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# A 21,000 year record of organic matter quality in the WAIS Divide ice core

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**Abstract.** Englacial ice contains a significant reservoir of organic material (OM), preserving a chronological record of materials from Earth's past. Here, we investigate if OM quality surveys in ice core research can provide paleoecological information on the dynamic nature of our Earth through time. Temporal trends in OM quality from

- 15 the early Holocene extending back to the Last Glacial Maximum (LGM) of the West Antarctic Ice Sheet Divide (WD) ice core were measured by fluorescence spectroscopy. Fluorescent intensity fluctuations and PARAFAC modelling of fluorescent OM from the LGM (27.0-18,0 kyrs BP; before present 1950), through the last deglaciation (LD; 18.0-11.5 kyrs BP), to the early to mid-Holocene (11.5-6.0 kyrs BP) provided evidence of different types of OM chemical species in the WD ice core over 21.0 kyrs. Two proteinaceous PARAFAC components (C1 and C2)
- 20 were characteristic of fluorescent OM prevailing in all climate periods, suggesting a strong signature of labile microbial OM. A humic-like component (C3), characteristic of terrestrial and marine OM fluorescence, was only observed during the Holocene, suggesting that recalcitrant OM may be an ecological marker of warmer climates. Fluctuations in WD ice core OM fluorescence over 21.0 kyrs BP may be driven by environmental changes at the source, and potentially its interaction with the atmosphere. We suggest that fluorescent OM signatures observed
- 25 during the LGM were the result of greater continental dust loading of microbially derived proteinaceous material in a drier climate, with lower marine influences when sea ice extent was higher, and continents had more expansive tundra cover. As the climate warmed, the OM quality record in the WD ice core changed, reflecting shifts in carbon productivity as a result of global ecosystem response.

# 30 1 Introduction

Ice cores are a powerful tool for reconstructing the timing and extent of past changes in Earth's climate, providing records of biological, chemical, and physical constituents over time (Dansgaard et al., 1993; Petit et al., 1999; Johnsen et al., 2001; Alley, 2002; Jansen et al., 2007; Luthi et al., 2008). Detailed paleorecords of temperature, precipitation, dissolved chemicals, and gas composition of the lower atmosphere, volcanic eruptions, solar

35 variability, sea surface productivity, anthropogenic emissions, and a variety of other climate and biogeochemical indicators can all be determined from ice core studies, providing an invaluable record of our past with implications for the future. In addition to the extraordinary range of materials catalogued within ice cores, ice also provides a unique environment for preserving microbes and other biological material (i.e. plant fragments, seeds, pollen grains,





fungal spores, and organic matter [OM]) (Priscu et al., 2007; Miteva et al., 2009; Barletta et al., 2012; WAIS Divide
Project Members, 2015). OM, comprised of biomolecules from living and decaying organisms, and also input from surrounding environments, plays a significant role in aquatic ecosystems affecting many biogeochemical processes that, in turn, influence its contribution to the global carbon cycle (Battin et al., 2008). Englacial OM may also contribute to global carbon dynamics upon its decomposition after being released from the ice lattice by melting and retreat (Priscu and Christner, 2004; Priscu et al., 2008). Therefore, as a reservoir of OM and a potential source of
carbon and biological material, determining ice core OM quality (chemical character) and reactive nature is essential

to understanding past carbon signatures that could impact our future.

Ice core studies rely on the paradigm that atmospheric deposition is the sole mechanism for specific gases and materials to become trapped in the ice. Extending that to include OM, the trapped material becomes a catalog of preserved paleoecological markers of Earth's history, that can be used to better understand biogeochemical

