ORGANIC COMPOUNDS ASSOCIATED WITH CARBONATE GLOBULES AND RIMS IN THE ALH84001 METEORITE.

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McKay et al. [1] examined material along fracture surfaces in the ALH84001 meteorite. They reported that polycyclic aromatic hydrocarbons (PAHs), which are frequently produced by the decay of living material, were "found in the highest concentrations in the regions rich in carbonates" [1]. The formation conditions of the carbonates in ALH84001 is highly controversial. These carbonates may have formed by precipitation from a fluid, possibly water, which flowed through cracks in the meteorite. McKay et al. also found magnetite and Fe-S grains, similar in size and shape to those produced by terrestrial bacteria, occurring in dark rims surrounding carbonate globules [1]. This close spatial association of a possible indicator of liquid water, mineral grains consistent with those produced by bacteria, and hydrocarbons consistent with biological decay material led McKay et al. to suggest that ALH84001 contained evidence of possible ancient biological activity on Mars [1].

However, the PAHs were detected by Laser Desorption Laser Ionization Mass Spectrometry, using an instrument with a sampling beamspot 50 micrometers in size [1], which is comparable to the size of entire carbonate globules (~50 to 100 micrometers), and much larger than the rims (~5 to 10 micrometers thick) or the individual magnetite crystals (tens of nanometers in size). In addition, this technique was sensitive only to PAHs, not other organic molecules which are less stable in the laser desorption process.

We employed the Scanning Transmission X-Ray Microscope (STXM) on beamline X-1A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory to determine the bonding states and the spatial distribution of carbon in ultramicrotome thin-sections of carbonates and rims on the carbonates from the ALH84001 meteorite [2]. The STXM has a 50 nanometer analysis beamspot, comparable to the size of the individual magnetite and Fe-S crystals associated with the carbonates in ALH84001. Use of the STXM allows the spatial association of carbon bearing compounds with the mineral phases in ALH84001 to be examined with a resolution ~1000 times better than that achieved by McKay et al. [1].

We then examined the same thin-sections using a Spectra-Tech Fourier Transform Infrared (FTIR) spectrometer, installed on beamline U4-IR at the NSLS, to identify the carbon bonds in each sample The FTIR allows examination of these samples for a wide range of organic compounds, not just the PAHs detected by McKay et al. [1], using analysis spots down to ~3x3 microns in size.

Samples and Preparation: Fragments of ALH84001 carbonate and rim material were embedded in elemental sulfur, ultramicrotomed to a thickness of ~200 nanometers, and deposited on an SiO substrate. This sample preparation procedure avoids exposure to the carbon-bearing epoxies and the carbon substrates normally used in preparation of samples for Transmission Electron Microscope (TEM) and STXM examination. TEM examination of the ALH84001 carbonate globule samples indicated they consisted mostly of large crystals of Mg-Fe-carbonate with some regions of fine-grained Mg-Fe-carbonate and magnetite. TEM examination of the ALH84001 dark rim samples indicated they were dominated by feldspathic glass, but included large (~5 micron) chromite and small regions of fine-grained magnetite, sulfide, and Mg-Fe-carbonate similar to the rim material described by McKay et al. [1].

STXM Examination: The STXM can be used to determine the spatial distribution and the bonding state(s) of carbon in the samples. In the mapping mode, the energy of the incident monochromatic x-ray beam is fixed and the sample is scanned beneath the beam. The absorption of the sample is measured at each pixel. Since the absorption of carbon increases sharply at the carbon K-edge energy while the absorptions of other elements are approximately constant in a narrow range of energy near the carbon K-edge, a pixel showing an increase in absorption between the map just below the carbon K-edge (e.g., 280 eV) and the map just above the carbon K-edge (e.g., 300 eV) contains carbon. In Carbon-X-ray Absorption Near Edge Structure (C-XANES) mode the sample position is fixed, and the monochrometer is scanned over the energy range from 270 to 310 eV. Absorptions in this region are characteristic of particular carbon bonds. The C-O bond in carbonate gives rise to a strong absorption near 290 eV but no absorption near 285 eV, while C-C, C=C, and C-H bonds have strong absorptions in the 284 to 287 eV range. Thus, C-XANES is a sensitive technique to detect organic (or graphitic) carbon in a matrix of carbonate, making the STXM particularly well suited to identifying non-carbonate carbon in a matrix of carbonate (as is the case for the ALH84001 carbonate and rim samples).

The C-XANES spectra of the carbonate globule samples showed a strong absorption at 290 eV, characteristic of the C-O bond in carbonate. These samples also showed weaker absorptions at 284.8 eV, 286.5 eV, and 288.2 eV (shown in reference 2). The relative intensities of the latter three absorption peaks were approximately constant (where they could be detected) over the sample, suggesting that throughout the carbonate globule samples a single additional carbon-bearing phase dominated the absorption. However these three peaks varied in intensity with position on the sample. Individual 50 nanometer spot analyses varied from spots showing only the 290 eV carbonate peak to spots showing strong absorptions at at 284.8 eV, 286.5 eV, and 288.2 eV but no detectable 290 eV carbonate peak. This indicates the second carbon-bearing phase is distributed inhomogeneously, on the scale of the 50 nm beamspot, within the carbonate. Work is in progress to correlate the locations of this carbon-bearing phase with TEM mineralogy

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of the section.

