PROCEEDINGS OF THE TWENTY-EIGHTH ANNUAL KECK RESEARCH SYMPOSIUM IN GEOLOGY

April 2015
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ANTARCTIC PLIOCENE AND LOWER PLEISTOCENE (GELASIAN) PALEOCLIMATE RECONSTRUCTED FROM OCEAN DRILLING PROGRAM WEDDELL SEA CORES:
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JAMES HALL, Wesleyan University
Research Advisor: Suzanne OConnell

INTRODUCTION

Plio-Pleistocene Antarctic Glacial History

The Pliocene epoch is in many ways a climatic analogue to our current world, with atmospheric CO$_2$ levels reaching over 400 ppm during the mid-Pliocene climatic optimum (Haywood et al., 2009), a level that was surpassed in May of 2013 (Blunden, 2014). Therefore, the epoch can shed light on the consequences of current climate change. The stability or lack thereof of the East Antarctic Ice Sheet (EAIS) is now an area of study experiencing much contention and is one of the focal points of this study. Holding ~27 million km^3 of ice, the EAIS has the potential to raise global sea levels tens of meters (http://lima.nasa.gov/antarctica/). While previously thought to have remained stable during the Pliocene and Pleistocene epochs, it now seems conceivable that the EAIS coastline could have deglaciated throughout the late Pliocene as well as the early Pleistocene (Raymo et al., 2006)

The Ocean Drilling Program

The Ocean Drilling Program (ODP), now the International Ocean Discovery Program (IODP), is a multi-country deep-sea drilling collaboration that provides ocean floor geological data and samples to aid research on the history and dynamics of Earth. The samples used in this research were taken from cores recovered during January and February of 1987 on the 113th expedition of ODP. ODP Expedition 113 traveled to the Weddell Sea, Antarctica, with the goal of acquiring information that could be used in subsequent studies to better understand the processes involved in Antarctic ice sheet formation, Antarctic bottom water formation, and other phenomena.

The site at which our samples were recovered has a geographic coordinate position of -70.8315° latitude, -14.5735° longitude. It is located in the eastern Weddell Sea in a water depth of 2359m (Figure 1). It is in close proximity to the Wegener Canyon. The cores from this site include sediments that were deposited during the early Cretaceous to the present. The primary focus of this study is on fully recovered core sections from the Pliocene (Core 113-693-A8R) and the early Pleistocene (Core 113-693-A-2R).

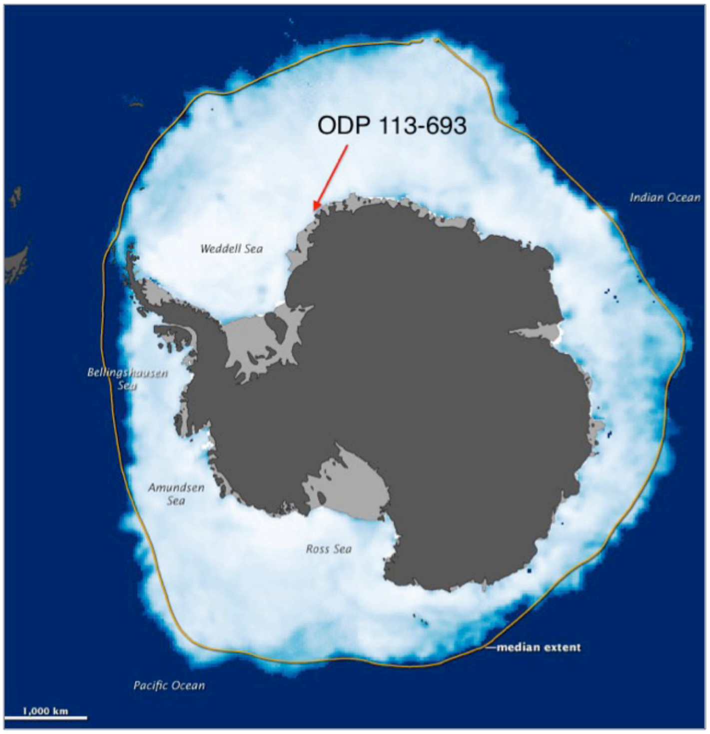


Figure 1. Location of ODP 113-693A indicated by red arrow (Dunbar, 2012).

