Source-specific characteristics of aerosol OM over the North Atlantic Ocean: Implications for the identity of potential Fe binding ligands

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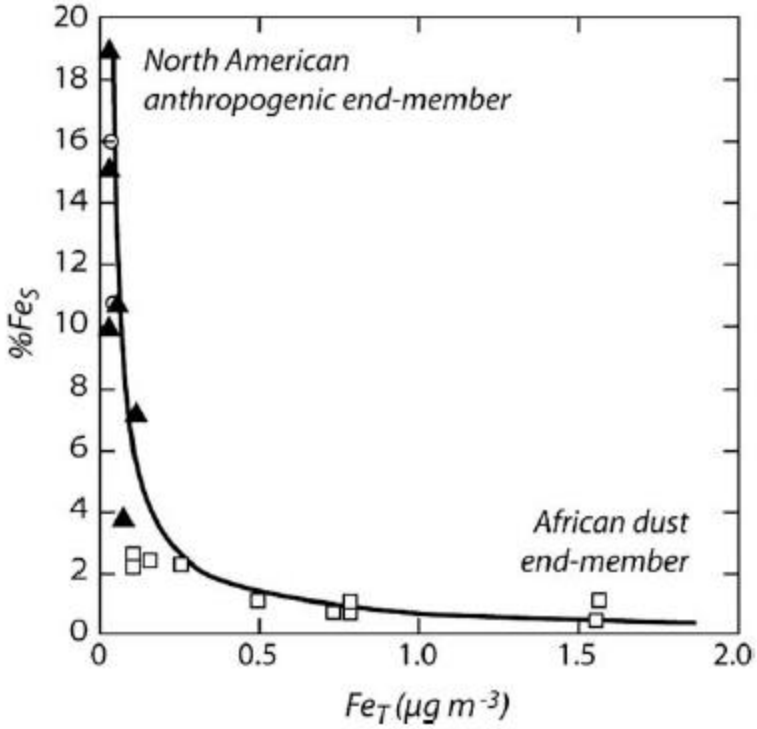
What do aerosols have to do with Fe?

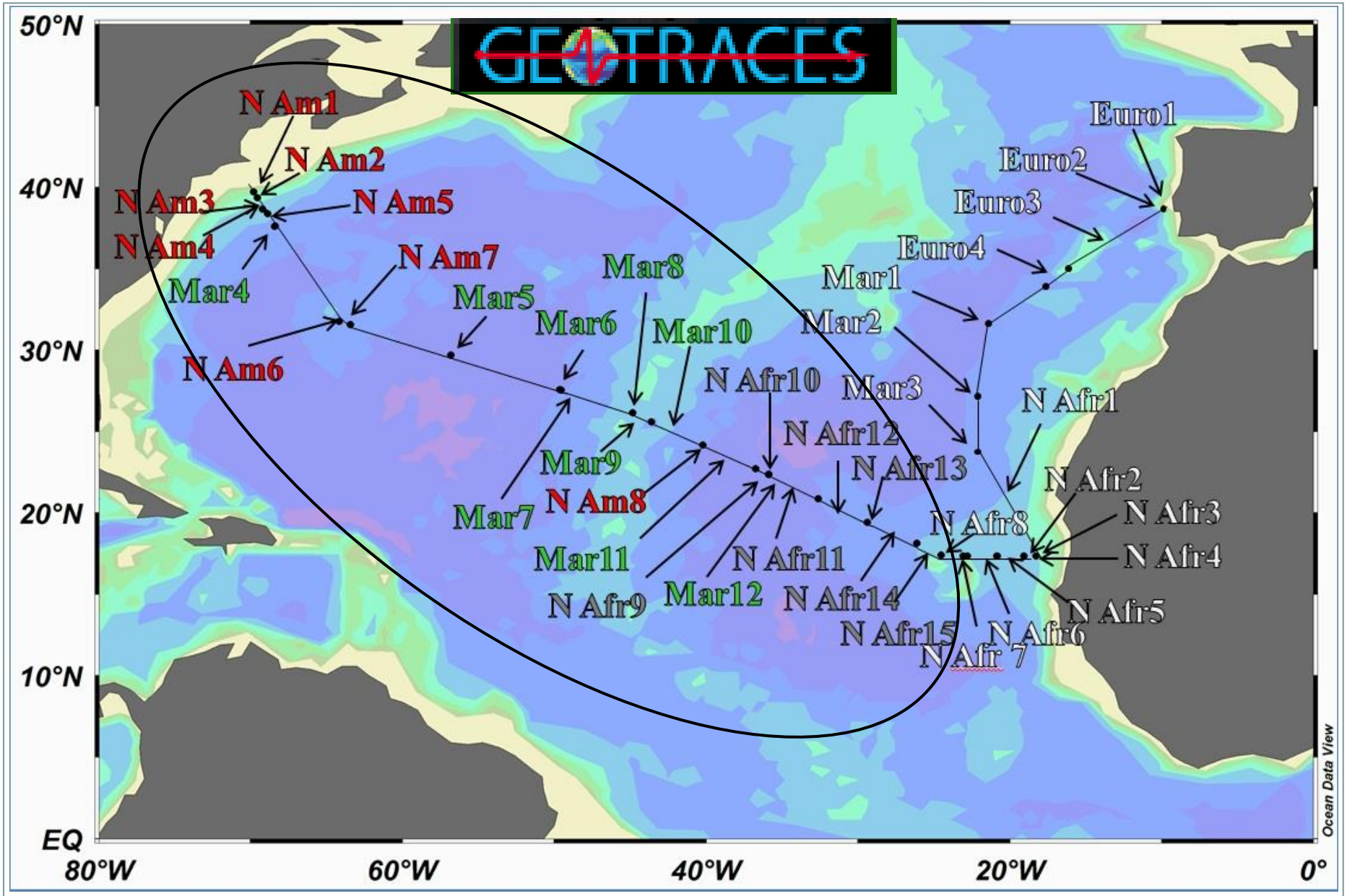


(Sholkovitz et al., 2009)

- Primary source of Fe to the ocean
- Mineral-dust influenced
  - i.e. North African
  - High Fe_T but low $\%Fe_S$ (<1%)
- Anthropogenic-combustion influenced
  - i.e. North America, Europe
  - Low Fe_T but high $\%Fe_S$ (up to 20%)

<u>Hypothesis</u>: Combustion sourced aerosol OM is molecularly distinct from mineral-dust aerosol OM facilitating increased Fe solubility

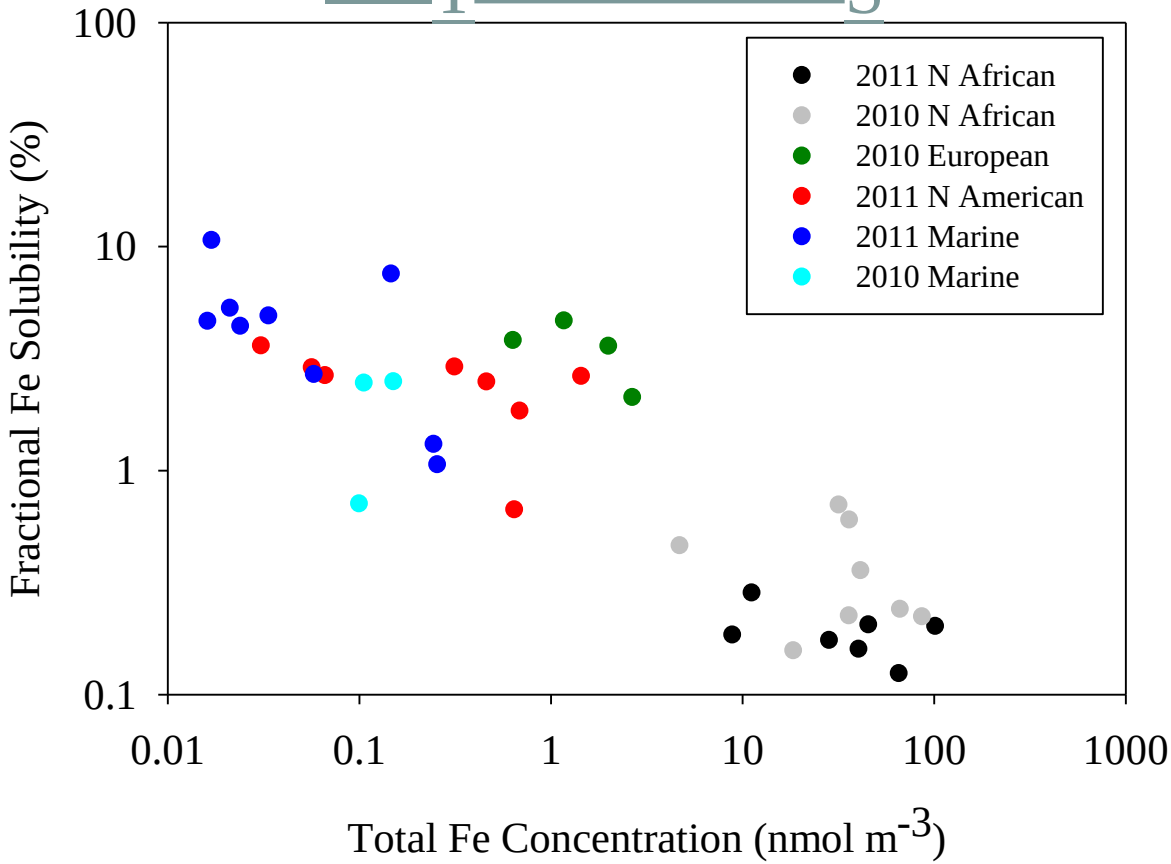
(Wozniak et al., 2013; Sedwick et al., 2007; Mahowald et al., 2005, Sholkovitz et al., 2012)


