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

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FORMATION OF BASEMENT-INVOLVED FORELAND ARCHES: INTEGRATED STRUCTURAL AND SEISMOLOGICAL RESEARCH IN THE BIGHORN MOUNTAINS, WYOMING
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Students: *JESSE DAVENPORT*, College of Wooster, *KRISTINA DOYLE*, Amherst College, *B. PARKER HAYNES*, University of North Carolina - Chapel Hill, *DANIELLE LERNER*, Mount Holyoke College, *CALEB O. LUCY*, Williams College, *ALIANORA WALKER*, Smith College.

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Students: *ERIN CAMP*, Amherst College, *EVAN N. DETHIER*, Williams College, *HAYLEY CORSON-RIKERT*, Wesleyan University, *KEITH M. KANTACK*, Williams College, *ELLEN M. MALEY*, Smith College, *JAMES A. MCCARTHY*, Williams College, *COREY SHIRCLIFF*, Beloit College, *KATHLEEN WARRELL*, Georgia Tech University, *CIANNA E. WYSHNYSZKY*, Amherst College.

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Faculty: *KELLY MACGREGOR*, Macalester College, *CATHERINE RIIHIMAKI*, Drew University, *AMY MYRBO*, LacCore Lab, University of Minnesota, *KRISTINA BRADY*, LacCore Lab, University of Minnesota

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Students: *BRIANA BERKOWITZ*, Beloit College, *DAENA CHARLES*, Union College, *MELLISSA CROSS*, Colgate University, *JOHN MICHAELS*, North Carolina State University, *ERDENEBAYAR TSAGAANNARAN*, Mongolian University of Science and Technology, *BATTOGTOH DAMDINSUREN*, Mongolian University of Science and Technology, *DANIEL ROTHBERG*, Colorado College, *ESUGEI GANBOLD*, *ARANZAL ERDENE*, Mongolian University of Science and Technology, *AFSHAN SHAIKH*, Georgia Institute of Technology, *KRISTIN TADDEI*, Franklin and Marshall College, *GABRIELLE VANCE*, Whitman College, *ANDREW ZUZA*, Cornell University.

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KECK SIERRA: MAGMA-WALLROCK INTERACTIONS IN THE SEQUOIA REGION
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EOCENE TECTONIC EVOLUTION OF THE TETONS-ABSAROKA RANGES, WYOMING
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Students: *JESSE GEARY*, Macalester College, *KATHERINE KRAVITZ*, Smith College, *RAY MCGAUGHEY*, Carleton College.

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Keck Geology Consortium: Projects 2010-2011
Short Contributions— Front Range, CO

INTERDISCIPLINARY STUDIES IN THE CRITICAL ZONE, BOULDER CREEK CATCHMENT, FRONT RANGE, COLORADO
Project Faculty: DAVID P. DETHIER: Williams College, WILL OUIMET: University of Connecticut

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Research Advisor: Anna Martini

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CORING A 12KYR OMBROTROPHIC SPHAGNUM PEAT BOG: A HISTORY OF ATMOSPHERIC MERCURY

ERIN CAMP, Amherst College
Research Advisor: Anna Martini

INTRODUCTION

Elemental mercury (Hg^0) is primarily transported through the atmosphere, where it has an average residence time of one year and can be deposited worldwide (Bindler, 2003). Hg^0 is deposited both naturally and anthropogenically in the environment, where it can chemically transform into a highly toxic methylated form of mercury (Vandal et al., 1993). Mercury is introduced naturally into the environment through volcanism, geothermal activity, and emission from the biosphere and water bodies, and anthropogenically through coal combustion, waste incineration, and metal ore processing (Bindler, 2003). Additionally, mercury retention is known to increase in colder temperatures, thus can be used as a paleotemperature proxy (Martínez-Cortizas et al., 1999).

Ombrotrophic peat bogs topped by Sphagnum moss are excellent archives of elemental Hg deposition because they receive all their nutrients from the atmosphere and allow little vertical mixing (Madsen, 1981; Lodenius et al., 1983). The Colorado Front Range has a rich history of gold and silver mining, smelting and mercury amalgamation, thus it is an ideal location for mercury studies (Nriagu, 1994). This project has measured the amount of Hg deposition in North Boulder Creek Bog, CO in order to 1) identify the natural background Hg deposition for this location, 2) correlate concentrations with natural and anthropogenic historical events, and 3) calculate the amount of anthropogenically deposited mercury in this location.

