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UNDERSTANDING CLIMATE: BIOGENIC SILICA AS A PROXY FOR INTERGLACIAL AND GLACIAL PERIODS 3 TO 5 MILLION YEARS AGO

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ABSTRACT

Paleoclimatology, the study of Earth's past climate, allows us to determine how Earth systems responded to different climatic conditions. This field is particularly relevant due to its potential applications to current global climate change. As Earth's climate continues to warm, areas of high latitude such as Antarctica experience the most warming, drawing concern to ice melt and consequent sea level rise. The dominant contributor to current climate warming is the increase in atmospheric CO_2, which now exceeds 400 ppm. During parts of the Pliocene Epoch, 5.3 to 2.6 million years ago, atmospheric CO_2 is also thought to have exceeded 400 ppm. One control on atmospheric CO2 levels is the amount of carbon that can be sequestered by down welling and biological productivity, especially in the Southern Ocean. Through biosilica analysis of sediment cores from Site 697 from the northwestern Weddell Sea north of the Antarctica Peninsula, we seek to understand when during glacial and interglacial periods productivity is highest. We hypothesize that high biosilica content corresponds to increased productivity and to warm interglacial periods. Through this study, we attempt to establish a more detailed understanding of the environmental changes likely to occur in the earth's climate and the Antarctic ice sheet's response.

INTRODUCTION

Biosilica refers to marine sediments that are formed through biological processes. The main contributors to biosilica in today's oceans are diatoms and radiolarians, although silicoflagellates, discoasters and sponge spicules can also contribute. Diatoms and radiolarians are both single cellular organisms that live at varying depths in the water column. Diatoms are algal photo synthesizers and radiolarians are zooplankton that feed on other single cellular organisms in an amoeba like fashion. As these organisms grow they make their skeleton from silica (SiO_2) (Demaster 1981). When the organism dies it sinks to the bottom of the ocean and its silica skeleton is deposited in the marine sediment below.

It should be noted that the deposition of silica in marine sediment is quite rare. The reason being that the earth's oceans are under saturated in silica so the biosilica is dissolved by the ocean water. The only exceptions to this are areas of high productivity where there are so many diatoms and radiolarians that some of their silica skeletons reach the seafloor and are buried. The Antarctic is an area of high productivity due to the upwelling of nutrients and therefore our site in the Weddell Sea in Antarctica has a record of biosilica.

Microfossils can be used as proxies for climate. When identified by species, diatoms can tell us about the range of oceanic temperatures because every species has specific parameters for survival (see Robakiewicz, this volume). The presence of diatoms themselves tells us one extremely important fact; ice in the form of permanent sheets must not have been present. Diatoms cannot photosynthesize under ice sheets, although some live in and on ice sheets. If they are present in the sediment record, ice sheets must not have extended to this area of the Weddell Sea. By examining the fluctuations in diatom levels we can begin to establish

a pattern of warm interglacial periods with high diatom abundance and cooler glacial periods with little to no diatom presence.

The record of biosilica we examine in this study dates back 3 to 5 million. The dynamic past of the Antarctic ice sheets is unknown and given the current pattern of global warming it is highly relevant to study the response of these ice sheets to high levels of carbon dioxide in the past.

METHODS

The biosilica analysis procedure was adapted from the National Lacustrine Core Facility of the University of Minnesota. Below is a brief summary of the three-part process. All samples for this study were collected from a marine sediment core drilled on ODP Leg 113 Hole 697B.

Part 1: Initial Preparation

1. Freeze dry sediment samples overnight to remove any moisture.
2. Take a portion of each dried sample and grind into a fine powder with a mortar and pestle. Store each unique sample in a labeled one-dram vial.
3. Make all reagents according to the guidelines in LabCore manual with the following exception: use 40 g of NaOH to make one molar NaOH instead of 0.5 molar.
4. Make four sets of 15 mL tubes with twenty-four tubes per set. Label the caps of these tubes A1-C8. Additionally label your sets as 60 minutes, 90 minutes, 120 minutes, and 200 minutes.
5. Use a pipette to fill each 15mL tube with 4 mL of double deionized water.
6. Label twenty-four 50 mL tube caps from A1 to C8. Use a pipette to fill each tube with 38 mL of one molar NaOH.
7. Select 10 of one-dram samples to analyze. Label 20 one-dram caps A1-C8. Weigh out 25 mg of each sample into the labeled one-dram caps and record weights. Make sure to duplicate each sample so that you have 20 caps of sediment per 10 unique samples.
8. Three of the remaining caps were left empty to serve as operational blanks. The other cap was filled with 25 mg of a laboratory biosilica standard made from extra sediment from the core.

