H\(_2\) or CO\(_2\) + H\(_2\) requires temperatures less than \(-400^\circ\)C and the presence of metal or oxide catalysts and is facilitated by high abundances of CO, CO\(_2\), and H\(_2\), and low abundances of H\(_2\)O (e.g., Bilenko and Schachtler, 1981; Anderson, 1984). In either the martian or terrestrial crust, magnetite represents a likely catalyst for reactions (1–4). High pressure favors the stability of hydrocarbons, especially high molecular weight and condensed compounds (e.g., Domine, 1991; Zolotov and Shock, 1999).

To explore the stability of hydrocarbons, we calculated equilibrium constants for net metastable reactions like (1–4) using thermodynamic properties for condensed \( n \)-alkanes and PAHs from Helgeson et al. (1998) and Richard and Helgeson (1998). Table 1 lists the hydrocarbons that are considered. Our modeling is constrained by the stability of solid and liquid hydrocarbons and we adopted unit activity for this species. The equilibrium constants were used to calculate the positions of saturation curves for hydrocarbons as functions of the fugacities \( f \) of gases, bulk composition, and temperature. The formation of thermodynamically stable methane and graphite were precluded because the formation of these species is kinetically inhibited below 300–600 °C in rapidly cooling natural or experimental systems (Ziengelein and Johannes, 1980; Shock, 1992; Luque et al., 1998; see Zolotov and Shock, 1999, for a review). To model the equilibrium speciation in thermal gases, we used the Gibbs free energy minimization method.

In our calculations we assume that the possible formation of hydrocarbons does not affect significantly the abundances of reactants (H\(_2\), CO, CO\(_2\)) and products (H\(_2\)O) in local environments. Nevertheless, the abundances of gases can change during natural hydrocarbon synthesis and, therefore, our evaluations represent upper limits for saturation conditions, especially for less stable hydrocarbons.

### HYDROGEN/CARBON ATOMIC RATIO AND THE STABILITY OF HYDROCARBONS

In hydrocarbons, the H/C ratio varies from 4 in methane to almost zero in high molecular weight PAHs. Alkylated PAHs have higher H/C ratios than their parent species. It is reasonable to expect that the bulk H/C ratio in the H–C–O system affects the stability of hydrocarbons. This raises the question of whether or not the patchy association of aliphatic hydrocarbons and mostly unalkylated polycyclic aromatic compounds observed at least in ALH 84001 reflects the bulk composition of the system in which martian hydrocarbons formed.

To explore the effect of the H/C ratio with respect to hydrocarbons in martian meteorites, we evaluate the stability of various \( n \)-alkanes and PAHs in cooling H–C–O gases with variable C/H ratios. We assume that magmatic or impact-generated gases are in chemical equilibrium at a high temperature and quench directly after cooling begins. At high temperatures, the equilibrium speciation of the H–C–O system is modeled at the CO\(_2\) controlled by the quartz–fayalite–magnetite (QFM) buffer:

\[
3\text{SiO}_2 + 2\text{Fe}_2\text{O}_3 = 3\text{Fe}_2\text{SiO}_4 + \text{O}_2 \quad (5)
\]

which is a reliable proxy for terrestrial (Carmichael, 1991; Kasting et al., 1993) and martian (Stolper and McSween, 1979; McSween, 1994) gas–rock–magma systems. Some martian magmatic gases (McSween et al., 1996; Ghosal et al., 1998) and some impact-generated gases (Mukhin et al., 1989; Kasting, 1990) can be more reduced than QFM, which would enhance the stability of metastable hydrocarbons when these gases cool (Zolotov and Shock, 1999, 2000).