Most spots on the rim samples showed no absorption at 290 eV, consistent with the absence of carbonate. Some spots on these sections showed two absorption peaks at 284.5 eV and 288.2 eV, indicating the presence of C-C, C=C, C-O, or C-H bonds. The differences in absorption peak energies and the absence of the third peak in the rim sample indicate that the dominant carbon-bearing phase in the rim is different from that in the carbonate globule. Correlation of the STXM carbon map with the TEM mineralogy indicates the carbon-rich phase is associated with the fine-grained magnetite and sulfide, and may also occur as veins or inclusions in the feldspathic glass.

FTIR Examination: To determine if the dominant carbon-bearing compound is different in the rim samples and the carbonate globule samples and to determine if these phases are organic, the same samples analyzed by STXM were examined by FTIR. These FTIR measurements were performed using a Spectra-Tech FTIR instrument installed on beamline U4-IR of the NSLS, which produces an intense, stable infrared beam, resulting in a signal/noise ratio about 100 times better than the laboratory instrument using a glowbar infrared source [3].

The FTIR spectra of the rim samples showed a broad absorption near 1000 cm^{-1}, characteristic of silicate glass, and two weaker features at 2918 cm^{-1} and 2850 cm^{-1}, consistent in position and relative depths with the symmetric and asymmetric stretching vibrations of C-H$_2$ in an aliphatic hydrocarbon (see Figure 1).

The FTIR spectra of the carbonate globule samples showed a narrow absorption at ~1500 cm^{-1}, characteristic of carbonate, and a weaker absorption at 2964 cm^{-1}. The feature at 2964 cm^{-1} is characteristic of the C-H$_3$ asymmetrical stretching vibration. Although a weaker C-H$_3$ symmetrical stretching vibration generally occurs near 2870 cm^{-1}, this feature is absent in the carbonate globule spectrum, and is suppressed in certain compounds containing C-H$_3$ groups. Two even weaker features at 2920 cm^{-1} and 2850 cm^{-1}, consistent with C-H$_2$, were also detected at some spots on the carbonate globule samples. One particularly good spectrum of the carbonate globule sample appears to show a weak, broad absorption over the range 2990 cm^{-1} and 3060 cm^{-1}. This feature could indicate the detection of C-H stretching vibrations of a mixture of PAHs, which would have an absorption centered near 3030 cm^{-1}. Follow-up measurements to determine if we have located the PAHs are planned.

Bishop et al. [4] have reported the detection of three absorption features in a bulk sample of ALH84001 at positions consistent with the three absorption bands we detected (2964, 2918, and 2850 cm^{-1}). However, because their analyses were on a bulk sample of ALH84001, they were unable to associate these absorption features with specific mineral phases in the meteorite.

Conclusions: The STXM results demonstrate the close spatial association of carbon-bearing phases containing C-C, C=C, C-O, and/or C-H bonds with the carbonate globules and rims in ALH84001. The carbon detection limit of the STXM is of order percent level. The bulk carbon contents of

other SNC meteorites have been reported to be in the 400 ppm to 700 ppm range [5]. If ALH84001 has a similar bulk carbon content, then these STXM results demonstrate that compared to the bulk meteorite relatively large concentrations of non-carbonate carbon are associated with the carbonate globules and rims from ALH84001.

The FTIR measurements indicate the rim material contains an aliphatic hydrocarbon whose absorption is dominated by the C-H$_2$ group, while the absorption in the carbonate globule is dominated by the C-H$_3$ group, thus the rim and the globule contain different carbon-bearing compounds.

The combined STXM and FTIR measurements confirm, at a much smaller scale than was possible in the McKay et al. [1] measurements, the close spatial association between organic material and the carbonate globules and rims in ALH84001. Furthermore, these results seems to rule out the simplest form of organic contamination of ALH84001, simple evaporation of an organic-rich fluid, which would be expected to leave the same residue in both the carbonate globules and the adjacent rim material. However, we cannot exclude contamination by selective absorption of different organic species onto the different mineral substrates.

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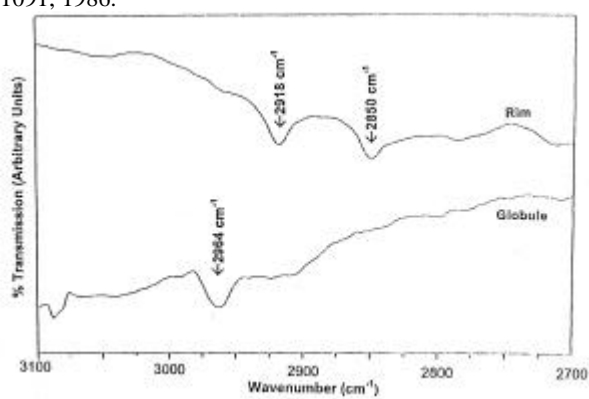

Figure 1: FTIR spectra of the C-H stretching region of a Rim sample (top) and a Carbonate Globule sample (bottom) from the ALH84001 meteorite. The Rim sample shows two strong absorptions, at 2918 and 2850 cm^{-1}, consistent with the positions and relative intensities of the C-H$_2$ stretching vibrations in an aliphatic hydrocarbon. The Carbonate Globule sample shows a single strong absorption at 2964 cm^{-1}, consistent with a C-H$_3$ stretching vibration, and a weaker, broad absorption from 2900 to 2950 cm^{-1}. This sample may also show a very weak, broad feature from 2990 to 3060 cm^{-1}, possibly associated with PAHs.