A COMPARISON OF THE STRUCTURE AND BONDING OF CARBON IN APEX CHERT KEROGENOUS MATERIAL AND FISCHER-TROPSCH-TYPE CARBONS. B. T. De Gregorio[1], T. G. Sharp[1], and G. J. Flynn[2], [1]Department of Geological Sciences, Arizona State University, P. O. Box 871404, Tempe, AZ, 85287-1404: degregorio@asu.edu, [2]Department of Physics & Department of Mathematics, SUNY Plattsburgh.

Introduction: Microbial-like features preserved in the 3.5 Ga Apex chert are possibly the oldest fossils on Earth [1]. However, despite their cellular appearance, the fact that they exist in an ancient hydrothermal system and few pristine (unaltered) microbial morphologies exist has led some researchers to look for alternative models for their formation [2]. The kerogenous carbonaceous material that composes these features [3] could be created by an abiotic organic synthesis reaction and preserved in a microbial-like morphology. Many different types of simple and complex organic molecules can be synthesized by a Fischer-Tropsch-type (FTT) reaction, which only requires sources of reactants, hydrothermal temperatures, and a proper catalyst. All three of these requirements may be met in an ancient hydrothermal vent crosscutting basalts, as the Apex chert does.

Micro-laser Raman spectroscopy has been previously used to investigate the amount of graphitization in the Apex carbonaceous features, suggesting that the material is very poorly graphitized [1-2]. However, the peaks in the Raman spectra are very diffuse, suggesting that the Apex carbonaceous material may actually be completely amorphous, which may imply a biogenic origin. Electron energy-loss spectroscopy (EELS) and x-ray absorption near-edge spectroscopy (XANES) can be used to characterize kerogen and other disordered carbons. EELS has been used to characterize kerogen preserved in *bona fide* microfossils of the Gunflint Formation [4]. Since EELS is performed using transmission electron microscopy (TEM), it is able to detect graphite crystallites that are not resolvable with Raman. XANES is analogous to EELS but uses x-rays rather than electrons to probe the electronic structure of the sample.

Methods: Apex chert carbonaceous material from the Chinaman Creek locality, which contains the proposed microfossils, was analyzed *in situ,* rather than extracting the carbon and possibly altering its structure and composition. Crushed black chert samples were embedded in sulfur droplets. Thin, electron and x-ray transparent sections (90-100 nm) were cut by ultramicrotomy and placed on copper TEM grids coated with a silicon monoxide film.

The two experimental FTT carbon products analyzed in this study were synthesized under hydrothermal conditions, using oxalic and formic acids as reactants and montmorillonite as a catalyst [5]. Total liquid extracts from experiments run at 175°C and 250°C, which match the estimated crystallization temperature of the Chinaman Creek hydrothermal vein [2], were prepared for analysis by dehydration onto copper TEM grids coated with a silicon monoxide film.

EELS analysis and high-resolution TEM imaging was performed on the Philips CM-200 microscope at Arizona State University. XANES analysis was preformed in the scanning transmission x-ray microscope (STXM) at the X1A beam line of the National Synchrotron Light Source. XANES analysis was always performed before EELS analysis because of potential beam damage effects caused by high-energy electrons in the TEM. Because of electron charging effects of the silicon monoxide film in the TEM, a thin coat of amorphous carbon was deposited on the samples prior to EELS analysis. This carbon coat can be shown to have a small but negligible effect on the EELS spectrum. No carbon film was necessary for EELS analysis of the FTT carbons.

Results: The EELS spectrum of carbonaceous material preserved in the Apex chert (Fig. 1d) contains a π^* peak at 285 eV and a broad, sloping σ^* peak at ~294 eV, which is distinctly different from the spectra of laboratory standard graphitized carbon (Fig. 1a) and amorphous carbon (Fig. 1e). The lack of a leading-edge σ^*_1 peak at 292 eV implies that the Apex carbon is completely ungraphitized, and the large π^* peak suggests a high abundance of carbon-carbon double bonds (C=C), either in aromatic or alkenyl functional groups. These results are similar to EELS spectra of kerogen in the Gunflint Formation [4].

Similar EELS spectra are obtained from both FTT carbon products (Fig. 1b, c). Both FTT carbons are ungraphitized and have a large number of aromatic or alkenyl groups (indicated by the broad σ^* and large π^* peaks, respectively). In addition, both spectra show the presence of a peak at 288.5 eV due to carbonyl groups (C=O). These results are consistent with previously published descriptions of these materials [5].

Apex chert carbonaceous material is also ungraphitized in the XANES spectrum (Fig. 2c). However, a carbonyl peak can now be detected at 288.5 eV that was not visible with the lower EELS energy resolution. In addition, the barely-visible carbonyl peaks seen in EELS spectra of the FTT carbon products are now more prominent in XANES spectra (Fig. 2a, b).