- 50 processing, carbon stocks, and cycling events. While still a novel addition to deep ice core research, chemically characterizing the OM constituents in englacial ice is of particular interest for several reasons: 1) OM character can be linked to its source (e.g., aquatic, terrestrial) describing different influences of past and present ecosystems, 2) OM character can serve as a proxy for englacial biological activity, potentially explaining anomalous concentrations of other gases (e.g., methane, carbon dioxide) in ice core research, and 3) OM could be a pivotal contributor to the
- 55 global carbon cycle if materials released to surrounding environments are metabolized to CO<sub>2</sub> in a warming climate. We hypothesize that Antarctic englacial ice contains a chronological record of OM that reflects changes following the Last Glacial Maximum (LGM). To test this hypothesis we used fluorescence spectroscopy to generate Excitation Emission Matrices (EEMs), a bulk analytical method commonly used to probe OM source and nature in aquatic ecosystems. Fluorescence spectroscopy is advantageous to employ for a large sample set with low sample
- 60 volumes due to rapid data acquisition and the wealth of information generated describing OM fluorescing components, chemical character, and source influences (Coble et al., 1990; Coble, 1996; Stedmon and Cory, 2014). For this study, all possible sources of OM detected within the West Antarctic Ice Sheet (WAIS) Divide ice cores were considered. A total of 1,191 meltwater samples of limited volume (~7.5 mL) were examined from 1400 m of deep ice, corresponding to 21.0 kyrs, extending from the LGM, through the last deglaciation (LD), to the mid-
- 65 Holocene. This is the first high temporal resolution analysis of englacial OM by fluorescence spectroscopy from the Antarctic ice sheet.

# 2 Methods

### 2.1 WAIS Divide sample site description

70 Ice cores were collected as a part of the multidisciplinary WAISCORES project at 79.467 °S and 112.085 °W, Antarctica (Figure 1), (WAIS Divide Project Members, 2013, 2015). Snow precipitation at this site is relatively high (~22 cm y<sup>-1</sup>), compared to other Antarctic locations, resulting in ice cores containing a high resolution record of trapped gases, chemicals, and biotic and abiotic constituents over the last 65,000 years (dating scale WDC06A-7 (WAIS Divide Project Members, 2013)) (Banta et al., 2008). The WAIS Divide (WD) ice core represents the first





75 continuous Southern Hemisphere equivalent paleoclimate record to the Greenland ice core GISP2, GRIP, and North GRIP projects.

## 2.2 Ice core collection, preparation, and melting

Ice core drilling and recovery was completed in 2012 to a depth of 3405 m, using a hydrocarbon-based drilling

- 80 solvent (Isopar-K; ExxonMobil Chemicals). Ice cores were transported to the National Ice Core Laboratory (NICL) in Denver, Colorado, for ice core processing. For this project, 1400 m of ice cores (depths: 1300 2700 m below the surface) dating from 6.0 to 27.0 kyrs BP [before present 1950] by the WDC06A-7 timescale (WAIS Divide Project Members, 2013)), were cut into 3x3x100 cm long sections and transferred to the Desert Research Institute (DRI) in Reno, Nevada, for continuous melting (4.5 mL min<sup>-1</sup>) in a closed continuous flow analysis (CFA) system
- 85 (McConnell et al., 2002; McConnell et al., 2007; McConnell et al., 2014). The quality of the ice cores was excellent, well below the brittle ice zone without cracks or fractures.

Meltwater (7.5 mL for each sample) from the inner most section of the ice cores was directed to a discrete sample collector (Gilson 223), and dispensed into combusted (425 °C for 4 h) septa sealed amber glass vials, maintained at 4 °C to minimize volatilization and atmospheric exposure. Deionized water blanks were routinely analyzed to ensure that the melting system remained contaminant free.

# 2.3 Ice core OM absorbance

Prior to fluorescence spectroscopy, absorbance spectra of WD core meltwater samples were collected from 190-1100 nm using a Genesys 10 Series (Thermo-Scientific) Spectrophotometer with a 1 cm path length cuvette and

- 95 VISIONlite software. Obtaining absorbance spectra is necessary to calculate the spectral corrections of primary and secondary inner filter effects when post-processing EEMs data (Acree et al., 1991; Tucker et al., 1992). WD core OM samples were optically dilute, with measured A<sub>254</sub> well below 0.3 a.u.; consequently, no sample dilution was required (Miller and McKnight, 2010; Miller et al., 2010). Spectra were blank corrected against purified water from a Milli-Q system each day.
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# 2.4 Fluorescence spectroscopy

EEMs were generated on a Horiba Jobin Yvon Fluoromax-4 Spectrofluorometer equipped with a Xenon lamp light source and a 1 cm path length quartz cuvette. Excitation (Ex) wavelengths were scanned from 240-450 nm in 10 nm intervals and emission (Em) was recorded between 300-560 nm in 2 nm increments. Data integration time was 0.25

- 105 s and data acquisition was carried out in signal/reference mode using a 5 nm bandpass on both Ex and Em monochromators, normalizing the fluorescence Em signal with the Ex light intensity. Post processing of the fluorescence data was completed in MATLAB to generate 3D EEMs, which included sample corrections for Raman scattering and blank water subtraction. EEMs were prepared for parallel factor multivariate analysis (PARAFAC) following a procedure previously outlined for sample classification, normalization, and subset selection (Cawley et Carrier State)
- 110 al., 2012) to model the WD fluorescent OM character. A three component PARAFAC model was generated for the subset of samples by drEEM and the N-way toolbox scripts in MATLAB (Murphy et al., 2013).