METHODS

X-Ray Fluorescence

X-Ray Fluorescence (XRF) is an analytical technique used to acquire information on the major and trace elemental concentrations of a material given in the form of element counts per area. A third-generation Avaatech XRF Core Scanner was used on Leg 113 sediment core sections at the IODP Texas headquarters on the Texas A&M campus in College Station, Texas. The cores were scanned down their centers in 2 cm intervals, except where gaps or low elevated sections within the cores occurred. At each interval, a 1cm^2 section of the core was irradiated for 20 seconds. 10kV and 30kV runs were conducted for every core section and 50kV runs were conducted for core sections from 113-693-A-2R and 113-693-A-8R. 10kV runs allowed for the detection of the major elements Al, Si, P, S, Cl, Ar, K, Ca, Ti, Cr, Mn, Fe, and Rh, whereas 30kV runs allowed for the detection of the heavier trace elements Ni, Cu, Zn, Ga, Br, Rb, Sr, Y, Za, Nb, Mo, Pb, and Bi. 50kV runs allowed for the detection of even heavier elements: Ag, Cd, Sn, Te, and Ba, with our primary interest being the presence or absence of barium.

Magnetic Susceptibility

Magnetic susceptibility is an analytical technique that provides a dimensionless value indicating the amount of magnetic material present in the sediment. A multi-track sensor was used at the IODP Texas headquarters to conduct magnetic susceptibility analyses on cores 8R and 2R. The cores were scanned down their centers in 0.05 cm intervals.

Calibration of XRF Data to Oxide Weight Percent

The acquisition and analysis of element counts per area from XRF is a popular research method in the geosciences (Marce et al., 2006; Shelley et al., 2014), though it remains hindered by its purely qualitative and non-quantitative nature. It remains practical for many purposes, such as identifying clear depositional changes within a core, but it does not necessarily represent the elemental composition of a material.

To correct for this, fourteen samples from Site 693 were selected for XRF analysis at the University of Massachusetts Amherst X-Ray Fluorescence Laboratory. This analysis provided weight percent data for the following oxides: SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, and P_2O_5. Using the median weight percent for each of these oxides for all fourteen samples, the XRF data in the form of element count per area was calibrated to oxide weight percent data. Element counts were collected for Si, Ti, Al, Fe, Mn, Ca, K, and P, and all were calibrated to their respective oxides using the two-step process developed by Lyle et al. (2012).

<u>Step 1:</u>

$S_e = \text{Med\%}_e \times (\text{PeakArea}_e/\text{PeakArea}_e\text{, med})$

Where,

S_e = non-normalized oxide weight percent (wt%) at a given interval,

$\text{Med\%}_e$ = median of the wt% of each oxide obtained from the XRF sediment sample (for example, for Al, the median of the wt% of Al_2O_3 was used),

PeakArea_e = intensity of an element from the XRF core scanner at a given interval,

PeakArea_e, med = median for each element obtained from the XRF core scanner.

<u>Step 2:</u>

$\text{NMS}_o = (S_e \text{ x } 100)/\text{raw sum}$,

Where,

NSM_o = normalized median-scaled data for a specific oxide at a specific interval, e.g. Fe_2O_3 at 21.2 mbsf,

S_e = non-normalized oxide wt% of a specific oxide at a specific interval,

Raw sum = sum of the raw oxide wt% at an interval (Chin, 2013; Lyle et al., 2012).

<u>Example:</u>

Step 1: $\text{Med\%}_e$ = 67.2 wt. % SiO_2, PeakArea_e = 78,922 at 60.62 mbsf, and PeakArea_e, med = 107,650. Thus, $S_e = 67.2 * (78{,}922/107{,}650) = 49.27$ wt. %.

Step 2: S_e = 49.27 wt. %, raw sum = 68.02 wt. %. Thus, NMS_o = (49.27 x 100)/68.02 = 72.43 wt. % SiO_2.

