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

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DOM in ice cores

The WAIS (West Antarctic Ice Sheet) Divide ice coring project is a multi-disciplinary effort to collect a deep ice core from the flow divide in central West Antarctica (Figure 1a). The WAIS Divide ice coring project is the first to include chemical characterization of dissolved organic matter (DOM) and particulate organic matter. Analysis of the ice core will allow us to develop a series of interrelated climate and biologic records focused on understanding interactions of atmospheric global systems throughout history.

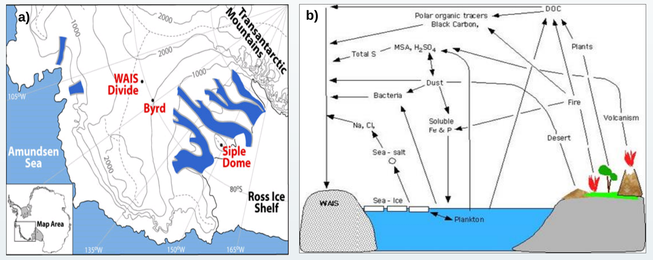


Figure 1: a) Location of WAIS Divide in Antarctica and b) sources and interactions of chemical and biological signatures to be investigated at the WAIS Divide.

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). It is a significant component of aquatic and glacial ecosystems and can affect many biogeochemical processes such as nutrient cycling, contaminant transport, and microbial growth. Materials trapped in ice cores provide evidence 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 organic matter, present in the atmosphere at the time of deposition (Figure 1b). 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.

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 (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.

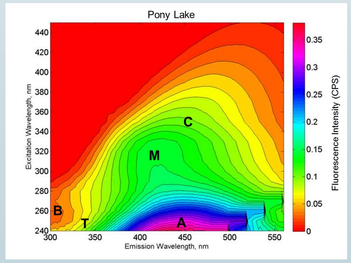


Figure 2: Excitation Emission Matrix of Pony Lake (Antarctica) DOM that shows the major fluorescing components of DOM. A and C are humic-like components, M is a marine humic-like signature, and B and T both denote the protein-like fluorescing components tyrosine and tryptophan.

Materials & Methods

Early Holocene cores (1300-1700m) were melted by a closed continuous flow analysis system at the Desert Research Institute in Reno, Nevada (Figure 3). The interior melt was directed to a sample collector (Gilson) for direct analysis and discrete sample collection for offline analysis at Montana State University. Discrete sample analysis included: EEMS 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) WAIS Divide particles.

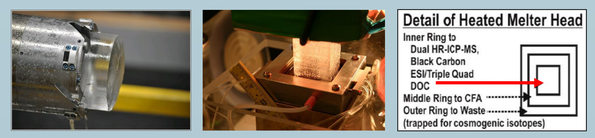


Figure 3: (left) WAIS Divide ice, (middle and right) heated melter head system. Temperatures range from 40-70˚C.

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).

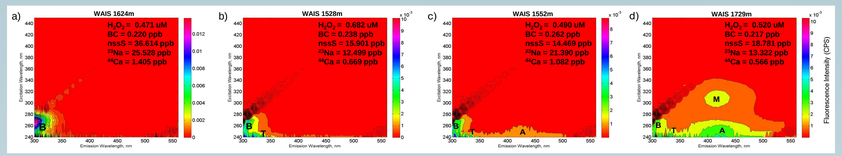


Figure 4: WAIS Divide EEMS and corresponding geochemical data of a) tyrosine-like DOM fluorescence from 1624.376m, b) tyrosine- and tryptophan-like DOM fluorescence from 1528.66m, c) tyrosine-, tryptophan-, and humic-like DOM fluorescence from 1552.731m, and d) tyrosine-, tryptophan-, humic- and marine humic-like DOM fluorescence from 1729.391m.

All WAIS Divide samples contain proteinaceous fluorophores suggesting a strong microbial influence on the ice core DOM character. Approximately 3% of DOM from these ice cores show a shift to more humic material present and represent areas of potential geochemical interest.

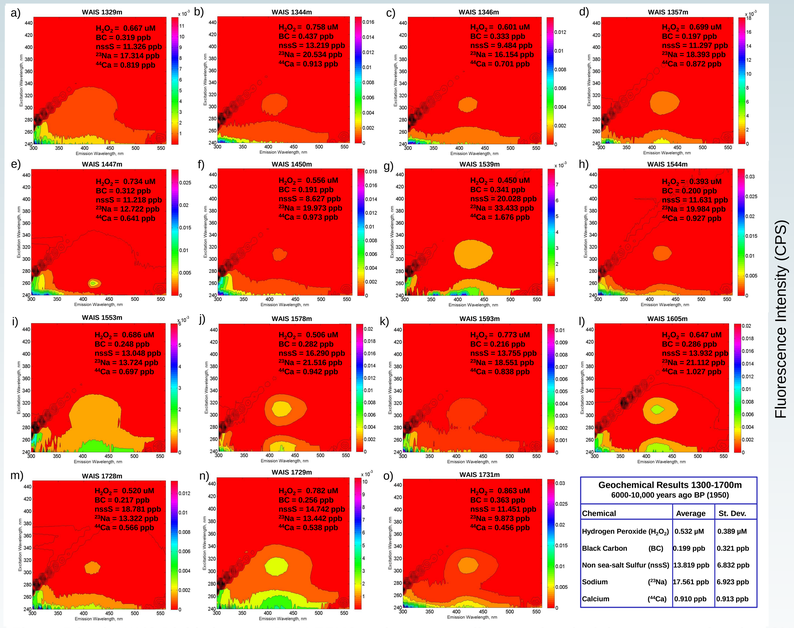


Figure 5 (a-o): WAIS Divide ice core DOM EEMS and corresponding geochemical data representing the ~3% of samples showing humic-like fluorescence. The ice core depths starting at 1329m and finishing at 1731m [6272-9439 years ago BP (1950)] increase alphabetically from (a) to (o) EEMS.

