Carbon Functional Groups Identification and Source Apportionment of Fine Particulate Matter with C(1s) NEXAFS Spectroscopy

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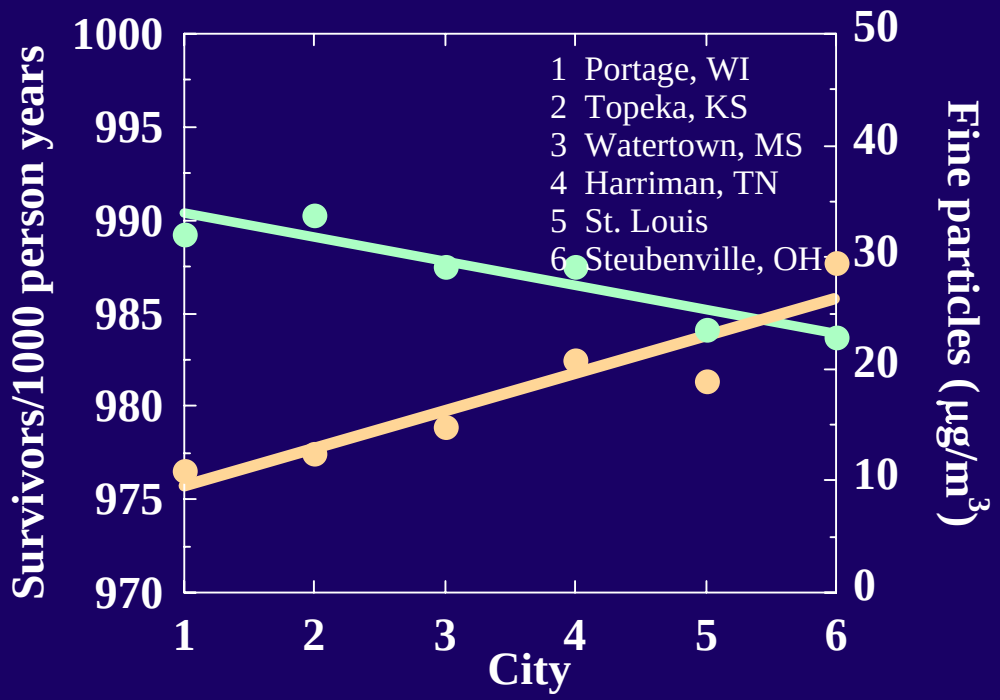
Airborne fine particulate matter - *Feinstaub*

Direct correlation: Particle concentration ~ Mortality ratio

Suspected role in global climate forcing

"The 6 Cities Study"
D.W. Dockery et.al., New Engl. J. of Medicine (1993):329/24 1753-1759.



Soot takes center stage
W.L. Chameides, M. Bergin;Science (2002) 297 2214

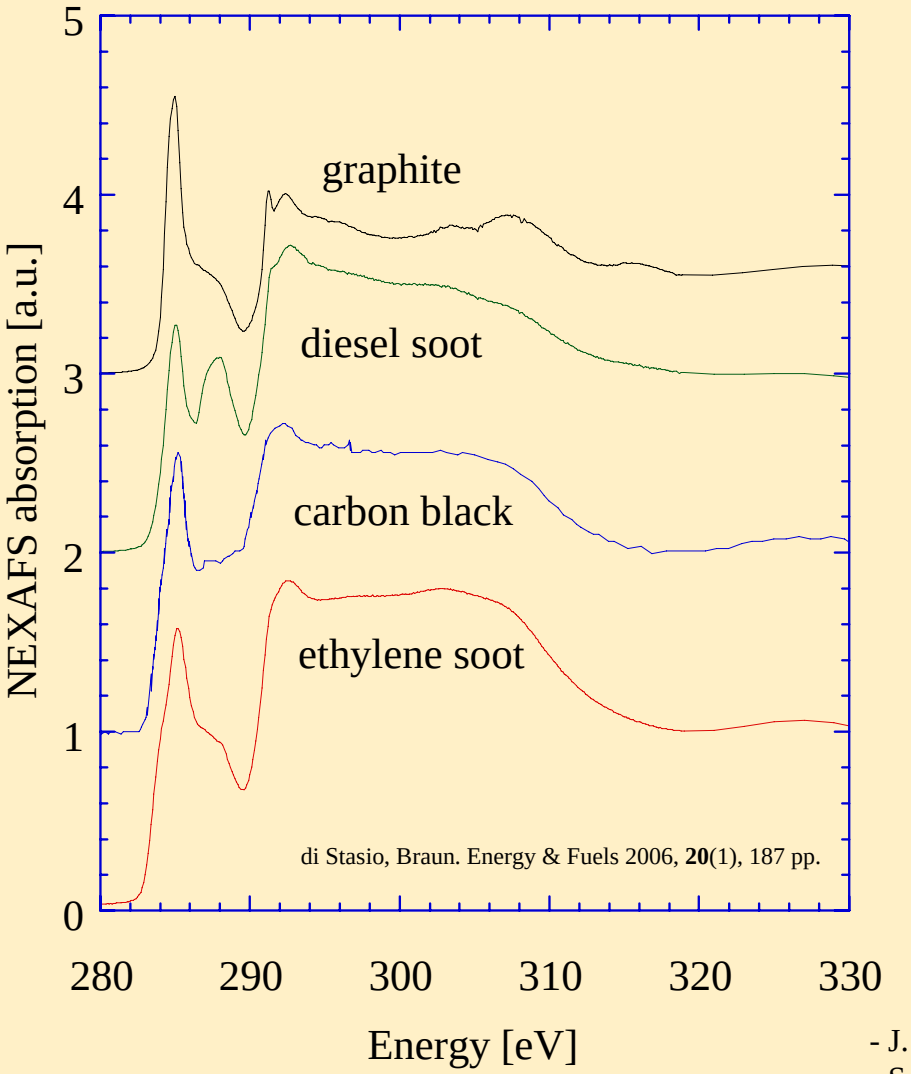
NEXAFS

- Near-edge X-Ray Absorption Fine Structure Spectroscopy
- For the analysis of soot molecular structure
- Element specific – **here we focus on the carbon**

X-ray spectroscopy has been used for PM speciation before, but not for carbon speciation !

Environm. Sci. & Technol. 41 (2007) 173.

C(1s) NEXAFS spectroscopy



Element specific

- Sensitive to molecular structure
- Soot shows strong peak at 285 eV from C=C double bonds such as graphite or PAH
- Surface functional groups, SOM
- Goal: molecular fingerprint for source attribution
- Quantitative ?

- J. Stöhr, NEXAFS Spectroscopy, Springer, 1992, NY.
- S.C.B. Myneni, Rev. Miner. Geochem. 49 (2002) 485.
- A. Braun, J. Env. Monitoring., 2005, **7**(11), 1059.

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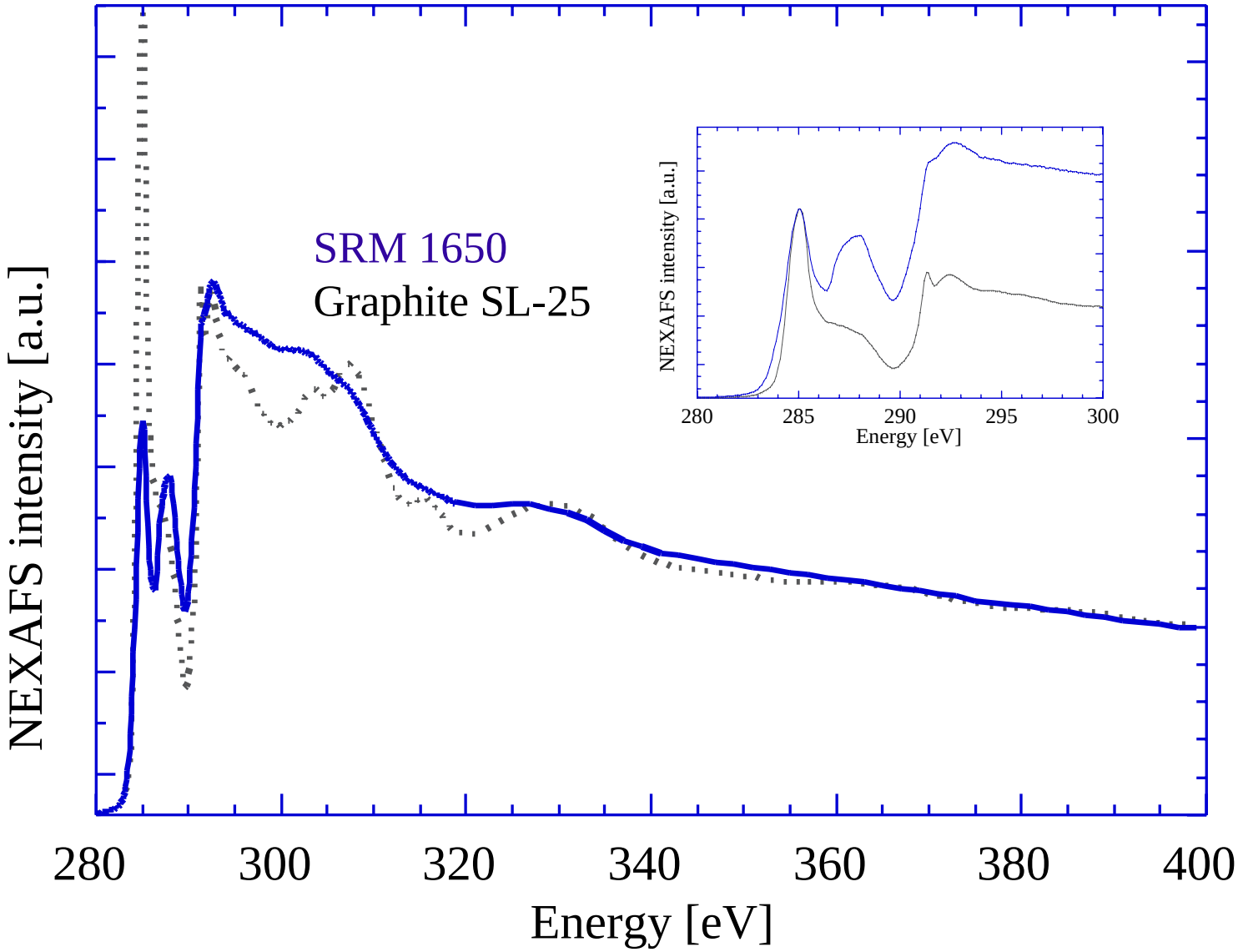
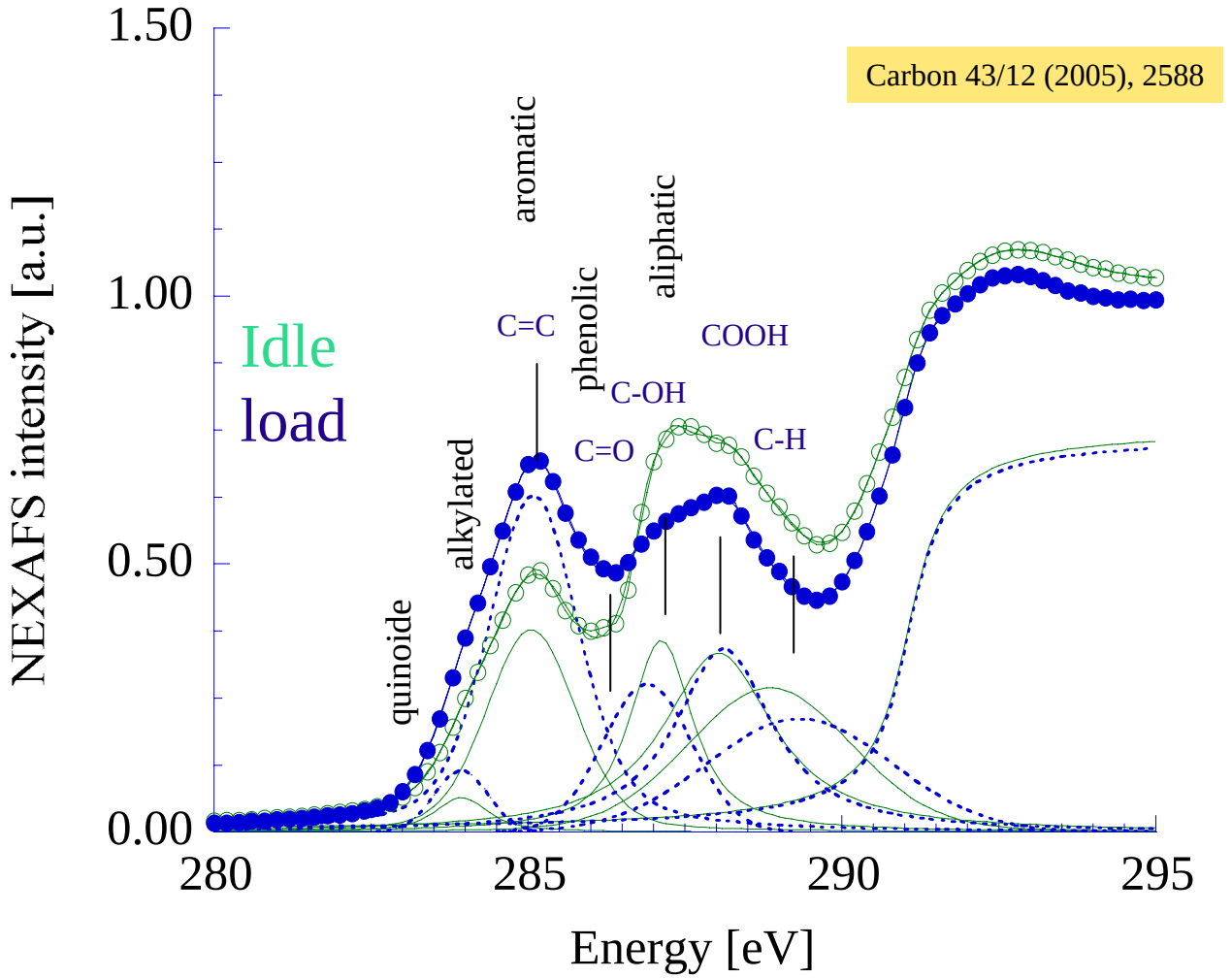