The speciation in a high-temperature H–C–O gas depends on the bulk H/C ratio, as shown Fig. 1. In H-enriched compositions, which predominate in terrestrial volcanic gases (Symonds et al., 1994), steam is the major volatile component present. In H-depleted compositions that are suggested by the composition of martian meteorites (Karlsson et al., 1992; Bodnar, 1999), CO\(_2\) is the major species. Quenching of the gas compositions shown in Fig. 1 permits hydrocarbons to form metastably below ~230 °C depending on the speciation and the H/C ratio (Fig. 2). The highest saturation temperature for each hydrocarbon, corresponding to the maximum thermodynamic drive for its formation, occurs at the bulk H/C ratio equal to the ratio in that species. For example, pyrene (H/C = 0.625) has its maximum saturation temperature at the bulk H/C ratio of 0.625, which corresponds to the H\(_2\)O/CO\(_2\) ratio of 0.313 at 1100 °C if the CO\(_2\) is controlled by QFM. In the H\(_2\)O-rich part of

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**TABLE 1.** The hydrocarbons included in the present study.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Molecular mass</th>
<th>H/C atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )-alkanes ((C_{n+2}H_{2n+2}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n )-decanes</td>
<td>( C_{10}H_{22} )</td>
<td>142.2</td>
<td>2.2</td>
</tr>
<tr>
<td>( n )-eicosane</td>
<td>( C_{20}H_{42} )</td>
<td>282.6</td>
<td>2.1</td>
</tr>
<tr>
<td>PAHs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biphenyl</td>
<td>( C_{12}H_{10} )</td>
<td>154.2</td>
<td>0.833</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>( C_{10}H_8 )</td>
<td>128.2</td>
<td>0.800</td>
</tr>
<tr>
<td>1-methylnaphthalene</td>
<td>( C_{11}H_{10} )</td>
<td>142.2</td>
<td>0.909</td>
</tr>
<tr>
<td>1,4-dimethylnaphthalene</td>
<td>( C_{12}H_{14} )</td>
<td>156.2</td>
<td>1.000</td>
</tr>
<tr>
<td>1,3,5-trimethylnaphthalene</td>
<td>( C_{13}H_{16} )</td>
<td>170.3</td>
<td>1.077</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>( C_{12}H_{10} )</td>
<td>178.2</td>
<td>0.714</td>
</tr>
<tr>
<td>Anthracene</td>
<td>( C_{14}H_{10} )</td>
<td>178.2</td>
<td>0.714</td>
</tr>
<tr>
<td>Pyrene</td>
<td>( C_{20}H_{22} )</td>
<td>202.2</td>
<td>0.625</td>
</tr>
<tr>
<td>1-methylpyrene</td>
<td>( C_{13}H_{22} )</td>
<td>216.3</td>
<td>0.706</td>
</tr>
<tr>
<td>Chrysene</td>
<td>( C_{18}H_{22} )</td>
<td>228.3</td>
<td>0.667</td>
</tr>
<tr>
<td>Triphenylene</td>
<td>( C_{19}H_{22} )</td>
<td>228.3</td>
<td>0.667</td>
</tr>
</tbody>
</table>

*Only two of the \( n \)-alkanes considered with \( n = 5-20 \) are presented.
Fig. 1. Calculated equilibrium abundances of H–C–O gases as a function of H/C atomic ratio at 1100 °C and 1 bar. The $f$O$_2$ corresponds to the quartz–fayalite–magnetite (QFM) buffer (Eq (5)). Dashed lines mark the range of H/C ratios in terrestrial volcanic gases from Symonds et al. (1994).

the system, which is typical for terrestrial volcanic gases, aliphatic hydrocarbons (exemplified by eicosane) can form at almost the same temperatures as PAHs, yielding a metastable aromatic–aliphatic mixture below 150–200 °C. However, in dry systems (lower H/C ratios), PAHs can form at significantly higher temperatures than aliphatic hydrocarbons. Moreover, aliphatic hydrocarbons will not form if reaction (1) is inhibited at low temperatures, and PAHs will predominate among the condensed hydrocarbons. Figure 2b shows that in wet gases (high H/C ratio), methylated PAHs have higher thermodynamic potentials than their parent compounds, whereas low H/C ratios suppress the formation of methylated PAHs. The hydrocarbon saturation lines in Fig. 2e demonstrate that synthesis from CO + H$_2$ (reactions like (1) and (2)), rather than reduction of CO$_2$ (reactions like (3) and (4)), is thermodynamically favored at higher temperatures and can be responsible for hydrocarbon synthesis in cooling gases, regardless of the H/C ratio.

