FTIR and Fluorescence Spectroscopic Analyses of NWA 7034: Organic Terrestrial Contamination and its Association with High Nickel Regions . S. Wirick[1], G. J. Flynn[2], J. Brandes[4], L. Miller[3], R. Smith[3], [1]Center for Advanced Radiation Sources, Univ. of Chicago, Chicago, IL 60637, USA,(swirick@bnl.gov), [2]Dept. of Physics, Plattsburgh University NY 12901, USA, [3]Photon Science Dept., Brookhaven Nat. Lab., Upton, NY 11973 USA, [4]Skidaway Institute Oceanography, Savannah, GA 31411 USA

Introduction: NWA 7034 and its pairings are the first meteorites to be identified as containing Martian surface soil [1]. The meteorite was collected in the Western Sahara and is believed to have formed on and near the surface of Mars by either volcanic material mixing with surface material to form a regolith breccia or by multiple impact events mixing with Martian soil [2,3,4,5]. Grady, et al. [6] reported that NWA contained an order of magnitude more terrestrial carbon than any other Martian meteorite. We have characterized this carbonaceous matter using FTIR spectroscopy and mapped Fe and Ni to determine associations with this organic matter.

Samples and Methods: An ~ 0.3 g of NWA 7034 was examined. Two thirds of this piece was ground and embedded in sulfur and microtomed to a thickness of ~ 100 nm. Microtomed sections were placed onto Mo TEM grids backed with formvar/carbon. The grids had been previously analyzed for trace metal content. For metals analysis, the X26A microprobe beamline located at the National Synchrotron Light Source (NSLS) was used. This beamline has a 10 micron focused beam size and ~10x9 photons per sec in the focused beam. Flyscan mode was used to collect element maps and fluorescence spectra were extracted from regions of interest in these maps. A pixel size of 5 microns was used. The Continuum FTIR microscope located at the U2B beamline, also at the NSLS, was used to collect FTIR spectra. This instrument was set to a 10 micron aperture and the infrared synchrotron source is ~ 1000 times brighter than a globar source. FTIR spectra were collected using a count time of 1000 scans.

X-ray Results: A total of 7 grids were made with an average of 10 sections on each grid. For the metal analysis we have only analyzed the data from grid 6 and grid 7. Grid 6 contained 75 Fe hot spots ranging in size from a single pixel (5 microns) to 25 microns. Only 9 Ni hot spots were identified on this grid and out of these only one Ni hot spot also contained detectable levels of Fe and the Fe/ Ni in this spot was 1.36. This spot also contained Si, S, Ca, Ti, and Cu. For comparison, the CI Fe/Ni is ~18 and the Fe/N in an Fe, Ni rich area in a large cluster IDP, L2009R2, cluster 14 had an Fe/Ni of 8.7. This area also contained S, Ca, Cr, Cu and Zn. Grid 7 contained only 9 Fe hot spots and 2 Ni hot spots, with Fe/Ni ratios of 0.7 and 2.6l. Spot 1 on grid 7 also contained Si, S, Ca, Ti, Cr, Cu and Zn. Spot 2 contained S, Ti, Cu, and Zn. The detection of Si and S at this beamline is limited due to the low photon flux at these energies. The cluster IDP was not microtomed but was transferred still in the silicon oil it was collected into on to a 7 micron thick kapton tape for X-ray fluorescence analysis.

FTIR Spectral Results: Since 2009 we have collect over 600 FTIR spectra from: crushed, dry mounted; crushed wet mounted; and microtomed thin sections on silicon monoxide or formvar backed, copper TEM grids and now Mo TEM grids, formvar/carbon backed on 9 different meteorites. These include 3 Martian meteorites, ALH84001, NWA 7034 and Tissint, and the carbonaceous chondrites, Bells, Jbilet Winselwon, Murchison, Murray, Sutterôs Mill, and Tagish Lake. Four meteorites, NWA 7034, ALH84001, Jbilet Winselwan and Sutterôs Mill contain material that gives FTIR spectra showing the amide I and amide II and the amide A bands, indicative of the presence of proteins or peptides. ALH84001, NWA 7034 and Jbilet Winselwan are finds and the Sutterôs Mill meteorite was exposed to rain 2 days after its fall so it is no surprise that proteinaceous material is found in these meteorites. FTIR spectra were collected from grids 2,6, and 7 from NWA 7034. For NWA 7034, only 2 areas (on grids 6 and 7) out of 22 spots analyzed had FTIR spectra showing the amide bands. These areas also contained high Ni but low or no detectable Fe. Other FTIR spectra from NWA 7034 show ketone carbonyl functional group, aliphatic C-H, O-H stretch, carbonates, silicates, and clays. 14 of the 22 spectra collected contained strong absorptions between 900-1200, 1000-1300, 1500, 1400-1500, 1600, 1700, 2850-2950 cm-1 and were significantly different from each other with only the amide containing spectra being the same. Both of these spectra occurred in areas with high Ni.