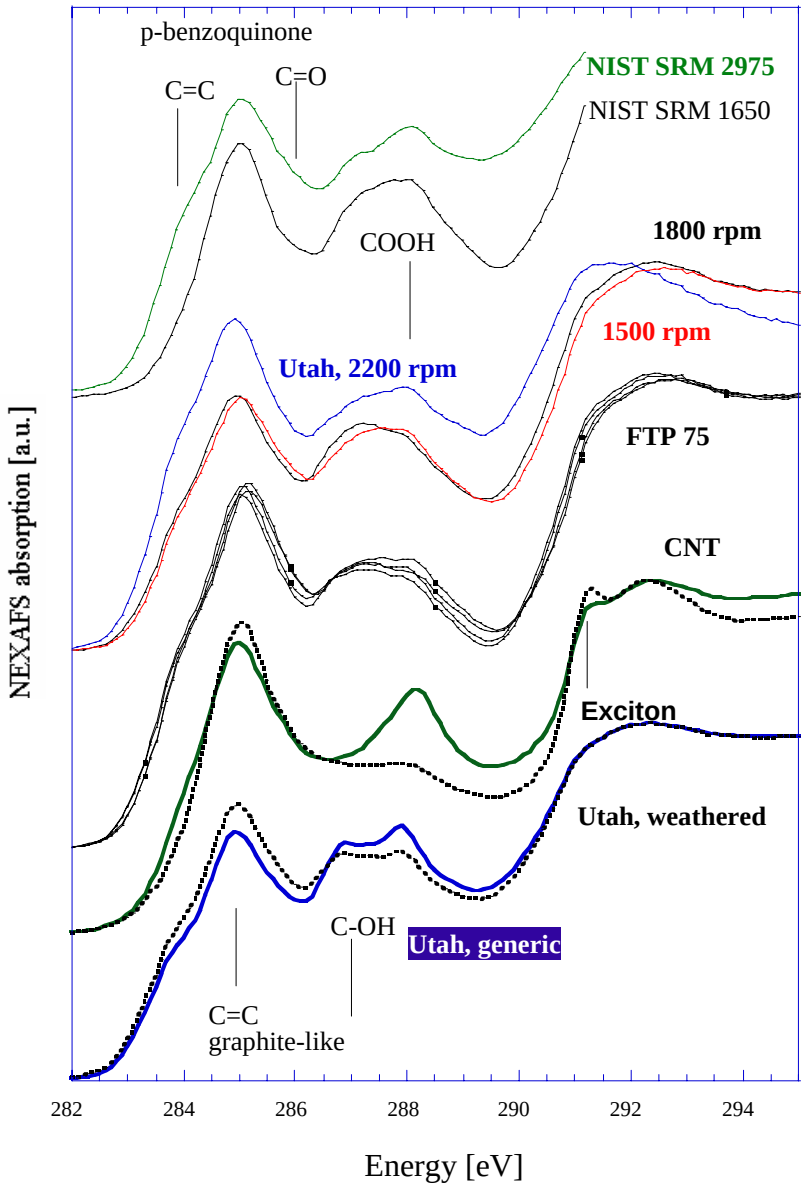
Environm. Sci. & Technol. 41 (2007) 173.

NEXAFS of idle and load diesel soot

Load soot contains more graphitic material. Idle soot contains significantly more aliphatic material, incl. volatiles, residual oil, fuel, soluble organic matter,… .

