

An Abiotic Organic Synthesis mechanism on Mars. Steele, A¹., Fries, M¹., Amundsen, H.E.F²., Mysen, B¹., Fogel, M¹., Schweizer, M³., L. Kater¹, Boctor, N¹.

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Introduction: Carbonate minerals in Martian meteorites and in particular ALH84001 bear witness to the processing of volatile and biologically relevant compounds (CO₂, H₂O) on Mars. In the debate to understand whether relic Martian life is present in ALH84001, significant research has been conducted to understand the presence and provenance of organic materials and specifically polyaromatic hydrocarbons (PAHs) in this meteorite (1-3, 6). The initial finding of PAHs helped spark the debate as to the presence of a possible Martian biota (3). However, whilst there is debate on the provenance of PAHs in the meteorite there is a pool of macromolecular carbon (MMC) both within the carbonate globules and the host pyroxene that is indigenous to the meteorite (3, 4). The nature, provenance and formation mechanism of both these pool of MMC remains unknown. Although in the case of MMC within the carbonate globules both biogenic and meteoritic in fall have been suggested (1)⁴.

We reported on the use of confocal micro-Raman imaging spectroscopy analysis coupled with 3-D montage light microscopy and scanning electron microscopy (SEM) of a number of carbonate globules, diffuse carbonates and features within the bulk rock (4). Analysis was conducted on fresh fracture surfaces throughout 5 allocations of ALH84001 that constitute a complete depth profile of the meteorite. To understand further the mechanism of formation of the carbonate globules and to confirm any observations on a terrestrial analogue, studies were undertaken on carbonate globules contained in xenoliths from the Bockfjord Volcanic Complex (BVC) on Svalbard. These have been shown to be similar in mineralogy to those found in ALH84001 (5). In many of the ALH 84001 globules MMC is associated with magnetite both in the rims and around small magnetite particles inside fresh internal carbonate surfaces. MMC also occurs in the magnetite associated with slab carbonates either as individual grains or clusters and with irregularly sized areas of magnetite throughout crack surfaces. Out of twenty globules imaged throughout the depth profile, five showed blebs and/or bands of MMC from areas within the rims. Eight globules have small blebs of MMC within the inner sideritic zones of the carbonate globules where they are always associated with small regions of magnetite. Out of

eight patches of magnetite analyzed in the matrix, seven contain evidence of MMC.

MMC in ALH 84001 varies from very ordered (almost pure graphite) to very disordered (similar to IDPs). The vast majority of MMC found in ALH 84001 is relatively amorphous, with crystalline graphite occurring in two localities among the matrix magnetite assemblages analyzed. Indigenous MMC, which may include PAHs, have been found within ALH 84001 (1-4). PAHs have also been detected in the MMC/graphitic component of carbonaceous chondrites and IDPs using the same techniques as applied to ALH 84001 by the McKay et al team i.e. two step laser ablation mass spectrometry (7). Raman spectroscopic analyses of similar material (i.e. carbonaceous chondrites and IDPs) show a peak distribution of MMC similar to that found in this study. We conclude therefore, that the PAHs originally found in ALH 84001 by McKay et al., (1996) are related to the pool of carbon analyzed in this study.

Graphite has been previously detected by Raman spectroscopy in the Martian meteorite NWA1068. The Raman peak distribution in ALH 84001 shows broad peaks at both ~1600 and 1350 cm⁻¹ (G and D band) that are indicative of MMC and not of poorly crystalline or crystalline graphite. Whilst Pasteris and Wopenka (2003) have shown that this peak distribution does not indicate a biological or abiological origin for MMC, however, the peak distribution of graphite and poorly ordered graphite are significantly different from kerogen or MMC. Therefore, to reiterate, the D and G bands of carbon Raman spectra cannot discriminate between known biological signal (say a Gunflint microfossil) and the non-biological carbon in IDPs.

We conclude that the carbonaceous material detected in our study is composed of MMC containing a range of compounds including polyaromatic species and that the D and G band Raman peak distribution of MMC is similar to that found in carbonaceous chondrites and IDPs. Becker et al. (1999) demonstrated the presence of macromolecular carbon in the matrix of ALH 84001].

The presence of MMC within carbonate globules in lherzolite xenoliths from BVC suggests that macromolecular carbonaceous material can be generated during carbonate deposition within mantle

rocks on Earth. Thermodynamic calculations and experimental data on the thermal breakdown of siderite show that PAHs, graphite, and MMC are produced and this observation has been used previously to explain the presence of PAHs in ALH 84001. (5, 16). Although a thermal decomposition of siderite origin for PAHs in ALH 84001 is alluring, the studies on BVC show that magnetite and carbonates associated with MMC can form during primary development of the globules.

An explanation of the development of BVC and ALH 84001 carbonate assemblages requires an understanding of the phase relationships of iron oxides, graphite and CO₂ over a range of pressure, temperature and oxygen fugacities (13 - 14). The stability field for siderite is small in temperature/*f*O₂ space compared to that for magnetite and graphite. Therefore, during formation of both the BVC and ALH84001 globules large fluctuations in oxygen fugacity (up to ~ -40 log units of *f*O₂) and temperature were possible. However, as the temperature decreases from 400°C to 0°C, so does *f*O₂ in a system buffered by hematite and magnetite. This is not an unreasonable assumption given the presence of both hematite and magnetite in BVC and ALH 84001 (13). For BVC globules, this situation is rational given the fact that after ejection from Sverrefjell, the BVC xenoliths were exposed to arctic temperatures. Hot, CO₂-containing, aqueous fluids cooled rapidly, during which time the oxygen fugacity fell, thus promoting the formation of reduced carbon phases alongside magnetite. During this process the conditions in BVC samples evidently entered the magnetite/graphite stability field twice, as MMC carbon with magnetite is detected in both the center and the outer rims of the carbonate globules. While the stability field that includes reduced carbon technically describes the carbon as graphite, the low temperatures, and corresponding lack of kinetic energy for crystalline graphite formation should reasonably produce the macromolecular carbon and PAHs found in this study and others. It has also been noted that the formation of macromolecular carbon and PAHs is energetically favorable even at moderately high H₂ fugacities (16). Hydrogen would be present in this system from dissociation of water and perhaps linked to dissolution of the host mineral matrix. These conditions would all predispose the formation of MMC observed in both BVC carbonates and ALH 84001. Similar interaction between CO₂ and FeO have also been proposed as being responsible for MMC reservoirs in meteorites and interplanetary dust particles, although it has not

previously been confirmed as a process in Martian samples or indeed terrestrial mantle rocks.

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