

**PRELIMINARY XANES ANALYSIS OF LABORATORY ANALOGS OF TITAN THOLINS.** M. Nuevo<sup>1,2,\*</sup>, E. Sciamma-O'Brien<sup>1</sup>, S. A. Sandford<sup>1</sup>, F. Salama<sup>1</sup>, C. K. Materese<sup>3</sup>, and A. L. D. Kilcoyne<sup>4</sup>, <sup>1</sup>NASA Ames Research Center, Moffett Field, CA 94035, USA, <sup>2</sup>BAER Institute, NASA Research Park, Moffett Field, CA 94035, USA, <sup>3</sup>NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA, <sup>4</sup>Advanced Light Source, Berkeley, CA 94720, USA. \*e-mail: michel.nuevo@nasa.gov

**Introduction:** Titan, the largest moon of Saturn, is a fascinating object. It is the only other object in the Solar System, besides Earth, with a dense (1.5 bar at the surface) atmosphere whose composition is dominated by N<sub>2</sub>, with CH<sub>4</sub> as the second most abundant gas. A complex organic chemistry between N<sub>2</sub> and CH<sub>4</sub>, induced by solar UV photons and energetic particles, results in the formation of a large variety of organic compounds, including hydrocarbons (e.g., C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>), nitriles (e.g., HCN, HNC, HC<sub>3</sub>N, CH<sub>3</sub>CN, C<sub>2</sub>N<sub>2</sub>), as well as larger molecules that include aromatic and heteroaromatic compounds [1]. This complex organic chemistry also leads to the formation of aerosols that play an important role in Titan's atmospheric dynamics, climate, as well as surface composition and processes. Because of its N<sub>2</sub>-based dense atmosphere, and its CH<sub>4</sub> cycle that resembles the hydrological cycle on Earth, Titan is often considered to be an analog of early Earth. In recent years, Titan's atmosphere and surface were monitored in detail by the NASA *Cassini* mission, which orbited the Saturnian system from 2004 to 2017, as well as the ESA *Huygens* probe, which plunged into Titan's atmosphere and landed on its surface in 2005.

Many laboratory studies have been conducted in the past four decades to understand the organic chemistry taking place in the atmosphere of Titan. These experiments simulate Titan's atmospheric chemistry using various energy sources to induce the dissociation and ionization of N<sub>2</sub> and CH<sub>4</sub>, in order to trigger subsequent reactions that result in the formation of refractory organic materials that are analogs of Titan's aerosols and referred to as 'tholins'. These tholins have been studied with a wide variety of techniques in order to determine their chemical compositions as well as physical, chemical, and optical properties. These studies showed that Titan's atmospheric aerosols are probably macromolecular materials consisting mainly of carbon, nitrogen, and hydrogen, with a mixture of aliphatic and aromatic structures [2].

In this preliminary study, we analyzed laboratory tholins produced in the NASA Ames COSmIC facility from four different initial gas mixtures: N<sub>2</sub>:CH<sub>4</sub> (90:10), N<sub>2</sub>:CH<sub>4</sub>:C<sub>2</sub>H<sub>2</sub> (89.5:10:0.5), N<sub>2</sub>:CH<sub>4</sub> (95:5), and N<sub>2</sub>:CH<sub>4</sub>:C<sub>2</sub>H<sub>2</sub> (94.5:5:0.5), using X-ray absorption near-edge structure (XANES) spectroscopy to obtain

information on their chemical structures as well as their elemental C/N ratios.

**Methods:** Tholin samples were produced using the Titan Haze Simulation (THS) experiment on the NASA Ames COSmIC facility [3,4]. In the COSmIC/THS, a supersonic expansion is used to cool down gas mixtures to Titan-like temperatures (150 K) and decrease the gas pressure to 30 mbar. A plasma discharge (–800 V) is then generated in the stream of that expansion to induce chemistry between the different molecular species of the gas mixture. Similar to the processes occurring in Titan's atmosphere, larger species are formed in the gas phase and result in the formation of solid particles, analogs of Titan's aerosols. These tholins can be jet-deposited onto substrates, which can be collected at the end of a run for ex-situ analyses. In the study presented here, tholins were produced from the four gas mixtures and deposited for 1–2 hrs onto silicon nitride substrates, then collected under argon atmosphere in a glove box, and stored in sealed containers.

