A comprehensive imaging and Raman spectroscopy study of ALH84001 and a terrestrial analogue from Svalbard. Steele, A[1]., Fries, M[1]., Amundsen, H.E.F[2]., Mysen, B[1]., Fogel, M[1]., Schweizer, M[3]., Boctor, N[1].
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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 (CO_2, H_2O) 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*). 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 infall have been suggested (*1*)[,4].

We report 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. 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*).

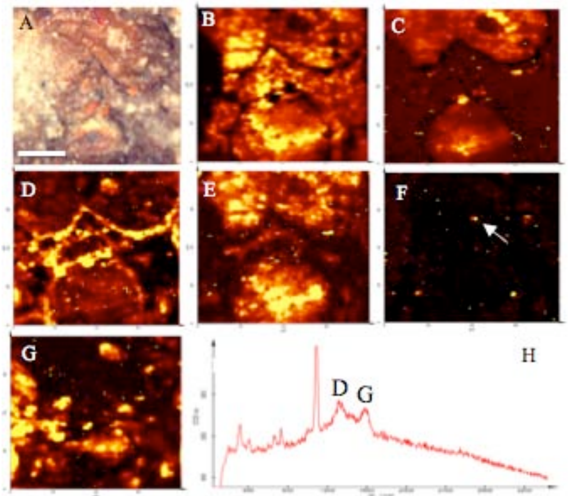
Materials and Methods: Analysis was conducted on ALH84001 samples 380, 357, 347 and 336 representing a depth profile through the meteorite with 380 and 357 containing fusion crust, 336 from near the centre and 347 at the centre of the meteorite. Samples were removed from curation vials and placed onto clean glass slides. No further mounting agents were used except in the case of one sample from the 347 allocation which was mounted into SEM mounting putty to place a single defined globule as close as possible into a single focal depth field. Svalbard xenolith samples were obtained in the Arctic Mars Analogue Svalbard Expedition (AMASE 2003 and 2004) to the Sverrefjell volcano, Bockfjorden volcanic complex, Svalbard. Raman spectra and images were collected of carbonate globules, globule rims, slab carbonates and matrix features in ALH84001 and Svalbard Xenoliths. Raman imaging was performed using a WITec α-SNOM instrument. The excitation source is a frequency-doubled solid-state YAG laser (532nm) operating at between 1-20 mW output power as measured at the laser.

Results: Raman microprobe imaging and spectral data of a cross section of one of the BVC carbonate globules occurring in an interstitial pocket in a spinel lherzolite xenolith. These globules have a centre comprised of carbonate, hematite and magnetite followed by magnesite rich carbonate bounded by an outer rim of hematite, magnetite and magnesite. MMC is present between the hematite and magnetite zones at both the centre and periphery of the globule as identified by the ordered and disordered Raman peaks of carbon at 1350 and 1610 cm^{-1}.

Figure 1 shows the results of mapping the distribution of certain characteristic spectral peaks across three globules in ALH84001 (380) shown in Figure A (peak assignments are contained within the figure caption). Hematite and pyrrhotite are distributed throughout the globules in a very heterogeneous fashion. Magnetite is mostly concentrated within the rims of the globules but can also be found as discrete patches of small (1 - 5μm) grains within the carbonate globules. MMC material (Figure 1H) appears as discrete small patches mostly within the magnetite rims. Out of twenty globules imaged throughout the depth profile, five showed MMC from areas within the rims. Eight globules have small patches of carbon within the inner zones of the carbonate globules. These are always associated with small patches of magnetite. The relationship of magnetite with MMC is found also within the diffuse carbonates, within the centre of scratched carbonate globules and in discrete patches within the matrix of the meteorite itself.

Figure 1. Raman mapping of three carbonate globules from ALH84001 357. A – Light microscopy (scale bar - 40 μm), image montage of a trio of carbonate globules. Figures B - G Raman mapping (80 x 80μm) of, B - carbonate (~1090cm^{-1}) (note the lighter the

color the more intense the signal), C - pyrrhotite (215cm^{-1}), 3D – Magnetite (677cm^{-1}), 3E – Hematite (1315 cm^{-1}), F – Carbon G band (1610 cm^{-1}) 3G – Pyroxene (1010 cm^{-1}), H – Averaged spectra of areas containing the 1610 cm^{-1} of the carbon G band. Ordered and disordered carbon peaks are shown with the letters D and G respectively.



Indigenous MMC that may include Polyaromatic Hydrocarbons (PAHs) have been found within ALH84001 (*1, 3, 6, 7*). In other studies PAHs have been detected in the MMC / graphitic component of carbonaceous chondrites and IDPs using the same technique as applied to ALH84001 by the McKay et al team (*8*). Raman spectroscopy analysis of this same material shows a peak distribution of ordered and disordered carbonaceous material similar to that found in this study (Fig 2h) (for example see (*9*, *10*)). The Raman peak distribution in ALH84001 (Fig 3h) shows broad peaks at both 1610 and 1350 cm^{-1} that is indicative of MMC and not of poorly crystalline graphite (*11*). Together with previous studies showing the presence of PAHs in this meteorite this leads us to conclude that the carbonaceous material detected in this study is composed of MMC containing a range of compounds and potentially polyaromatic species.

The confocal Raman microscope used for this study has confirmed the presence of pervasive fine-grained hematite inside the carbonate globules. Therefore to correctly interpret oxygen isotope data a hematite - carbonate standard series as well as pure carbonates should be calibrated against in any measurement (E. Hauri personnel communication). Therefore the heterogeneous distribution of hematite within the globules is likely to be responsible for the wide variations measured in oxygen isotopes and must be corrected for to gain an accurate measurement of the temperature of formation of the ALH84001 globules.

We have shown that MMC, when present in either the carbonate globules (both externally or internally), diffuse carbonates or bulk rock is always associated with fairly course-grained magnetite. We conclude therefore that the indigenous MMC found in previous studies within ALH84001 probably formed by known abiogenic means, constrained by the conditions and reactions of the Fe-C-O system. MMC formed either as a primary phase during deposition, as seen with similar reduced carbon species within carbonate globules of terrestrial BVC mantle xenoliths, or by the effects of an impact shock. Therefore, observations in this present study broadly support the Treiman (2003) hypothesis of an abiogenic production mechanism for the carbonates and some portion of the organic carbon and MMC in ALH84001 (*12*). This conclusion does not rule out the possibility that indigenous Martian life was somehow trapped or was contained within ALH84001. It does however make the task of finding evidence for indigenous Martian life more difficult. However, the separation of multiple carbon pools is the task that needs to be undertaken to enable life detection on Mars to advance with any reasonable degree of confidence at a particular result. Indeed studying how life can perturb a particular abiotic signal may be the simplest form of life detection strategy, as no inference on the nature of an unknown type of organism is needed. Whether ALH84001 does contain evidence of relic biogenic activity is therefore still a matter of debate. However, the meteorite does contain evidence of abiotic reduced carbon synthesis mechanisms that are indigenous to Mars. There has been much speculation as to the presence of hematite and the lack of carbonates on Mars. This study provides an interesting insight into the fate of carbonate on Mars. At the risk of over interpreting the data from a single rock to espouse global phenomena it never the less intriguing that this data shows that carbonate may be converted to hematite, potentially via impact mechanisms.

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