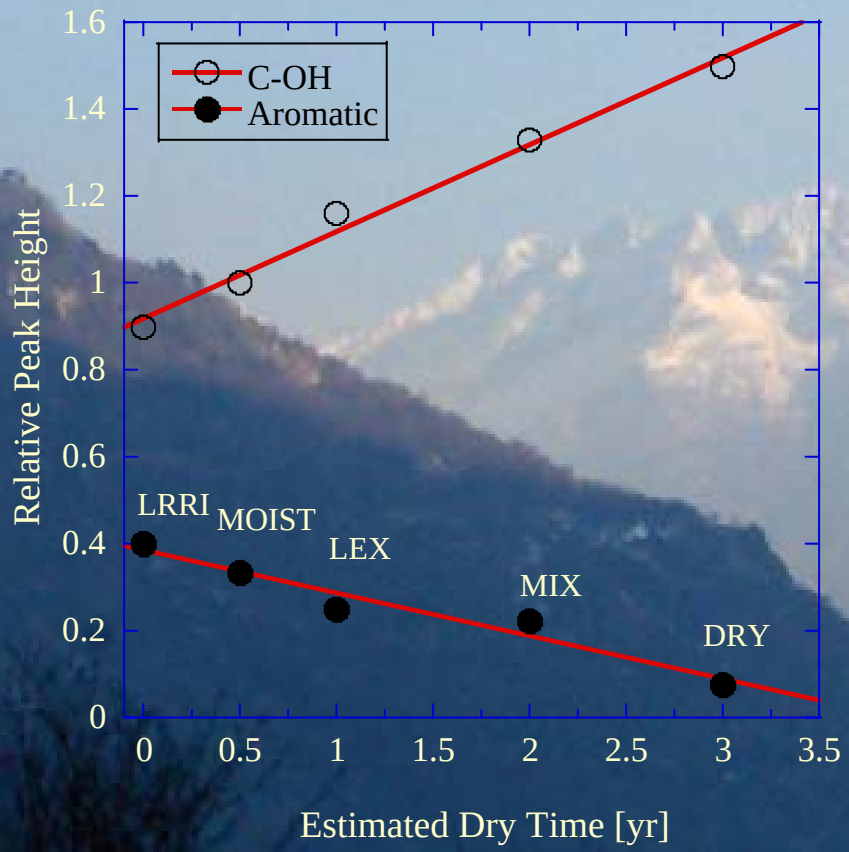


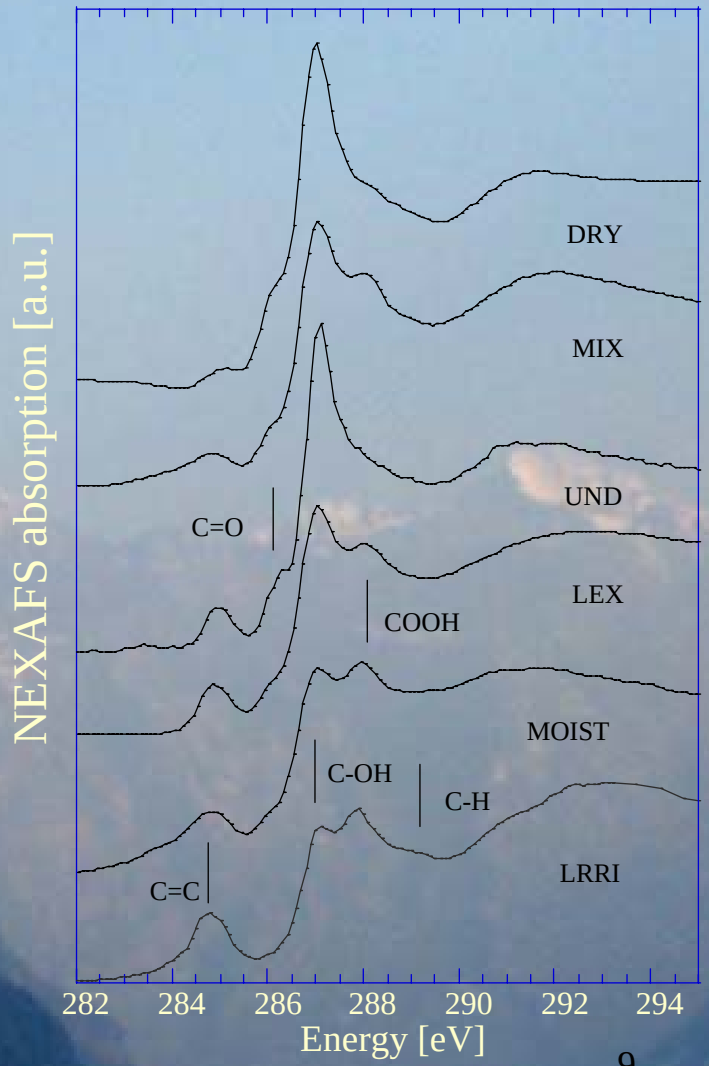
Comparison of various DPM samples



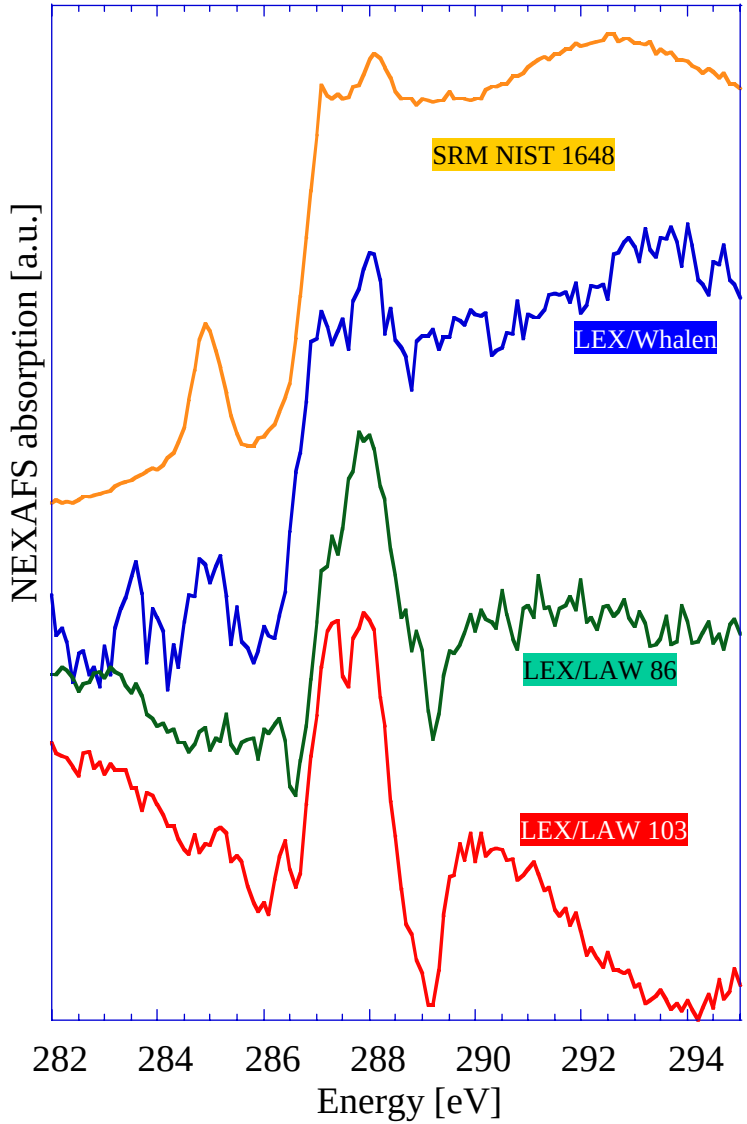
Wood Smoke Studies

Kreosote from dry wood and moist wood yields entirely different spectra

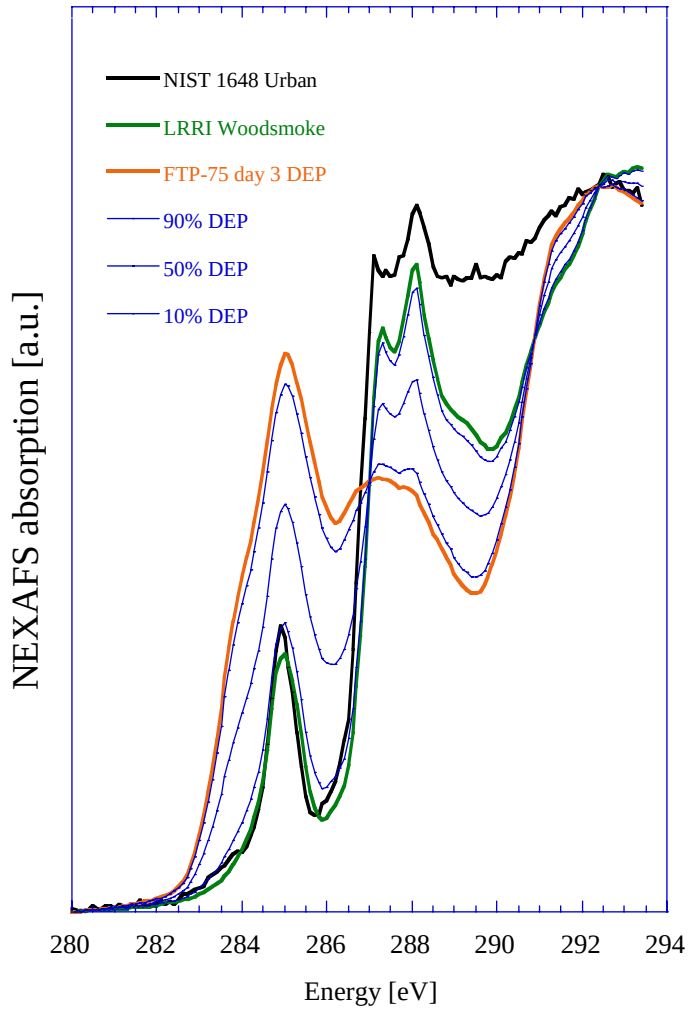




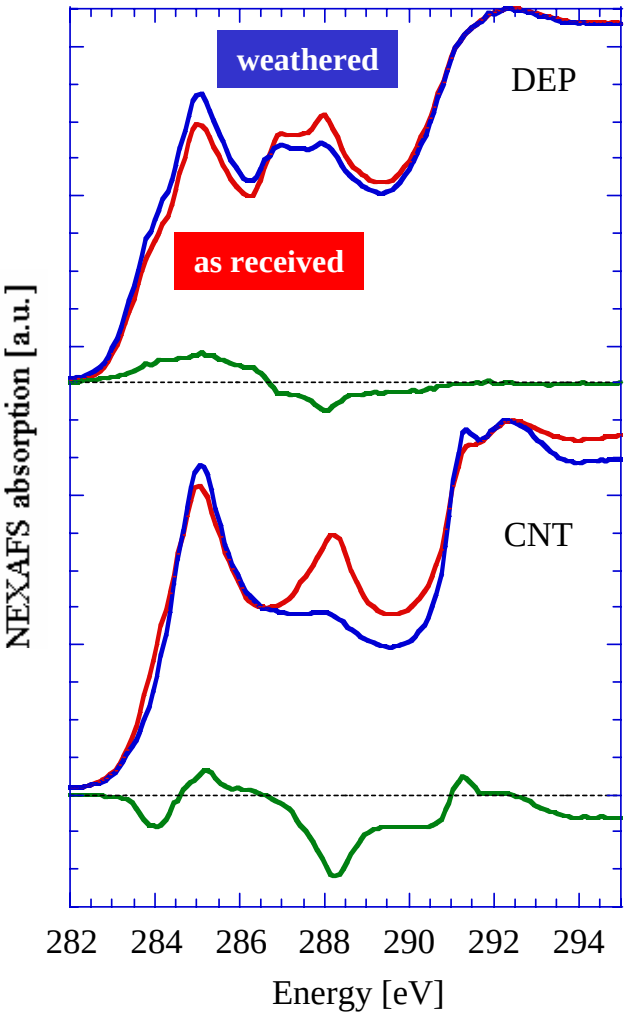
Can We „Model“ Urban PM ?



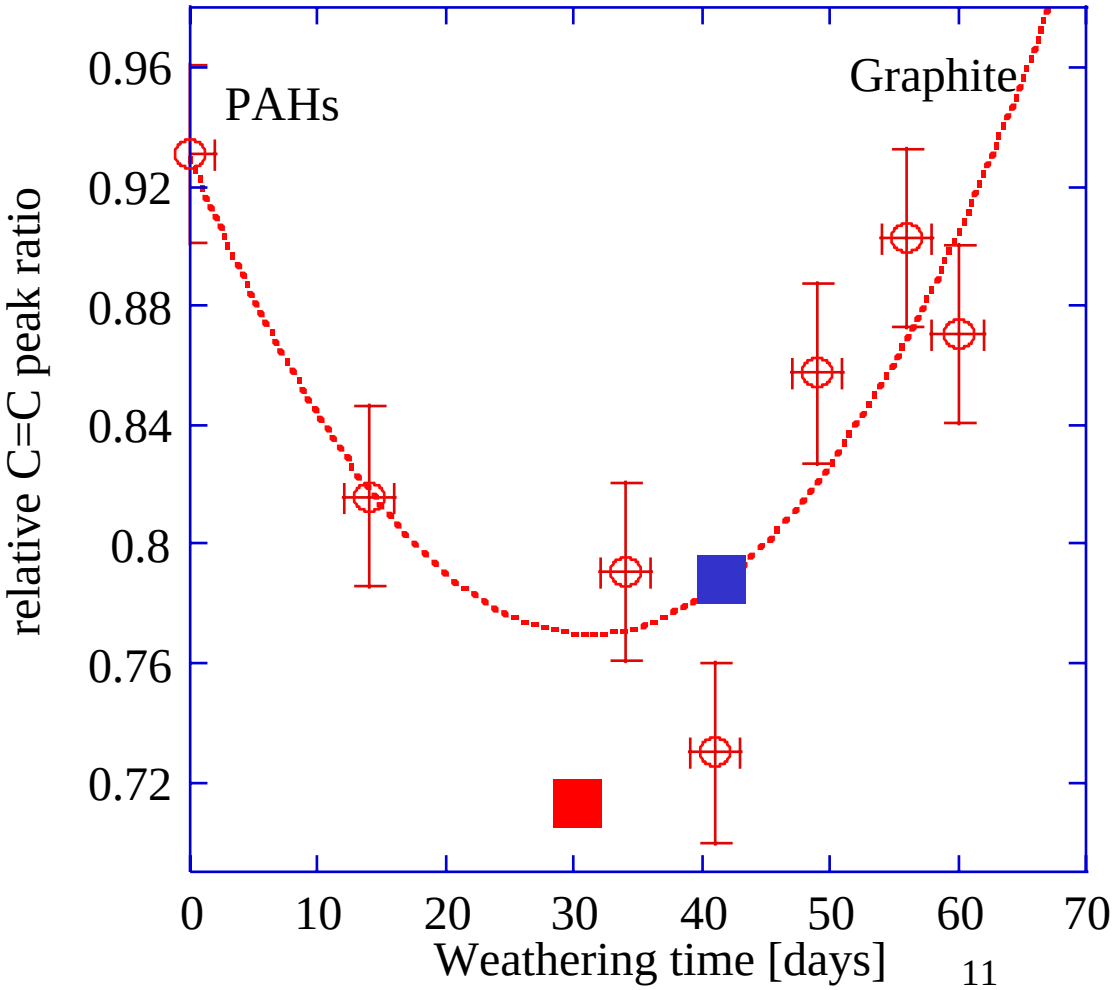
c · Woodsmoke + (1-c) · DEP = Urban ?



