ABIOTIC ORIGIN FOR PAHs AND ALIPHATIC HYDROCARBONS IN ALH84001 AND NAKHLA MARTIAN METEORITES: SYNTHESIS IN TRAPPED MAGMATIC AND/OR IMPACT GASES.

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Introduction: The association of polycyclic aromatic hydrocarbons (PAHs) with carbonates in the martian meteorite ALH84001 has been interpreted as a sign of biological activity on ancient Mars [1]. In contrast, Anders [2] has argued that PAHs found in that meteorite could have formed through some kind of abiotic (e.g., Fischer-Tropsch (FT) [3] type) synthesis from simple inorganic molecules. Our prior reports [4,5] show that PAHs can form metastably together with aliphatic hydrocarbons from carbon oxides (CO, CO_2) and H_2 in cooling hydrothermal fluids, or in volcanic and fumarolic gases on Mars and Earth. Here we (1) argue that new analytical data on the distribution of PAHs and aliphatic hydrocarbons in ALH84001[6-11] and Nakhla [11] support an abiotic origin of these compounds, (2) discuss an abiotic formation of these hydrocarbons in cooling magmatic gases trapped during magma crystallization as the rocks (ALH84001 and Nakhla) formed on Mars and (3) consider the formation of hydrocarbons in cooling impact gases formed during shock event(s) in ALH84001.

Arguments for abiotic synthesis of hydrocarbons: We suggest that the following analytical data support abiotic rather than biological origins of hydrocarbons in ALH84001:

- The nearly uniform distribution of PAHs among impact feldspar glass, carbonate and magmatic orthopyroxene in ALH84001 [6].
- The presence of the same type(s) of organic compounds in the investigated carbonate globule and the feldspathic rim in ALH84001 [8,9].
- The close association of PAHs with aliphatic hydrocarbons in ALH84001 [7,9] and Nakhla [11].

Several arguments presented in [1,10,12] show that PAHs appear to be indigenous to ALH84001. The presence of hydrocarbons in orthopyroxene [6] and feldspathic glass [6-9] also argues against terrestrial contamination in ALH84001.

The similarity of C-XANES spectra for PAHs and aliphatic hydrocarbons in ALH84001 and Nakhla [11] indirectly indicate an abiotic extraterrestrial origin of hydrocarbons in Nakhla.

The concept: The presence of similar hydrocarbons in minerals, which crystallized from magma, in two distinct martian rocks could indicate that these substances formed in a single process which is not dependent on martian biological activity. We suggest that this process may be FT type synthesis via the net reaction

$$a\ CO + b\ H_2 \rightarrow c\ C_xH_y \text{ (hydrocarbon) } + d\ H_2O$$

in cooling magmatic or/and impact gas. The formation of hydrocarbons in FT type of synthesis requires relatively low temperature (< ~400°C), the presence of metal/oxide catalysts, and is facilitated by high abundances of CO + H_2 and low abundances of H_2O [e.g., 3]. High pressure favors the synthesis of hydrocarbons, especially high molecular weight and condensed species. The formation of hydrocarbons from CO_2 and H_2 is also possible at a low rate [13], however our results [5,14] show that despite CO_2 predominance over CO in magmatic/volcanic gases, the formation of organic species from CO (+H_2) is at least thermodynamically more favorable.

Synthesis of hydrocarbons in trapped magmatic gases: On Earth, magmatic temperatures of ~1100-1200°C at the condition of the quartz-fayalite-magnetite (QFM) oxygen buffer usually provide percent level abundances for CO and H_2 owing to thermochemical equilibria in the C-O-H system [15]. During magma crystallization, magmatic gases released from magmas could be trapped in mineral defects and fluid inclusions. In contrast to emitted volcanic gases that dilute with cooling, trapped gases can maintain their concentrations if rapid cooling prevents complete reequilibration. The source of various hydrocarbons in terrestrial igneous rocks [e.g., 16-19] is unclear, but they may have formed through FT type processes as trapped gases cooled [19,14]. Our theoretical models [5,14] show that trapped gases typical of terrestrial volcanoes have a high 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 CO_2-rich fluid inclusions in magmatic minerals in ALH84001 and Nakhla [20] provides vivid evidence of the presence of trapped gases. Rapid cooling of these trapped gases would have provided the thermodynamic drive for the formation of the observed metastable hydrocarbons. However, there is one complication in the trapped-gas hypothesis. Neither ALH84001 nor Nakhla represent the types of volcanic rocks that cool rapidly enough to quench trapped gases. Slower cooling is more likely to lead to sequential reequilibration of trapped gases, decreases in the abundances of CO and H_2, and establishment of stable rather than metastable states.