**EFFECT OF THE CARBON MONOXIDE/CARBON DIOXIDE RATIO**

The CO/CO$_2$ ratio in high-temperature crustal gases depends on the oxidation state of surrounding magmas and rocks, temperature, and pressure. Equilibrium with respect to the reaction

$$2\text{CO}_2 = 2\text{CO} + \text{O}_2$$  \hspace{1cm} (6)

requires that the CO/CO$_2$ ratio increases with decreasing $f$O$_2$ and decreasing pressure and, at the same time, the ratio increases with rising temperature. Except in very reduced Fe-O-bearing environments that could have existed only at the earliest stages of planetary evolution, CO$_2$ always predominates in magmatic gases even at low-pressure subvolcanic conditions and at high temperatures corresponding to ultramafic melts. However, in impact-generated gases (Mukhin et al., 1989; Kasting, 1990), and gases formed through thermal decomposition of ferrous carbonates (as described below), the abundances of CO and CO$_2$ are comparable.

The effects of variations in the CO/CO$_2$ ratio on the saturation temperatures of hydrocarbons with respect to reactions like (1–4) are shown in Fig. 3. The H/C ratio used to construct the plot in Fig. 3 is 0.001, which we use as a proxy to model dry magmatic and impact gases in ALH 84001. The saturation temperatures of hydrocarbons with respect to reactions like (1) and (2) increase with increasing CO/CO$_2$ ratios. In addition, hydrocarbon synthesis from CO + H$_2$ always exhibits a higher thermodynamic drive than synthesis from CO$_2$ + H$_2$.

Figure 3a shows hydrocarbon saturation curves as functions of CO/CO$_2$ ratio and temperature at fixed abundances of H$_2$ and H$_2$O corresponding to the H–C–O gas quenched at 1100 °C at QFM. This plot can be used to consider the effects of disequilibrium addition of CO into the cooling gases from external sources (for example, because of decomposition of ferrous carbonates). Figure 3b illustrates how oxidation state and the related CO/CO$_2$ ratio in high-temperature gases affect the saturation temperatures of hydrocarbons when the gases cool without reequilibration. More...
reduced conditions (lower \(f_{O_2}\) values) provide higher CO/CO\(_2\) and H\(_2\)/H\(_2\)O ratios at chemical equilibrium and lead to higher saturation temperatures for hydrocarbons. For example, gases quenched at the wüstite-magnetite buffer provide saturation temperatures of PAHs about 80 °C higher than gases quenched at QFM. The magnetite–hematite buffer does not favor hydrocarbon synthesis at temperatures at which reactions like (1–4) are allowed by kinetics (see Fig. 3b).

Reduced conditions in high-temperature gases also increase the thermodynamic drive to form hydrocarbons from H\(_2\) + CO\(_2\) (compare a and b in Fig. 3). The increase in the H\(_2\) abundance under reduced conditions causes an increase in saturation temperatures for hydrocarbon synthesis from CO\(_2\) + H\(_2\) despite the growing CO/CO\(_2\) ratio. This happens because the thermodynamic drives for reactions like (3) and (4) depend more on the abundance of H\(_2\) than those of CO\(_2\) and H\(_2\)O.

Reduced conditions corresponding to high CO/CO\(_2\) ratios also affect stabilities of methylated PAHs relative to their parent species. Under these conditions, the saturation curves for methylated species lie at progressively lower temperatures than for parent PAHs as exemplified by pyrene and naphthalene in Fig. 3c. To explain this behavior, we propose that an increase in temperature leads to a decrease in the stability of methylated PAHs at a fixed H/C ratio. Therefore, a high CO/CO\(_2\) ratio in cooling gases becomes an additional factor that favors the formation of unalkylated PAHs, in addition to a low H/C ratio.

