

ORGANIC CARBON IN MARS METEORITES: A COMPARISON OF ALH84001 AND NAKHLA: G. J. Flynn¹, L. P. Keller², C. Jacobsen³ and S. Wirick³, ¹Dept. of Physics, SUNY-Plattsburgh, Plattsburgh, NY 12901 (FlynnGJ@splava.cc.plattsburgh.edu), ² MVA, Inc., 5500 Oakbrook Pkwy, S. 200, Norcross, GA 30093, ³Dept. of Physics, SUNY-Stony Brook, Stony Brook, NY 11794.

Introduction: We previously reported Scanning Transmission X-Ray Microscope (STXM) carbon mapping, X-ray Absorption Near Edge Structure (XANES) spectroscopic measurements, and Fourier Transform Infrared (FTIR) spectroscopic measurements on carbonate globule and opaque “rim material” from the ALH84001 meteorite [1]. The carbonate globule was consistent with the material described by McKay et al. [2]. However, the opaque “rim material” was dominated by feldspathic glass [1], appearing opaque mainly because of the presence of chromites, and containing only minor amounts of the carbonate, magnetite, and sulfide which are major components in the rims described by McKay et al. [2]. Percent-level organic carbon was found associated with both the carbonate globule and the opaque “rim material.” FTIR spectroscopy indicated the presence of aliphatic hydrocarbons, having different ratios of C-H₂ to C-H₃ bonds, in the two samples [1]. Since then, Jull et al. [3] have demonstrated that a significant fraction of the non-carbonate carbon in bulk ALH84001 is terrestrial, presumably contamination during residence of the ALH84001 meteorite in the Antarctic. To follow-up on our earlier measurements, we have examined a new sample of carbonate with attached rim material from the ALH84001 meteorite as well as friable material extracted from a freshly broken surface of Nakhla.

ALH84001: A carbonate globule with attached rim material was extracted from a freshly broken surface of a chip of ALH84001 (ALH84001,255). This sample was embedded in elemental sulfur, a series of ultramicrotome thin sections were prepared and deposited on an SiO substrate. Several sections included a small (~2x2 microns) area of rim material attached to an ~8 micron globule fragment, preserving the spatial associations between the rim and the globule.

Transmission Electron Microscope examination of the section analyzed indicates it contains three distinct regions. Fine-grained rim material consisting of carbonate, magnetite, and rare sulfides, and coarse-grained carbonate in the globule interior are separated by a region containing coarse-grained, porous carbonate and sparse, fine-grained magnetite. This new sample has a rim consistent in mineralogy with that described by McKay et al. [2].

The sample was examined using the STXM in a new stack-imaging mode which eliminates problems previously experienced due to sample drift during acquisition of C-XANES spectra, allowing us to take full advantage of the ~50 nanometer spatial resolution of the STXM for spectroscopy. In stack-imaging mode, the absorption of focused, monochromatic x-rays is measured at each pixel.

Typically 150 to 200 absorption images are taken over the range 270 to 310 eV, with an energy spacing of ~0.1 eV in the pre-edge region. The images are aligned, correcting for sample drift during the sequence. The C-XANES spectrum is extracted either at a point by examining the image-stack along a pixel, or over a region of interest by adding pixels corresponding to that region in each image.

The highest quality spectra are obtained by averaging over the largest number of pixels. The average C-XANES spectrum over the rim material showed four strong pre-edge peaks. Three peaks, at 285 eV, 286.2 eV, and 288 eV, are similar to the peaks, at 284.8 eV, 286.5 eV, and 288.2 eV, detected in the carbonate globule from ALH84001 examined previously [1]. The fourth peak, at 290 eV, is indicative of carbonate. The globule material and the porous carbonate separating the rim from the globule interior show the same four peaks. In each C-XANES spectrum we can measure the ratio of the absorption at 290 eV to that at 288 eV to monitor the ratio of carbonate to organic carbon. The rim has a higher ratio of organic carbon to carbonate than does the globule. The porous carbonate appears to have approximately the same ratio of organic carbon to carbonate as the globule interior. Analyses of individual carbonates within the globule showed weak, but distinct, organic absorptions accompanying the strong carbonate absorption, indicating the presence of the organic component either within or associated with the large carbonates. The highest ratio of organic carbon to carbonate was found in isolated spots within the rim. Thus far, however, we have been unable to isolate regions in the rim which showed only the organic or only the carbonate absorption feature(s), suggesting that organic carbon is intimately mixed with the carbonate on the scale of ~100 nanometers in the rim. The C-XANES spectrum of this organic carbon is similar to that of acid insoluble extract from the Murray carbonate chondrite.

FTIR measurements on this section showed no detectable absorptions in the C-H stretching region.