Part 2: Digestion

1. Set a hot water bath to 85° C. Use a rack to place the 50 mL tubes of NaOH inside the water bath.
2. Once up to temperature begin digestion by dropping each cap of sediment into its corresponding NaOH tube. Make sure to record your starting time. You have 30 seconds to deposit each cap of sediment into each tube and shake the tube.
3. Repeat step 2 for each sample.
4. Take your recorded start time and calculate when 60, 90, 120, 150, 180, and 200 minutes will have passed. 1 mL extractions of the NaOH will be taken at 60, 90, 120, and 200 minutes. At 150 and 180 minutes each sample will be shaken for 30 seconds to suspend sediment.
5. After 60 minutes have passed use a pipette to extract 1 mL aliquot from each NaOH tube and deposit it in its corresponding 15 mL tube with double deionized water. Change tips every time you extract an aliquot. You have 30 seconds to collect an aliquot for each of the 24 digestion tubes.
6. Repeat step 5 for each of the extraction times.

Part 3: Analysis

1. Turn on spectrophotometer and set to read 860 nm wavelength.
2. Set up four sets of 10 mL plastic beakers corresponding with your set of aliquots for 60, 90, 120 and 200 minutes. Additionally, make a set of 10 mL beakers for your silica standards to create your absorbance curve.

3. Pipette 2 mL of Molybdate solution into each plastic beaker.

4. Pipette 0.5 mL of each aliquot into its corresponding plastic beaker. Change pipettes for each sample. Record the time you pipette the last sample.

5. Dispense 4 mL of double deionized water into each of the beakers within 15 minutes of pipetting the last aliquot.

6. Dispense 3 mL of reducing solution into each beaker within 15 minutes of pipetting the last of the double deionized water into beakers.

7. Wait at least 3 hours for color of the samples to fully develop. Do not wait more than 5 hours to analyze.

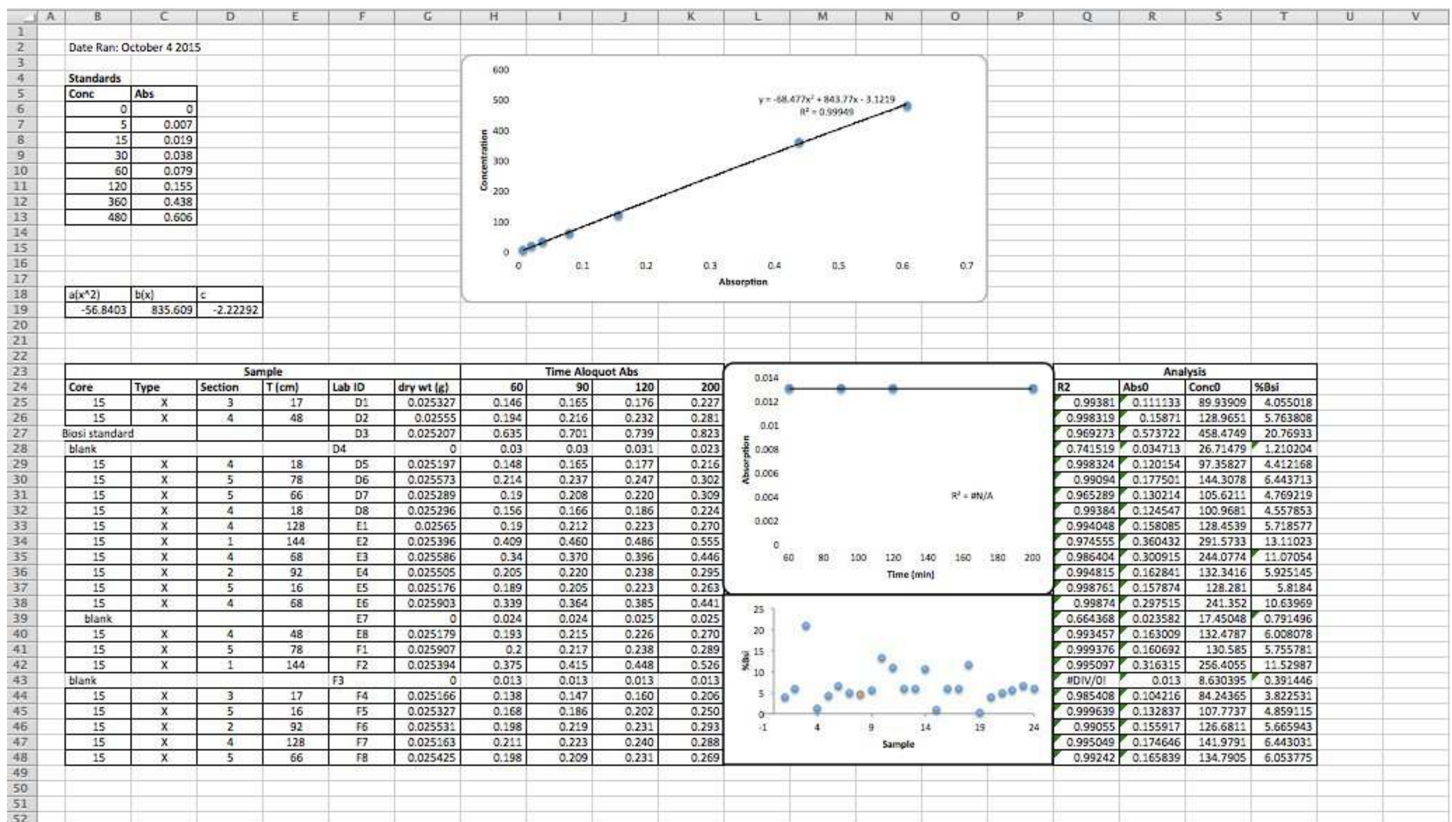
8. After enough time has passed, run double deionized water through the spectrophotometer.