SYNTHESIS IN TRAPPED MAGMATIC GASES

On Earth, magmatic temperatures of approximately 1100–1200 °C at the condition of the QFM buffer yield percent level abundances for CO and H\(_2\) owing to thermochemical equilibria (Symonds et al., 1994). During magma crystallization, released gases are commonly trapped in mineral defects and fluid inclusions. In contrast to emitted volcanic gases that are diluted upon cooling, trapped gases can maintain their concentrations if rapid cooling prevents reequilibration below magmatic temperatures. The source of various organic compounds, mostly hydrocarbons, in terrestrial igneous rocks is unclear (Markinu and Podkletnov, 1978; Petersile and Pavlova, 1978; Mathez, 1987; Tingle et al., 1990, 1991; Krot et al., 1994; Gennadiyev and Pikovsky, 1996), but they may have formed through FT-type processes as trapped gases cooled (Mathez, 1987; Tingle et al., 1990, 1991). Our theoretical models of metastable low-temperature equilibria (Zolotov and Shock, 2000) show that trapped gases typical of terrestrial volcanoes have the potential to form hydrocarbons below 200–250 °C from CO and H\(_2\), and below ~150 °C from CO\(_2\) and H\(_2\), if metastable equilibrium states can be attained. The presence of hydrocarbons in quickly cooling objects such as mantle xenoliths (Tingle et al., 1991), kimberlites (Krot et al., 1994), volcanic bombs, and the uppermost parts of lava flows (Gennadiyev and Pikovsky, 1996) is consistent with the hypothesis of FT-type synthesis of hydrocarbons from a variety of cooled magmatic gases.

The CO\(_2\)-rich fluid inclusions in pyroxene in ALH 84001 (Bodnar, 1999) may represent trapped magmatic gases. As demonstrated above, high-temperature quenching of CO\(_2\)-rich, H-depleted gases of this type would have provided a thermodynamic drive for the formation of the observed hydrocarbons. However, one complication in the trapped gas hypothesis remains. The ALH 84001 meteorite does not represent the type of volcanic rock that cools rapidly enough to quench trapped gases. Slower cooling could have led to sequential reequilibration of trapped gases, decreases in the abundances of CO and H\(_2\), establishment of stable
rather than metastable states, and inhibition of hydrocarbon formation. In the remainder of this section, we explore how low-temperature reequilibration in slowly cooling magmatic gases would affect the stability of hydrocarbons.

There are two endmember paths for the reequilibration of cooling thermal gases. One is the reequilibration in a closed gaseous system that remains unaffected by surrounding rocks. This cooling path readily occurs in high-temperature rapidly flowing magmatic fumaroles (Giggenbach, 1987). At the other extreme, the \( f/O_2 \) of the gas is controlled by the oxidation state of the surrounding rocks. The latter path usually corresponds to a low gas/rock ratio and might be applied to magmatic cumulates such as ALH 84001. It should be emphasized that reactions become sluggish as temperature decreases and some gases may quench over a wide temperature interval below the temperature of the magma. In addition, the predominance of CO \(_2\) rather than CH\(_4\) in fluid inclusions in typical terrestrial igneous rocks of mafic to ultramafic composition (e.g., Naumov and Kovalenko, 1986) as well as in ALH 84001 (Bodnar, 1999) indicates that the formation of methane can be inhibited at temperatures less than \( \sim 300 \)°C.

The speciation of a H–C–O–S gas continuously equilibrated at QFM below magmatic temperatures is shown in Fig. 4. In this example of a magmatic gas with a low H/C ratio, CO\(_2\) predominates at all temperatures. If methane forms, it is the dominant H-bearing species below \( \sim 200 \)°C, and the abundances of Hz and H\(_2\)O fall abruptly. If the formation of methane is inhibited, which seems to have occurred in ALH 84001, the abundances of Hz, H\(_2\)S, and H\(_2\)O change less sharply. In either case, the abundance of Hz remains nearly constant down to temperatures where the formation of hydrocarbons becomes possible. Although preserved concentrations of Hz and the decrease in abundance of H\(_2\)O below 300 °C favor hydrocarbon synthesis with respect to reactions (1–4), the decrease in the abundance of CO does not. However, equilibration of C–O gases can be sluggish at temperatures higher than those at which S–H–O gases equilibrate (e.g., Barnes, 1987; Giggenbach, 1987), leading to quenching of elevated CO concentrations somewhere below magmatic temperatures (as indicated schematically in Fig. 4).