GEOTRACES
50°N
40°N
30°N
20°N
10°N
EQ
80°W
60°W
40°W
20°W
0°
N Am1
N Am2
N Am3
N Am4
N Am5
N Am6
N Am7
N Am8
Mar1
Mar2
Mar3
Mar4
Mar5
Mar6
Mar7
Mar8
Mar9
Mar10
Mar11
Mar12
Euro1
Euro2
Euro3
Euro4
N Afr1
N Afr2
N Afr3
N Afr4
N Afr5
N Afr6
N Afr 7
N Afr8
N Afr9
N Afr10
N Afr11
N Afr12
N Afr13
N Afr14
N Afr15
Ocean Data View

Experimental Methods

- 2011 US GEOTRACES North Atlantic cruise aerosol samples
- Aerosol samples (n=24) with N. American-, N. African-, and marine influenced air masses were analyzed for:
  - Fe_T & % Fe_S
  - WSOC
  - Molecular characteristics of WSOM using ^1H NMR
- PCA is used to identify molecular characteristics source-specific to N. American, N. African, and Marine influenced aerosol WSOM sources.

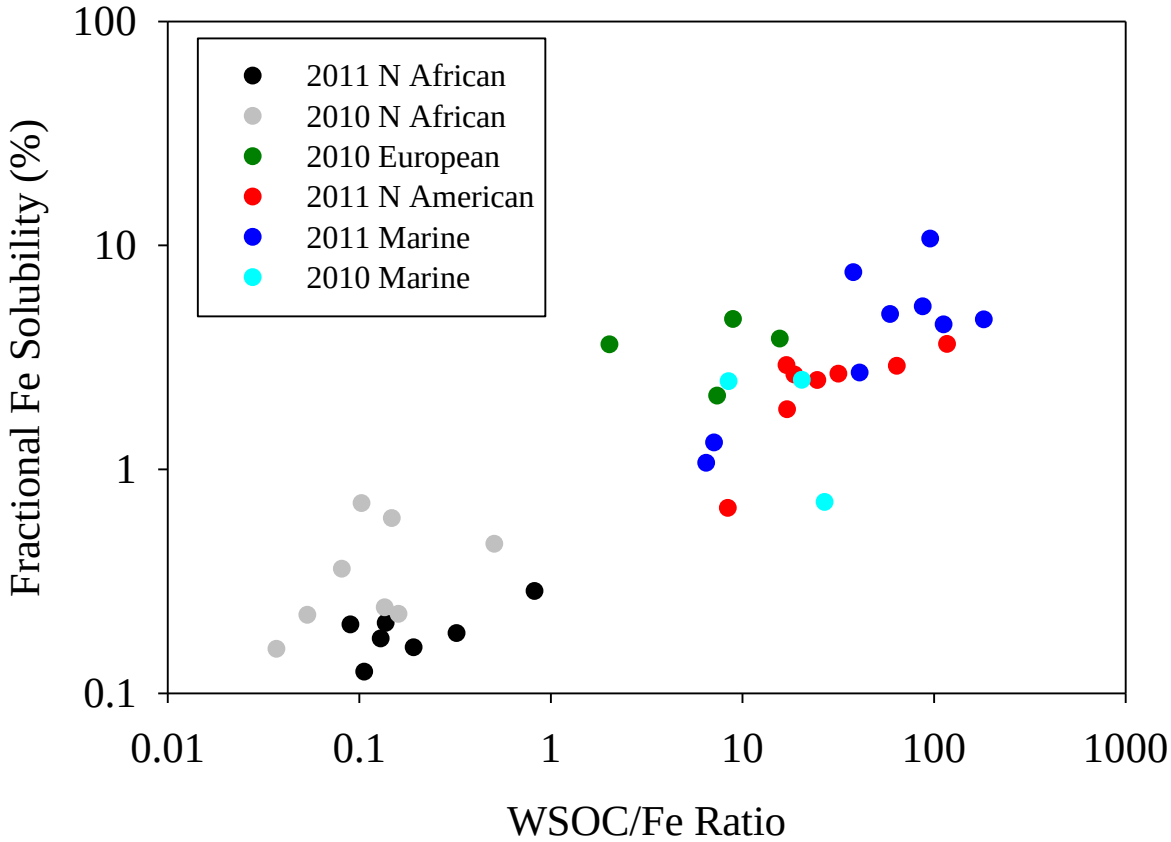
Fe_T vs. $\%Fe_S$



- Anthropogenic samples show lower Fe_T concentrations but much higher $\%Fe_S$
- Mineral-dust samples show higher Fe_T concentrations but lower $\%Fe_S$

(Sholkovitz et al., 2012)

WSOC/Fe_T vs. %Fe_S

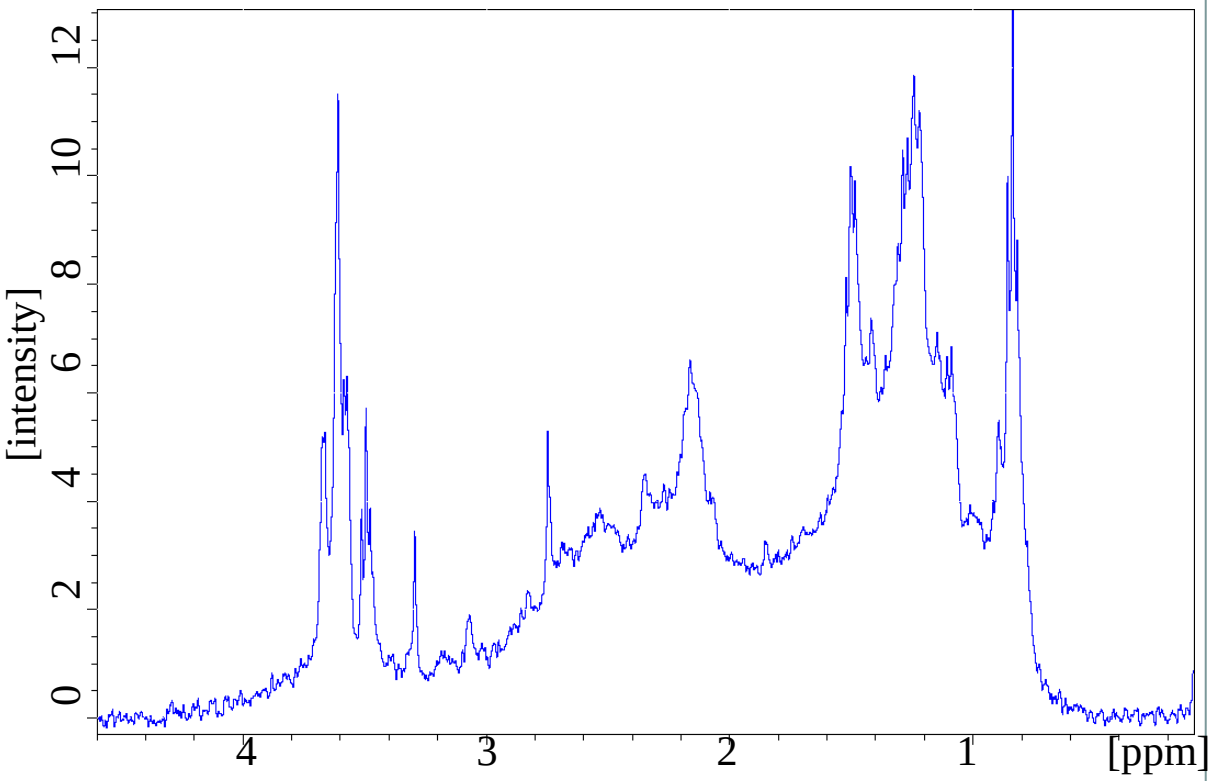


- Anthropogenic-influenced samples are high in %Fe_S and WSOC/Fe_T ratios
- Mineral-dust samples are low in %Fe_S and WSOC/Fe_T ratios

