Aerosol Water Soluble Organic Matter Molecular Characteristics and Iron Solubility from the 2011 US GEOTRACES Cruises in the North Atlantic Ocean

*[1]**A. S. Wozniak**, [2]R. U. Shelley, [1]A. S. Willoughby, [1]S. D. McElhenie, [2]W. M. Landing, and [1]P. G. Hatcher

[1]Department of Chemistry & Biochemistry, Old Dominion University, [2]Department of Earth, Ocean, and Atmospheric Science, Florida State University, *Corresponding author, awozniak@odu.edu

1. Introduction

- Fe is thought to limit net community production in ~1/3 of the world's oceans (Boyd et al., 2007). Its atmospheric delivery in bioavailable (soluble) form is vital to 1° production, CO_2 drawdown, and climate.
- Mineral dust aerosols have orders of magnitude higher total Fe (Fe_t) concentrations, but fractional Fe solubilities (%Fe_s) that are orders of magnitude lower than combustion-influenced aerosols.
- Carboxylate organic matter (OM) ligands that bind with Fe represent one of several mechanisms that could contribute to the higher %Fe_s observed for aerosols from combustion-influenced sources.
- *This work uses chemometrics (principal component analysis (PCA) and 2D correlation spectroscopy) of molecular level water soluble OM (WSOM) characteristics to identify the unique features of N. American combustion-influenced aerosol WSOM that could represent Fe-binding ligands.*

2. Approach

- Aerosol particulate samples (n=24) with North America-influenced, North African-influenced, and marine air mass trajectory classifications were collected during the GEOTRACES Nov-Dec 2011 cruise aboard the R/V Knorr (Figure 1).
- PPL extracts (in MeOH) of water extracted aerosol filters (WSOM) were run on a 12 T Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FTICR-MS) in the negative ion mode. Peaks assigned molecular formulas after Wozniak et al. (2008).
- Fe_t, soluble Fe, V, Al measured by inductively coupled plasma mass spectrometry. %Fe_s = Fe_s/Fe_t. WSOC measured by Shimadzu TOC-V.

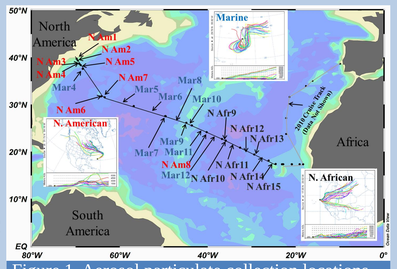

Figure 1. Aerosol particulate collection locations during the 2011 US GEOTRACES cruise. Arrows pointing to a dot were collected on station. Arrows pointing to the line were collected in transit. Representative North American-influenced (N Am), North African-influenced (N Afr), and marine (Mar) air mass back trajectories are displayed and correspond to sample labels.

3. Results

3a. Fe_t, %Fe_s, WSOC/Fe, V/Al

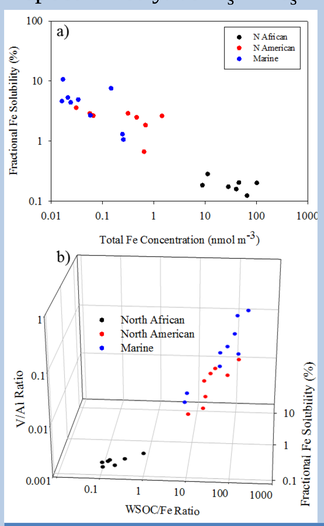

Figure 2. Aerosol a) total Fe (nmol m^{-3}) vs. Fe fractional solubility (%) and b) WSOC/Fe ratio vs. Fe fractional solubility (%) vs. V/Al ratio for aerosols collected on the 2011 US GEOTRACES cruise in the North Atlantic Ocean influenced by N. African, N. American, and marine air masses.