High-temperature quenching of CO increases the saturation temperature for hydrocarbons as shown in Fig. 5a. The higher the quenching temperature, the higher the temperature at which hydrocarbons can form. This figure also demonstrates that PAHs may form even if the QFM buffer controls the abundance of CO at the temperature of synthesis. Figure 5b shows that high-temperature quenching of Hz is not as important for hydrocarbon synthesis as quenching of CO. However, comparison of a and b in Fig. 5 shows that the saturation temperatures of hydrocarbons depend more strongly on the abundance of Hz than CO. We conclude that although high-temperature quenching of magmatic gases favors hydrocarbon synthesis, reequilibration of slowly cooling gases does not prevent synthesis.

**SYNTHESIS IN IMPACT GASES**

An alternative to hydrocarbon synthesis from magmatic gases is provided by shock events that can create local CO-, Hz-rich atmospheres, and a newly formed magnetite catalyst. The ALH 84001 meteorite retains signs of impact event(s), and at least some of them occurred after the formation of the carbonates (Treiman, 1998; Scott *et al.*, 1997, 1998; Scott, 1999). Petrographic
observations indicate that during shock events carbonates were affected thermally, partially decomposed (Breatley, 1998; Scott, 1999), or even melted (Scott et al., 1997; 1998). In particular, carbonates were eroded on contact with the impact feldspathic melt (Breatley, 1998; Schwandt et al., 1999).

The complex composition of Fe-Mg-Ca carbonates in ALH 84001 (Mittelefeldt, 1994; Treiman, 1995; Harvey and McSween, 1996) might have led to a distinct dissociation of various components. The preservation of carbonates in the shocked rock and the lack of Ca and Mg oxide phases indicate little if any dissociation of Ca,Mg-carbonates via

\[
(Ca,Mg)CO_3 \rightarrow (Ca,Mg)O + CO_2. \tag{7}
\]
(calcite, magnesite)

However, as shown in Fig. 6, decomposition of siderite (FeCO₃) in thermal events provides significantly higher amounts of gases than the decomposition of other carbonates. The siderite component of carbonates in ALH 84001 has local mole fractions as high as 0.3–0.4 (Mittelefeldt, 1994; Treiman, 1995; Harvey and McSween, 1996) and could have been an important source for impact-generated gases.

The presence of magnetite in the contact zone between carbonates and impact feldspathic glass (Breatley, 1998), rather than wüstitte, iron metal, or graphite (all of which sometimes form from decomposing siderite (Giardini and Salotti, 1969; Gallagher et al., 1981), allows us to suggest the dissociation of ferrous carbonate in ALH 84001 via

\[
3FeCO_3 \rightarrow Fe_3O_4 + 2CO_2 + CO. \tag{8}
\]
(siderite) (magnetite)

This reaction is also consistent with a common association of magnetite with porous (possibly dissociated) Fe-rich carbonates (McKay et al., 1996) as well as with several arguments for an abiotic origin of magnetite grains in ALH 84001 (Scott, 1999). In many cases, laboratory thermal decomposition of siderite also leads to the formation of magnetite (e.g., Giardini and Salotti, 1969; Gallagher et al., 1981; Stubina and Toguri, 1988). In ALH 84001, reaction (8) would have created a CO-rich local gas phase with a CO/CO₂ ratio of 0.5 in the limiting case corresponding to the dissociation of Ca- and Mg-carbonates.

It is likely that impact heating would have led to liberation of water from decomposing hydrous minerals and from moisture trapped or adsorbed at mineral grain boundaries. In a CO-rich gas mixture, water vapor can be consumed partially via

\[
H_2O + CO \rightarrow H_2 + CO_2. \tag{9}
\]

At the low H/C (H₂O/CO₃⁻, H₂O/CO) ratio in ALH 84001, the abundance of CO in the impact gas would not have been greatly affected by progress of reaction (9). However, an increase in the H₂/H₂O ratio provided by this reaction could have enabled hydrocarbon synthesis from gas mixtures with high CO contents.