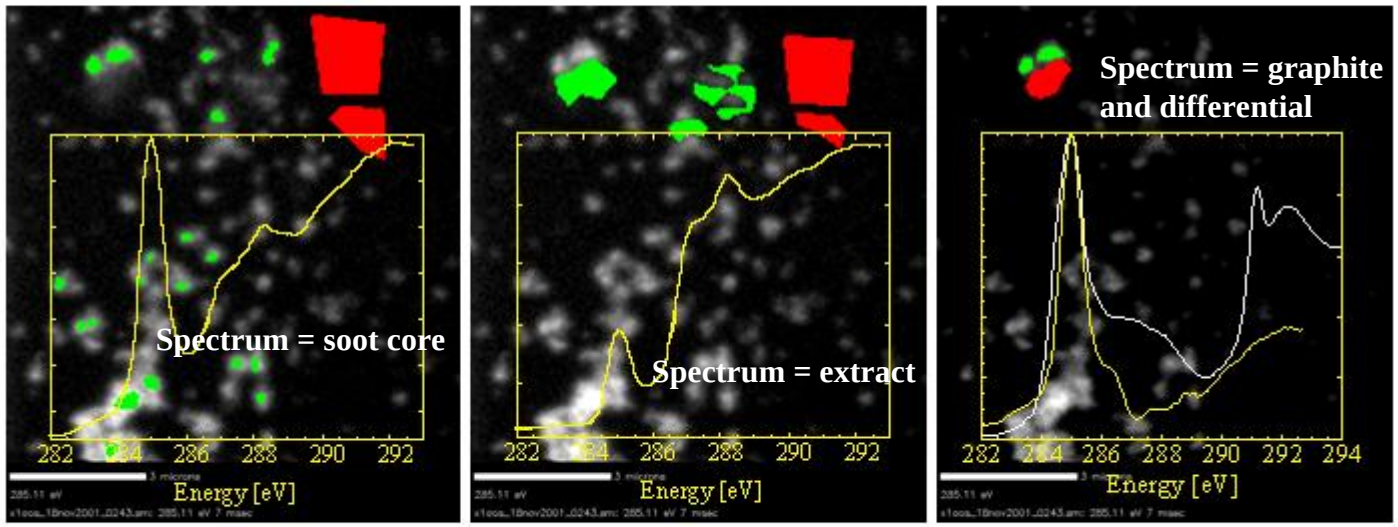
Diesel PM Weathering Study



DPM exposed to air, humidity, sun light for 2 months
NEXAFS peak heights change
Aromatic C=C peak decreases , then increases
PAHs decomposed ?



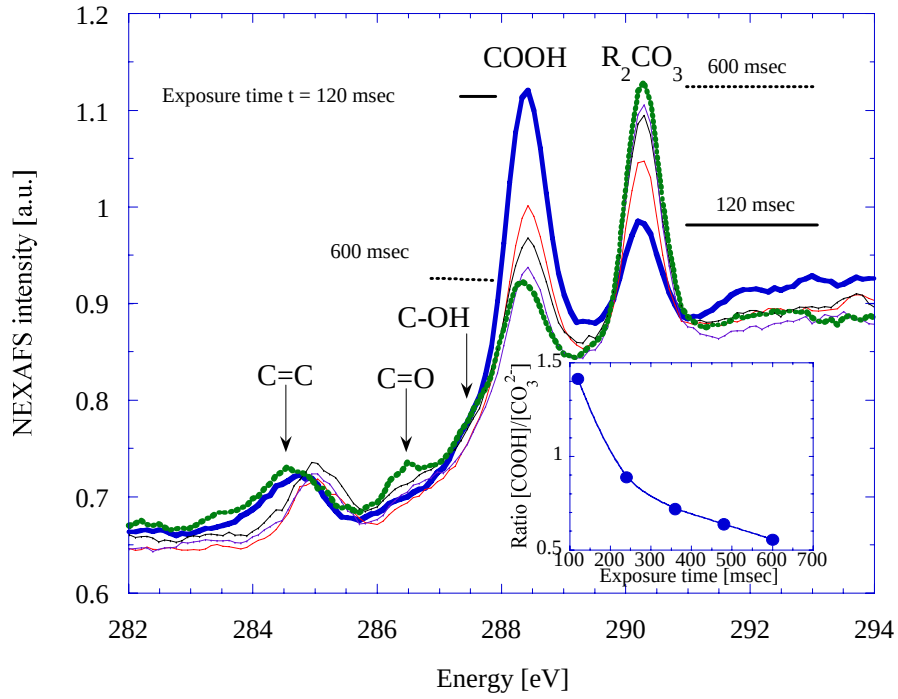
Scanning Transmission X-ray Micro-spectroscopy



STXM is X-ray microscopy with chemical contrast
Resolution: ~ 100 nm, and chemical contrast of ~ 0.1 eV
Soot core and extracts have different spectral characteristics

Fuel (2004) **10** 7/8, 997

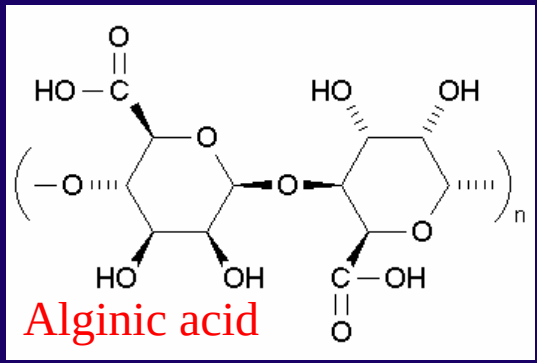
Photochemistry and De-carboxylation



Intense X-ray beam of the STXM microscope generates nascent oxygen from air.

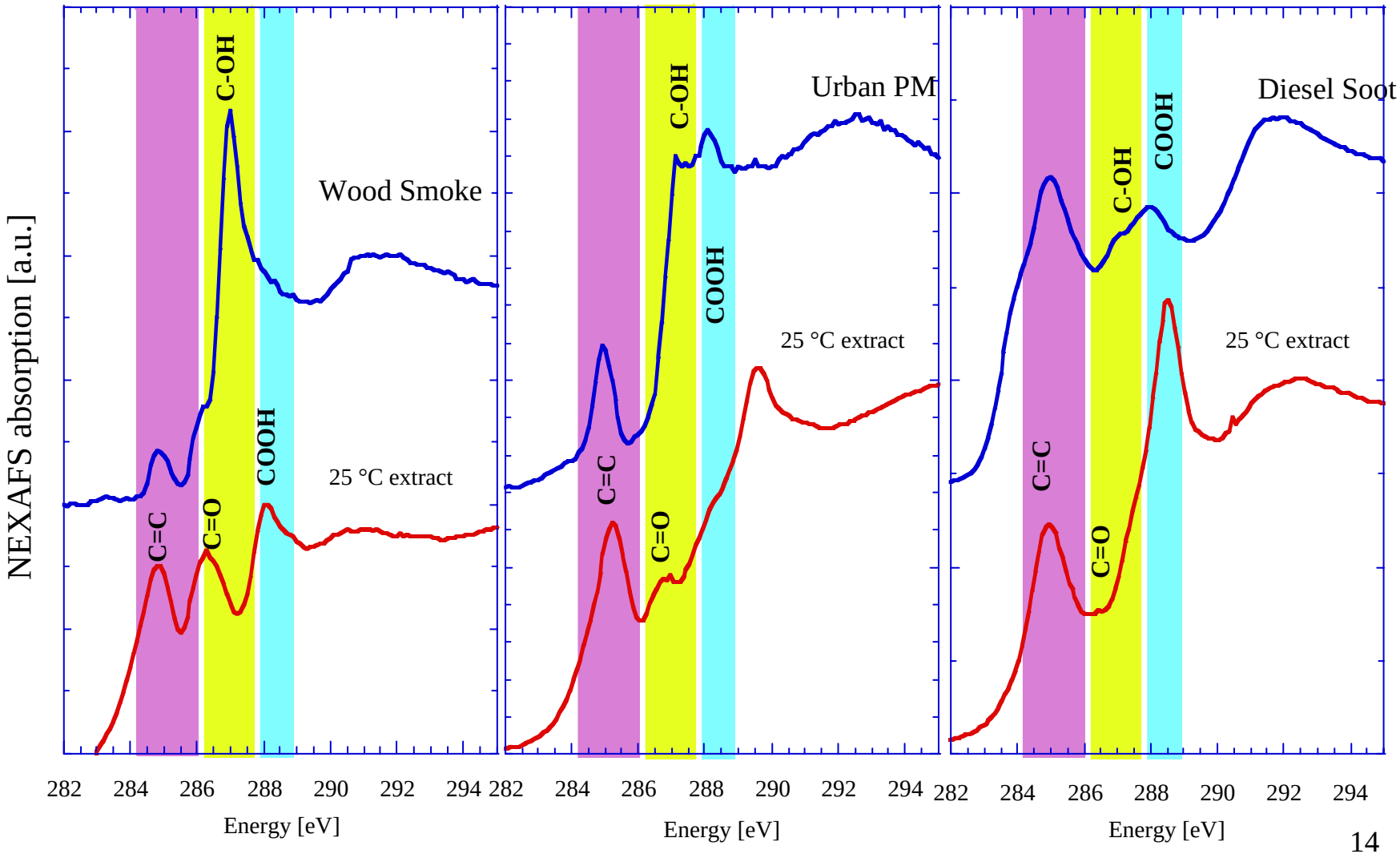
Upon irradiation, COOH carboxyl peak intensity decreases, and new peak evolves - probably from an organo-carbonate.