Nakhla: A large, single stone of the Nakhla meteorite, which fell in Egypt in 1911, was made available by the British Museum for comparison with ALH84001. Since this Nakhla specimen had an almost complete fusion crust, it was hoped that it might have been protected from terrestrial contamination. Certainly, Nakhla was not exposed to the same sources of terrestrial contamination (other than in the Curatorial Facility and during STXM preparation) as ALH84001, which resided in the Antarctic before recovery.

We extracted tan-colored, friable material from a freshly broken interior chip from the British Museum Nakhla sample. FTIR analysis of this tan material indicates the presence of major phyllosilicates with minor carbonate and sulfate. Because of difficulties in micro-toming this friable material, fragments of this material were directly deposited onto a TEM grid with a SiO₂ substrate for STXM examination. We located several fragments which were thin enough (<40 nanometers thick) for STXM examination.

We performed a preliminary survey of more than 30 spots on three Nakhla fragments. Most spots showed flat C-XANES spectra, indicating significant absorption but no carbonaceous material. A few spots showed flat spectra except for the pair of potassium L-lines, indicating the presence of a K-rich phase but no carbonaceous material. One fragment of the tan-colored, friable material, included a linear region, possibly a vein, about 5 μm long and about 1 μm wide which was rich in carbonaceous material. Within this vein we identified spots showing:

- 1) carbonate (290 eV peak) plus a weak organic carbon signature (two peaks near 285 eV and 288.6 eV),
- 2) K-rich material (297 and 299 eV peaks) plus organic carbon (with two strong absorptions at 285 eV and 288.6 eV plus a weaker absorption at 286.8 eV), and,
- 3) organic carbon (strong absorptions at 285 eV and 288.6 eV and a weaker peak at 286.8 eV) alone.

The organic carbon in Nakhla has C-XANES absorptions at similar (but not identical) energies to those we previously reported for the first ALH84001 carbonate globule (284.8 eV, 286.5 eV, and 288.2 eV) [described in reference 1] and the second ALH84001 carbonate globule (285.0 eV, 286.2 eV, and 288 eV) described above. This Nakhla sample shows the same associations of organic carbon with carbonate, K-rich material, and alone that we previously reported in ALH84001 carbonate, rim, and feldspathic glass.

A second fragment of the tan, friable material from Nakhla was examined by FTIR. This fragment shows three strong absorptions in the C-H stretching region:

- 1) at 2928 cm⁻¹ and 2862 cm⁻¹ consistent with C-H₂ stretching vibrations in an aliphatic hydrocarbon,
- 2) at 2965 cm⁻¹, consistent with C-H₃ stretching vibrations, and,
- 3) a possible weak feature at about 3016 cm⁻¹, consistent with PAHs.

We previously observed similar aliphatic absorption features in the "rim" (mostly feldspathic glass) and carbonate globule samples from ALH84001 [1]. The center of the C-H₃ feature is at the same position (2964 vs 2965 cm⁻¹) in both the ALH84001 and the Nakhla samples. However, the C-H₂ features are both shifted to higher wavenumber (by 10 to 12 cm⁻¹) in the Nakhla sample compared to ALH84001, suggesting the aliphatic compounds in the two samples may be different.

Conclusions: The same three organic absorption peaks occur with roughly the same peak height ratios in both the rim and the globule of this ALH84001 sample. This indicates that the rim and the underlying globule contain the same type(s) of organic compound(s). Analyses of individual carbonates within the globule showed weak, but distinct, organic absorptions accompanying the strong carbonate absorption, indicating the presence of the organic component either within or associated with the large carbonates. The porous carbonate beneath the rim exhibits the same four C-XANES absorptions, and the average spectrum of the porous carbonate is indistinguishable from that of the core carbonate. These new measurements confirm our earlier results indicating that relatively high concentrations (percent level) of organic carbon are spatially associated, at the 10 nanometer scale, with the carbonates and rims in ALH84001.

The absence of aliphatic hydrocarbon absorption features in the new ALH84001 sample indicates the C-XANES and FTIR techniques are most sensitive to different types of organic compounds, and the aliphatic hydrocarbons detected in our earlier sample of ALH84001 are absent (or present in significantly lower abundance) in the new ALH84001 sample.

The observation of organic carbon with similar C-XANES and FTIR spectra associated with carbonate and K-rich phases in ALH84001 and Nakhla suggests a similar origin for this organic matter in both meteorites. If so, then the detection of this organic in Nakhla would rule out an Antarctic source for the organic matter we have detected in the ALH84001 carbonate globule and rim material. However, the spectra of the organic matter are not identical in the two meteorites, and we cannot rule out terrestrial contamination of each meteorite in its respective terrestrial environment.

References: 1) Flynn, G. J. et al. *Lunar & Planetary Science XXIX*, Abstract #1156, 1998. 2) McKay, D. S. et al., *Science*, **273**, 924-927, 1996. 3) Julı, A. J. T., et al., *Science*, **279**, 366-369, 1998.