(Wozniak et al., 2013)

^{1}H NMR Analysis

400MHz NMR housed in the COSMIC facility at ODU



North American sample
4.6 - 0 ppm range

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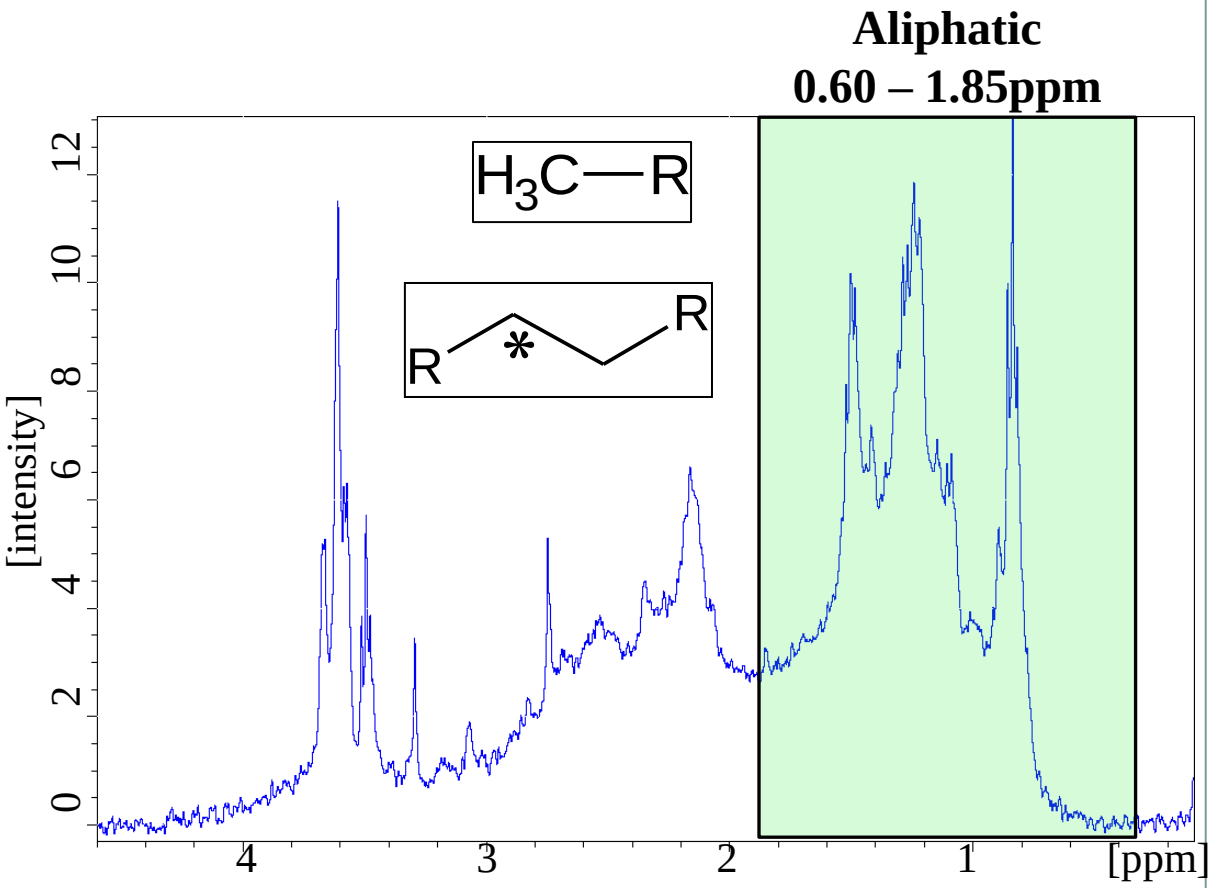
400MHz NMR housed in the COSMIC facility at ODU



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(Tagliavini et al., 2006)

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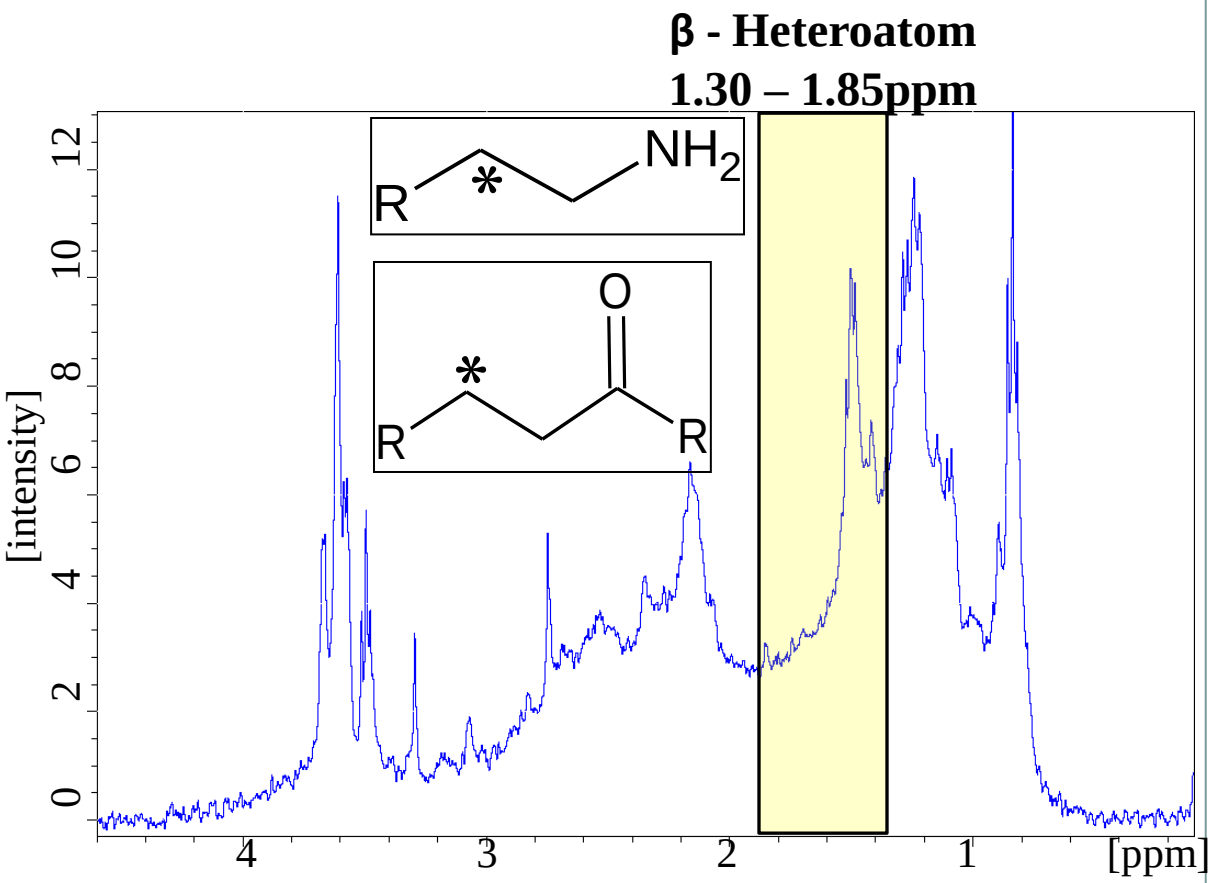

