Dissolved Organic Matter (DOM) in the WAIS Divide Ice Core

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DOM in Ice Cores

Materials trapped in ice cores allow us to reconstruct the timing and extent of past changes on Earth. Snowfall accumulation at WAIS Divide is 22cm/year and deposits with it a high resolution record of gases, dissolved chemicals, and biotic and abiotic particles present in the atmosphere (Figure 1). It is now clear that life in glacial environments contains complex communities of microorganisms and evidence continues to amass that glacial ice serves as a reservoir of biological cells and organic material (Priscu *et al*., 2008, Hodson *et al*., 2008, and Anesio *et al*., 2009). The WAIS Divide ice coring project is the first to explicitly include biologic activity and chemical characterization of dissolved organic matter (DOM), and is a significant addition to modeling global carbon dynamics.

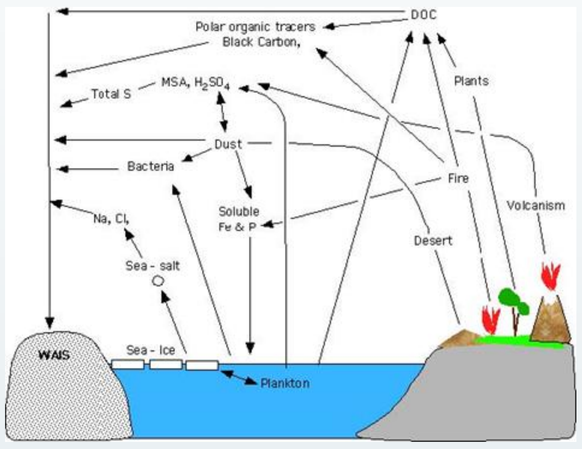

Figure 1: Sources and interactions of chemical and biological signatures to be investigated at the WAIS Divide.

DOM is a polydisperse mixture of organic compounds consisting of intact or transformed biomolecules released from living and decaying bacterial, algal, and higher plant organic material (Mopper *et al*., 2007 and Cory and McKnight, 2005). It is a significant component of aquatic ecosystems and can affect many biogeochemical processes such as metal redox cycling, contaminant transport, and microbial growth. Though glacial ice is now recognized as a potentially significant global organic carbon reservoir, DOM has received little attention in past glacial systems studies and ice coring endeavors. Therefore, determining the chemical and reactive nature of ice core DOM will greatly contribute to our understanding of glacial biological activity and atmospheric composition. When analyzed in conjunction with other collaborative WAIS Divide geochemical data, DOM characterization may reflect past and present climate change, volcanic activity, fluctuations in the bioavailability of nutrients, sea-ice extent, and biomass burning signatures.

Fluorescence Spectroscopy

The optical components of DOM provide information on the chemical properties of the bulk sample. The Excitation Emission Matrix Spectroscopy (EEMS) technique has become widely used to evaluate sources and sinks of DOM. The principle of EEMS is that excitation, emission, and fluorescence intensity are simultaneously scanned over a range of wavelengths and plotted on a single map of optical space (Figure 2) (Hudson *et al*., 2007). EEMS are used to characterize the DOM based on the presence of different classes of fluorophores and by the positions of their excitation/emission maxima. The most common fluorophores of DOM and their descriptions are presented in Figure 2.

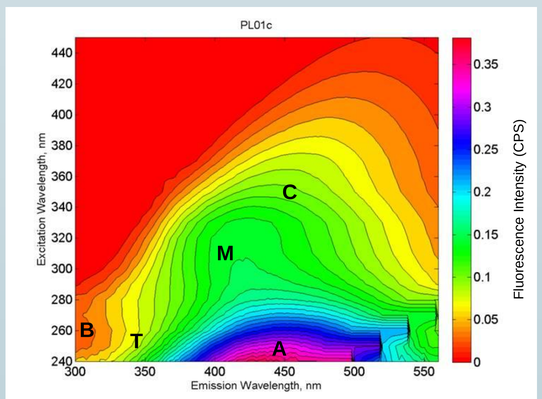

Figure 2: Representative Excitation Emission Matrix of Pony Lake (Antarctica) DOM that shows the major fluorescing components of DOM. A and C are humic-like components, M is a marine humic-like signature, and B and T both denote the protein-like fluorescing components tyrosine and tryptophan

Before characterizing WAIS Divide DOM, a group of carefully selected standards were run by EEMS as a reference for the major fluorescing components or contaminants that could be found in ice core samples (Table 1).

