ORGANIC CARBON IN CARBONATE AND RIM FROM ALH84001. G. J. Flynn[1], L. P. Keller[2], C. Jacobsen[3], and S. Wirick[3], 1) Dept. of Physics, SUNY-Plattsburgh, Plattsburgh, NY 12901, 2) MVA, Inc, 5500 Oakbrook Pkwy, Norcross, GA 30093, 3) Dept, 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) spectroscopy, and Fourier Transform Infrared (FTIR) spectroscopy on a carbonate globule and opaque "rim material" from the ALH84001 meteorite [1]. The 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 associated with both the carbonate globule and the opaque material. The carbon-XANES spectrum of the organic compound in the globule was different from that in the opaque material [1]. FTIR spectroscopy indicated the presence of aliphatic hydrocarbons, having different ratios of $C\text{-}H_2$ to $C\text{-}H_3$ groups, in the two samples [1].

New Sample: To follow-up on those measurements, 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 (~2 x 2 micron) area of rim material attached to an ~8 micron globule fragment. These sections preserve the spatial associations between the rim and the globule.

Transmission Electron Microscope examination indicates the sections contain 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. The rim is 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 the acquisition of carbon-XANES spectra. The stack-imaging mode allows us to take full advantage of the ~50 nanometer spatial resolution of the STXM for spectroscopy. In the stack-imaging mode, the absorption of focused, monochromatic x-rays is measured at each pixel on a thin-section. 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 single pixel, or over a region of interest by adding the pixels corresponding to that region in each image. At each energy, the reference intensity (on the substrate) and sample intensity are measured on the same image, rather than in two successive spectra which are sometimes offset slightly in energy due to nonreproducibilities in the monochrometer motion (a problem being addressed in a STXM redesign).

C-XANES Results: Figure 1 shows the STXM image of the entire sample. The highest quality spectra are obtained by averaging over the largest number of pixels on the sample. Figures 2 through 4 show C-XANES spectra averaged over the rim material, the globule interior, and the region containing coarse-grained, porous carbonate and fine-grained magnetite which separates the globule interior from the rim.

Pre-edge (π^*) absorptions occur at photon energies corresponding to induced electron transitions from the K-shell to unoccupied outer orbitals whose energies are very sensitive to the types and locations of neigh- boring atoms. The rim material showed four strong π^* peaks (Figure 2). 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]. Those peaks were associated with organic carbon by Fourier Transform Infrared spectroscopic examination of that globule [1]. The fourth peak, at 290 eV, is indicative of carbonate. The globule material (Figure 3) and the porous carbonate (Figure 4) separating the rim from the globule interior show the same four π^* peaks.

Figure 1: STXM image of an ultramicrotome thin section of ALH84001. The top consists of large carbonate in the interior of the globule. The lower ~2 µm is fine-grained rim. These two regions are separated by coarse-grained, porous carbonate.

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. Comparing the average C-XANES spectrum over the carbonate globule with the average over the rim indicates that 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.

The highest ratio of organic carbon to carbonate was found in isolated spots within the rim. Thus far, however, we have been unable to locate regions in the rim which show 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.

Conclusions: The same three organic absorption peaks occur with roughly the same peak height ratios in both the rim and the globule. This indicates that, in this sample, the rim and the 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 100 nanometer scale, with the carbonates in ALH84001. They differ from the earlier results in that this sample of rim material, consisting of fine-grained carbonate, magnetite, and sulfides (i.e., the type of rim described by McKay et al. [2]), contains an organic component that is identical in its C-XANES spectrum to that of the carbonate globule to which it is attached. The opaque sample we analyzed previously, which was dominated by feldspathic glass and chromite, has a C-XANES spectrum which differs in absorption peak energies and height ratios from these rim and globule samples. FTIR measurements, to identify specific carbon functional groups in this sample, are in progress.

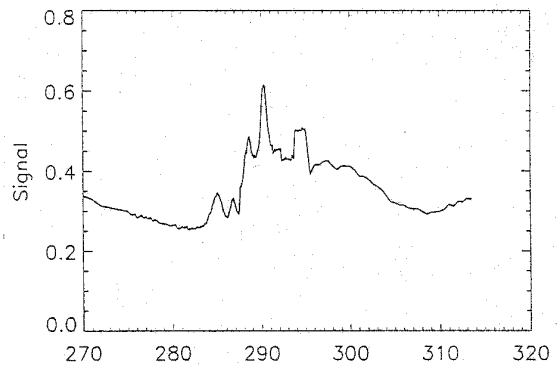

Figure 2: C-XANES spectrum averaged over the rim of the ALH84001 sample shows three π* peaks, at 285 eV, 286.2 eV, and 288 eV, indicative of organic carbon and a peak at 290 eV from carbonate.

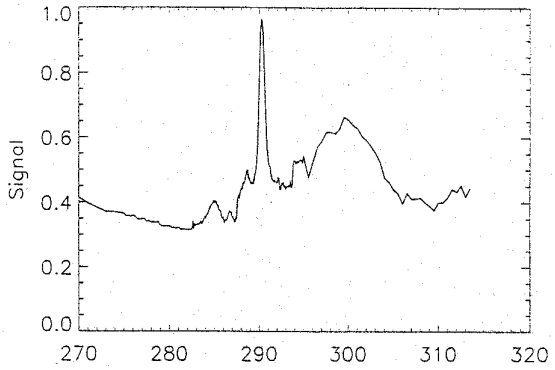

Figure 3: C-XANES spectrum averaged over the globule interior. The ratio of the intensity of the carbonate peak to the organic peaks is higher in the globule interior than in the rim (shown in Figure 2).

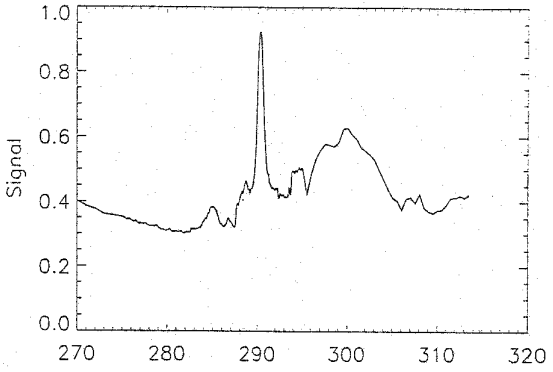

Figure 4: C-XANES spectrum averaged over the porous carbonate, located between the rim and interior. The spectrum is very similar to that of the carbonate in the interior (shown in Figure 3).

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.