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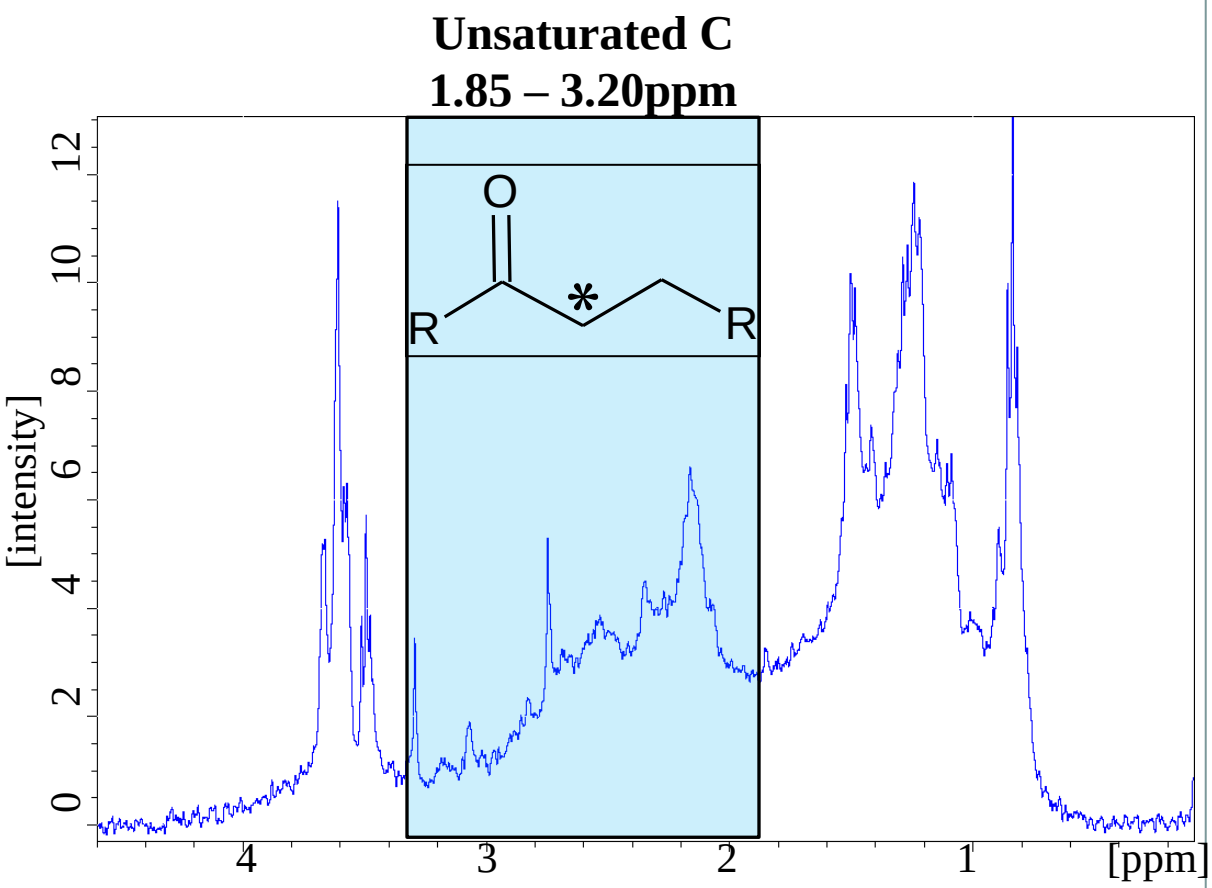

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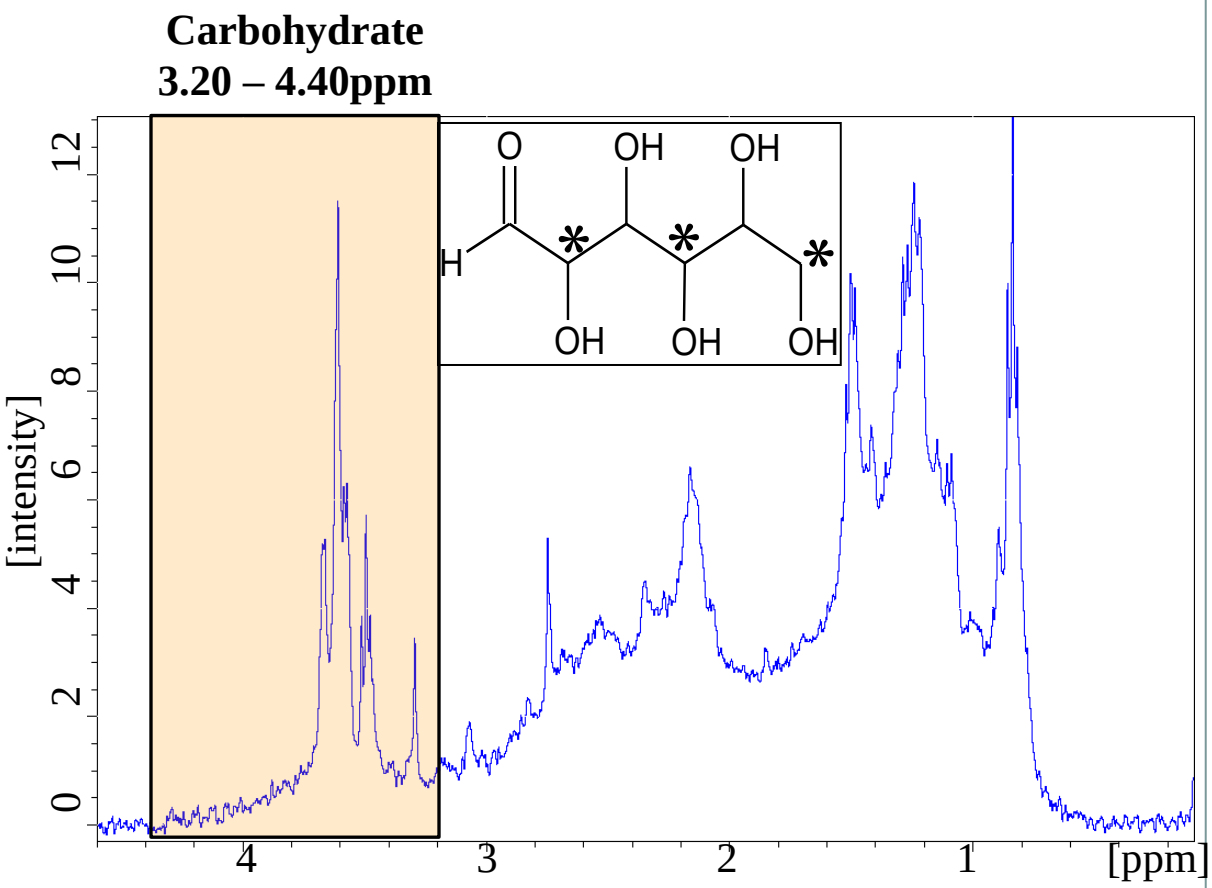
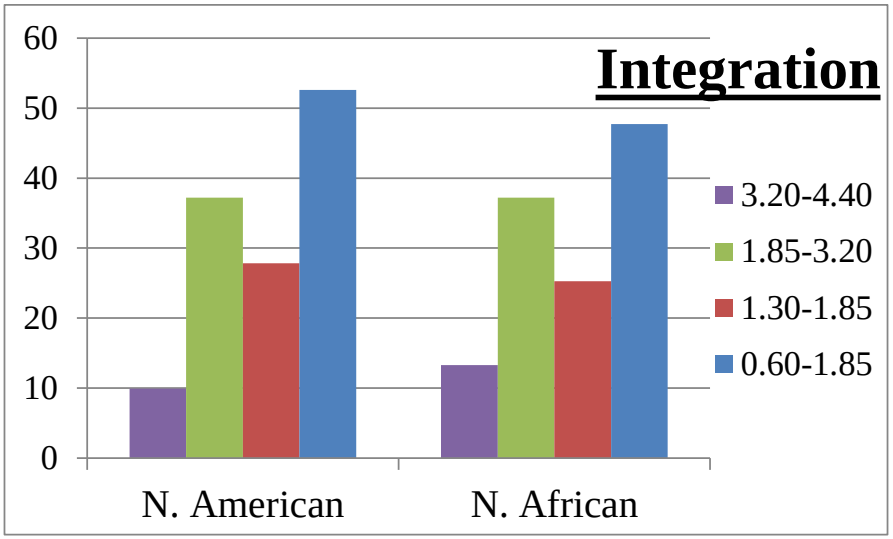
400MHz NMR housed in the COSMIC facility at ODU