# **2.5 Elemental Analysis**

Meltwater from the interior section of the ice core was also used for a broad range of elemental analyses including sodium (Na), sulfur (S), calcium (Ca), manganese (Mn), and strontium (Sr) as co-registered datasets. From the CFA system, meltwater was directed through Teflon tubing to two Inductively Coupled Plasma Mass Spectrometers (ICPMS, Element 2 Thermo Scientific) located in an adjacent class 100 clean room for continuous trace element

analysis (McConnell et al., 2007). Sea-salt sodium (ssNa) as well as non-sea-salt sulfur (nssS) and calcium (nssCa) were calculated following standard procedures from measured total concentrations of Na, S, and Ca using

120 abundances in sea water and mean sediment (Bowen, 1979).

## **3 Results**

# 3.1 Fluorescent OM in the WD core

- WD EEMs (1,191 samples covering 1400 m of ice core) dating from the LGM (27.0 18.0 kyrs ago BP) to the mid
  Holocene (11.5 6.0 kyrs BP) were analyzed to characterize the OM fluorescing components in ice. All samples contained amino acid-like fluorescence characteristic of bioavailable carbon species at low Ex/Em wavelengths (240-270 nm / 300-350 nm), while fewer contained OM fluorescence at higher Ex/Em wavelengths (2.5%), characteristic of more recalcitrant species (examples in Supplement Figure 1a-b). The LGM was characterized by relatively high total OM fluorescence intensities (Raman Units; Figure 2), however the largest increase occurred in
- 130 the early Holocene, spanning 37 discrete EEMs samples that corresponded to 0.318 kyrs between 9.738-10.056 kyrs ago BP. Since OM is a complex mixture containing a broad range of molecules and potentially overlapping fluorescent regions, the application of PARAFAC was used to resolve the representative subset of samples into individual OM fluorescing components characterized by their Ex/Em maxima in different climate periods. Three WD OM PARAFAC components were identified (Figure 3a). Ice from the LGM and LD time periods contained
- 135 fluorescence characterized by PARAFAC components one and two (C1 and C2), while the Holocene was characterized by fluorescence of all three components.

PARAFAC component C1 showed maximum fluorescence in a region analogous to the secondary fluorescence of fluorophore peak B (tyrosine-like, Ex: 240 nm and Em: 300 nm), which is typically associated with microbial processing in aquatic environments (Coble et al., 1990; Coble et al., 1998). C2 also corresponded to amino

- 140 acid-like fluorescence, however this component displayed overlap between the tyrosine- and tryptophan-like fluorescent regions. Because of this overlap, C2 was further evaluated to investigate its variation as a function of climate (Figure 3). Component C2 was found to be red shifted to longer Em wavelengths from the LGM to the LD, and blue shifted to shorter Em wavelengths from the LD to the Holocene ice (Figure 3b); thus explaining the overlapping fluorescence in C2 in the overall PARAFAC model (Figure 3a).
- 145 Component C3 displayed fluorescence commonly associated with more humic-like material. Two humiclike fluorescing regions were identified that comprised C3: fluorescence at 1) Ex/Em: 240-260/380-460 nm, characteristic of fluorophore peak A, commonly associated with terrestrial plant and/or soil origin, (Coble, 1996; Marhaba et al., 2000), and 2) Ex/Em: 300-320/380-460 nm, characteristic of fluorophore peak M, commonly





associated with marine environments (Coble, 1996) and also linked with higher molecular weight, reduced aromatic
chemical species potentially exposed to microbial processing in aquatic environments (Stedmon et al., 2003; Cory and McKnight, 2005; Stedmon and Markager, 2005; Murphy et al., 2008; Balcarczyk et al., 2009; Fellman et al., 2010). The C3 maximum fluorescence intensities fluctuated mildly in the Holocene, but intensities were higher at lower Ex wavelengths (fluorophore peak A region). WD ice core OM PARAFAC components were uploaded to the OpenFluor database to compare and contrast C1, C2, and C3 with other environments, however, no component matches were determined (Murphy et al., 2014).