Varimax-rotated Principal Component Analysis

Principal component analysis (PCA) is an exploratory statistical technique used to reduce large, cryptic datasets to more easily interpretable "components" with the goal of elucidating an underlying structure behind the dataset. Principal components, i.e. combinations of variables in the original dataset, are created. The first component explains the largest possible amount of variance within the dataset, the second explains the second largest possible amount of variance (with the stipulation that it is orthogonal to the first principal component), and so on. The principal components can then be used in scatterplots, regressions, and other statistical techniques.

Many variations of this technique exist, with the most popular being Varimax-rotated principal component analysis (VPCA). Rotated PCA methods allow variance to be more widely distributed across principal components, thereby increasing the number of "loadings" for variables on the components that follow the leading component. This allows the components to be more easily interpreted. Professor Joseph Ortiz of Kent University and several of his students have used VPCA extensively to examine orbital loadings in XRF and VNIR data from the Arctic and Antarctica (Cope, 2009; Siriwardana, 2011). Similar applications have been conducted in this study using both of our XRF datasets (count ratios and calibrated oxides). It should be noted that PCA (including VPCA) is exploratory and not confirmatory, and thus inferences and general trends, not conclusions, can be drawn from these methods.

The Varimax-rotated principal component analyses were conducted in RStudio. These techniques were conducted on two sediment cores: 693A-2R and 693A-8R, deposited during the Pleistocene and the Pliocene, respectively. Components were created and compared using the raw element count per area data as well as the calibrated data in the form of oxide weight percent.

The element ratios used in creating the components for the raw element count per area data were Ag/Ti, Ba/Ti, Ca/Ti Cd/Ti, Cl/Ti, Cr/Ti, Cu/Ti, Fe/Ti, K/Ti, Mn/Ti, Mo/Ti, Ni/Ti, P/Ti, Rb/Ti, S/Ti, Sn/Ti, Sr/Ti, Zr/Ti, and Zn/Ti. Ratios with Ti as the denominator were used to account for terrigenous sources as titanium comes from land. The oxides used in creating the component for the oxide weight percent data were Al_2O_3, CaO, Fe_2O_3, K_2O, MnO, P_2O_5, SiO_2, and TiO_2.

Wavelet Analysis

Wavelet analysis is a statistical analysis technique used to identify levels of periodicity within a time-series dataset (Torrence and Compo, 1998). It is widely used within the paleoclimate reconstruction and geophysics communities, as Earth's climate is reliant on many periodicities (e.g. those driven by eccentricity, precession, and obliquity).

To prepare the dataset for wavelet analysis, it was necessary to first interpolate and then detrend the component data. The datasets were interpolated (i.e. the data were expanded to intervals not captured in the actual XRF scanning procedure) for every 2-centimeter interval between the lowest meters below sea floor (mbsf) value and the highest mbsf value. The data was then detrended by creating a 2^{nd}-degree polynomial trendline for the cores (2R and 8R), inserting the depth at each interval into the equation for the trendline, and subtracting the value obtained from the trendline equation from the original value at each interval. After detrending the data, cyclical patterns become more easily identifiable. Both the interpolation and the detrending methods were conducted in RStudio.

The data from each component created from the element count and oxide weight percent data as well as the magnetic susceptibility data were then inputted into Interactive Wavelet Plot (http://ion.exelisvis.com/), a free online program that provides wavelet power spectrums to aid in the identification of cycles within a dataset. The settings were adjusted such that zeroes were padded to the end of the datasets and a line representing 30% red noise was included to better identify cycles from misleading spikes.

Using the wavelet power spectrums, linear sedimentation rates were calculated using the period length of a cycle and the lengths of Milankovitch cycles. By experimenting with Milankovitch cycle lengths, trends were identified in the linear sedimentation rate and wavelets within the dataset were matched with Milankovitch cycles. The estimated linear sedimentation rates and matched Milankovitch cycles were compared with those from a similar study by Tavo True-Alcara (2015) using diffuse spectral reflectance (DSR) data to further increase confidence in the conclusions being drawn.

RESULTS

Varimax-Rotated Principal Component Downcore Plots

Twenty Varimax-rotated principal components were created for this study: five from the raw element count ratio data for each core, four from the oxide weight percent data for each core, and one from the magnetic susceptibility data for each core.