Potential tool for in-situ reaction studies !
(ozone + soot, etc…)

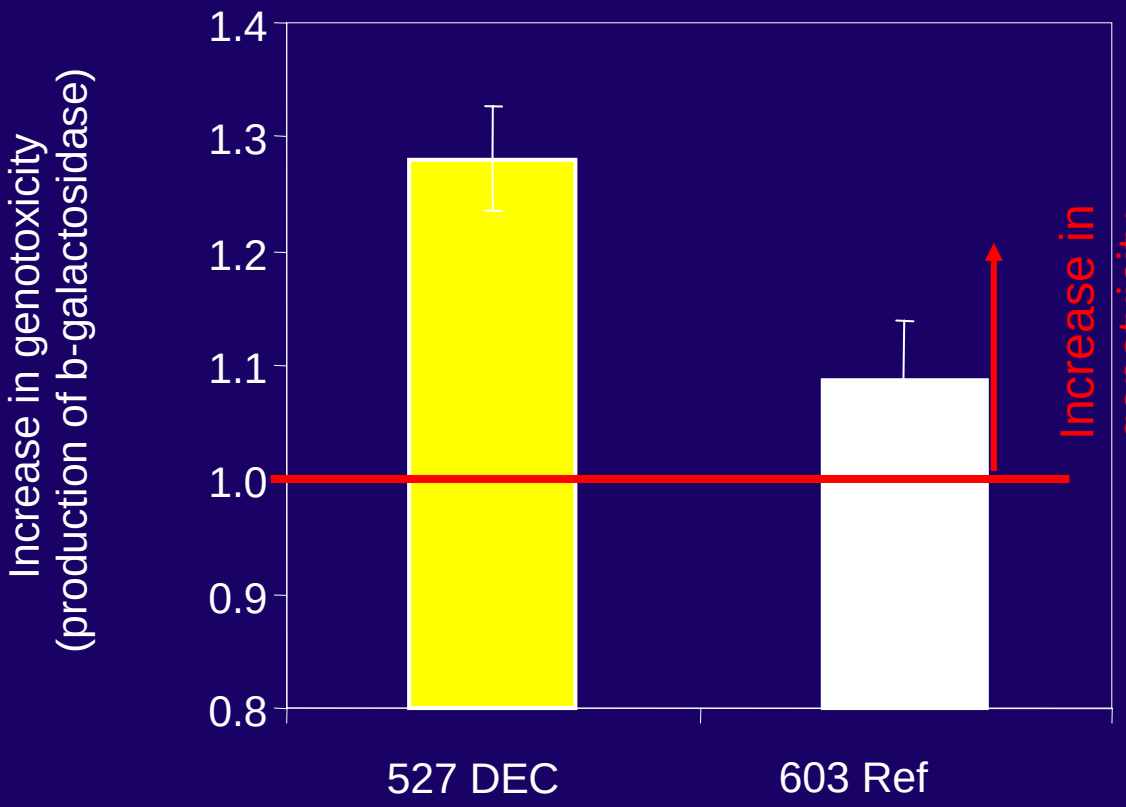


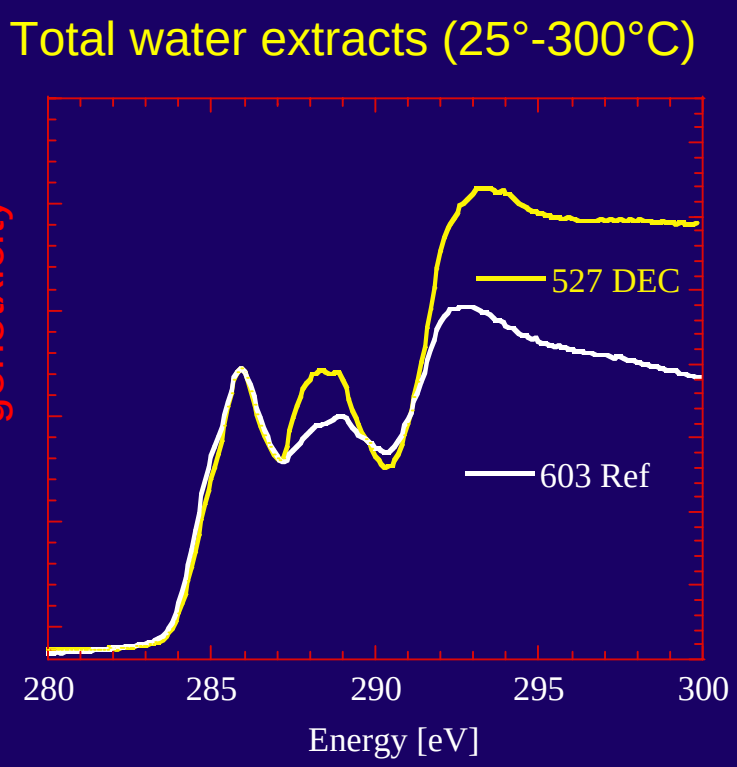
Atm. Environment 40/30 (2006) 5837
and Special Issue in J. Electron Spectr. & Related Phenomena on Radiation Damages; in press

PM and extracts may have entirely different, if not controversal spectral characteristics



Diesel exhaust PM generated with oxidizer has higher genotoxicity



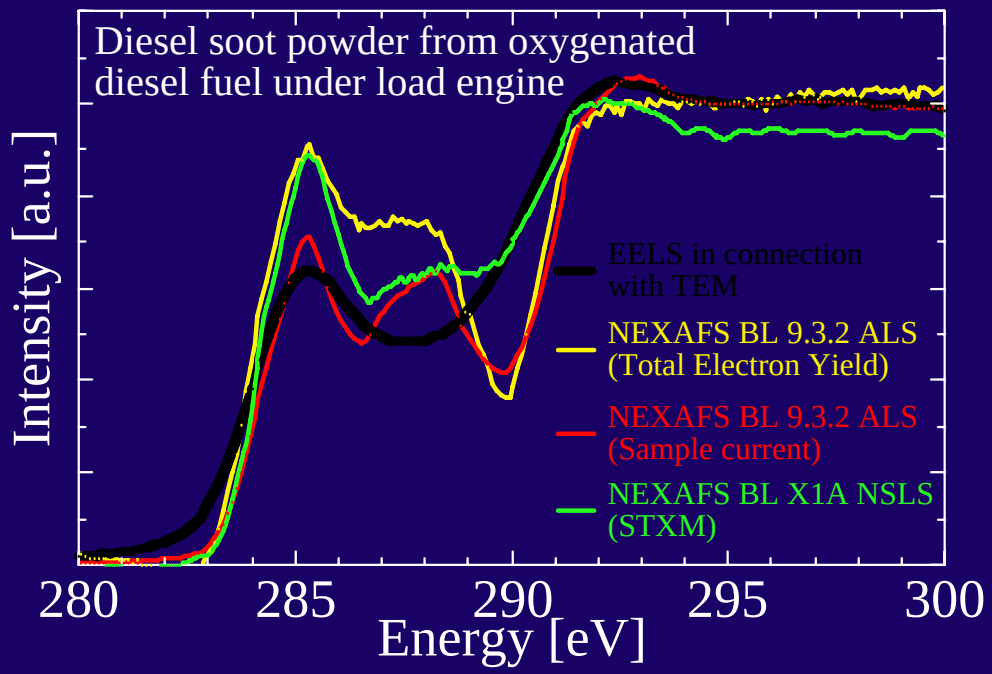


A. Kubatova, A Braun, in preparation

De Marini et al., Bio-assay directed fractionation and mutagenicity of exhaust particles, Env. Health Persp. 2004, 112(8), 814-819


Thank you

NEXAFS vs. EELS

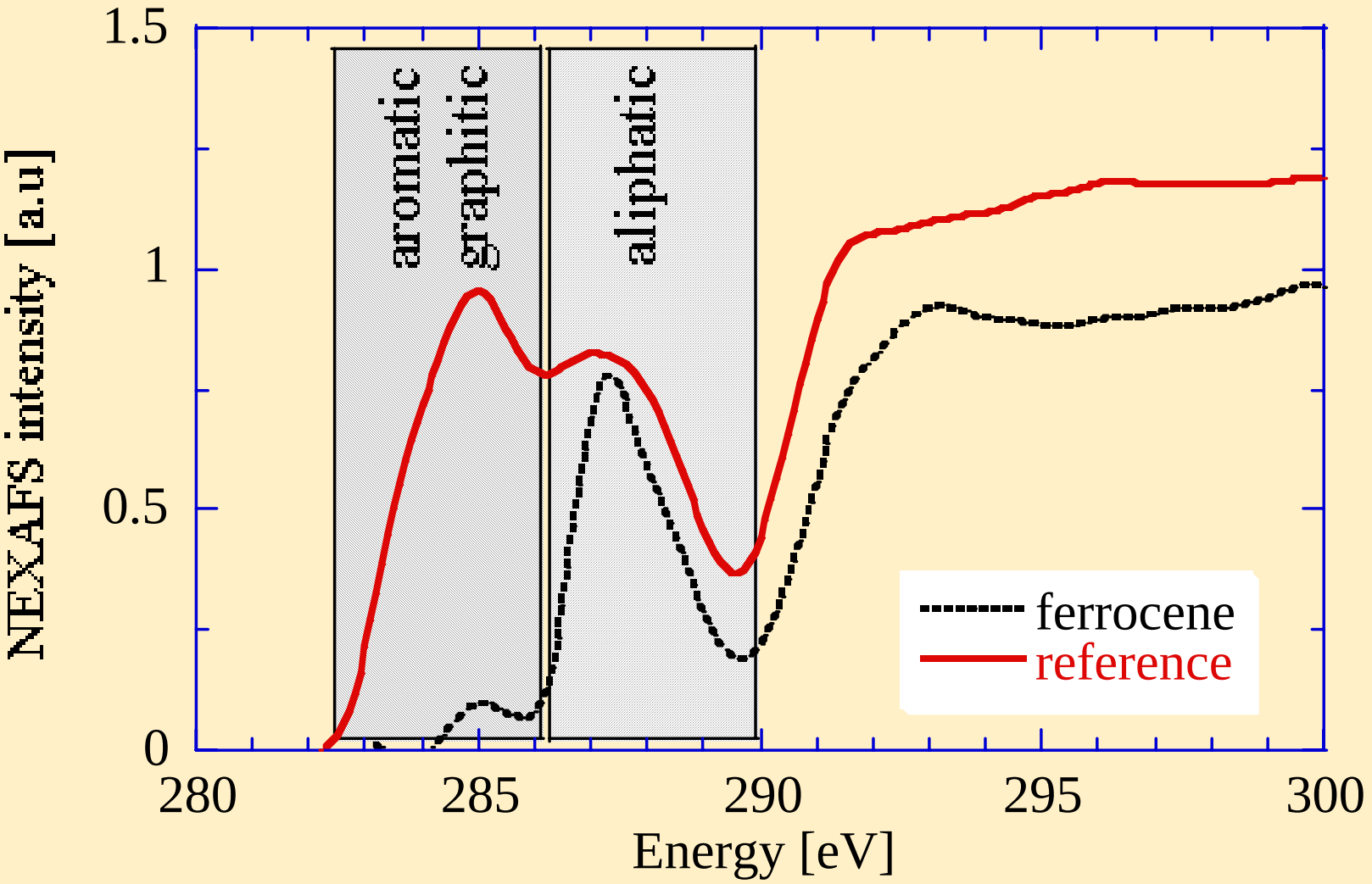


EELS and NEXAFS have similar spectra. TEM microscopes often come with an EELS spectrometer. But EELS spectra from TEM look blurred, almost entirely useless for quantitative studies.