Rapid cooling after the shock event(s) would have favored high-temperature quenching of H₂-bearing, CO-rich impact gases. Therefore, when the rocks cooled to approximately 300–200 °C, these gases are likely to have consisted of disequilibrium mixtures of CO, H₂, CO₂, and H₂O. The high concentrations (up to tens of mole percent) of reduced gases (CO + H₂), low temperatures, and the presence of a freshly formed fine-grain magnetite catalyst with a high surface to volume ratio should have favored FT-type hydrocarbon synthesis.

The saturation temperatures presented in Fig. 7 show that thermal decomposition of siderite favors hydrocarbon synthesis at temperatures >250 °C. This figure illustrates a conservative case because thermal heating ALH 84001 is likely to have exceeded 250 °C and the abundance of H₂ might have been higher than a few parts per million owing to progress of reaction (9). Comparison of Fig. 7 with Fig. 5 shows that the decomposition of siderite can provide higher saturation temperatures for hydrocarbons than trapped magmatic gases. In addition, the thermal decomposition of siderite leads to a larger difference in saturation temperatures between the low and high molecular weight PAHs than does synthesis in trapped gases. This difference in turn affects speciation of hydrocarbons as we discuss below.

**DISCUSSION**

The evaluation of hydrocarbon stability described above allows us to suggest that the presence of predominantly unalkylated PAHs...
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in ALH 84001 (McKay et al., 1996) reflects a low abundance of H2O in magmatic and impact gases if they are the abiotic source of hydrocarbons on Mars. Indeed, it has been argued that martian meteorites formed in relatively dry magmatic conditions (Karlikson et al., 1992; McSween, 1994), and those in which ALH 84001 formed were the driest (Treiman, 1998; Bodnar, 1999).

The evaluations of hydrocarbon stability presented here and elsewhere (Zolotov and Shock, 2000) reveal the energetic possibility for hydrocarbon synthesis even from percent levels of CO + H2 in a gas phase that corresponds to typical magmatic gases on Earth and possibly on Mars. In impact gases, the abundances of CO and H2 can be as high as tens of percent (e.g., Mukhin et al., 1989; Kasting, 1990), which would increase both the potential for hydrocarbon synthesis and formation temperatures for individual compounds. The formation of gaseous and condensed hydrocarbons from C- and H-bearing gases during impact experiments has been demonstrated by Bar-Nun and Shaviv (1975), Mukhin et al. (1989), Sugisaki et al. (1994), and Gerasimov et al. (2000). It is worth noting that the presence of impact-generated O2 in some of these experiments does not prevent the formation of hydrocarbons. Although an experimental impact treatment of siderite has not been reported, hydrocarbon syntheses related to thermal decomposition of ferrous carbonates have been observed in a variety of experiments (Giardini and Salotti, 1969; Salotti et al., 1970; Cherns and Tsarev, 1984; Weng et al., 1996).

Thermal decomposition of ferrous carbonate in ALH 84001 may not have been the only source for CO. An additional amount of CO can be produced from CO2 because of the shifting of equilibrium (6) to the right under thermal shock. Reduction of CO2 in impact-generated gases is consistent with the results of impact vaporization of a calcite–silicate mixture (Gerasimov et al., 1996) and dolomite (Rietmeijer et al., 1999). Condensation of soot and complex C agglomerates of fullerene-type observed in those experiments provides vivid indications of locally reduced environments that should favor hydrocarbon synthesis if molecular hydrogen is present. In addition, a CO/CO2 ratio of about unity has been reported in impact experiments on carbonate-free mafic and ultramafic rocks and meteorites (Mukhin et al., 1989). Impact heating should have affected trapped magmatic gases, possibly allowing them to reequilibrate. If so, high-temperature reequilibration would have led to a higher CO/CO2 ratio than originally was in the trapped magmatic gases, improving the chance for hydrocarbon synthesis upon cooling of quenched gases.