Downcore plots for each component were created to aid in identifying cycles and/or lithologic changes. Online interactive graphs were built using Shiny, a user-built package for R, to allow readers to examine the data in a more user-friendly way. The interactive graphs can be found using the following web addresses:

http://jthall.shinyapps.io/components_2R/ (693-A-2R, element count plots)

http://jthall.shinyapps.io/components/ (693-A-8R, element count plots)

http://jthall.shinyapps.io/components_lyle_2R (693-A-2R, oxide weight percent plots)

http://jthall.shinyapps.io/components_lyle_8R/ (693-A-8R, oxide weight percent plots)

Extrapolation of Milankovitch Cycles using Power Spectrums

The data for the detrended/interpolated Varimax-rotated components were inputted into Interactive Wavelet Plot and wavelet power spectrums were returned and analyzed for each of the twenty components (Figure 2 and Figure 3). Using the wavelets' lengths, the dominant Milankovitch cycles for each core were identified. Tables 1 and 2 show the linear sedimentation rates (centimeters/thousand years) for each Pliocene and Pleistocene component, respectively, calculated by dividing the length of each individual wavelet by the length of the assigned Milankovitch cycle and multiplying that value by 1,000. The derived linear sedimentation rates from the XRF count data, XRF oxide wt. % data, and magnetic susceptibility data are then compared with the derived linear sedimentation rates from diffuse spectral reflectance data. The same statistical techniques were used to derive sedimentation rates from this fourth dataset, i.e. Varimax-rotated principal component analysis followed by wavelet analysis and Milankovitch cycle assignments.

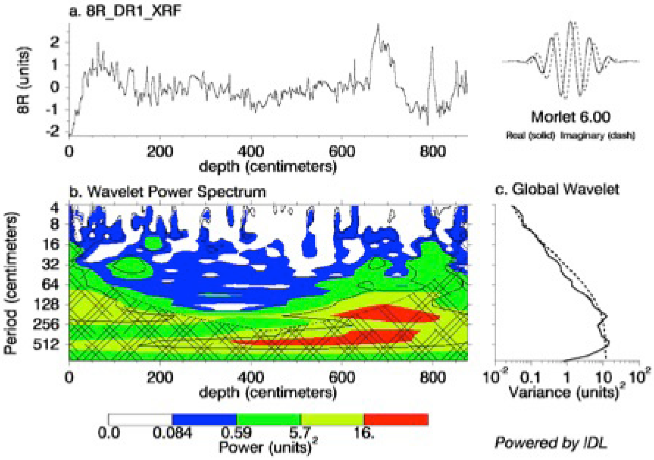


Figure 2. Wavelet output for the first XRF count components for 8R. Peaks are around 515 cm and 170 cm and are significant beyond our chosen red noise level.