These tholins were then analyzed with a scanning transmission X-ray microscope (STXM) installed on beamline 5.3.2.2 of the Advanced Light Source of the Lawrence Berkeley Laboratory, providing photons in the 250–700 eV range with a 10<sup>7</sup> photons s<sup>–1</sup> flux [5]. XANES spectra of these tholins were measured in the 275–580 eV energy range in order to span the carbon, nitrogen, and oxygen 1s X-ray absorption edges with an energy step size of 0.1 eV in the fine structure regions, and 1–2 eV in the pre- and post-edge regions. C-, N-, and O-XANES spectra provide information on the functional groups present in the samples. In addition, the relative contributions of each element C, N, and O from known mass absorption coefficient curves [6,7] can be estimated from full-range XANES spectra, which allows for the determination of the C/N and C/O ratios in each tholin sample.

**Results:** For all tholins, the C-XANES spectra show the presence of functional groups such as aromatic carbon (285.1 eV), imines (286.2 eV), and nitriles (286.9 eV), with relative proportions with each other and with other bands that vary widely from one sample to another. These bands are much more intense for tholins produced from mixtures containing acetylene (C<sub>2</sub>H<sub>2</sub>) (Fig. 1). In particular, the increase in the formation of aromatic compounds when acetylene is present is consistent with the fact that C<sub>2</sub>H<sub>2</sub> is a known

precursor of benzene. For all tholins, the C-XANES spectra also show the presence of multiple weak bands associated with amorphous carbon around 284.5, 290, and 297 eV. In the spectrum of  $\text{N}_2:\text{CH}_4$  (90:10), a strong band associated with the presence of aliphatic carbon (287.1 eV) is detected. This band is also observed in the C-XANES spectra of the other three tholin samples but with a significantly smaller intensity. N-XANES spectra (not shown here) of the four tholin samples show similar trends, with more intense bands associated with nitriles and imines in tholins produced from mixtures containing  $\text{C}_2\text{H}_2$ . The main bands observed in the spectra of our  $\text{N}_2:\text{CH}_4$  tholins are consistent with those observed in a previous study conducted on Titan tholins produced in a different experimental set-up [8].

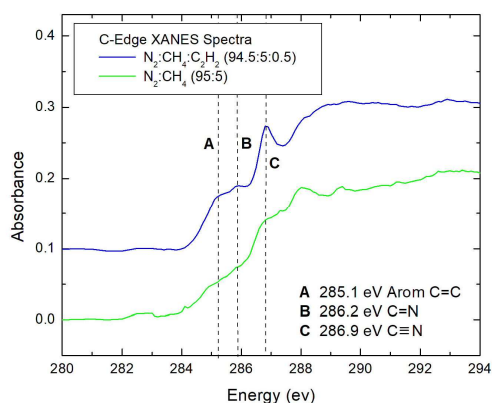


Figure 1: C-XANES spectra of the tholin samples produced from the  $\text{N}_2:\text{CH}_4$  (95:5) and  $\text{N}_2:\text{CH}_4:\text{C}_2\text{H}_2$  (94.5:5:0.5) mixtures, showing differences of intensities for the aromatic C and nitrile bands.