Standard	Tracer Description	TOC concentration	EEMS Ex/Em Maxima
Tryptophan	Protein-like fluorescence	4.4 ppm	250/350nm
Tyrosine	Protein-like fluorescence	4.8 ppm	270/300nm
Phenylalanine	Protein-like fluorescence	9.9 ppm	250/300nm 250/560nm
Benzoquinone	Quinone-like fluorescence	10.4 ppm	285/325nm
Vanillic Acid	Biomass-burning	9.4 ppm	250/325nm and 280/325nm
Methanesulfonic Acid	Oceanic sulfur	3.2 ppm	240/300nm
*Isopar-K Hydrocarbon Fluid	Drilling fluid contaminant	0.083 ppm	240/300nm 240/410nm and 280/410nm
*Exxsol D-40 Dearomatized Hydrocarbon Fluid	Drilling fluid contaminant	1.6 ppm	265/300nm and 240/410nm
IHSS Suwannee River	Humics	6.3 ppm	240/450nm and 340/450nm
IHSS Pony Lake	Fulvics	7.8 ppm	240/450nm and 320/420nm

*Denotes the water layer mixed with each drilling fluid and subsequently separated for experimentation. Neither drilling fluids are suitbale to experiment with by EEMS.

Table 1: Summarizes the standards, tracers, total organic carbon (TOC) concentrations in parts per million (ppm), and the EEMS response describing the centers of excitation and emission maxima. IHSS refers to the International Humic Substance Society.

Materials & Methods

Early Holocene cores (1300-1700m) were melted by a CFA closed system at the Desert Research Institute in Reno, Nevada (Figure 3). The interior melt was directed to a Targeted Ultraviolet Biological Sensor (TUBS) and a sample collector (Gilson) for direct analysis and discrete sample collection for offline analysis back at Montana State University (MSU).

Figure 3: (left) WAIS Divide ice and (right) heated melter head system.

TUBS was used to investigate the fluorescence (UV excitation at 224nm) and resulting emission (280-400nm) nature of WAIS ice cores to characterize the DOM. We are currently compiling and analyzing these data.

MSU samples included: EEMS analysis and cell counts by flow cytometry. We are currently using a BD AccuriC6 flow cytometer, optimized for enumerating bacterial cell counts to measure the frequency distribution of total DNA stained (SYBR Gold) particles on the remaining discrete samples. This poster focuses on preliminary results from our EEMS measurements.

Results: EEMS

EEMS were generated using a Horiba Jobin Yvon Fluoromax-4 Spectrofluorometer and externally processed to remove inner filtering effects, Raman scattering, and blank signal fluorescence (see below). All EEMS were normalized to the water Raman signal. 90% of the DOM in the 484 samples was dominated by the presence of both tyrosine- and tryptophan-like protein fluorescent signatures. Proteinaceous fluorophores (B and T) are believed to reflect the production of amino acids during microbial metabolism (bacterial origin) and are typically more labile than DOM with significant humic signatures (A, C, and M).

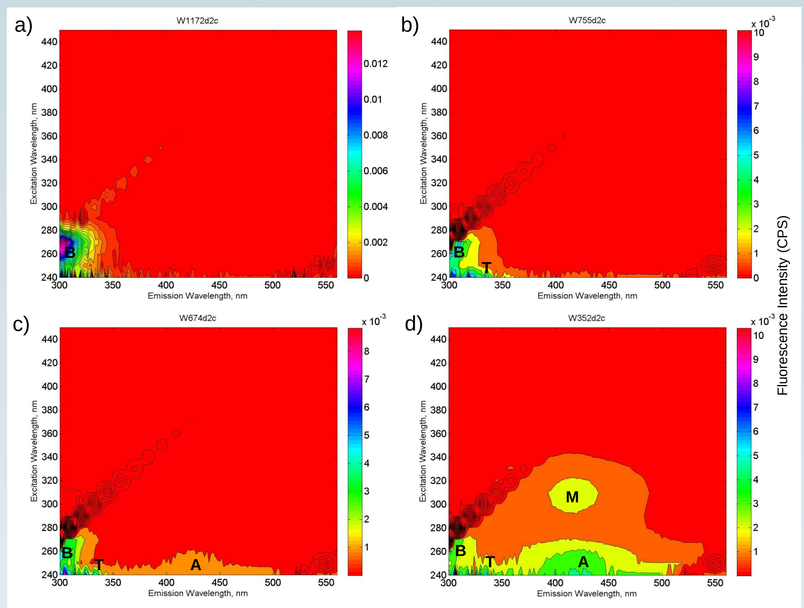

Figure 4: WAIS Divide EEMS of a) tyrosine-like DOM fluorescence from ~1400m, b) tyrosine- and tryptophan-like DOM fluorescence from ~1540m, c) tyrosine-, tryptophan-, and humic-like DOM fluorescence from ~1560m, and d) tyrosine-, tryptophan-, humic- and marine humic-like DOM fluorescence from ~1730m.