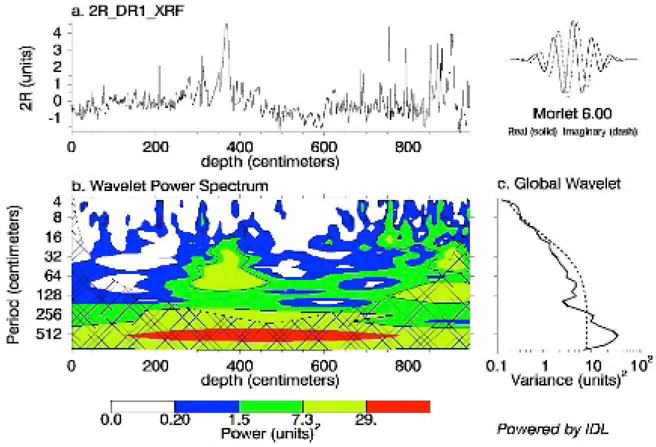
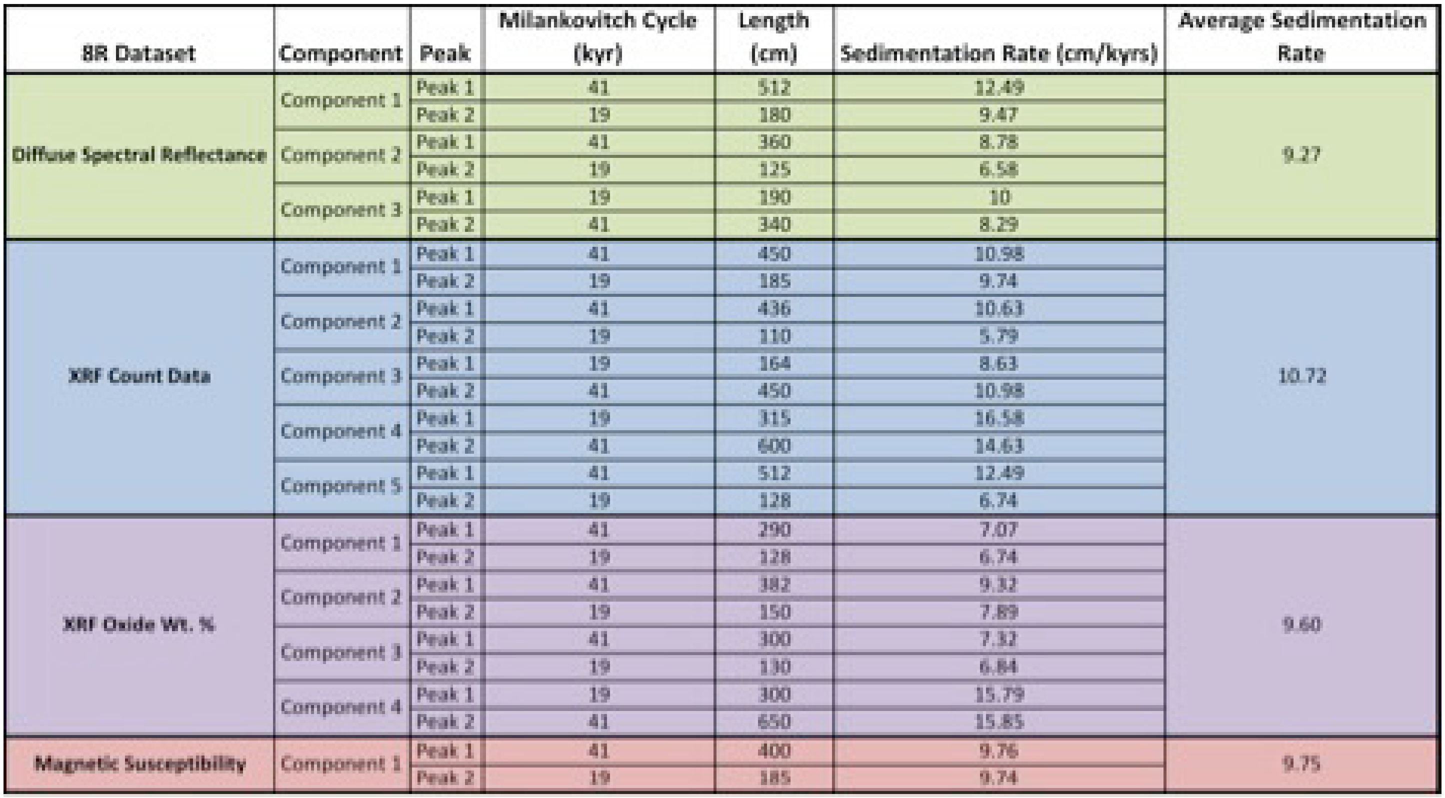
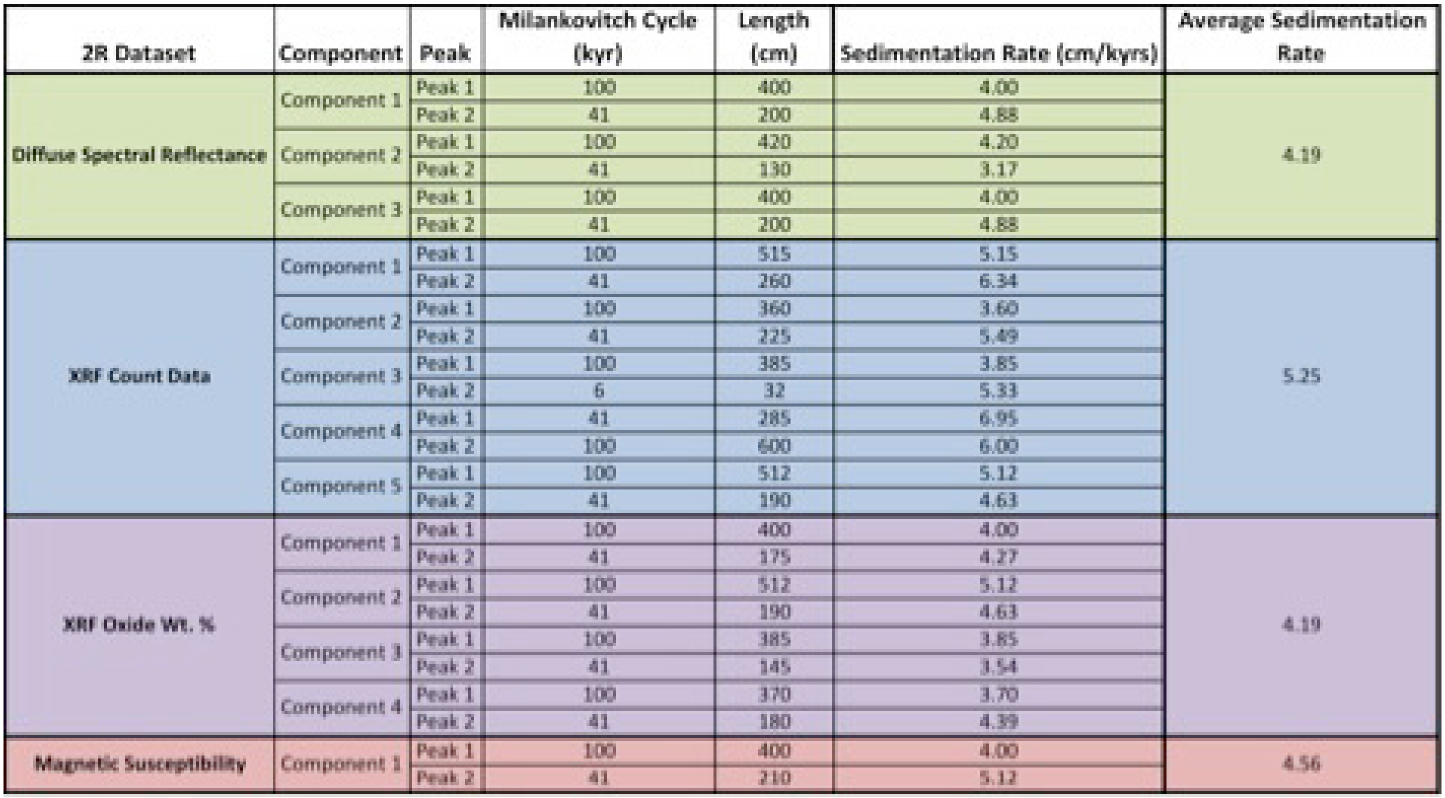