# 3.2 Trace element concentrations

The extent of terrestrial dust contributions to the OM in the WD ice core was explored by analyzing the concentrations of elemental nssCa, Mn, and Sr, commonly used to reconstruct past atmospheric composition in

- 160 paleoclimate research. Figure 4 shows the concentrations of nssCa, Mn, and Sr together with the WD ice core OM PARAFAC components and the co-registered the  $\delta^{18}$ O temperature record for reference (Marcott et al., 2014). The highest concentrations of nssCa, Mn, and Sr were observed during the LGM (Figure 4), indicating greater dust loads to Antarctica in the older ice. The transition between the LGM and the LD was characterized by a decrease in nssCa, Mn, and Sr concentrations over 2.0 kyrs, followed by concentrations that, on average, remain considerably lower
- 165 than reported for the LGM. A strong positive correlation between nssCa and Sr was found throughout the WD ice core ( $R^2 = 0.894$ ), with nssCa and Mn, and Sr and Mn less strongly correlated ( $R^2 = 0.516$  and  $R^2 = 0.478$ ).

## **4** Discussion

# 4.1 Deep englacial OM nature and origin

- 170 The worlds glaciers and ice sheets are believed to hold nearly six petagrams of carbon (Hood et al., 2015), representing a significant component of the global carbon cycle. Ice environments function as sinks of allochthonous OM by atmospheric deposition and aeolian transport (Stubbins et al., 2012), yet our understanding of the OM source and its reactivity in these reservoirs, especially in deep ice, is in its infancy. We applied fluorescence spectroscopy to determine the climate specific differences in OM source material and reactive nature throughout history. OM
- 175 fluorescence represented by PARAFAC components C1 and C2 was present in all climate periods in the WD ice core, providing a consistent record of microbial OM signatures throughout history. Of the two components, OM containing tryptophan-like fluorescence (C2) has been shown to represent intact dissolved proteins, considered to be freshly derived from microorganisms (Mayer et al., 1999; Stedmon et al., 2003; Cory and McKnight, 2005; Stedmon and Markager, 2005; Murphy et al., 2006; Fellman et al., 2010). Miteva et al. (2016) reported that the presence of
- 180 microorganisms in deep ice cores also suggests the possibility of *in situ* OM processing, which could have important implications for gaseous climate records (Rhodes et al., 2013; Miteva et al., 2016; Rhodes et al., 2016). Including *in situ* biological OM transformations in ice core research was recently proposed as an alternate mechanism for CH<sub>4</sub> production in ice from firn layers of the WD ice core (Rhodes et al., 2016).

Humic-like fluorescent OM was not detected in the older ice from the LD and LGM periods, suggesting lower abundances produced in external environments or lack of transport to Antarctica during colder periods. The





first appearance of humic-like OM fluorescence was reported at 11.061 kyrs old BP, 500 yrs after the Holocene began. The two regions of fluorescence maxima ascribed to PARAFAC component C3 describe a pairing of different types of more recalcitrant OM species produced from terrestrial and aqueous environments. Throughout the Holocene, the fluorescent maximum at Ex/Em: 240-260/380-460 nm consistently had higher fluorescent intensities

190 than its pair at Ex/Em: 300-320/380-460 nm, describing more fluorescent chemical species characteristic of OM derived from terrestrial plants and/or soils in the younger ice. With no humic-like signatures detected for the LGM or the LD, we hypothesize that warmer temperatures during the Holocene were associated with more expansive vegetation cover and increased production and degradation of OM in terrestrial, freshwater, and marine environments.

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# 4.2 Continental dust in the WD ice core

Concentrations of nssCa, Sr, and Mn have been shown to be proxies of terrestrial crustal dust in paleoclimate ice core records (McConnell et al., 2007; Gornitz, 2009; Lambert et al., 2012). As such, it is plausible to envisage a link between concentrations of these dust tracers and other transported materials influenced by aeolian deposition, (e.g.,