Synthesis of hydrocarbons in impact gases: The ALH84001 meteorite possesses vivid signs of impact events, and at least some of them occurred after the formation of carbonates [21,22]. These post-carbonate impact(s) could have led to thermal dissociation of carbonates into carbon oxide gases via net reactions

$$(Ca,Mg,Fe)CO_3 \Rightarrow (Ca,Mg,Fe)O + CO_2 \quad \text{and}$$

$$2\ CO_2 \Rightarrow 2\ CO + O_2.$$

As a result, high-temperature dissociation can produce a reduced local environment [23], probably caused by a high amount of CO. In some impact experiments the

CO/CO_2 ratio exceeds unity [24]. Water vapor (trapped/adsorbed at mineral grain boundaries, and/or liberated from hydrous minerals) can dissociate simultaneously via the net reaction

$2\ H_2O \Rightarrow 2\ H_2 + O_2$.

Rapid cooling after the impact would have favored a high-temperature quenching of impact-generated gases. Therefore when the rocks cooled to ~400-200°C they should have contained a disequilibrium mixture of CO, H_2, CO_2 and O_2. The high concentrations (up to tens of mole percent) of reduced gases (CO + H_2) and low temperatures are ideal for the synthesis of metastable hydrocarbons [3-5,14]. If the temperatures are high enough, the hydrocarbons would have formed in a gaseous phase and then condensed. Theoretical results show the possibility of this type of synthesis in cooling volcanic gases that contain less than a few % of CO + H_2 [5,14]. The formation of condensed hydrocarbons and other organic compounds from CO-, H_2-bearing impact gases has been experimentally demonstrated [24]. It is interesting that the presence of impact-generated O_2 in these experiments does not prevent the formation of hydrocarbons.

The ALH84001 meteorite crystallized from the magma with low water content [e.g., 21]. The predominance of CO_2 (in the carbonates plus inclusions) over H_2O (or OH^-) in ALH84001 before the impact(s) should have favored a high CO/H_2 ratio in impact-generated gases. That high ratio could have led to the formation of condensed hydrocarbons as PAHs (which have H/C ratios of ~0 to 0.8) rather than aliphatic hydrocarbons (such as methane and other alkanes which have H/C ratios of ~2 to 4). The formation of methane and other light alkanes could have been inhibited in such fast cooling processes [e.g., 25].

If some of the carbonate globules in ALH84001 are indeed enriched in PAHs [1] and other hydrocarbons [9], they may record higher CO_2 + CO partial pressures that existed locally in the impact-affected carbonate grains.

The proposed synthesis of hydrocarbons in cooling impact gases in ALH84001 is consistent generally with the suggested impact melting of preexisting carbonates [22] and with the model of formations of carbonates from a CO_2-rich impact gas, which formed due to shock decomposition of other carbonates outside the rock [26].

Discussion: Impact heating should have affected trapped magmatic gases, possibly allowing them to reequilibrate. High-temperature reequilibration could have led to a higher CO/CO_2 ratio than originally in the trapped magmatic gases. The effects of the impact(s) treatment on early-formed carbonates, hydrous minerals, adsorbed gases, moisture and trapped magmatic gases could have been to produce an homogenized gas mixture in the whole rock. Subsequent rapid cooling could have led to a similar mixture of metastable hydrocarbons. This mechanism is consistent with the nearly uniform distributions of PAHs in ALH84001 [6].

The formation of hydrocarbons from trapped and/or impact gases may have been catalyzed by magnetite [2,3]. Decomposition of Fe-rich carbonate may have resulted to formation of magnetite during crystallization of the impact melt [22]. In addition, a low gas/rock ratio should favor catalysis.

High pressure during magmatic crystallization and/or impact event(s) would have favored the synthesis of PAHs in ALH84001. At least the high molecular weight (>300) alkylated PAHs in ALH84001 may be attributed to that process.

Summary: The polycyclic aromatic and aliphatic hydrocarbons in ALH84001 could have formed metastably from CO (CO_2) and H_2 in cooling magmatic and/or impact gases. The origin of hydrocarbons in Nakhla is unclear, but the trapped-gases hypothesis seems to be reasonable. Tests of the pathways of hydrocarbon synthesis that we propose will be possible given new information about the distribution, speciation, and isotopic compositions of hydrocarbons in at least these two martian meteorites. Testing the existence of metastable states in these meteorites should motivate a search for gaseous or condensed hydrocarbons in recently discovered fluid inclusions [20].

Acknowledgements: This work was supported by the NSF Grant CHE-9714060.

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