The Effects of Glacial Melting on Precipitation Patterns in Jellyfish Lake, Palau Derived from Hydrogen Isotopes in Algal Lipids

Alana N. Kraft

alanak2@uw.edu

University of Washington

School of Oceanography, Box 357940

Seattle, WA 98195-7940

Abstract

A meltwater-induced disruption of the Atlantic Meridional Overturning Circulation (AMOC) 8.5-8 kyr impacted climate globally, with evidence from around the continental Pacific suggesting large perturbations to rainfall patterns. Modeling indicates a southward shift of the tropical rainbands during this time. However, this is largely untested due to a lack of paleoclimate data where the Intertropical Convergence Zone (ITCZ) is well defined. In this project, I analyze hydrogen isotopic data ($^{2}H/^{1}H$) from well-dated sediment cores taken from Jellyfish Lake, Palau that imply a southward shift of the ITCZ during this time. Due to this lake being a uniquely undisturbed area with a high rate of sediment accumulation, the isotopic composition of dinosterol in these sediments can provide a detailed reconstruction of past rainfall in the tropics. Dinosterol is an organic compound produced exclusively by dinoflagellates, a taxa of photosynthetic microalgae. Through this "molecular fossil," I can reconstruct the $^{2}H/^{1}H$ ratio of the lake water and its salinity, both of which are directly tied to rainfall in Palau. To identify and purify the dinosterol found in sediment core samples, I use High-Performance Liquid Chromatography (HPLC), Gas-Chromatography-Mass Spectrometry (GC-MS), and Gas Chromatography-Flame Ionization Detection (GC-FID) instruments. Using Gas Chromatography-Isotope Ratio Mass Spectrometry (GC-IRMS), I found large and systematic fluctuations in the $^{2}H/^{1}H$ ratios of dinosterol. Thus, the preliminary data demonstrate a trend toward a drier climate in Palau at the time of the glacial meltwater pulse into the North Atlantic 8,200 years ago, consistent with a southward shift of the ITCZ. Over the past century, there has been a substantial increase in glacial melting due to anthropogenically-induced climate change. This paleoclimatic data has important implications in furthering our understanding of how drastic alterations in ocean circulation could affect climate on a global scale.

Plain Language Summary

A catastrophic outburst of glacial meltwater into the Labrador Sea 8,200 years ago disrupted oceanic circulation in the North Atlantic. This is thought to have resulted in a southward shift of the tropical rainbands, but direct paleoclimate evidence from the Pacific Ocean is lacking. This project aims to address this data deficiency. Jellyfish Lake, Palau is a uniquely undisturbed area with a high rate of sediment accumulation. The organic compound, dinosterol, found in these sediments contains an exclusive ratio of hydrogen atoms of differing atomic weights that is directly tied to rainfall in Palau via the mixing of freshwater and saltwater that occurs in the lake, and increased precipitation and humidity in the tropics. To extract the dinosterol from the sediment core samples, I used instruments that run hot solvent through the samples and pulled out the dissolved organic compounds. The purification of the dinosterol then occurs via a series of instruments that further isolate the compound and quantify the isotopic ratio of hydrogen. The preliminary data demonstrate a trend toward a drier climate in Palau at the time of the glacial meltwater pulse into the North Atlantic 8,200 years ago, consistent with a southward shift of the rainbands. This paleoclimatic data is of increased importance today due to the substantial increase in glacial melting as a result of human-induced climate change.

Introduction

The relatively stable climate of the Holocene was interrupted by a period of abrupt climate change 8.5-8 ka BP, when an outburst of glacial meltwater into the Labrador Sea disrupted the Atlantic Meridional Overturning Circulation (AMOC), plunging the North Atlantic region into cold conditions and impacting climate globally (Keigwin et al. 2005). This palaeoceanographic data on abrupt climate change scenarios is of increased importance in today's society due to rapid changes in Earth's greenhouse gas and polar ice budgets (Clark et al., 2018). With mountain glaciers such as the Greenland ice sheet melting rapidly due to anthropogenically induced climate change, it is possible a similar disruption might occur (Thomas et al., 2006).