- 200 OM concentration and character, microbial biomass, and pollen grains). WD shallow ice core data showed a positive relationship between the concentrations of dissolved organic C and both nssCa and Sr (Supplement Figure 2). While organic C concentrations were not available for this study, we present the fluorescent chemical character of the OM measured concurrently with nssCa, Mn, and Sr concentrations to classify various transport mechanisms of specific types of fluorescing OM throughout history (Figure 3).
- 205 The LGM contained the highest concentrations of nssCa, Mn, and Sr, when annual snowfall deposition was low (WAIS Divide Project Members, 2013). We speculate that the larger nssCa, Mn, and Sr concentrations measured during the LGM likely originated from increased continental dust loading as well as more efficient atmospheric transport. At the end of the LGM, concentrations of nssCa, Sr, and Mn declined around 18.0 – 16.0 kyrs BP, near the beginning of the LD, reflecting a decrease in continental dust loading as the climate warmed.
- 210 Throughout the LD and the Holocene, abrupt increases or spikes in nssCa, and Sr, and Mn concentrations were observed over shorter time scales. These increases in the LD and Holocene may be linked to other atmospheric events, emphasizing a plethora of mechanisms by which OM can be transported to Antarctica.

# 4.3 OM source fluctuations over time

- 215 Fluctuations in ice core OM fluorescent quality may be driven by a multitude of variables, including: ecosystem productivity, changes in precipitation and accumulation due to temperature shifts, sea ice extent, wind patterns, fires, and volcanic activity, most of which are in some way governed by the relative climate conditions. Sea ice extent was determined from the concentration of ssNa in the WD ice core (WAIS Divide Project Members, 2013), the results of which were used in this study as a proxy to evaluate marine influences on OM quality from the LGM to the early
- 220 Holocene. Higher concentrations of ssNa was associated with more extensive sea ice cover in colder climates, whereas decreased ssNa concentrations coinciding with  $\delta^{18}$ O enrichment, implied less sea ice extent during warmer climates (WAIS Divide Project Members, 2013). Higher OM fluorescence intensities in the LGM, may indicate





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higher concentrations of transported OM at WD. Changes in atmospheric circulation could also affect OM transport to WD and has been reported as a possible explanation for the decrease in ssNa concentrations at the end of the LGM (WAIS Divide Project Members, 2013). We speculate that extensive sea ice cover is associated with less

marine influences on the WD ice core OM, compared to open ocean.

During the LGM, tundra ecosystems covered more expansive areas of the Earth (Ciais et al., 2012) and while C was cycling, productivity in the environment differed from warmer climates (Ciais et al., 2012, and references within). We attribute the qualitative changes in the WD fluorescent OM record to be a function of

- 230 changing environmental influences throughout time. At the onset of warming, the years in between the LGM and the Holocene (6.0 kyrs) were a transitional period, encompassing a climate with rising temperatures and decreasing sea ice extent. Intriguingly, PARAFAC components C1 and C2 were present in both the LD and the LGM (Figure 3), despite relatively rapid changes in climate. OM from the LD alone, after the LGM, showed a slight red shift in C2 (Figure 3b), suggesting more freshly produced fluorescent OM from external environments. Decreased continental
- 235 dust loads and the potential for more marine inputs may be important factors contributing to differences in OM character between the LD and LGM.

The years between 13.0-11.5 kyrs BP, at the end of the LD, defined as the Antarctic cold reversal, incorporate a depression of temperature, just prior to the early Holocene, where reports of Ca and dust concentrations increase (Delmonte et al., 2002). Also measured in the WD ice core (Figure 4), these environmental

240 fluctuations during the Antarctic cold reversal, may also explain the fluorescent OM variation in the LD (Figure 3b). We submit that the C2 fluorescent OM red shift, observed in the LD, is a result of a multitude of environmental changes (i.e. more marine, terrestrial, and microbial influences) occurring in the transitory period between the LGM and the Holocene.

The Holocene was the only period shown to contain evidence of a more humic-like OM PARAFAC

- 245 component (C3). The Holocene is characterized by higher levels of C productivity and vegetation cover (Ciais et al., 2012), with atmospheric temperatures and the potential for marine influences at their highest. With gross terrestrial C production estimated to be double that of the LGM (Ciais et al., 2012), it is reasonable to predict that the Holocene would contain the most heterogeneous mixture of OM from marine, freshwater, and terrestrial environments, comparatively. As such, the Holocene contains both bioavailable C species of microbial origin and
- 250 more recalcitrant humic-like OM (Figure 3a). With temperatures rising rapidly, Earth's atmosphere changed drastically in the Holocene, and atmospheric concentrations of CO<sub>2</sub> and CH<sub>4</sub> increased substantially (WAIS Divide Project Members, 2013, 2015) from natural processes. Reports of higher concentrations of CO<sub>2</sub> and CH<sub>4</sub> also suggests evidence of increased levels of C utilization and production in the Holocene, which agrees with the more degraded types of fluorescing OM observed in the youngest ice.
- 255 Volcanic eruptions inject particles, aerosols, and gases into the atmosphere (e.g., H<sub>2</sub>O, SO<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>S, HCl, and HF) regionally and globally depending on the height of the volcanic plume (Robock, 2000). Therefore, volcanic eruptions increase the potential for particles and chemicals to be transported to Polar regions and deposited onto ice-sheets. Concentrations of non-sea-salt sulfur (nssS) are commonly used to trace volcanic signatures in polar ice cores and to reconstruct past volcanic activity on Earth (Sigl et al., 2013; Sigl et al., 2014; Sigl et al., 2015). The