A small percentage (~3%) of DOM from these ice cores show a strong shift to more humic material present in the DOM and represent areas of potential geochemical interest.

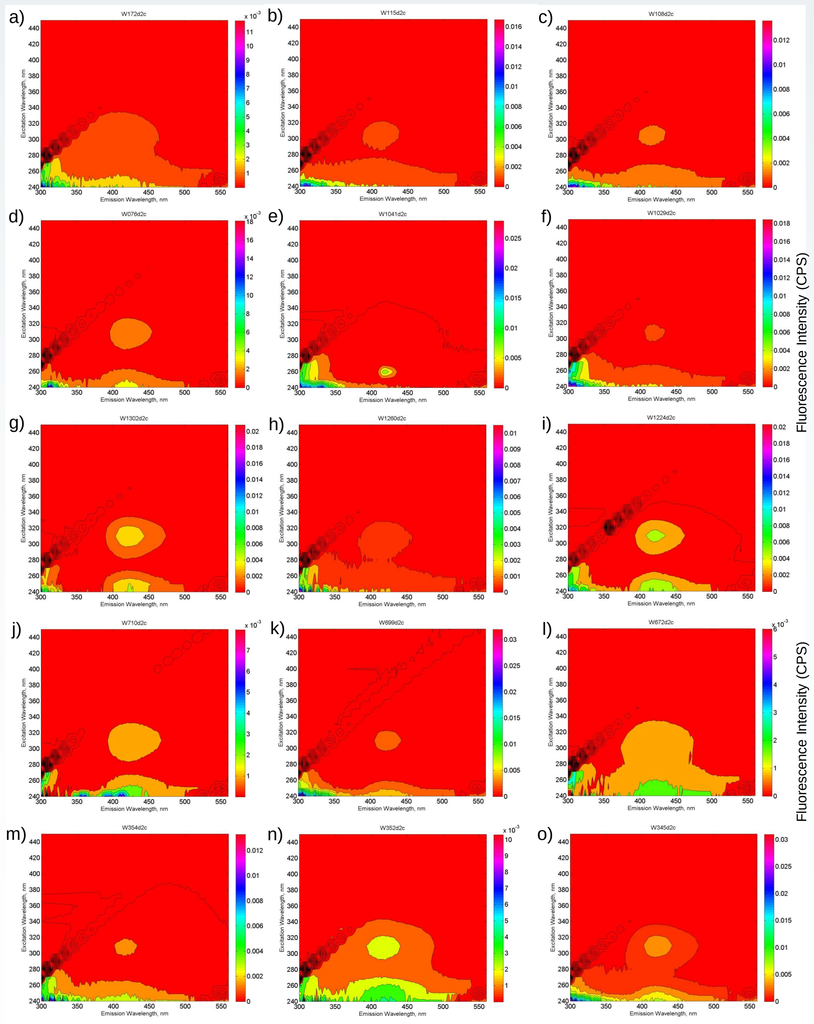

Figure 5 (a-o): WAIS Divide ice core DOM EEMS representing the ~3% of samples showing humic-like fluorescence. The ice core depth starting at 1300m and finishing at 1700m increases alphabetically from (a) to (o) EEMS.

Results: PARAFAC

We applied Parallel Factor Analysis (PARAFAC) to all WAIS EEMS to resolve each DOM sample into specific fluorophores characterized by their excitation and emission spectra. A previously published model was used to compare and contrast WAIS DOM with 7 quinone-like, 2 amino acid-like, and 4 unknown components (Cory and McKnight, 2005). Since DOM is a complex chemical mixture that contains a broad range of fluorescence and overlapping fluorophore regions, PARAFAC analysis is ideal for a more thorough characterization of fluorescent DOM.