PROJECT LOCATION

North Boulder Creek Bog (40.007349º,-105.560421º; Fig. 1) is a 3-meter deep subalpine Sphagnum moss-coated ombrotrophic bog that began to accumulate organic sediment at 12,000 cal. ^{14}C years BP (yBP; present refers to 1950) (Leopold and Dethier, 2007; Leopold, 2010 personal communication). The bog is located in the Front Range of Colorado, situated within a kettle hole associated with the Pinedale glaciation, and flanked by a glacial moraine on its eastern side (Richmond, 1960; Fig. 1). North Boulder Creek Bog is believed to have formed after the rapid drainage of Lake Devlin about 13,000 years ago (Leopold pers. comm. 2010; Madole, 1985).

Figure 1: Google Earth image of project location, illustrating the perimeter of the bog and the surrounding glacial moraine.

METHODS

The coring, performed with a modified Livingstone piston corer (Livingstone, 1955), produced a complete 1.8m core that had been compacted by an average of 50%—slightly less near the top and more near the bottom—representing a 3.65m core. Sampling of the core was performed at 2.5cm intervals, representing ‘expanded’ intervals of 5cm. All depths referred to in this paper are ‘expanded’ depths. All samples were dried overnight—maximum of 12 hours—at 105ºC. All seventy-four samples were ground with mortar and pestle, and run individually in a direct combustion cold vapor AA instrument (Hydra-C, Leeman Labs) for total mercury concentration. The machine was calibrated using a marine sediment standard with a precision of ±6.03% and an accuracy (recovery) of 103.6%. Following these runs, higher resolution sampling was conducted at 2cm 'expanded' intervals near the uppermost section of the core, in order to obtain more precise data during modern times. Six samples were taken near 35cm depth, and five additional samples were taken from the top 5cm of the core. Additionally, five samples were sent to the Woods Hole NOSAMS Facility for AMS radiocarbon analysis. These samples were extracted from various locations along the core at 100, 160, 265, 315, and 365cm depths. Radiocarbon age is calculated from the $\delta^{13}C$-corrected Fraction Modern (Fm) according to the following formula:

$$\text{Age} = -8033\ln(\text{Fm}).$$

Figure 2: Photos of top two sections of the core. Top photo represents the first meter of core, compacted to 48cm. Bottom picture represents the second meter of core, compacted to 46cm.

RESULTS

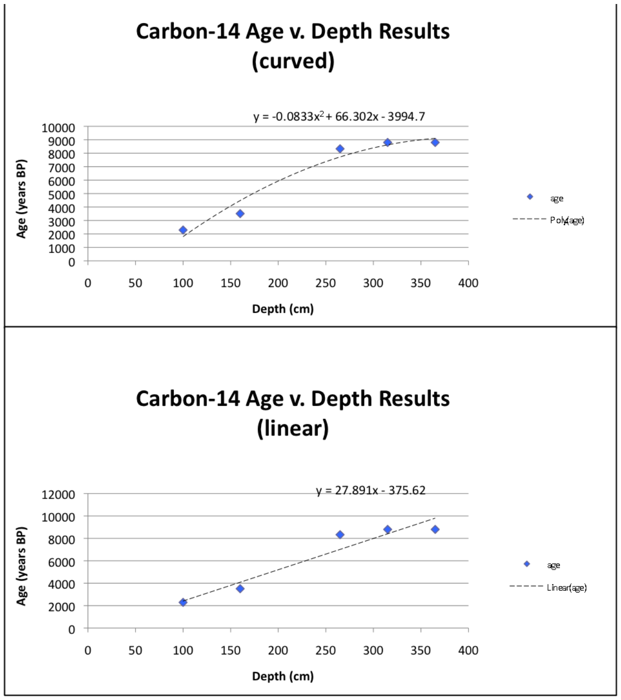

Figure 3: Age-depth graphs for C-14 data of the five bog samples, calibrated at Woods Hole HOSAMS facility. Top graph is a polynomial regression; bottom graph is a linear regression. Reporting of ages and/or activities follows the convention outlined by Stuiver and Polach (1977) and Stuiver (1980). Ages are calculated using 5568 years as the half-life of radiocarbon and are reported without reservoir corrections or calibration to calendar years. Boxed inset is illustrated in Figure 5.

The radiocarbon data yield a typical, slightly curved age vs. depth trend. With a linear regression analysis, the bog has a deposition rate of 0.36 mm yr^{-1}. A polynomial regression was used in order to fit the data at the shallowest and deepest parts of the core, where the best fit line tapers off in a convex fashion (Fig. 3). The polynomial regression suggests a calibrated age of 9105 yBP at the deepest part of the core.