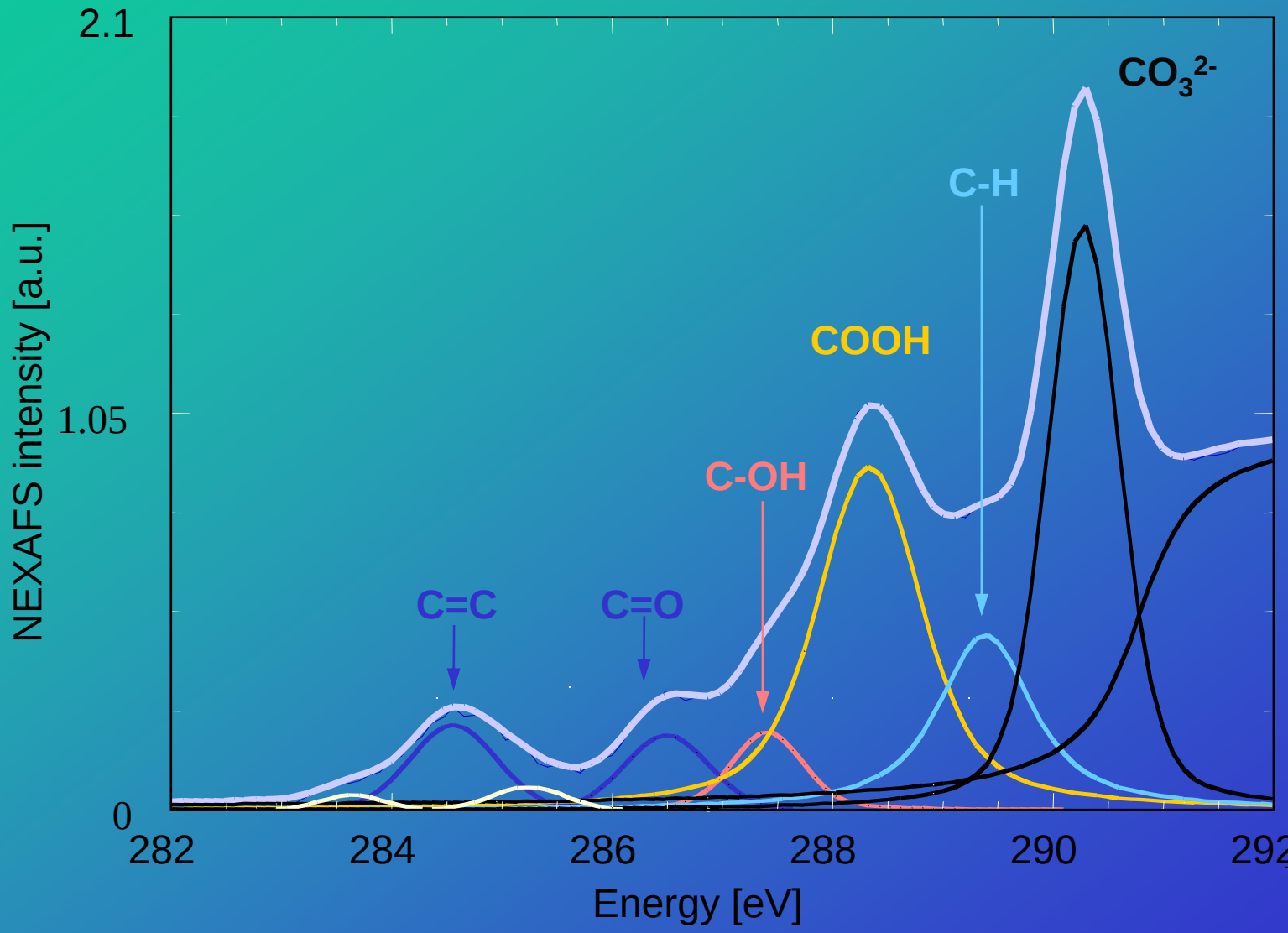
Carbon, **43**(1), (2005) 117-124.

Note: this concerns not ISEELS such as the ones by Hitchcock & coworkers

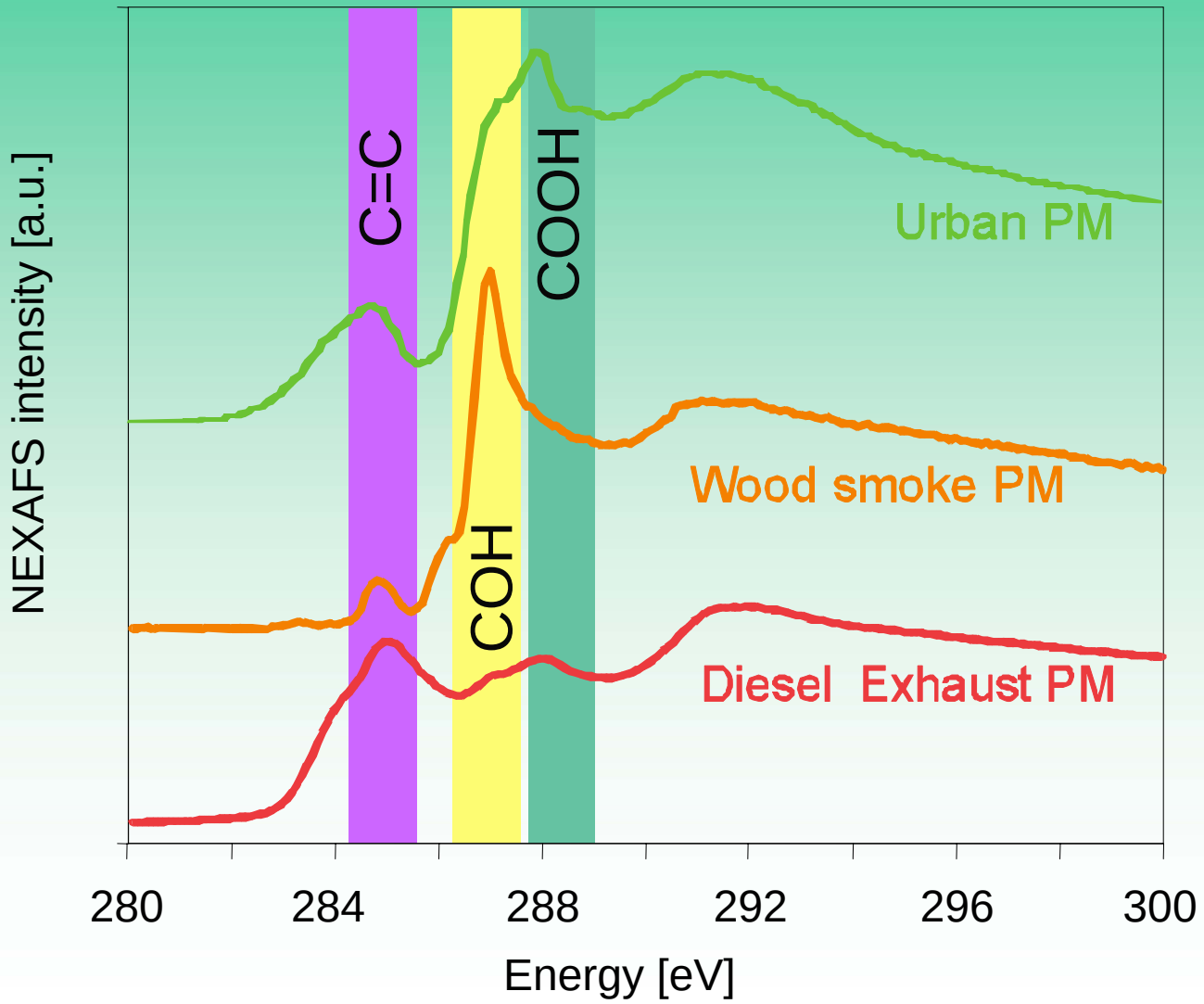
C(1s) NEXAFS confirms WAXS results: catalytic suppression of soot formation by ferrocene



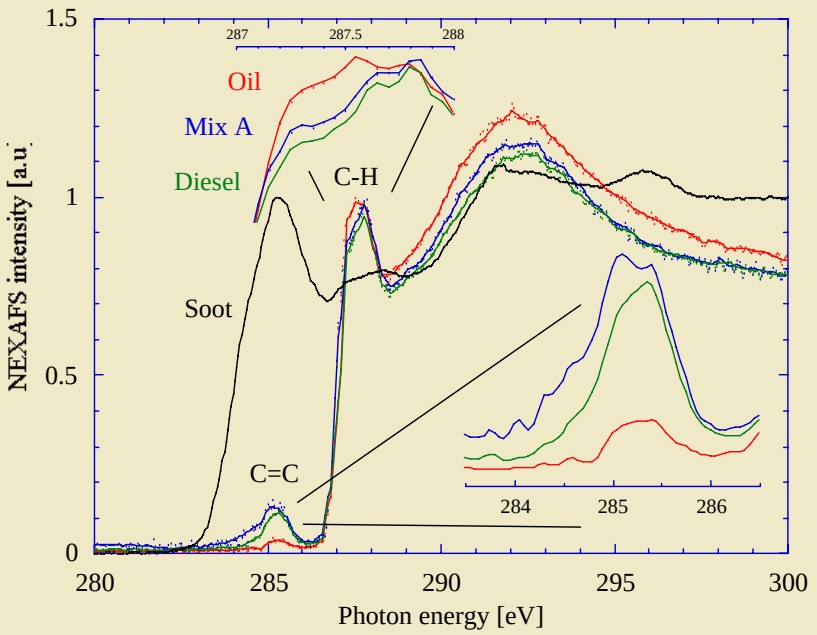
Suggested NEXAFS Peak Assignments for DPM Extract



Different PM samples show complex patterns in NEXAFS which cannot be easily attributed to the PM polarity



NEXAFS of soot, oil, and fuel



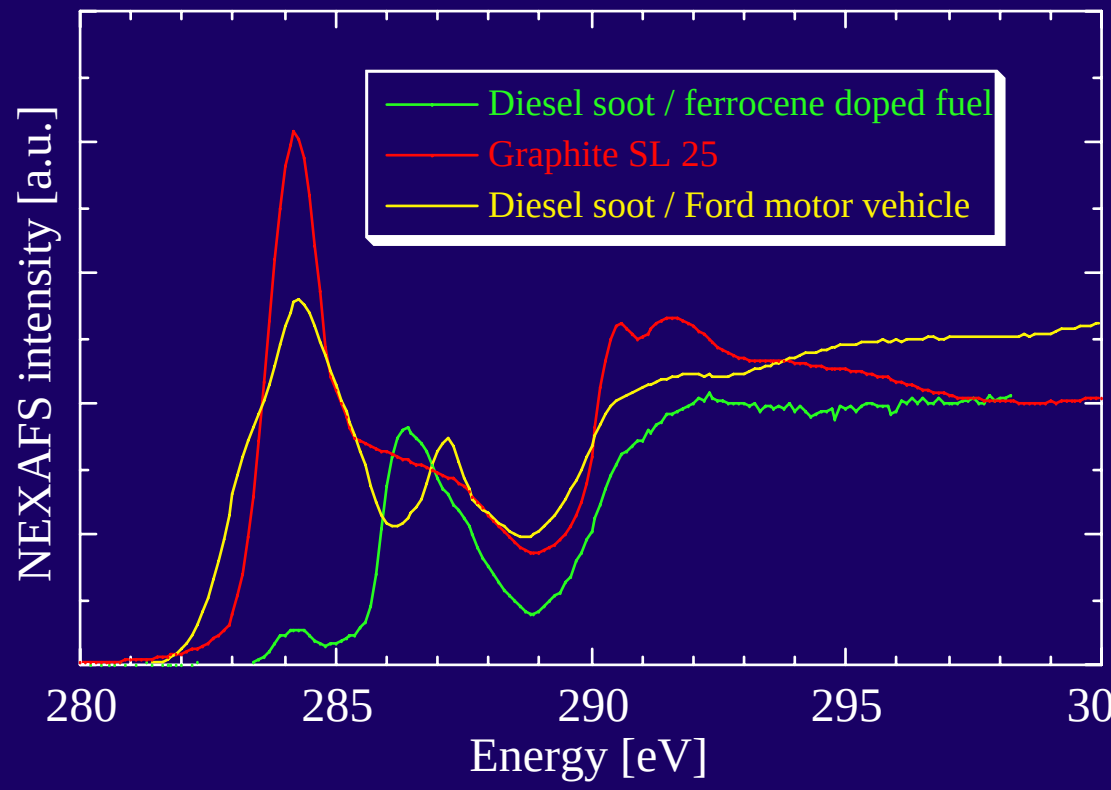
Spectra of soot, lubricant, fuel.