- N. American and marine aerosols showed higher %Fe_s (up to 10%) than N. African aerosols (<1%) which had much higher Fe_t (Figure 2a) as reviewed by Sholkovitz et al. (2012 and refs therein).
- %Fe_s also correlates positively with V/Al (combustion marker) and WSOC/Fe ratios (Figure 2b).
- Combustion-influenced aerosols have orders of magnitude more WSOM compounds per g of Fe than do dust aerosols and therefore a higher potential for Fe-OM ligand interaction.

3b. FTICR MS PCA

- The relative magnitudes of the top 500 most abundant peaks in each sample (2408 molecular formulas) input to a PCA.
- The first 3 PC scores separated the 24 samples into 5 distinct groups (Figure 3a).
- The PCA loadings (Figure 3b) represent the contributions from the input variables (molecular formulas) to each PC and define these groups.
- Using the defining OM formulas and air mass trajectories, the groups in Figure 3 are defined as:

- **Primary Marine** (N. Am 6, 7).
- **Mixed Marine** (Mar 4,8,10,11 N. Am 8).
- **Aged Marine** (Mar 5,6,7,9,12).
- **Continental Combustion** (N. Am 1-5).
- **Continental Desert Dust** (N Afr 9-15).

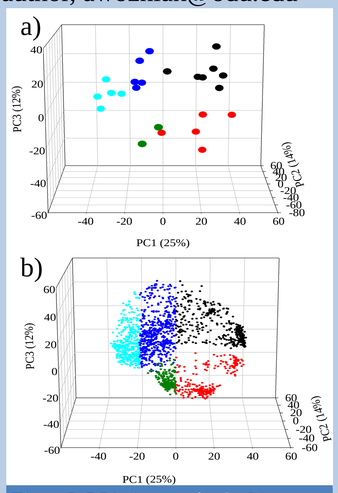

Figure 3. PCA a) scores for the 24 aerosols and b) loadings for the 2408 input variables (formulas) separated into groups defined as Primary Marine, Mixed Marine, Aged Marine, Continental Combustion (N Am), and Continental Desert Dust (N Afr). Adapted from Wozniak et al. in review.

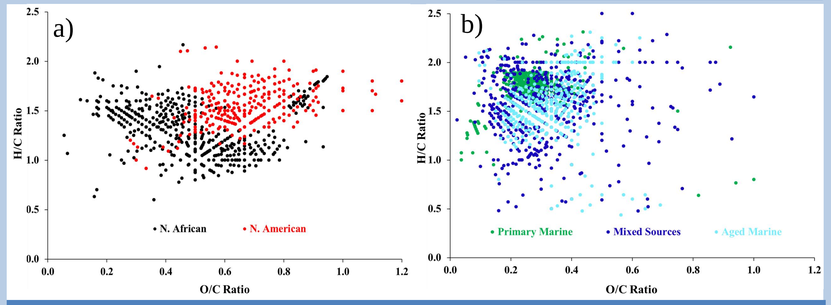

Figure 4. van Krevelen diagrams for the defining molecular formulas for the a) continental and b) marine sample groups as defined by PCA scores, air mass trajectories, and average molecular characteristics. Adapted from Wozniak et al. in review.

- Marine-derived aerosol WSOM generally characterized by lower O/C and higher H/C ratios than continentally-influenced WSOM (Figure 4).
- N. American-influenced samples are more aliphatic (high H/C) and oxygenated (high O/C) than N. African samples.
- N. American-influenced samples show high contributions from high O/C CHO and CHOS (organosulfate and nitrooxyorganosulfate) compounds.
- High O/C CHO formulas are consistent with aliphatic polycarboxylate Fe binding ligands suggested by Wozniak et al. (2013).

3c. 2D Correlation Spectroscopy: O/C, H/C ratios

- FTICR-MS aerosol WSOM molecular formula H/C and O/C ratios binned in increments of 0.01, and summed relative spectral magnitudes of each used as sample variable inputs for 2D correlation.
- Evaluates correlations in changes of O/C, H/C ratio relative spectral magnitude over gradient of V/Al (combustion influence).