The data from our mercury analysis, shown in Figure 4, range from 5.2 ppb to 201.2 ppb (ng/g). The highest values are recorded at shallow depths in the core, at recent times with greater anthropogenic influence, while the lowest values are recorded deep within the core, during historic times. The natural mercury background concentration for the North Boulder Creek Bog was calculated at approximately 23.2 ppb. Discernable peaks in mercury concentration occur at 0.5cm (158.9 ppb), 20cm (201.2 ppb), 42cm (125.8 ppb), 70cm (61.9 ppb), 80cm (49.4 ppb), 105cm (58.6 ppb), 135cm (54.6 ppb), and 230cm (72.5 ppb).

DISCUSSION

CARBON DATING

The oldest date calculated using ^{14}C was 8,800 BP at 365cm. Radiocarbon dating of this bog from previous studies demonstrated a maximum age of approximately 12,000 yBP (Leopold and Dethier, 2007), which suggests that our core location may not have been at the deepest or oldest part of the bog, or the core may not have reached the bottom of the bog.

Accumulation rates in peat bogs from other studies range anywhere between 0.015-0.920 mm yr^{-1} (Bindler, 2003; Biester et al., 2002). The average peat accumulation rate in North Boulder Creek Bog was calculated at 0.359 mm yr^{-1}, indicating a slow to intermediate deposition rate. This value is likely slow due to the subalpine location of the bog, where there are minimal organic inputs.

MERCURY ANALYSIS

Each sample represent approximately 28 years, yet there is a large gap of approximately 140 years between each sample due to the 5cm interval, due to the difficulty of high-resolution sampling. Additionally, there is typically much more compaction at depth within bogs. Thus, there may be events within these gaps of time that are not recorded by our mercury analysis. At the top of the core, however, sampling was conducted at tighter intervals and there is likely to be much less compaction.

The mercury concentration data from the core show reliable signals at appropriate depths, matching closely with results from other mercury studies of peat bogs (Martínez-Cortizas et al., 1999; Biester et al., 2002; Givelet et al., 2003; Schuster et al., 2002, Bindler, 2002). Results from this core demonstrate a set of peaks in mercury concentrations in the top 75cm depth, with a major drop in mercury concentration approaching the top of the core above 20cm. These peaks are all well above 50 ppb, indicating an additional source of mercury in addition to the natural deposition.

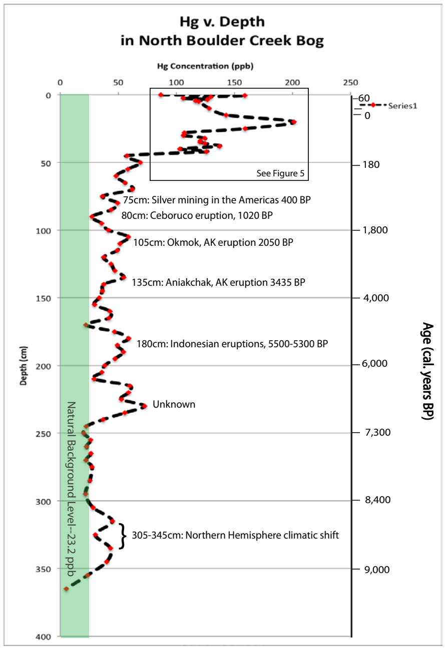

Figure 4: Mercury concentrations with depth in the complete North Boulder Creek Bog core, correlated to ^{14}CyBP. Red dots represent individual samples, and the dashed black line is the interpreted flux in concentration.

From 75-70cm depth, mercury concentration rises sharply to 61.9 ppb. According to the age-depth model, 75cm corresponds to an age of 509 yBP, closely following the onset of silver mining in the Americas in the 1550s when mercury was used to amalgamate the silver from its natural compounds. The sharp peak above 75cm depth likely represents the first clear distinction between natural and anthropogenic mercury deposition. Below this depth, it can be inferred that the majority of mercury deposition was due to natural causes, including dust loads, volcanic events, and climatic fluxes (Pirrone et al., 2010; Martínez-Cortizas et al., 1999). Alternatively, above 75cm it can be inferred that anthropogenically-induced mercury deposition is a significant contributor in addition to the natural mercury deposition. Thus, according to historic data, the mercury deposited above 70cm would have originated from modern mining, industrial pollution, waste incineration, WWII, coal burning, volcanic events, and climatic shifts (Hylander and Meili, 2003; Pirrone et al., 2010).