The broad and heterogeneous distribution of hydrocarbons in ALH 84001 can be interpreted in terms of spatial variations of the H/C ratio and may reflect the distribution of moisture, hydrous minerals, carbonates, and trapped gases before the impact(s). A local enrichment in the H2O-carbonate ratio could have led to a decreased PAHs/aliphatic ratio. The lower extent of alkylated PAHs in carbonates than in silicate matrix (Clemett et al., 1998, Becker et al., 1999) could be attributed to lower H/C ratios, higher CO/CO2 ratios, or both in carbonate gloses during hydrocarbon synthesis. An enrichment of at least some carbonate gloses in PAHs (McKay et al., 1996) and other hydrocarbons (Flynn et al., 1999) may record higher CO2 + CO partial pressures that existed locally in the impact-affected carbonate grains. Finally, local temperature and pressure variations during impact event(s) could have affected the speciation of hydrocarbons.

A supply of CO from the thermal decomposition of siderite could have affected the speciation of hydrocarbons formed from CO + H2. As shown in Fig. 7, low-molecular-weight hydrocarbons might form at temperatures significantly lower than high-molecular-weight compounds. This large temperature range could have inhibited formation of low-molecular-weight PAHs. In ALH 84001, this may explain the observed deficiency of PAHs lighter than phenanthrene.

In the absence of iron metal, which is the predominant case in the martian crust, magnetite seems to be the most likely catalyst for FT-type synthesis (Hayatsu and Anders, 1981; Berndt et al., 1996; Salvi and Williams-Jones, 1997). Magnetite dispersed in igneous minerals in ALH 84001 (McKay et al., 1996) could have catalyzed hydrocarbon synthesis in trapped magmatic gases. Catalytic activity of fine-grain magnetite formed from decomposed siderite is also consistent with the enrichment of PAHs (Flynn et al., 1999) and magnetite (McKay et al., 1996; Brearley, Flynn et al., 1999) in the rims around carbonate gloses. The predominance of long-chain aliphatic hydrocarbons in the magnetite-rich rims is in contrast with the presence of short-chain hydrocarbons in magnetite-poor gloses (Flynn et al., 1998a) and could be interpreted as resulting from more effective magnetite-catalyzed FT-type synthesis in the rim.

If the impact-generated temperatures were high enough (more than 200–300 °C), the hydrocarbons would have formed in a gaseous phase and then condensed. In ALH 84001, condensates could have formed on the boundaries of mineral grains and crack surfaces as suggested for carbonaceous films in terrestrial mantle xenoliths and their alkali basalt host (Mathez, 1987; Tingle et al., 1990, 1991). It follows that carbonaceous films on the surfaces of orthopyroxene crystals in ALH 84001 (McKay et al., 1997) may represent abiotic hydrocarbon condensates rather than "biofilms."

High temperature, pressure, or both caused by shock events could have led to aromatization of hydrocarbons formed previously (including hydrocarbons formed from trapped magmatic gases). This type of process has been observed during the impact aromatization of benzene, which leads to PAHs with a high degree of alkylalkylcation (Momura, 1995). In ALH 84001, the high-molecular-weight (greater than ~300 amu), mostly alkylated PAHs (McKay et al., 1996) may be attributed to an aromatization process of this type. Experiments of Momura (1995) and pyrolysis of organic extracts of the Murchison meteorite by Becker et al. (1999) show that higher molecular weight PAHs form at the expense of lighter PAHs. Therefore, hydrocarbon generation and alteration during impact event(s) in ALH 84001 could overprint hydrocarbon synthesis from trapped gases, if any.

Our proposed synthesis mechanisms for hydrocarbons are not connected closely with the origin of the carbonates. If the carbonates precipitated from low-temperature plays brines as proposed by McSween and Harvey (1998) and Warren (1998), then impact-driven synthesis would be required. However, our model does not exclude the suggested formation of carbonates from a CO2-rich impact gas, which formed because of shock decomposition of other carbonates outside the rock (Harvey and McSween, 1996).