Low V/Al → High V/Al

N. African dust-influenced → N. American combustion-influenced

- Marine samples (Figure 3a) removed due to low Fe_t and because marine WSOM molecular characteristics dominate the WSOM.

Red = Positive cross correlation/'In-phase' change
Blue = Negative cross correlation/'out of phase' change

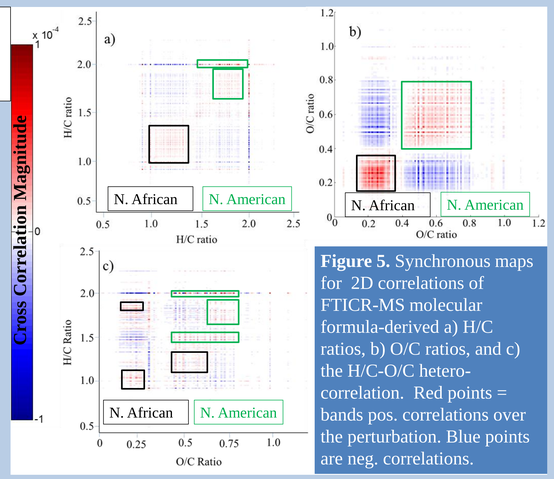

Figure 5. Synchronous maps for 2D correlations of FTICR-MS molecular formula-derived a) H/C ratios, b) O/C ratios, and c) the H/C-O/C hetero-correlation. Red points = bands pos. correlations over the perturbation. Blue points are neg. correlations.

- Changes at H/C ~1.0-1.4 (Figure 5a) and O/C ~0.15-0.33 (Figure 5b) correlate with themselves. The raw data show a loss of spectral magnitude along the gradient from N. African to N. American-influence.
- Changes at H/C ~1.67-1.95, 2.0 (Figure 5a) and O/C ~0.45-0.8 (Figure 5b) correlate with themselves. The raw data show an increase in these regions toward the N. American end member.
- Trend toward higher H/C and O/C ratios with combustion influence.
- Heterocorrelation show synchronous cross correlations between specific H/C and O/C bands. These represent relative losses in spectral magnitude from the N. African dust end member (e.g., O/C~0.15-0.33 x H/C~0.95-1.1) or gains in spectral magnitude toward the N. American end member (e.g., O/C~0.67-0.80 x H/C~1.67-1.95) (see boxes Figure 5c).
- 2D correlation of individual molecular formulas can identify families of formulas contributing to the observed correlations

4. Summary and Future Directions

- Aerosol Fe_t and V/Al ratio followed established relationships w/ %Fe_s.
- WSOC/Fe ratios in N. American aerosols are orders of magnitude higher than in N. African aerosols
- Chemometrics performed on FTICR-MS data show N. American aerosol WSOM to have higher contributions from compounds with higher H/C and O/C ratios than N. African.
- WSOC/Fe and molecular data are consistent with a role for aliphatic carboxylate aerosol WSOM ligands binding with Fe as a plausible mechanism for facilitating higher %Fe_s in combustion aerosols.
- Future work will examine 2D correlation spectroscopy using individual FTICR-MS peaks, ^{1}H NMR spectra, and ^{1}H NMR/FTICR-MS peak heterocorrelations as well as 2D ^{1}H-^{13}C HSQC and ^{1}H-^{1}H TOCSY experiments to provide structural characteristics of potential ligands.
- Studies examining aerosol OM-Fe relationships and any other mechanisms (e.g., photochemistry, acidity) that facilitate %Fe_s will increase our understanding of aerosol source-Fe-oceanic 1° production relationships and their potential impact on CO_2 drawdown and climate.

5. Acknowledgments

This material is based upon work supported by NSF Grant # OCE-1234166 awarded to ASW and PGH. The authors acknowledge assistance from the ODU COSMIC facility, Dr. Rachel Sleighter and Sarah Gurganus for FTICR-MS analyses, the US GEOTRACES program and the crew of the R/V Knorr.