In addition to the onset of ore mining and processing, the climate was also changing rapidly at this time in the Northern Hemisphere. Colder temperatures are known to sequester higher quantities of elemental mercury, thus shifts to a colder climate may have caused a higher retention of mercury in the bog near 70 cm (Martínez-Cortizas et al., 1999). The Little Ice Age took place from 500-250 yBP (Mann et al., 2009), and could have contributed to the higher retention of mercury.

PRE-ANTHROPOGENIC

Below 70cm, anomalous mercury peaks occur at 80cm, 105cm, 135cm, 180cm, and 230cm in the core. From 85 to 80cm depth, mercury concentration rises to a small peak of approximately 50 ppb. At 85cm, the age-depth model estimates an age of 1039 yBP, and at 80cm an estimate of 776 BP. At 1020 ± 200 BP, the Mexican volcano Ceboruco erupted, releasing about 1.1 ± 0.08 x 10^{10} m^3 of volcanic material and producing an explosion rated as a 6 on the Volcanic Explosivity Index (Smithsonian Institution, Global Volcanism Program). Given a time window of 1039-776 yBP, the mercury peak at 80cm likely resulted, in part, from the 1020 ± 200 BP eruption, which took place 2,090km away from the bog.

The next peak of 58.6 ppb Hg is recorded at 105cm, corresponding to an age of 2048 yBP. This peak may in part be explained by the Okmok eruption in the Aleutian Islands in 100 ± 50 BC (2050 BP). This eruption was a VEI 6 and ejected 5.0 ± 1.0 x 10^{10} m^3 of tephra (Smithsonian Institution). The Okmok Caldera is located just 4,828km from North Boulder Creek Bog and may be a contributor to the anomalous mercury peak that occurs just two years after its alculated eruption date.

The 54.6 ppb Hg peak at 135cm corresponds to an age of 3437 yBP, just following the Aniakchak eruption in Alaska, US. This eruption was rated a VEI 6 and released over 5 x 10^{10} m^3 of tephra (Smithsonian Institution). The extreme magnitude of the Aniakchak eruption and its close proximity to the deposition site (6,700km) make it a likely candidate for the anomalous peak at 135cm.

Climate may also have an effect on the amount of mercury deposited in the bog between 3438 and 2048 yBP, when the two previously mentioned mercury peaks were likely deposited. The cooler time period between 3,500-2,500 yBP in the Northern Hemisphere was characterized by ice rafting in the North Atlantic, high latitude cooling, and alpine glacier retreat, and is believed to be a period of Rapid Climate Change (RCC) resulting from a decline in solar output (Mayewski et al., 2004).

At 180cm depth mercury rises to 58.8 ppb, but re mains at high values between 195-175cm (5932-5056 yBP). This lengthy increase in mercury concentration may be partly due to the combined effects of the two eruptions of Luzon in Indonesia, which occurred at 5530 and 5500 yBP at Taal and Pinatubo, respectively. Together the VEI 6 eruptions released a total of 6.3 x 10^{10} m^3 of tephra into the atmosphere (Smithsonian Institution). Alternatively, the sustained rise in mercury concentration in this part of the core may also be due to a shift to colder temperatures between 6000 and 5000 BP—similar to the climate shift that also took place between 3,500-2,500 yBP. The colder climates in the Northern Hemisphere during this time are similarly attributed to solar variability (Mayewski et al., 2004).

From 245cm to 230cm depth, another peak climbs from 22.4 ppb Hg to a maximum of 72.5 ppb Hg. At 245cm, our age-depth model approximates an age of 7118 yBP (5,168 BC). Sufficient volcanic or climatic events cannot be correlated with the timing of this peak; therefore the mercury concentration at this depth cannot be attributed to a single point source. Higher resolution mercury analyses at this depth may yield more informative data.

Finally, there is an anomalous increase in mercury concentration between 345 and 305 cm in the core, representing a plateau just slightly above the background concentration. This plateau seems to linger for approximately 500 years, between 8962 and 8477 years BP, with a slight drop at 325 cm. Northern Hemispheric climate experienced a rapid shift to colder temperatures at 8,200 years BP, when the North Atlantic region received a large meltwater burst from proglacial lakes, causing both deepwater circulation and Northern Hemisphere temperature regulation to weaken (Born and Levermann, 2010). Due to the improbability of sustained volcanic influence during the time at which this plateau appears, it is highly likely that Holocene climate shifts played a large role in the retention of mercury in North Boulder Creek Bog.