Allows for chemical speciation of samples, and determination of oxidation states.

Fuel (2004) **10** 7/8 997-1000.

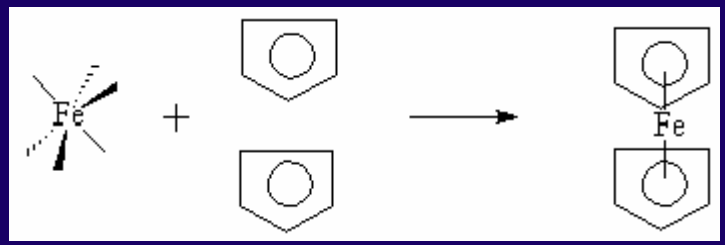
Catalytic suppression of soot formation in diesel engines

Mixing diesel fuel with ferrocene



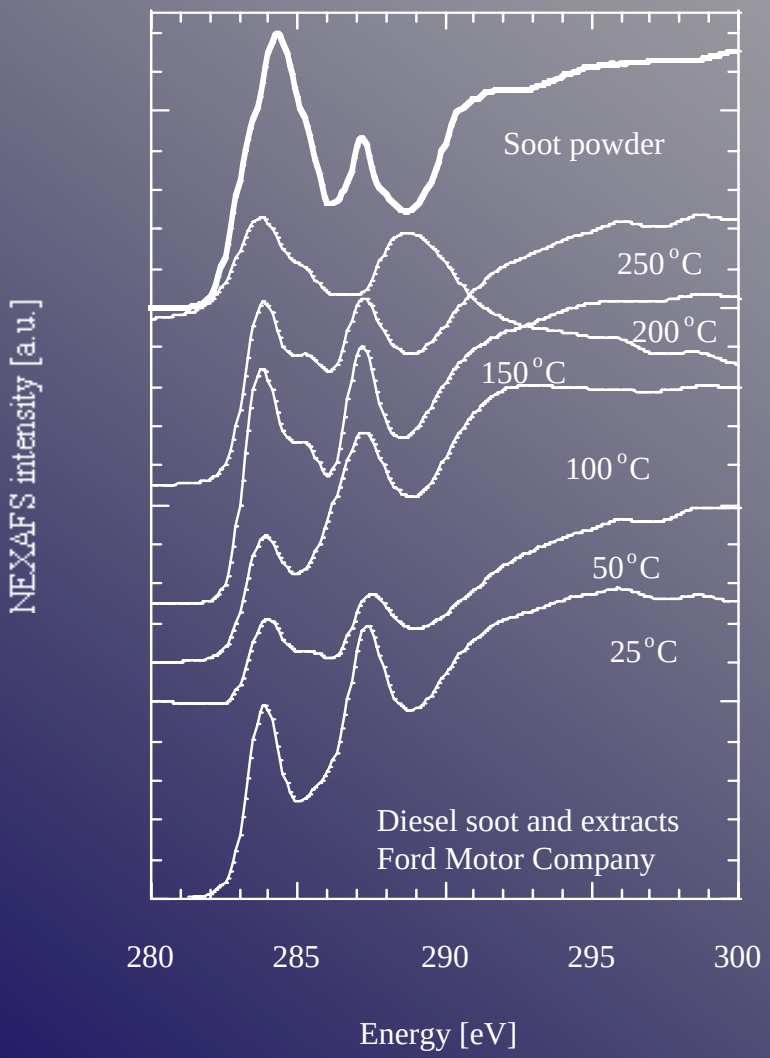
Ferrocene

Metastable molecule = **iron** atom sandwiched between two cyclopentadienyl rings.

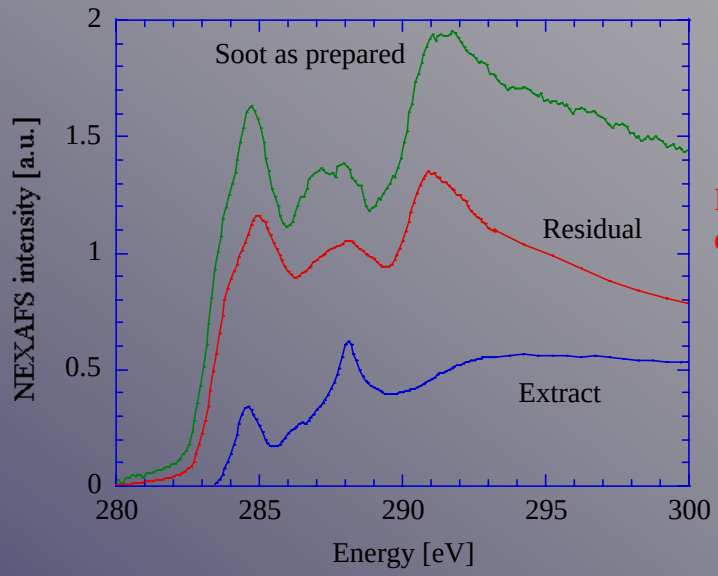


Dramatic decrease of C=C bond contribution in soot; increase in aliphatics

Soot Extracts



Separation of diesel soot into solid core and volatile fractions with sub-critical water facilitates subsequent decomposition of NEXAFS spectra.

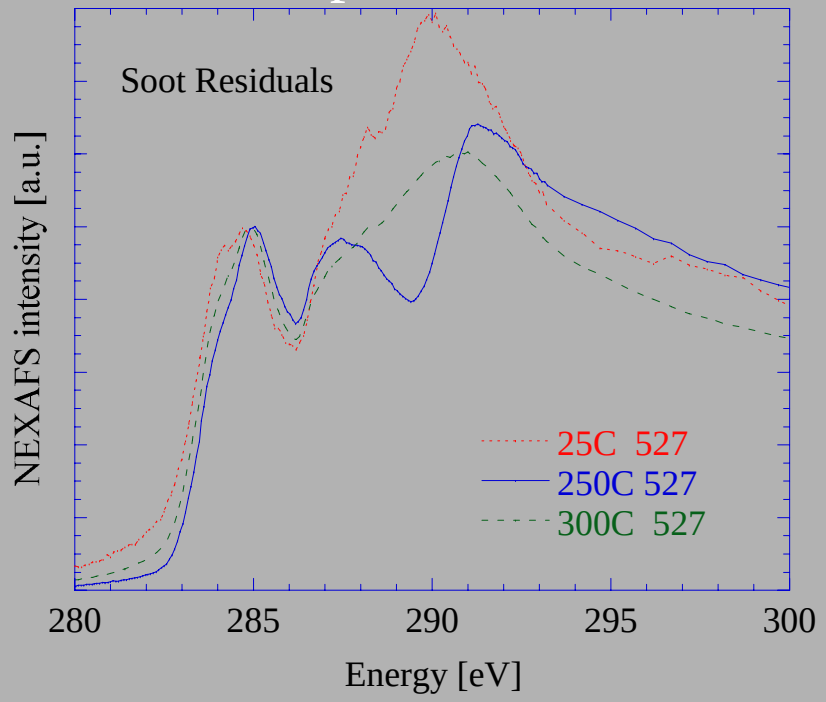


From reference diesel fuel

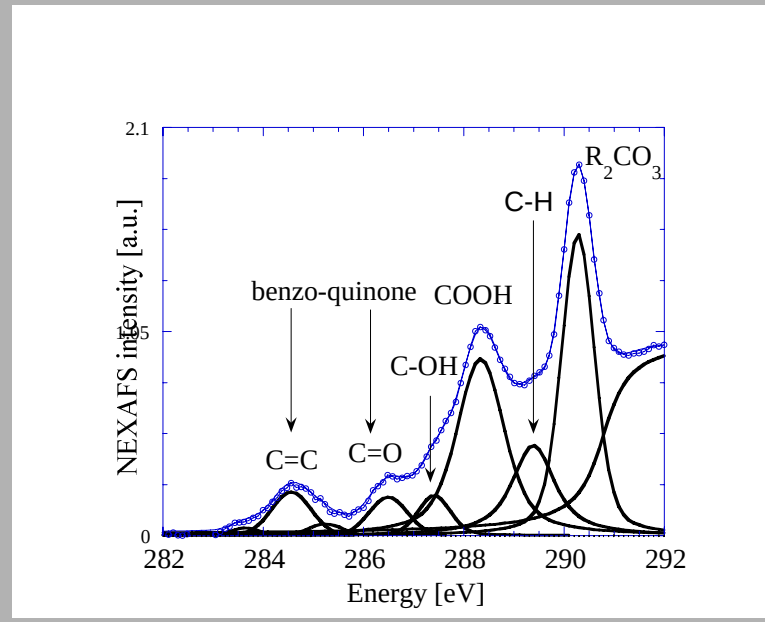
Extracts do contain material with C=C bonds

Soot Residuals

Separation of diesel soot into solid core and volatile fractions with sub-critical water facilitates subsequent decomposition of NEXAFS spectra.