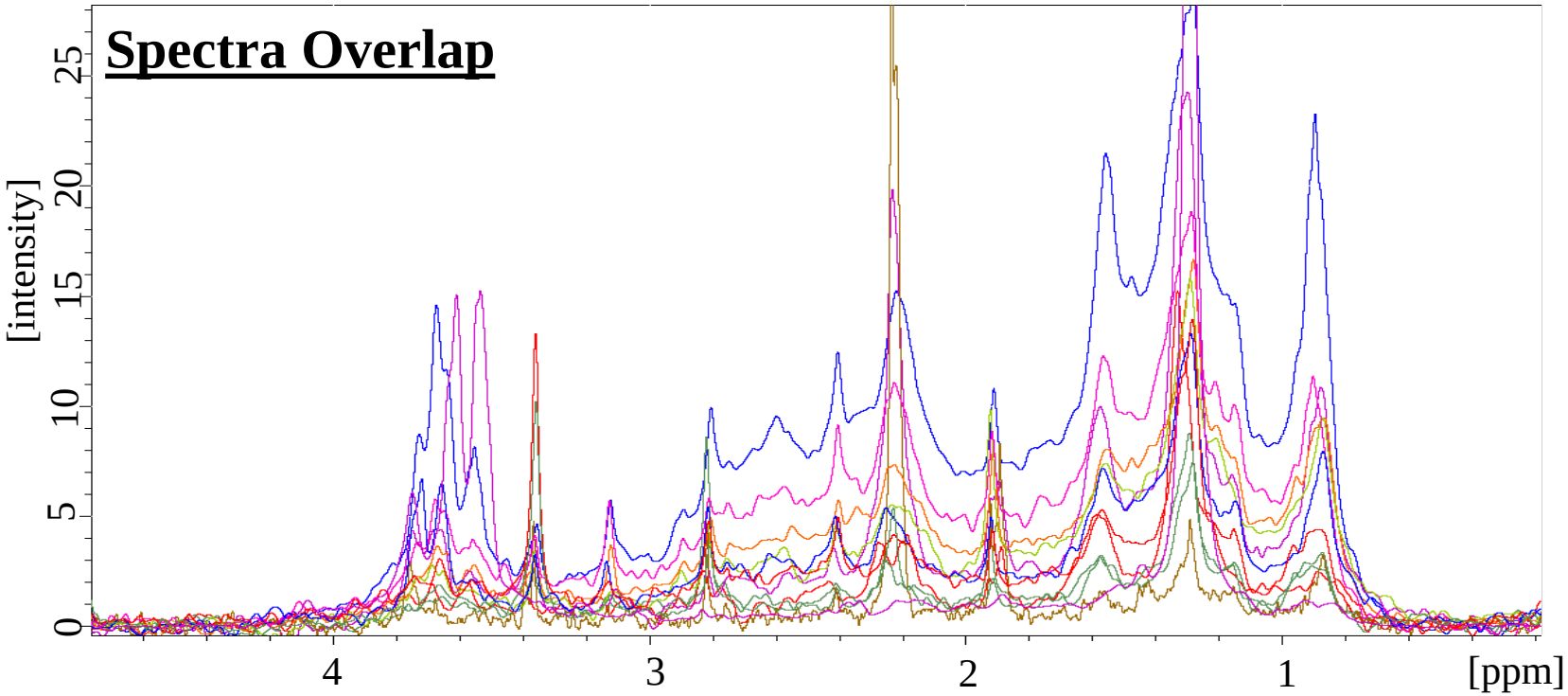


North American sample
4.6 - 0 ppm range

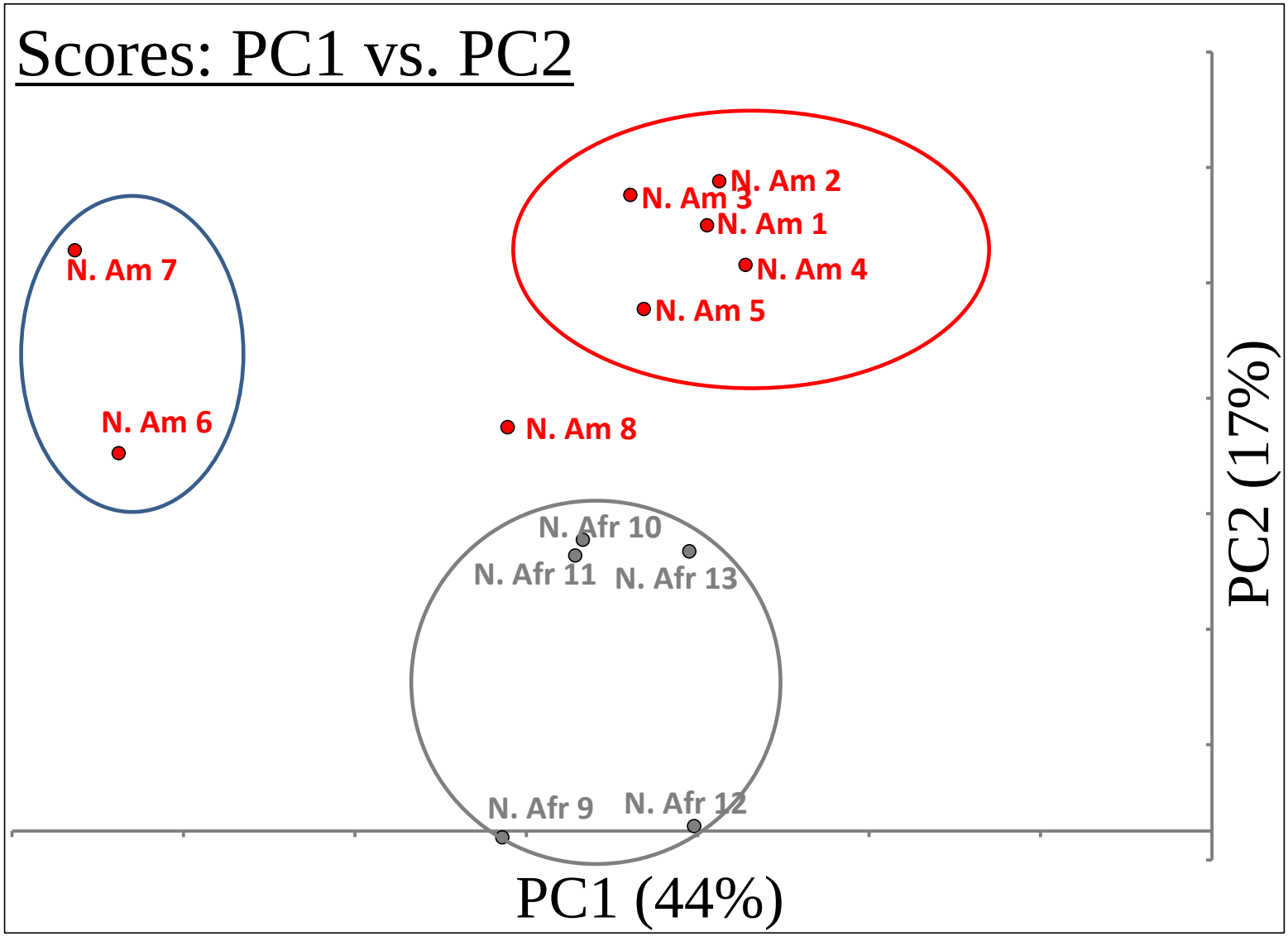
(Tagliavini et al., 2006)