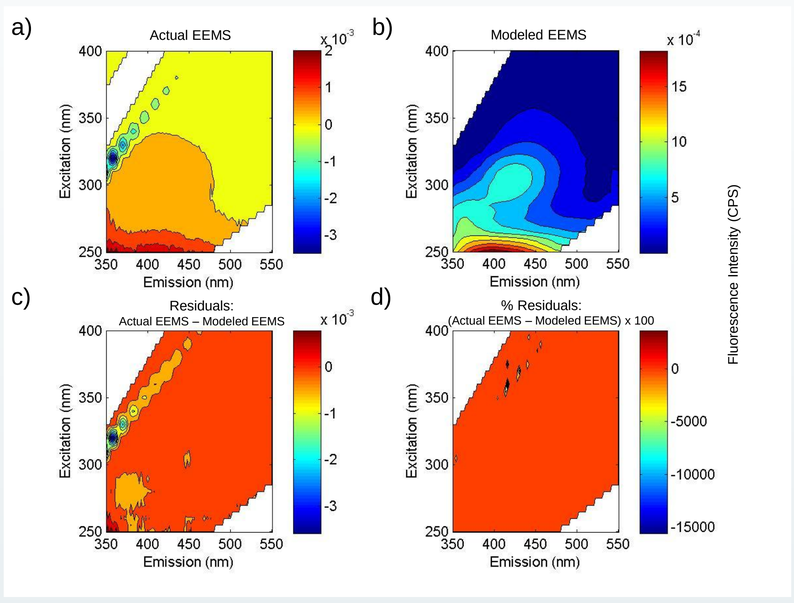

Figure 6: PARAFAC results of a WAIS sample ~1700m showing a) the actual EEMS, b) the modeled EEMS against the 13 components of the Cory McKnight (2005) model, c) calculated residuals (unexplained signal i.e. noise and un-modeled variation), and d) percentage of residuals.

Depth (m)	Q1	Q2	Q3	SQ1	SQ2	SQ3	HQ1	Tyr	Trp	U1	U2	U3	U4
1300-1400	9%	21%	21%	1%	0%	0%	16%	2%	17%	2%	0%	6%	6%
1400-1500	6%	24%	22%	1%	0%	0%	19%	0%	21%	1%	1%	2%	3%
1500-1600	6%	19%	23%	0%	0%	0%	20%	0%	13%	2%	0%	2%	4%
1600-1700	6%	16%	26%	1%	0%	1%	22%	0%	18%	2%	2%	2%	4%

Table 2: Percentages of the components identified by the Cory McKnight (2005) model of early Holocene WAIS ice. The first seven are quinone-like (oxidized to reduced forms), followed by tyrosine, tryptophan, and then four unknown components not yet associated with a specific molecular class.

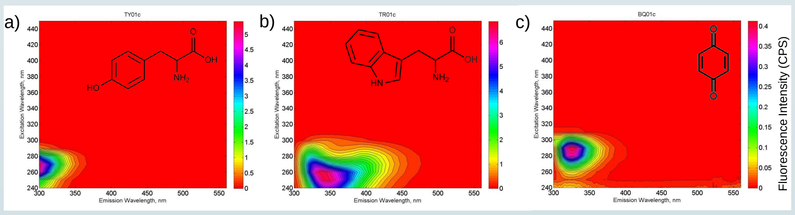

Figure 7: EEMS and chemical structures of a) tyrosine, b) tryptophan, and c) benzoquinone standards.

Discussion/Questions/Future Work

- We will compare all 484 EEMS with the co-registered geochemical datasets which will allow us to better understand the DOM trends through the southern hemisphere records.
  Questions to consider:
  1. Does the DOM chemical character change after a volcanic event?
  2. How does DOM relate to other environmental nutrients/elements? Will it continue to positively relate to marine derived Ca and Sr data from the McConnell laboratory?
  3. Will higher concentrations/more fluorescing material in the DOM directly correlate to less sea-ice cover?
  4. What periods in history correlate to low and/or high concentrations in DOM and its corresponding fluorescent nature?
- What will the UV nature of WAIS DOM by TUBS reveal?
- Will the DOM concentrations and fluorescing material increase and/or decrease with bacterial counts and biological matter?
- PARAFAC analysis against the Cory McKnight 2005 model confirms the presence of amino acid and quinone like contributions, however, with overlapping fluorescent regions a more refined model specific to glacial environments could yield more accurate results.
- Future work will include:
  1. Analysis of the TUBS and flow cytometry data to entirely characterize the biological and chemical constituents of the early Holocene WAIS Divide ice cores.
  2. Developing a new PARAFAC model based on glacial environments (Arctic and Antarctic).
  3. The second round of melting/experimentation will include ice cores extending from the early Holocene into the Last Glacial Maximum and will commence this fall.

Acknowledgements

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