The Case of Carbonaceous Chondrite Organic Matter in Allan Hills 84001

Stephan et al. (1999) reported a similarity of PAH composition in ALH 84001 with data obtained for CM and CI carbonaceous chondrites. This similarity may or may not indicate the presence of chondritic organic matter in the meteorite. Although the exogenous delivery of meteoritic or cometary organic material to the surface of Mars considered by Bell (1996) and Becker et al. (1999) is possible,
it is not likely to be responsible for indigenous hydrocarbons observed in ALH 84001. First, the presence of PAHs in magmatic minerals in ALH 84001 indicates an early source on Mars rather than an exogenous sources. Second, unlike organic compounds formed in the rocks, cometary or carbonaceous chondrite organic matter derived to the surface of Mars destabilized by ultraviolet light and oxidation by atmospheric ozone, oxygen, and peroxides. Third, the study of terrestrial rock samples and modeling experiments vividly demonstrate the possibility for abiogenic synthesis of hydrocarbons in postmagmatic (Konnerup-Madsen, 1989; Tingle et al., 1991), impact (Mukhin et al., 1989; Sugisaki et al., 1994; Gerasimov et al., 2000), and hydrothermal conditions (Berndt et al., 1996; Salvi and Williams-Jones, 1997). If life is absent on Mars, these types of processes should be responsible for organic compounds in the crust. It follows that exogenous delivery of organic compounds are not likely to contribute significantly to the total inventory of organic compounds on Mars.

CONCLUSIONS

Thermodynamic calculations of low-temperature metastable equilibria show that condensed PAHs and n-alkanes can form metastably from CO + H2 and CO2 + H2 (to a lesser extent) in cooling magmatic or impact gases. Low H/C and high CO/CO2 ratios in the gas phase facilitate synthesis of hydrocarbons with high aromatic/aliphatic ratios and low extents of alkylcation of the PAHs. Synthesis of this type is consistent with the speciation of hydrocarbons observed in the ALH 84001 martian meteorite. A plausible scenario for hydrocarbon synthesis in ALH 84001 involves the following steps: (1) FT-type synthesis of metastable hydrocarbons in H2O-depleted, (CO2 + CO)-rich trapped magmatic gases that could have quenched or reequilibrated below the temperature of magma. This stage is possible but not crucial for our model of abiotic hydrocarbon synthesis. (2) Impact event(s) led to dissociation of ferrous carbonates and formation of magnetite, reduction of liberated water vapor, and generation of a patchy local H2-bearing, CO-rich reduced environment. Thermal shock favors reequilibration of trapped magmatic gases and aromatization of hydrocarbons formed previously. (3) Rapid cooling and high-temperature quenching of impact gases lead to magnetite-catalyzed hydrocarbon synthesis from CO, (CO2 ?), and H2 below ~300 °C. Synthesis in trapped gases, if any, was likely to be overprinted. Several results from this scenario are consistent with observations from ALH 84001. Low H/C and CO2/CO ratios in the gas phase favor the formation of hydrocarbons with a high aromatic/aliphatic ratio and predominantly unalkylated PAHs. The formation of light PAHs as biphenyl and naphthalene is inhibited. Local variations in the H/C ratio, in the composition of carbonates, in the oxidation states of gases and minerals, in the distribution and grain size of magnetite, and in temperature and pressure during impact event(s) lead to creation of a patchy aromatic-aliphatic pattern.

Several observations can be made that would test our hypotheses of abiotic hydrocarbon synthesis in ALH 84001 and elsewhere. Suggestions include: (1) new analytical information about the distribution, speciation, and isotopic composition of hydrocarbons in ALH 84001 and other martian meteorites; (2) an investigation of possible carbonaceous films that could be hydrocarbon condensates; (3) identification of gaseous and condensed hydrocarbons in fluid inclusions; (4) experimental study of impact and thermal decomposition of siderite in the presence of H-bearing gases, minerals, or aqueous solutions to examine whether the predicted formation of a variety of hydrocarbons occurs; and (5) experimental study of FT-type hydrocarbon synthesis to model cooling igneous rocks and impactites.

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