9. Start running samples through the spectrophotometer beginning with your standards, then 60, 90, 120, and 200-minute sets. Record the spectrophotometer values. (Best done on the same spreadsheet data where you recorded the weight of your samples.

10. Run double deionized water through the spectrophotometer between each sample.

11. When all samples are finished run several rounds of double deionized water through the spectrophotometer and turn it off.

For instructions on how to set up the spread sheet see the LabCore manual.



Date Ran: October 4 2015

Standards

Conc	Abs
0	0
5	0.007
15	0.019
30	0.038
60	0.079
120	0.155
360	0.438
480	0.606

a(x^2)	b(x)	c
-56.8403	835.609	-2.22292

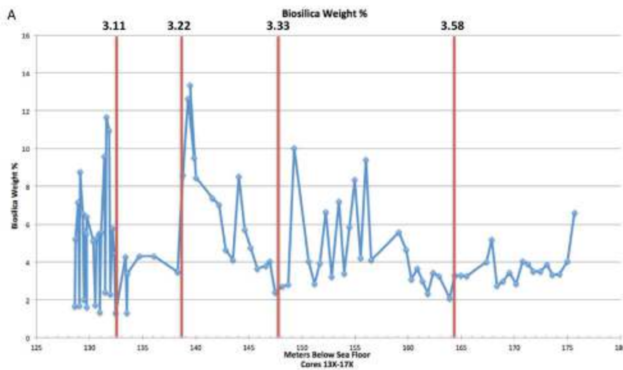
Sample						Time Aloquot Abs				Analysis			
Core	Type	Section	T (cm)	Lab ID	dry wt (g)	60	90	120	200	R2	Abs0	Conc0	%Bsi
15	X	3	17	D1	0.025327	0.146	0.165	0.176	0.227	0.99381	0.111133	89.93909	4.055018
15	X	4	48	D2	0.02555	0.194	0.216	0.232	0.281	0.998319	0.15871	128.9651	5.763808
Biosi standard				D3	0.025207	0.635	0.701	0.739	0.823	0.969273	0.573722	458.4749	20.76933
blank				D4	0	0.03	0.03	0.031	0.023	0.741519	0.034713	26.71479	1.210204
15	X	4	18	D5	0.025197	0.148	0.165	0.177	0.216	0.998324	0.120154	97.35827	4.412168
15	X	5	78	D6	0.025573	0.214	0.237	0.247	0.302	0.99094	0.177501	144.3078	6.443713
15	X	5	66	D7	0.025289	0.19	0.208	0.220	0.309	0.965289	0.130214	105.6211	4.769219
15	X	4	18	D8	0.025296	0.156	0.166	0.186	0.224	0.99384	0.124547	100.9681	4.557853
15	X	4	128	E1	0.02565	0.19	0.212	0.223	0.270	0.994048	0.158085	128.4539	5.718577
15	X	1	144	E2	0.025396	0.409	0.460	0.486	0.555	0.974555	0.360432	291.5733	13.11023
15	X	4	68	E3	0.025586	0.34	0.370	0.396	0.446	0.986404	0.300915	244.0774	11.07054
15	X	2	92	E4	0.025505	0.205	0.220	0.238	0.295	0.994815	0.162841	132.3416	5.925145
15	X	5	16	E5	0.025176	0.189	0.205	0.223	0.263	0.998761	0.157874	128.281	5.8184
15	X	4	68	E6	0.025903	0.339	0.364	0.385	0.441	0.99874	0.297515	241.352	10.63969
blank				E7	0	0.024	0.024	0.025	0.025	0.664368	0.023582	17.45048	0.791496
15	X	4	48	E8	0.025179	0.193	0.215	0.226	0.270	0.993457	0.163009	132.4787	6.008078
15	X	5	78	F1	0.025907	0.2	0.217	0.238	0.289	0.999376	0.160692	130.585	5.755781