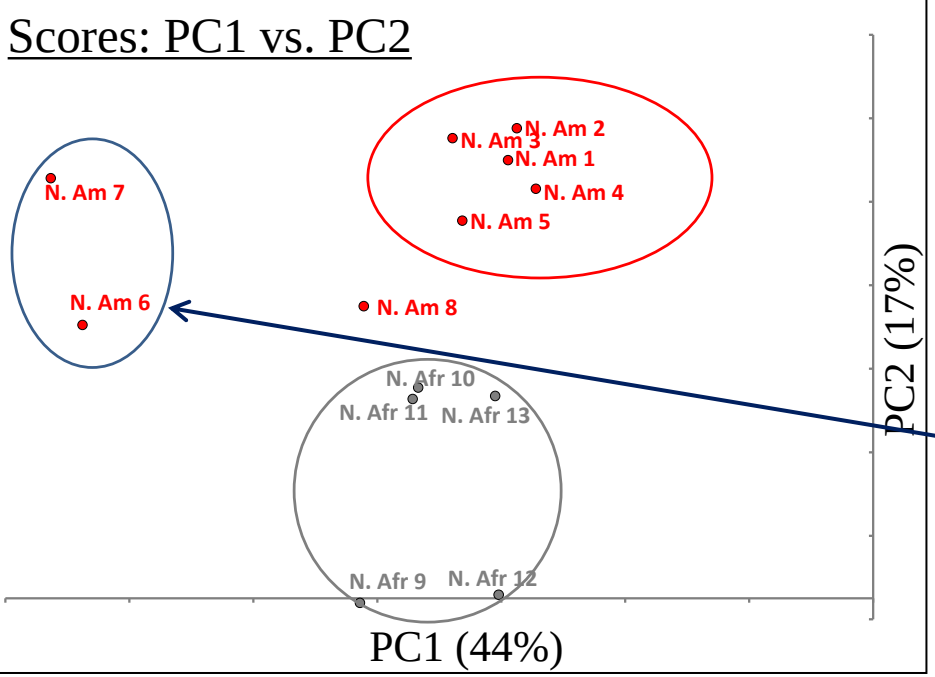
N. American & N. African Spectra

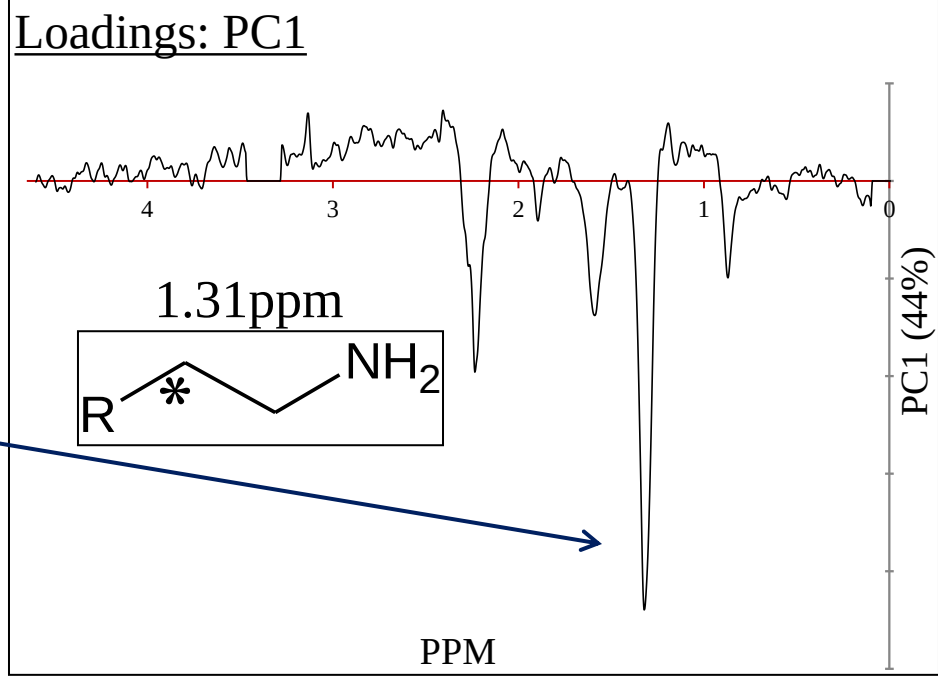




Principal Component Analysis (PCA)



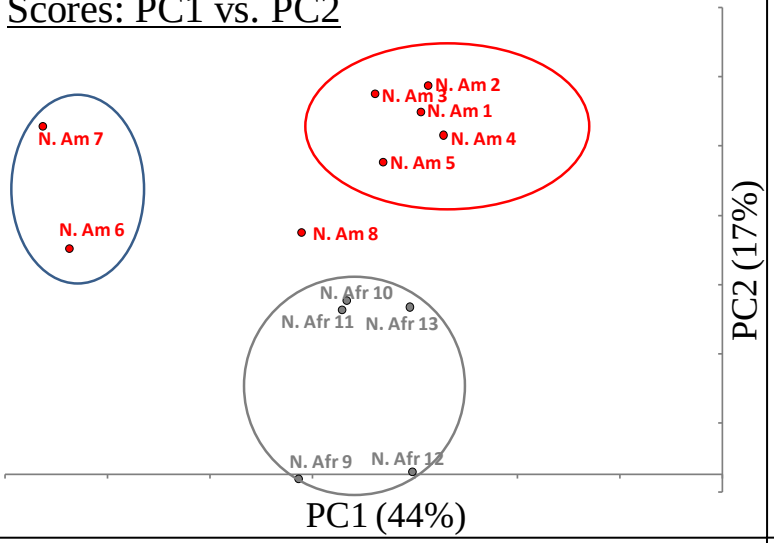




N. Am 7 & **N. Am 8** have an unusually high composition of N containing functional groups according to FTICR-MS

(Wozniak et al., in review)

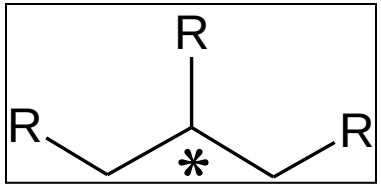
Scores: PC1 vs. PC2



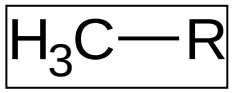
Total Aliphatic Region:

N. American samples are enriched in aliphatic H^+ relative to N. African samples

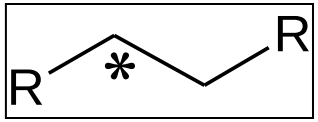
Loadings: PC2



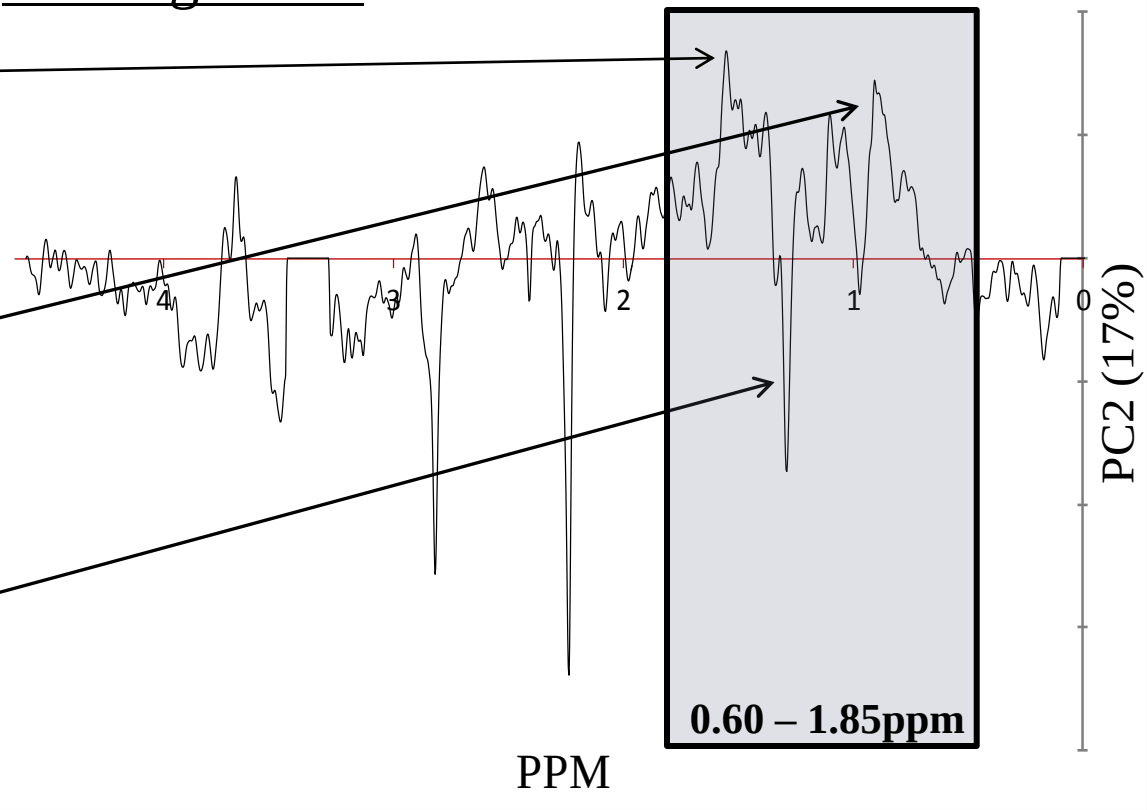
1.56ppm



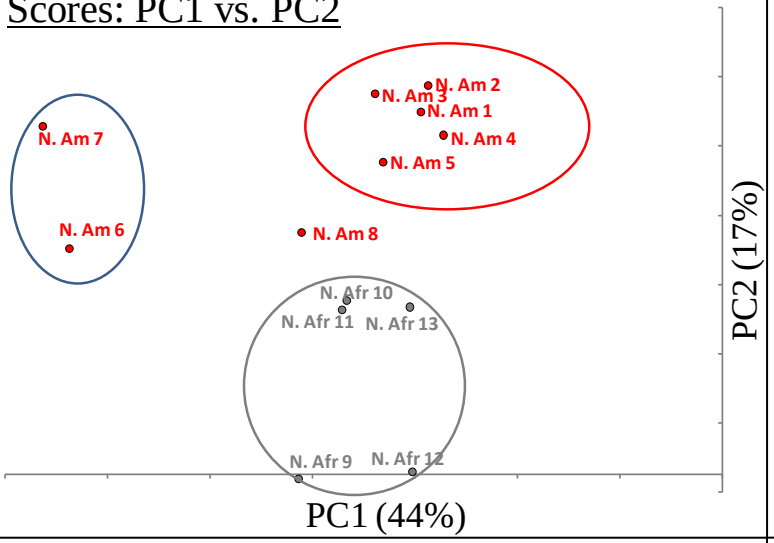
0.90ppm



1.29ppm

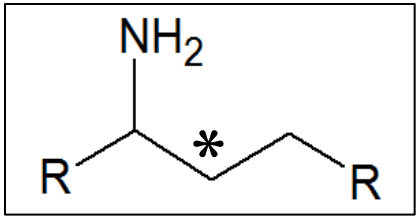


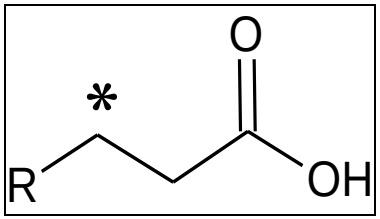
Scores: PC1 vs. PC2



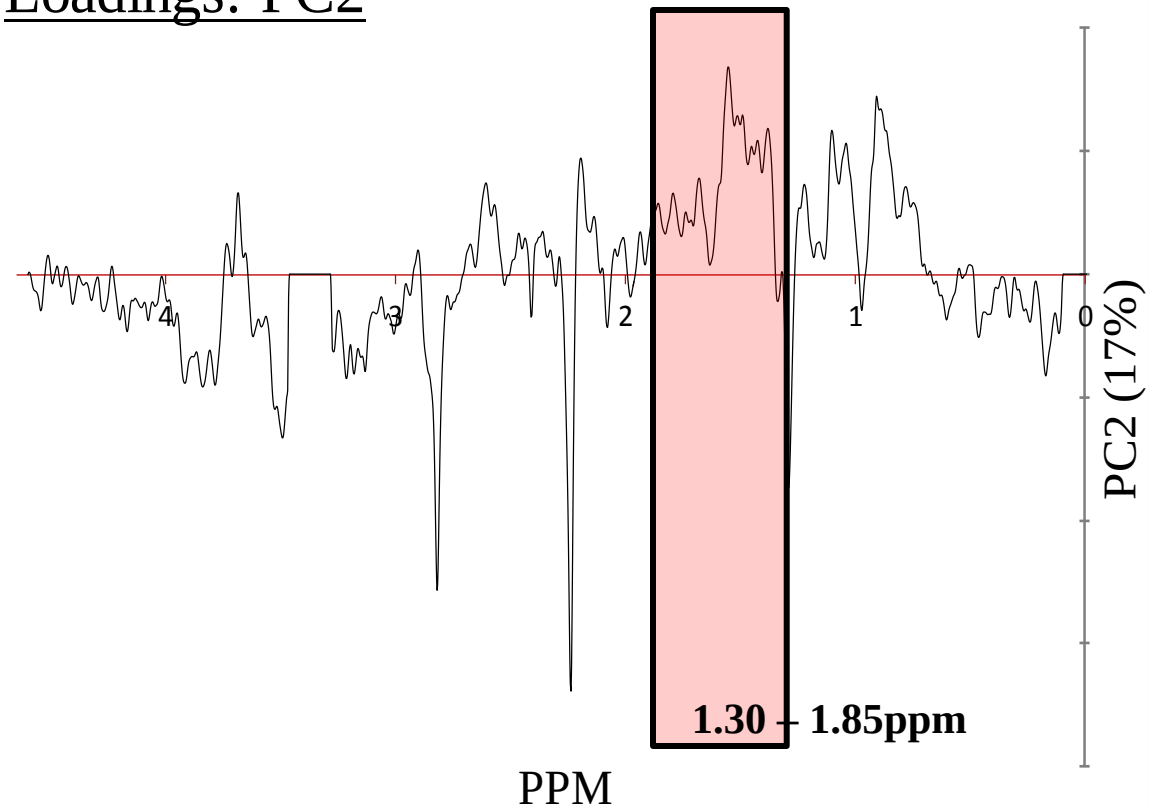
β - Heteroatom:

N. American samples are enriched in H^+ bound to C in β – position to heteroatoms relative to N. African samples.

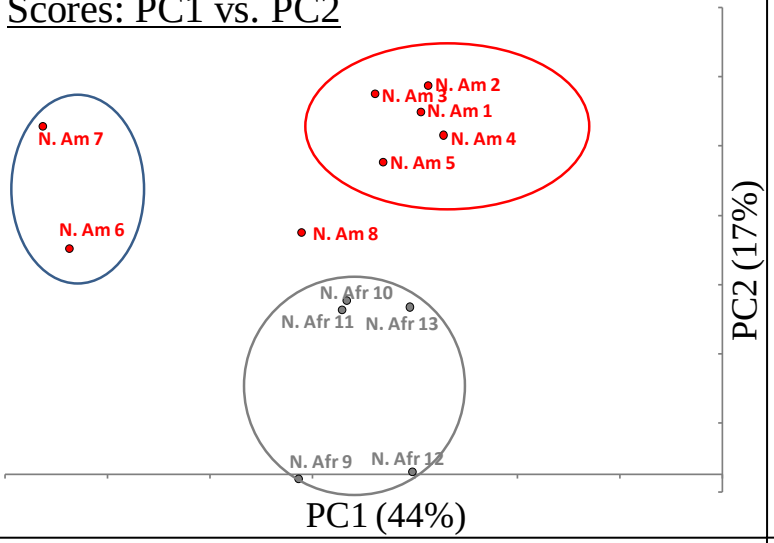




Loadings: PC2



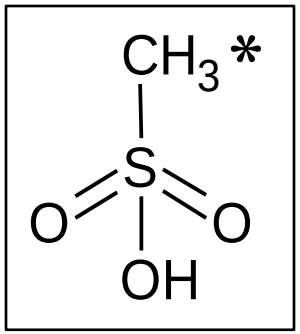
Scores: PC1 vs. PC2



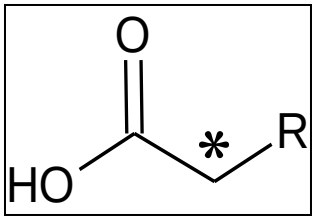
Unsaturated C Region:

N. American and N. African samples are enriched in H^+ that are bound to C in α–position to unsaturated C indicating oxygenated species.