Discussion: The ~15-25 micron aggregates containing both Fe and Ni also contained significantly more Ni, relative to Fe/Ni ratio of a CI. S is also present but may be left over from the embedding material. If we assume these particles contained only FeS with a density around 5 gm/cm3 the aggregates have a total mass of only ~11 ng, demonstrating the sensitivity of X-ray microprobes, even at second generation sources. With the advent of several next generation synchrotrons, X-ray fluorescence data obtained from these sources will be greatly improved. Both detection limits and spatial

resolution will increase, with measurements in the ppb range and spatial resolutions of 50 nm giving us the ability to resolve submicron grains in aggregates. But to take advantage of the very small spatial resolution, one needs to analyze samples that are near the thickness of the spatial resolution. At 10 Kev the escape depth for Zn is on the order of 100 microns, depending on the composition of the sample. With a 50 nm focused spot, a 30 micron thick "thin section" will be out of focus by almost that amount. Also, to analyze a single 200 nm sized mineral grain the sample thickness should be no more than the thickness of the smallest particles so one does not analyze minerals and glasses "behind" the mineral or glass of interest. We sectioned this sample of NWA 7034 with the hope of having beamtime on one of these new beamlines where we will be able to resolve single minerals and also to collect both C and N K-edge XANES spectra.

Why is the Fe/Ni in NWA 7034 Ni rich areas so different from the CI ratio? Yen, et al. analyzing data from the Mars rovers Spirit and Opportunity found that bright surface dust in the Gustav region is enhanced with Ni relative to the other soil components. The Gustav region on Mars is believed to be the area from which NWA 7034 and its pairings originated [1,7]. Yen et al. concluded that the addition of 3.4% chondritic material could be used to explain the elevated Ni. However, doing this caused mismatches in other elements and the surface dust at Gustev was not simply chondritic matter added to Martian surface matter. The Ni hot spots found in NWA 7034 that contain little or no detectable Fe may be the result of differentiation of chondritic material from an impact melt. Xu, et al. [11] found metal grains in 4 different lunar samples and concluded these grains were produced from impact melts. Some of these grains contained as much as 31 wt% Ni.

Why the amide containing material seems to be associated with the Ni rich regions is not clear but bacteria are known to absorb onto the surface of Ni containing compounds and so, may preferentially attach to any Ni rich regions in any rock and some strains of bacteria are used as bioaccummulators to remove Ni from industrial waste water [8]. The FTIR data also point to a significant variety of organic matter in NWA 7034. Although Grady et al. suggest the C isotope data identifies terrestrial contamination, it raises the question of how does one differentiated between terrestrial organic matter and extraterrestrial material if the C isotopic data is the same? With the reported multiple lithographies occurring in NWA 7034 one would expect any Martian carbon to be highly altered and in the case of carbon associated with high temperature and pressure events such as those found in volcanic or impact processes one would expect the carbon to be in an inorganic form, mostly amorphous carbon but also graphite and diamond. Some of the FTIR spectra may point to the presence of amorphous carbon but graphite has a strong, broad band at ~3500 cm-1 and we did not see this. Diamonds would likely be on the nanometer size and therefore not detectable by the FTIR microscope.

Conclusions: Coming from a semi-arid environment one has to wonder how NWA 7034 got contaminated with terrestrial organic matter if the meteorite was only on Earth for a short period of time. Tissint, a shergottite type meteorite was recovered 4 months after its observed fall in a region not far from where NWA 7034 was recovered and this meteorite did not contain any FTIR spectra that would point to terrestrial contamination. It has not yet been determined how long NWA 7034 and its pairings have been on earth but the Western Sahara is a dry region and so rainfall is limited. ALH84001 is believed to have been in the Allan Hills region of the Antarctic for ~13000 years and it is not very contaminated with terrestrial organic matter [9] and yet Antarctic ice and ice melts have been shown to support a diverse microbial ecosystem [12, 13] . W. S. Kiefer, et al. have reported a bulk porosity for ALH84001 of 9.1% and for NWA 7034, 7.4% [10]. NWA 7034 is less porous than ALH84001 and 13000 years of exposure to Antarctic summers and melting ice has resulted in significantly less terrestrial organic matter contamination for ALH84001 than NWA 7034. It is possible NWA 7034 was mishandled and the other pairings will contain less terrestrial organic matter. With its low porosity and exposure to minimal rainfall it is also possible NWA 7034 was on this planet for a significant amount of time before it was found.

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