ANTHROPOGENIC

Assuming the natural background level of mercury deposition has remained constant at this location, the anthropogenic input of mercury has ranged from about 13-136 ppb since the 1550s. Above 75cm in the core, the most prominent peak resides at 20cm (Fig. 5), which has been fit to other mercury curves in order to obtain an accurate date of 67 yBP, when Mount Krakatau erupted in Indonesia on August 26, 1883. The massive eruption was rated a VEI 6 and ejected 2.0 ± 0.2 x 10^{10} m^3 of tephra (Smithsonian Institution), and is therefore a reliable marker with which to pinpoint the date of that peak. There is a smaller peak just below Krakatau at 42cm depth, which is interpreted as the Tambora eruption of 1815 in Indonesia—a VEI 7 that erupted 1.6 x 10^{11} m^3 of tephra. Between these two peaks, the mercury concentration drops significantly before Krakatau, and remains at a small plateau between 38 and 32cm (137.2-120.4 ppb). This small plateau, less concentrated in mercury than the peak of Krakatau but slightly more than that of Tambora, is interpreted as the signal of mercury deposited by the American Gold Rush from 1850-1865, when mercury was used as an amalgamator for gold and silver ore processing.

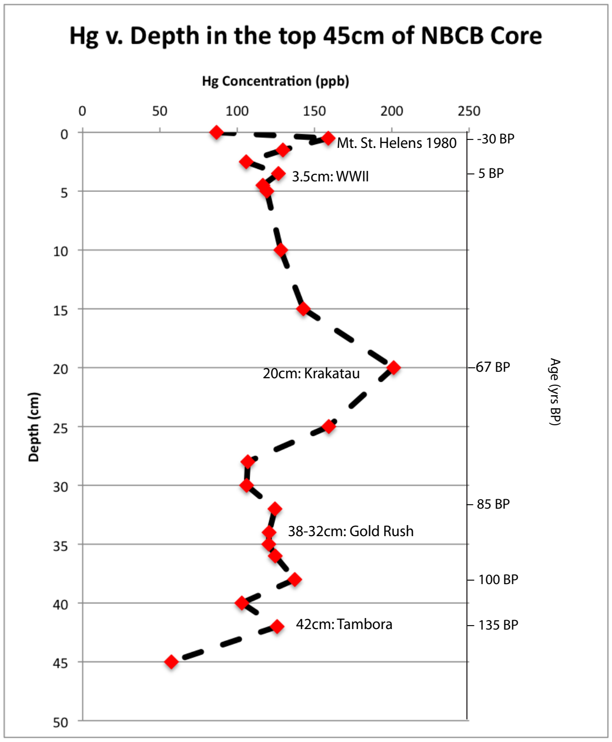

Figure 5: Zoomed inset from Figure 4. Mercury concentrations of high-resolution samples above 45cm in the core, calibrated to yBP. Red dots represent individual samples, and the dashed black line is the interpreted flux in concentration.

Above the 20cm peak, another significant peak of 158.9 ppb resides at 0.5cm. Due to its shallow position and extremely high mercury signal, this peak is interpreted as the mercury released and deposited during the Mount St. Helens eruption in March of 1980. The VEI 5 eruption, just 1510km away from the deposition site, released 7.4 x 10^7 m^3 of lava and 1.2 x 10^9 m^3 of tephra into the atmosphere (Smithsonian Institution). Below the Mt. St. Helens peak, there is a smaller increase in mercury concentration at 3.5cm (126.6 ppb). This small jump is likely a mercury signal deposited during WWII, when the defense industry was utilizing mercury to manufacture explosives.

Above the Mt. St. Helens peak, our data record the drop in atmospheric mercury concentration during the past few decades, marked by a total concentration of 86.6 ppb at 0cm, down from a peak of 158.9 ppb. This result is congruent with modern measurements that have shown a decrease in atmospheric mercury contributions from anthropogenic sources (Hylander and Meili, 2003). Given a natural background deposition of 23.2 ppb Hg, our most recent sample indicates an input of 63.4 ppb Hg from human activity at present, which includes coal combustion, industrial processes, and waste incineration.

CONCLUSION

As an ombrotrophic peat bog, North Boulder Creek Bog holds a well-recorded history of mercury deposition since approximately 9,000 yBP. The core used in this project did not reach the oldest portion of the bog, thus analyses on an additional core in a deeper location are recommended. A search for tephra using SEM analysis is recommended at the depths where we believe volcanic signals are located.

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