The Intertropical Convergence Zone (ITCZ) is a region that circles the Earth near the equator where the trade winds converge and buoyant air rises, thus it plays an important role in the global circulation system (Schneider et al., 2014). This rain belt migrates with the changing position of the thermal equator, making it responsible for the wet and dry seasons of the tropics. In many climate models, the ITCZ shifts south in response to a meltwater pulse. The truth of this response is largely untested due to a lack of paleoclimate data from oceanic regions where the ITCZ is well-defined. To address this data deficiency, hydrogen isotopic analyses of the microalgal lipid dinosterol (δ^2H_{dino}) was performed in lake sediments from Palau, located near the northern edge of the ITCZ. Thus, a drier Palau could imply a southward shift of the ITCZ ~8.2 ka BP (Sachs et al. 2018).

For this project, I focus on deuterium (δ^2H), an isotope of hydrogen containing 1 proton and 1 neutron. Isotopes are variants of a particular chemical element that differ in neutron number - this change in atomic mass results in unique physical properties of the isotopic species. Thus, deuterium is double the atomic weight of protium, or the hydrogen atom. Typically, the ratio of deuterium to protium, $^2H/^1H$, is reported in delta notation and compared to an international standard (Wiberg, 1955).

There are two processes that allow us to tie deviations in the $^2H/^1H$ ratio of the lake to precipitation, the first being the mixing of freshwater and saltwater. In Jellyfish lake, this mixing is heightened during precipitation events. Atmospheric water vapor and precipitation are deuterium depleted in relation to the ocean, which in delta notation is defined as zero. This is

due to the higher vapor pressure of atomically lighter material, causing it to evaporate more readily across the globe. Rainwater then has a lower hydrogen isotope ratio, which produces a more negative value in delta notation. Thus, when the mixing of freshwater and saltwater occurs in Jellyfish Lake, greater quantities of rainfall result in a lower, more negative delta value of lake water.

The second process that governs rain and its relation to lake water isotopes is the "amount effect" (Lee and Fung, 2007). The "amount effect" is based on observations at low latitudes. Regions in the tropical Pacific that receive greater monthly precipitation have a lower $^{2}H/^{1}H$ ratio. This is due to the continuous evaporation of raindrops as they fall towards the Earth, of which the lighter isotopes evaporate out more quickly. In some areas, the raindrops evaporate completely before reaching the ground. In areas with strong convective events, such as the tropics, precipitation occurs in large quantities very rapidly. Increased rainfall over a shorter period of time results in a more humid climate and decreased evaporation (Wolf et al., 2020). Thus, raindrops in wetter climates undergo less enrichment and result in more negative delta values. Combined with the heightened mixing of freshwater and saltwater, increased precipitation leads to a decrease in the $^{2}H/^{1}H$ ratio of Jellyfish Lake.

So, the quantity of deuterium present in lake sediment provides a record of past rainfall patterns. Jellyfish Lake, Palau, was chosen as the area of research due to being a remote, undisturbed lake with a high rate of sediment accumulation. The Republic of Palau is an archipelago in the Pacific Ocean, located approximately 8°N of the equator, and has multiple "rock islands" that are comprised of raised Miocene reefs. Cracks in the rocks that formed the islands allow for the mixing of freshwater and saltwater, resulting in a semi haline lake (Orem et al., 1991). Jellyfish Lake also contains a vertical density gradient, where freshwater rests on top of the lake, while denser saltwater at greater depths results in an anoxic zone. Decaying biomass and sediment from the surface of the lake sinks to the bottom, creating a layered sequence of the environmental history. For this project, sediment cores were taken from Jellyfish Lake that span the time of the cold snap, 8000 BCE to 2016 CE.