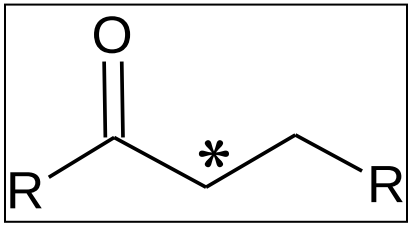
Loadings: PC2



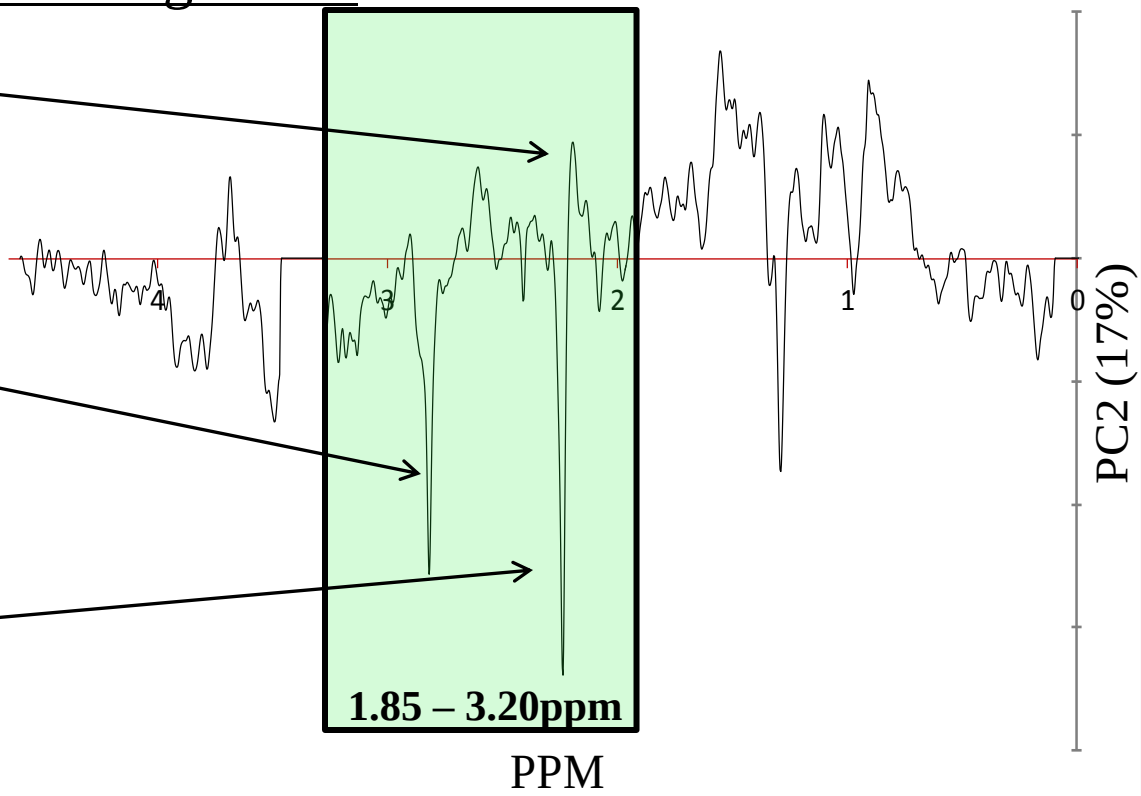
2.81ppm



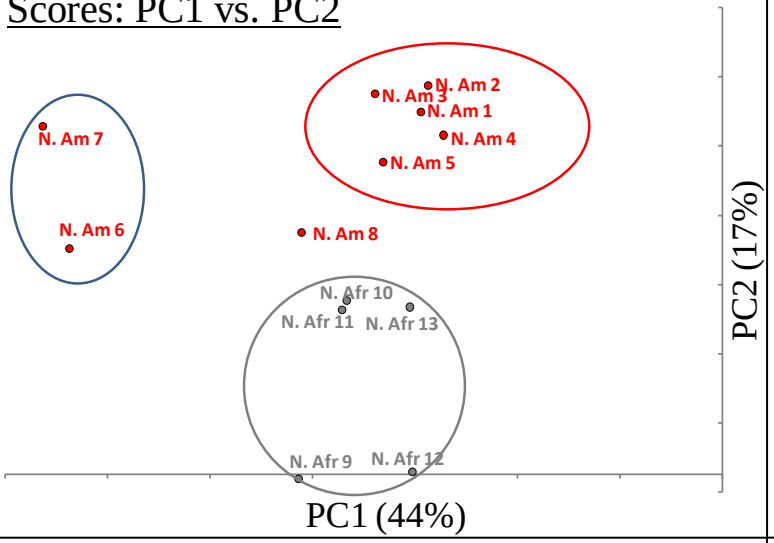
2.15ppm



2.23ppm



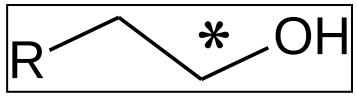
Scores: PC1 vs. PC2



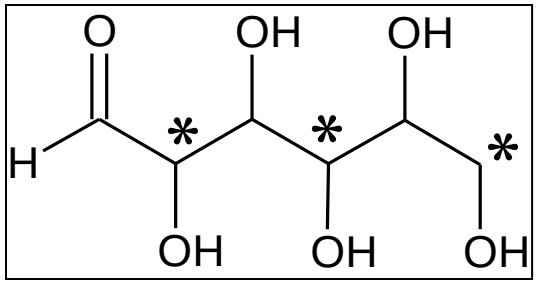
Carbohydrate Region:

N. African samples are enriched in H^+ bound to alcoholic, ether, or ester C relative to N. American samples.

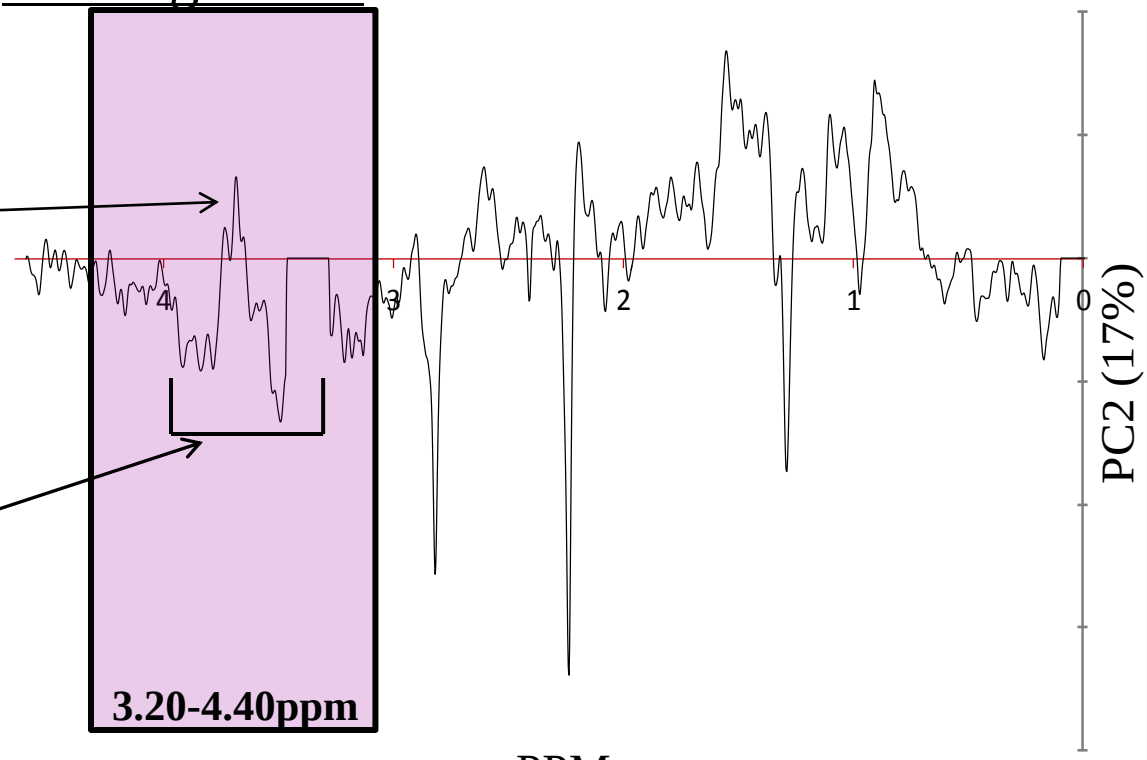
Loadings: PC2



3.64ppm



3.5 - 3.9ppm



Summary

- High solubility, anthropogenic-influenced samples have:
  - High WSOC/Fe_T ratios
  - Enriched in aliphatic, β-heteroatom, and carboxylic acid groups

- Low solubility, mineral-dust samples have:
  - Low WSOC/Fe_T ratios
  - Enriched in carbohydrate and carbonyl functional groups

- Preliminary results show the aliphatic, β-heteroatom, and carboxylic acid functionalities are consistent with the literature for OM ligands facilitating Fe solubility.

- Future Work: 2D NMR

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Acknowledgments:

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Amanda Willoughby

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GEOTRACES Project