Geochemical Results 1300-1700m
6000-10,000 years ago BP (1950)

Chemical		Average	St. Dev.
Hydrogen Peroxide (H_2O_2)		0.532 uM	0.389 uM
Black Carbon	(BC)	0.199 ppb	0.321 ppb
Non sea-salt Sulfur (nssS)		13.819 ppb	6.832 ppb
Sodium	(^{23}Na)	17.561 ppb	6.923 ppb
Calcium	(^{44}Ca)	0.910 ppb	0.913 ppb

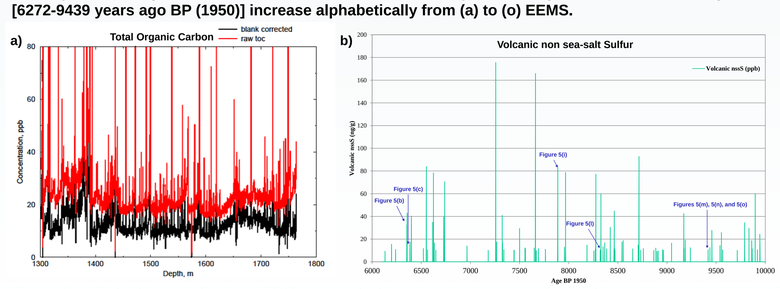


Figure 6: a) Total Organic Carbon (TOC) concentration showing large contamination spikes and b) Volcanic non sea-salt Sulfur concentration showing volcanic activity in the WAIS Divide ice core 1300-1700m.

Results: PARAFAC

We applied Parallel Factor Analysis (PARAFAC) to all WAIS EEMS to resolve each sample into specific DOM fluorophores characterized by their excitation and emission spectra. 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. We used the DOMFluor toolbox for MATLAB to run PARAFAC (Andersson & Bro, 2002 and Stedmon & Bro, 2008) on all EEMS to determine statistically significant glacial DOM components specific to WAIS Divide.

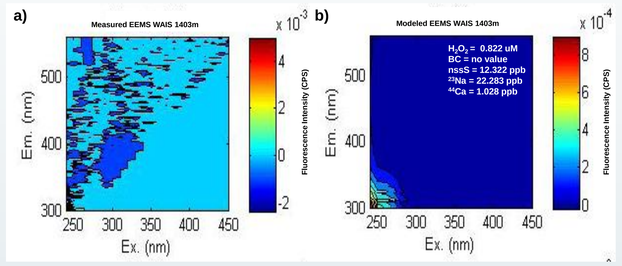


Figure 7: PARAFAC results of the 2-component model for WAIS sample 1403.714m showing a) the actual EEMS, and b) the modeled EEMS.

Two identified amino acid-like PARAFAC components were present in the WAIS samples from 1300-1700m. 98.1% of samples were found to be component 1 dominant, which describes samples with greater fluorescent intensity in that region than for component 2 (Figure 8).

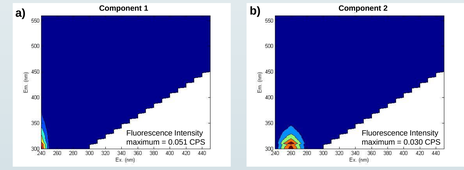
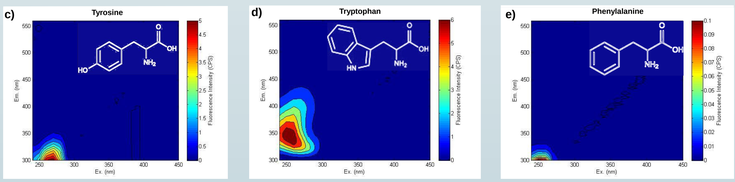


Figure 8: Amino acid-like components identified from PARAFAC analysis of WAIS Divide samples (1300-1700m depths) showing a) component 1, b) component 2, and the corresponding EEMS fluorescence and chemical structures of c) tyrosine, d) tryptophan, and e) phenylalanine.



Discussion & Future Work

- Proteinaceous fluorophores are dominant features in nearly all WAIS Divide samples suggesting DOM of bacterial origin having more labile character in the early Holocene ice cores.
- PARAFAC analysis identified 2 major components with amino acid-like fluorescence.
- Some EEMS display DOM character shifts to humic-like fluorescing material on or after a volcanic event.
- Early Holocene ice cores do not show strong links between environmental nutrient concentrations (H_2O_2, BC, ^{23}Na, ^{44}Ca, and nssS) and DOM fluorescing material.

  Questions to consider for the last glacial maximum:

  1. What periods in history correlate to low and/or high concentrations in DOM and its corresponding fluorescent nature?
  2. Will the DOM concentrations and fluorescing material increase and/or decrease with bacterial counts and biological matter?
- Future work will include: Last Glacial Maximum sample analysis, developing a new PARAFAC model based on glacial environments and analysis of flow cytometry data to characterize the biological and chemical constituents of the WAIS Divide ice cores.

Acknowledgements

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