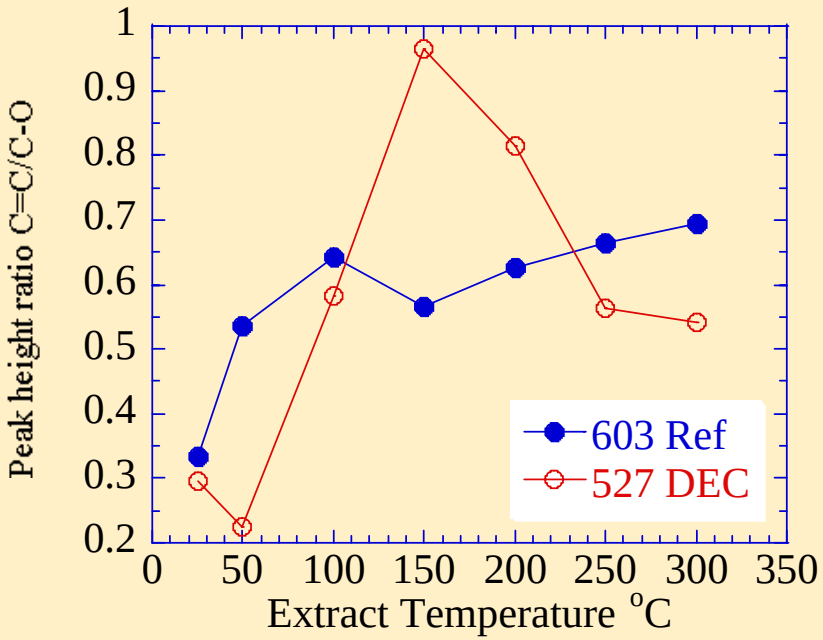
At low temperatures polar species like carboxylates and quinones are extracted.

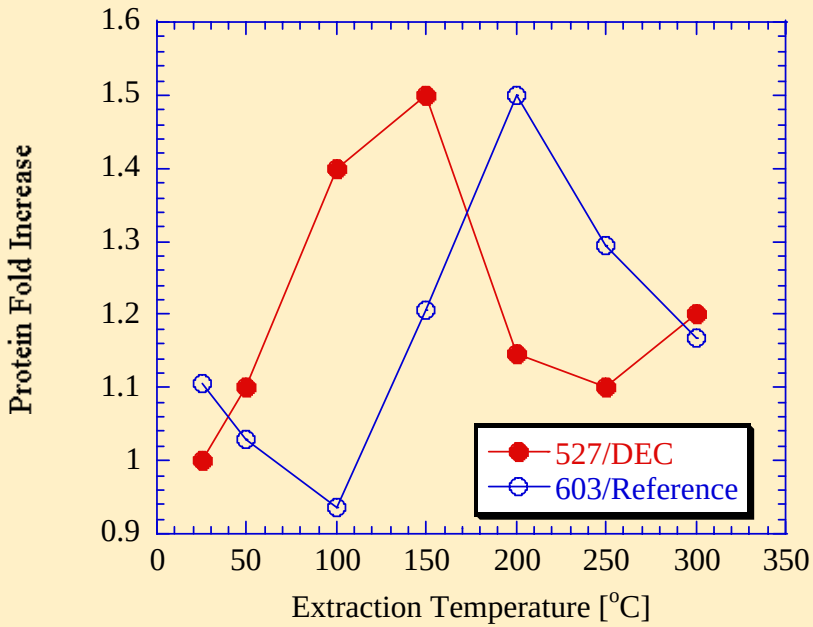


Proposed peak assignment for extracts.

Correlation of Toxicological Results and Spectra ?

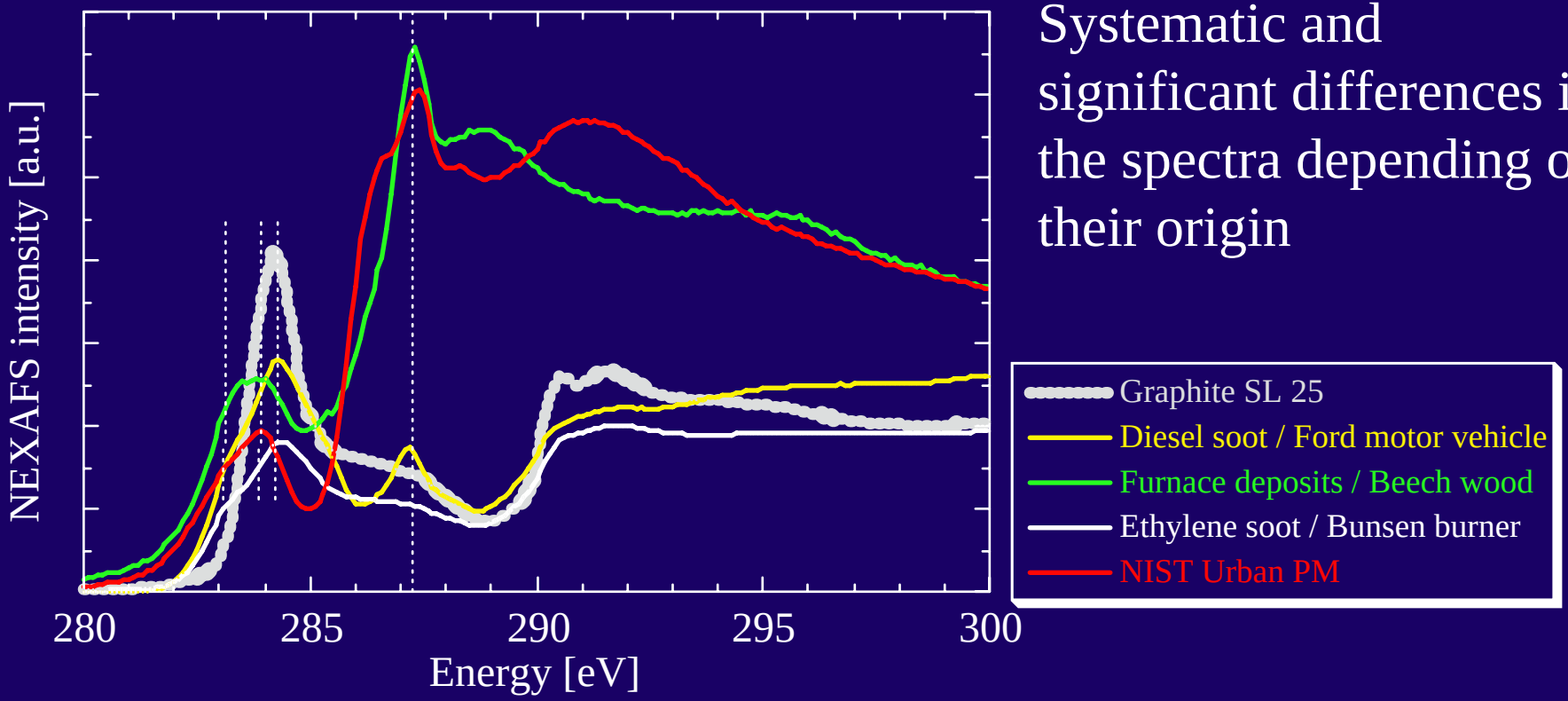
Cell cultures exposed to a series of subcritical water extracts.
Protein fold increase is a measure for toxic response.





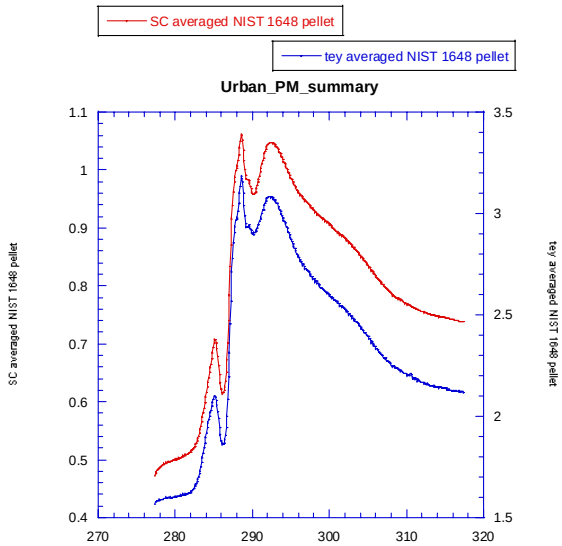
A. Kubatova, A Braun, in preparation

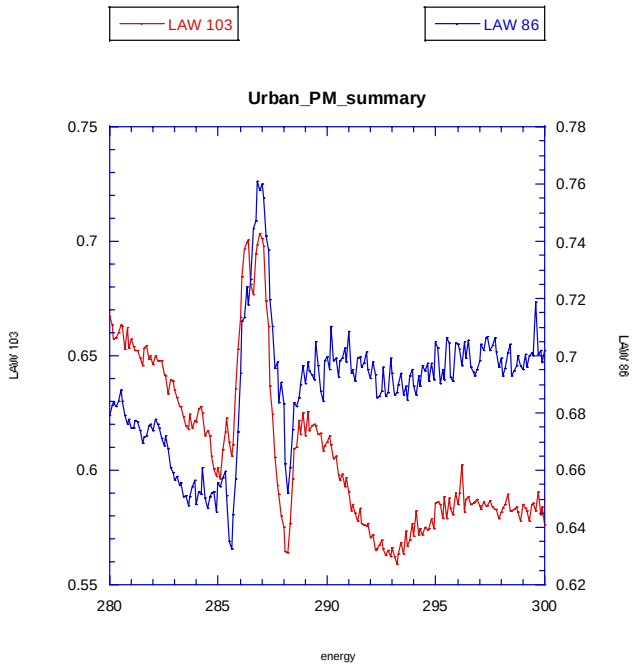
Spectra of some solid carbon samples

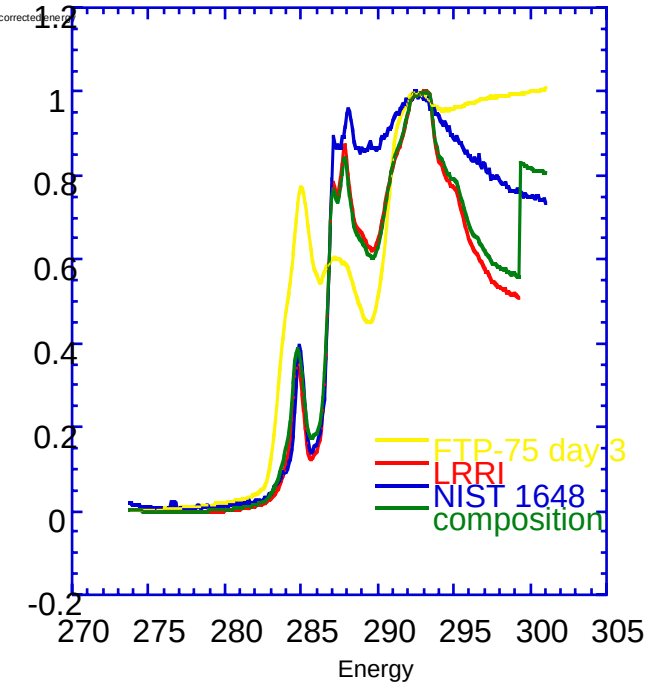


Systematic and significant differences in the spectra depending on their origin

Soot spectra contain significant intensity from C=C bonds ~ 285 eV.
Urban PM and wood creosote spectra contain significant intensity from aliphatics ~ 287 eV.


SC averaged NIST 1648 pellet
tey averaged NIST 1648 pellet
Urban_PM_summary
SC averaged NIST 1648 pellet
tey averaged NIST 1648 pellet
corrected energy


LAW 103
LAW 86
Urban_PM_summary
LAW 103
LAW 86
energy


FTP-75 day 3
LRRI
NIST 1648
composition
Energy