Figure 3. Wavelet output for the first XRF count components for 2R. Peaks are around 515 cm and 260 cm and are significant beyond our chosen red noise level.



8R Dataset	Component	Peak	Milankovitch Cycle (kyr)	Length (cm)	Sedimentation Rate (cm/kyrs)	Average Sedimentation Rate
Diffuse Spectral Reflectance	Component 1	Peak 1	41	512	12.49	9.27
		Peak 2	19	180	9.47	
	Component 2	Peak 1	41	360	8.78	
		Peak 2	19	125	6.58	
	Component 3	Peak 1	19	190	10	
		Peak 2	41	340	8.29	
XRF Count Data	Component 1	Peak 1	41	450	10.98	10.72
		Peak 2	19	185	9.74	
	Component 2	Peak 1	41	436	10.63	
		Peak 2	19	110	5.79	
	Component 3	Peak 1	19	164	8.63	
		Peak 2	41	450	10.98	
	Component 4	Peak 1	19	315	16.58	
		Peak 2	41	600	14.63	
	Component 5	Peak 1	41	512	12.49	
		Peak 2	19	128	6.74	
XRF Oxide Wt. %	Component 1	Peak 1	41	290	7.07	9.60
		Peak 2	19	128	6.74	
	Component 2	Peak 1	41	382	9.32	
		Peak 2	19	150	7.89	
	Component 3	Peak 1	41	300	7.32	
		Peak 2	19	130	6.84	
	Component 4	Peak 1	19	300	15.79	
		Peak 2	41	650	15.85	
Magnetic Susceptibility	Component 1	Peak 1	41	400	9.76	9.75
		Peak 2	19	185	9.74	