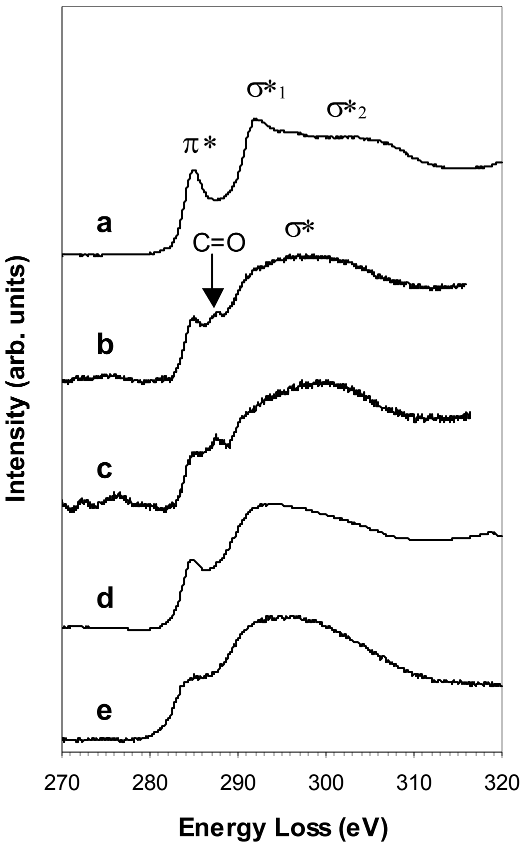

Figure 1: EELS spectra of (a) graphitized carbon, (b) FTT carbon synthesized at 250°C, (c) FTT carbon synthesized at 175°C, (d) Apex chert carbonaceous material, and (e) amorphous carbon.

Discussion: According to the combined EELS and XANES data, the carbonaceous material preserved in the Apex chert is structurally amorphous (ungraphitized), contains many carbon-carbon double bonds, and contains a small amount of carbonyl groups. Most of the C=C bonds indicated by the π* peak are most likely located in poly-aromatic domains rather than in alkene straight-chain hydrocarbons, which are less likely to survive diagenesis. These observations would also be expected of biogenic material preserved as kerogen. Although it would be premature to conclude, on the basis of our results, that the Apex chert carbonaceous material is biogenic, it can at least be said that this material is *kerogen-like* and consistent with the interpretation that the microbial-like features in the Apex chert are *bona fide* microfossils.

However, EELS and XANES spectra of synthetic FTT carbon products contain similar features to spectra of Apex chert kerogenous material. Both FTT carbons produced at 175°C and 250°C are structurally amorphous, contain a large amount aromatic and alkenyl groups, and contain carbonyl groups. Since the organic molecules produced by the FTT synthesis were primarily simple lipids [5], the π* peaks seen in EELS and XANES spectra are primarily due to alkenyl groups, but this cannot be concluded from the energy-absorption spectra alone. The most significant difference between the EELS and XANES spectra of Apex carbonaceous material and FTT carbons is the intensity of the carbonyl peak. However, if FTT carbon underwent diagenesis, much of the carbonaceous material would devolatilize, driving off CO_2 and H_2O. Depending on the preservation conditions, it is plausible that enough oxygen could be removed so that the energy-absorption spectra of the kerogen-like, mature FTT material would match the spectra of Apex chert carbonaceous material. If carbonyl is driven off by diagenesis, it is feasible, then, that an abiotic FTT reaction occurring in an ancient hydrothermal system could be responsible for the microbial-like features preserved in the Apex chert.

References: [1] Schopf J. W. et al. (2002) *Nature, 416,* 73-76. [2] Brasier M. D. et al. (2002) *Nature, 416,* 76-81. [3] De Gregorio B. T. and Sharp T. G. (2003) *LSPC XXXIV,* Abstract #1267. [4] Moreau J. W. and Sharp T. G. (2004) *Astrobiology, 4,* 196-210. [5] Rushdi A. I. and Simoneit B. R. T. (2001) *Orig. Life Evol. Biosph., 31,* 103-118

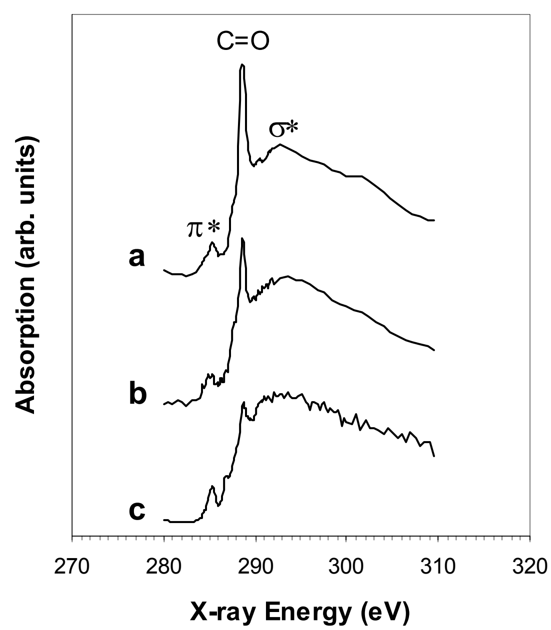

Figure 2: XANES spectra of (a) FTT carbon synthesized at 250°C, (b) FTT carbon synthesized at 175°C, and (c) Apex chert carbonaceous material.