15	X	1	144	F2	0.025394	0.375	0.415	0.448	0.526	0.995097	0.316315	256.4055	11.52987
blank				F3	0	0.013	0.013	0.013	0.013	#DIV/0!	0.013	8.630395	0.391446
15	X	3	17	F4	0.025166	0.138	0.147	0.160	0.206	0.985408	0.104216	84.24365	3.822531
15	X	5	16	F5	0.025327	0.168	0.186	0.202	0.250	0.999639	0.132837	107.7737	4.859115
15	X	2	92	F6	0.025531	0.198	0.219	0.231	0.293	0.99055	0.155917	126.6811	5.665943
15	X	4	128	F7	0.025163	0.211	0.223	0.240	0.288	0.995049	0.174646	141.9791	6.443031
15	X	5	66	F8	0.025425	0.198	0.209	0.231	0.269	0.99242	0.165839	134.7905	6.053775

Table 1. Here is an example of our biosilica data set. Standards made from known concentrations of biosilica make up our standard curve used to calculate the Weight % of Biosilica present in each sample. Each sample has its own ID and four aliquots. Every unique sample was run twice and the average of the two values was used as the actual % Biosilica for our data.

RESULTS

The overall goal of this project was to investigate if change in biosilica followed other proxy patterns of change in the Weddell Sea. We hypothesized: 1. High levels of biosilica would correlate with warmer temperatures and high IRD accumulation from melting icebergs. 2. The presence of chert in some samples might be correlated with high biosilica weight % values.

A total of 126 samples were analyzed for biosilica percentage and plotted versus time. The samples range from 1.30% to 13.35% percent abundance of biosilica.



B

Table 2. Ages of Magnetic Reversals Site 697 Hole B

Magnetic Reversals	Meters Below Sea Floor	Age
C2AN-2-T	132.8	3.11
C2AN-2-B	138.7	3.22
C2AN-3-T	147.6	3.33

Figure 1. Part A depicts the change in biosilica percentage for Site 697 Hole B cores 13X-17X. The red lines are ages from Part B. Part B magnetic reversal data comes from Hamilton and O'Brian (in prep) found in Pudsey 1990. The current ages come from Gee and Kent 2007.

When put side by side with a record of coarse fraction accumulation we see a similar pattern in their amplitude and synchronization at certain time intervals. This indicates that there must be some force driving change in both of these systems.