Table 1. Comparison of average Pliocene sedimentation rates from diffuse spectral reflectance (DSR) data, XRF count data, XRF oxide wt. % data, and magnetic susceptibility data.



2R Dataset	Component	Peak	Milankovitch Cycle (kyr)	Length (cm)	Sedimentation Rate (cm/kyrs)	Average Sedimentation Rate
Diffuse Spectral Reflectance	Component 1	Peak 1	100	400	4.00	4.19
		Peak 2	41	200	4.88	
	Component 2	Peak 1	100	420	4.20	
		Peak 2	41	130	3.17	
	Component 3	Peak 1	100	400	4.00	
		Peak 2	41	200	4.88	
XRF Count Data	Component 1	Peak 1	100	515	5.15	5.25
		Peak 2	41	260	6.34	
	Component 2	Peak 1	100	360	3.60	
		Peak 2	41	225	5.49	
	Component 3	Peak 1	100	385	3.85	
		Peak 2	6	32	5.33	
	Component 4	Peak 1	41	285	6.95	
		Peak 2	100	600	6.00	
	Component 5	Peak 1	100	512	5.12	
		Peak 2	41	190	4.63	
XRF Oxide Wt. %	Component 1	Peak 1	100	400	4.00	4.19
		Peak 2	41	175	4.27	
	Component 2	Peak 1	100	512	5.12	
		Peak 2	41	190	4.63	
	Component 3	Peak 1	100	385	3.85	
		Peak 2	41	145	3.54	
	Component 4	Peak 1	100	370	3.70	
		Peak 2	41	180	4.39	
Magnetic Susceptibility	Component 1	Peak 1	100	400	4.00	4.56
		Peak 2	41	210	5.12	

Table 2. Comparison of average Pleistocene sedimentation rates from diffuse spectral reflectance (DSR) data, XRF count data, and XRF oxide wt. % data.

DISCUSSION/CONCLUSION

Comparison across the results from all four of the 8R datasets—i.e. oxide weight percent, XRF element count ratio, magnetic susceptibility, and diffuse spectral reflectance—shows comparable sedimentation rates, ranging from 9.75 cm/kyr to 10.9 cm/kyr (Table 1). Furthermore, nearly all of the components across the four datasets are assumed to have 41,000 year obliquity as the most dominant Milankovitch cycle, followed by 19,000 year precession (there are several exceptions where the order of dominance is reversed). At such a high sedimentation rate we would fail to see 100,000 and 400,000 year eccentricity periodicities due to the length of the core, and therefore we cannot ascertain the dominance of these Milankovitch cycles during this time interval.

Comparison across the results from all four of the 2R datasets also shows similar sedimentation rates, ranging from 4.19 cm/kyr to 5.25 cm/kyr (Table 2). Furthermore, nearly all of the components across the four datasets are assumed to have 100,000 year eccentricity as the most dominant Milankovitch cycle, followed by 41,000 year obliquity.

The results from the wavelet power spectrums suggest that the long-term changes in the depositional environment at Site 693 during the Pliocene epoch were driven by obliquity (41 kyr) and to a lesser extent precession (19 kyr). The contribution from eccentricity cannot be assessed. Obliquity has been identified as the dominant pacer of the West Antarctic Ice Sheet (Naish et al., 2009), but this is the first time it has been identified for the Weddell Sea portion of the EAIS. The results also suggest that the long-term changes at Site 693 during the Pleistocene epoch were driven primarily by eccentricity (100 kyr) as well as obliquity (41 kyr), though obliquity to a lesser extent. Furthermore, the average sedimentation rate at our site during the Pliocene epoch was 10.24 cm/kyr, whereas during the Pleistocene epoch it was 4.55 cm/kyr.

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