- 260 direct effects of volcanic activity on OM quality and quantity were beyond the scope of this study, however, the nssS data from the WD ice core is referenced in this work to highlight volcanic activity as a possible mechanism for stimulating OM production. Volcanic eruptions detected in the WD ice core, using the nssS calculated volcanic detection threshold (Sigl et al., 2013), accounted for 4.5% of all OM characterized by EEMs (nssS concentrations shown in Supplement Figure 3). Although only a small percentage, volcanic activity was detected in all climate
- 265 periods, suggesting another possible mechanism for the fluorescent OM character changes since the LGM.

#### **5** Conclusions

OM is a complex mixture of heterogeneous, polydisperse, and polycyclic molecules, the nature of which may result from multiple sources. Analysis of the WD OM character by fluorescence spectroscopy allowed for the development

- 270 of a series of interrelated climate and chemical records focused on understanding changes of atmospheric global systems spanning 21.0 kyrs of Earth's history. PARAFAC modelling of the WD ice core fluorescent OM identified components used to better understand ecological influences in a changing climate. Proteinaceous fluorescence were dominant features in all WD samples over time, suggesting a strong microbial OM control of Earth's past ecosystems. More humic-like OM fluorescence, characteristic of recalcitrant material was only detected in the
- 275 Holocene, at a time when temperatures were warmer, precipitation and accumulation was greater, C productivity was higher, and tundra ecosystems were less expansive, advancing the probability for more organic materials to interact with the atmosphere. OM fluorescent character detected in the WD ice core within different climates may have fluctuated as a result of the diverse variables introduced as the atmosphere and microbial communities shifted over time. Taken together, proteinaceous fluorescent OM signatures in the WD ice core suggests that labile,
- 280 microbially derived OM prevailed in all climate periods, and were the greatest contributors to Earth's atmospheric compositions throughout history.

## Author contribution

C. Foreman, J. D'Andrilli, J. Priscu, and J. McConnell designed the experiments and J. D'Andrilli and M. Sigl
 carried them out. Both J. D'Andrilli and M. Sigl were a part of the ice core melting team. J. McConnell and M. Sigl
 calculated the dating scale for all samples. J. D'Andrilli prepared the manuscript with contributions from all coauthors.

## **Competing interests**

290 The authors declare that they have no conflicts of interest.

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- 305 expressed in this material are those of the authors and do not necessarily reflect the views of the NSF.

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470 Figure 1: Location of the West Antarctic Ice Sheet (WAIS) Divide in western Antarctica, with elevation contour lines: 112.085°W Longitude, 79.467°S Latitude, and 1,766m surface elevation (http://www.waisdivide.unh.edu/).







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Figure 2: Changes in West Antarctic Ice Sheet Divide ice core organic matter total fluorescence intensity, provided in Raman Units (R.U.), over time (kyrs before present 1950). Climate periods are labeled in shaded gray bars to describe the Last Glacial Maximum (LGM), the last deglaciation (LD), and the early to mid-Holocene.







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Figure 3: PARAFAC components identified for West Antarctic Ice Sheet Divide ice core organic matter showing a) component one (C1), component two (C2), and component three (C3) and the various overlapping features for the Last Glacial Maximum (LGM), last deglaciation (LD), and the Holocene climate periods. PARAFAC component variation for C2 is depicted in (b) for all climate periods.

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Figure 4: Trace element concentrations (ppb) from the West Antarctic Ice Sheet Divide ice core, dating from the Last Glacial Maximum (LGM), through the last deglaciation (LD), to the mid-Holocene for manganese (Mn), strontium (Sr), and non-sea salt calcium (nssCa), with the  $\delta^{18}$ O (per mil) temperature record, and the contributing OM PARAFAC components as a function of time (kyrs before present 1950).