However, when we plotted our IRD levels with our Biosilica data in a cross plot we see that there is no correlation. In fact, the highest values of biosilica correspond with the lowest levels of IRD and the lowest values of biosilica corresponded with the highest IRD values. Biosilica is therefore independent of IRD, disproving our initial hypothesis that high levels of IRD would correlate with high levels of

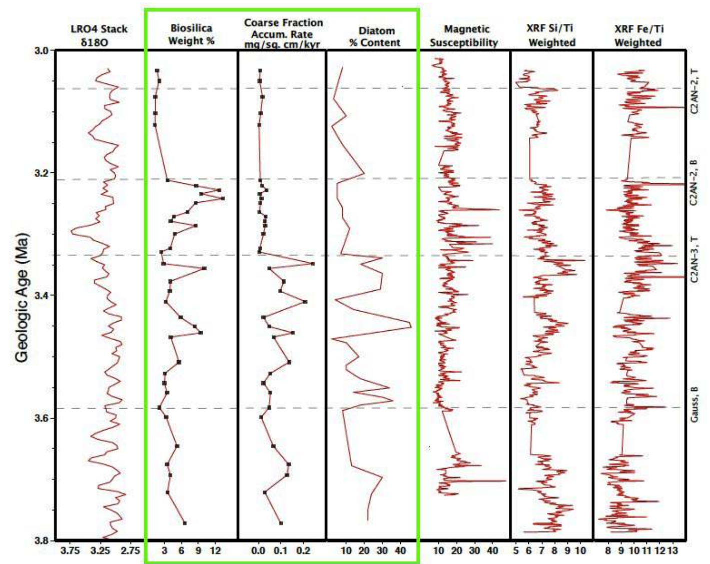


Figure 2. Side by side graph comparison of biosilica percentage, accumulation of coarse fraction over time, and diatom content by percent. Notice the slightly delayed peaks of all three components and their synchronization at several time intervals notably at from C2AN-3 to Gauss. (See Cullen in this volume.)

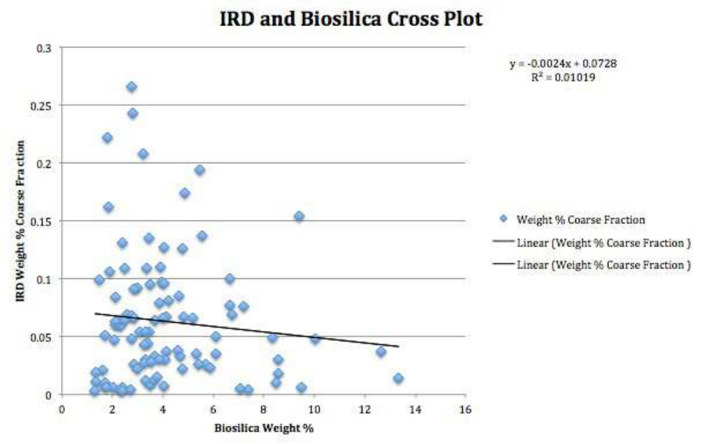


Figure 4. The cross plot above shows that there is no correlation between levels of IRD and Biosilica. The highest values of biosilica coincide with the lowest values of IRD, which is counterintuitive to our original hypothesis.

Biosilica because icebergs would indicate the melting of ice sheets.

Our second hypothesis also proved to be false. The presence of chert, which is a mineral composed of silica that has been warmed and compressed, in a sample has no correlation with the amount of Biosilica Weight %.

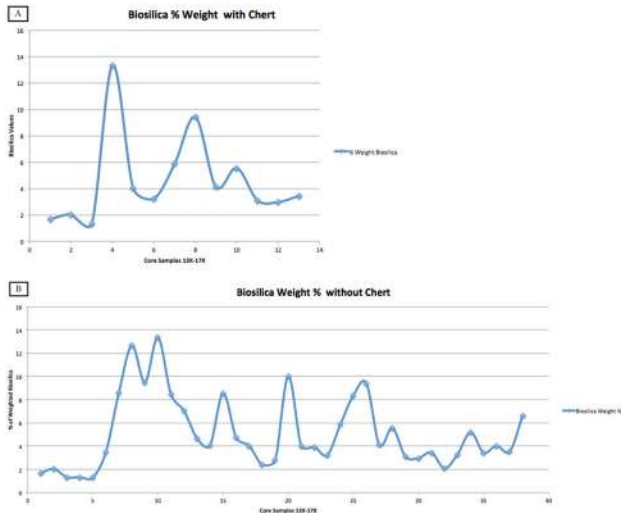


Figure 3. These figures represent the relationship between Biosilica Weight % and the presence of the mineral chert our samples (see Cullen in this volume). Part A is the fraction of samples with chert present and their corresponding Biosilica Weight % values. Part B shows samples without chert and their Biosilica Weight %. Neither of these graphs show no significant correlation.

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