The elemental C/N abundance ratios for the four tholins, obtained from their full-range XANES spectra were determined to be  $\sim 0.9$ – $1.3$  for tholins produced from starting mixtures that do not contain acetylene, and  $\sim 2.2$ – $2.4$  for tholins produced from mixtures that contain acetylene. These ratios highlight a significant difference depending on whether acetylene is present or absent in the initial gas mixture, with tholins produced from  $\text{N}_2:\text{CH}_4:\text{C}_2\text{H}_2$  mixtures showing C/N ratios larger by a factor of  $\sim 2$ . This observation is correlated to the increase in abundance of aromatic carbon, imines, and nitriles in  $\text{C}_2\text{H}_2$ -containing tholins (Fig. 1), and indicates that amounts of  $\text{C}_2\text{H}_2$  as small as 0.5% in the initial mixtures can result in a significant increase in the formation of chemical groups that consist of double and triple covalent bonds. In addition, a higher concentration of  $\text{CH}_4$  in the starting mixtures (10% vs. 5%) results in smaller C/N ratios, i.e., suggesting that more nitrogen is being incorporated into the tholins. On the other hand, for a given  $\text{CH}_4$  concentration, the addition of  $\text{C}_2\text{H}_2$  results in an increase of the C/N ratio, and

therefore less nitrogen being incorporated in the solid phase. A possible explanation for this observation resides in the design of the COSMIC experimental set-up, which truncates the chemistry due to the short ( $<4$   $\mu\text{s}$ ) residence time of the gas in the plasma discharge. A higher concentration of  $\text{CH}_4$  results in the formation of more bonds with nitrogen. However, because of the high reactivity of  $\text{C}_2\text{H}$  radicals with  $\text{C}_2\text{H}_2$ , mixtures containing  $\text{C}_2\text{H}_2$  may trigger a chemistry in which the formation of hydrocarbons is favored over that of N-bearing molecules, resulting in larger C/N ratios.

Finally, the XANES spectra of all tholins also show the presence of oxygen-bearing functional groups, in particular, alcohols and carbonyls, although none of the starting mixtures contained oxygen. The presence of these groups may be explained by the fact that in order for the X-rays from the STXM to penetrate through the full thickness of the samples, the tholin deposits must be very thin. Indeed, the tholin samples studied here were produced from experiments that lasted 1–2 hrs, resulting in samples that are much thinner than those produced for IR analysis, which are recovered after 10–40 hrs. Shorter experiments result in substrates covered with scattered individual grains separated from each other on the substrate, while for longer experiments the grains jet-deposited on the substrate stack on top of each other, forming a more homogenous layer of material. As a consequence, surface oxidation will affect a larger fraction of the samples produced from short experiments, as the ratio between the surface exposed to oxidation and volume of material is much higher for samples consisting of individual grains (i.e., shorter experiments) than for samples consisting of a homogenous deposit (i.e., longer experiments). XANES spectra of tholins are thus expected to show higher relative levels of oxidation, as confirmed by the high abundances of O-bearing groups. In a previous study, C- and N-XANES spectra of tholins produced in a different experimental set-up from  $\text{N}_2:\text{CH}_4$  (95:5) mixtures also showed strong bands associated with O-bearing groups such as carbonyls, alcohols, and ethers [8]. However, oxidation is not expected to significantly affect the C/N ratios in the bulk of the sample, although additional experiments are needed to confirm this statement.

**References:** [1] Hörst S. M. (2017) *J. Geophys. Res. Planets*, 122, 432–482. [2] Cable M. L. et al. (2012) *Chem. Rev.*, 112, 1882–1909. [3] Sciamma-O'Brien E. et al. (2014) *Icarus*, 243, 325–336. [4] Sciamma-O'Brien E. et al. (2017) *Icarus*, 289, 214–226. [5] Kilcoyne A. L. D. et al. (2003) *J. Synchr. Rad.*, 10, 125–136. [6] Henke B. L. et al. (1993) *Atom. Data Nucl. Data Tab.*, 54, 181–342. [7] Nuevo M. et al. (2011) *Adv. Space Res.*, 48, 1126–1135. [8] Kuga M. et al. (2014) *Earth Planet. Sci. Lett.*, 393, 2–13.