Water from the past cannot be sampled directly, but algae that grow in the lake use the hydrogen and deuterium from its water to make their lipids, or fats, so I analyzed the organic

compound dinosterol (Withers et al., 2001). With this "molecular fossil," I reconstructed both the $^{2}H/^{1}H$ ratio of the lake water and its salinity. In this study, I tested the null hypothesis that rainfall in Palau did not change appreciably during the 8.2 ka Event. However, since this was refuted with confidence via preliminary research, I evaluated the following alternative hypotheses:

H_1: During the 8.2 ka Event, Palau experienced anomalously dry conditions.

H_2: A multi-century hydroclimate anomaly occurred in the tropical Pacific between 9-8 ka.

H_3: Climatic variability is decreased via a simulated meltwater-induced southward displacement of the ITCZ in the tropical Pacific.

A potential impediment to this study is the examination of the singular lake in Palau. Future research conducted using lake sediment data from El Junco lake, located south of the tropical rainbands in the Galápagos, would increase confidence in the interpretations. Analysis of both study sites would provide substantial data to evaluate a southward shift of the Pacific ITCZ. Thus, if the Galápagos got wetter as Palau got drier, this would aid in confirming the null hypothesis that a multi-century hydroclimate anomaly occurred in the Tropical Pacific 9-8 ka.

Methods

i. Source of Data

For the collection process, a platform was assembled between two boats on Jellyfish Lake in September-October 2016, and sequential 1-m piston cores were driven into the underlying mud until bedrock was reached at ~14.5-15 m below the sediment surface. This was repeated at a nearby location in the lake in order to obtain duplicate sediment records. All sediment cores sections have been collected and have ^{14}C age control. I analyzed the 7-9 kyr ago interval that spanned the depth range of 11.10-13.60 m in the 14.60 meter-length core, and 11.60-13.40 m in the 14.85-meter core.

ii. Lipid Extraction and Saponification

All lake sediment samples were freeze dried and extracted three times for 5 minutes in a 9:1 mixture of dichloromethane (DCM) and methanol (MeOH) on an accelerated solvent extractor (ASE) Dionex 200 operated at 100°C and 1500 psi (Sunnyvale, CA, USA) (Nelson and Sachs, 2013). Excess solvent from the total lipid extract (TLE) was then evaporated under N_2 on a Turbo-vap system (Caliper, Hopkinton, MA, USA).

To the blown down sample, 10 mL of 1M potassium hydroxide (KOH) in MeOH was added to the TLE, then heated overnight at 70°C to free the sterols present and increase the yield. To neutralize the TLE, 15 mL of high-performance liquid chromatography (HPLC) grade water and 2 mL of a 6 M hydrochloric acid (HCl) were added to the sample. Three hexane extractions of 10 mL were then performed. A new 10 mL of HPLC water was added to the combined 30 mL of hexane, and the top hexane layer was pipetted through sodium sulfate (Na_2SO_4) tubes and evaporated under N_2 on the Turbo-vap system. An 5% aliquot of the TLE was then acetylated by adding 50 µl of acetic anhydride and 40 µl of pyridine and heating the sample at 70°C for 30 minutes. After the sample was cooled, the remaining reagents were evaporated under N_2.

iii. High Performance Liquid Chromatography

The dinosterol in the samples was purified on an Agilent 1100 HPLC-MSD instrument that separates compounds via a polarity gradient. Each sample was injected in 30 µl of 2:1

DCM:MeOH. An Agilent ZORBAX Eclipse EDB C_{18} column was used at a constant temperature of 30°C with a flow rate of 1.5 ml/min. The mobile phase transitioned from 5% MeOH in acetonitrile (ACN) for 10 minutes to 5:20:75 Meoh:EtOAc:ACN and was maintained for 145 minutes to elute the compounds within the samples. The retention time of dinosterol varied by approximately 10 seconds. To ensure complete recovery, the fraction collector on the HPLC acquired 30-s-long fractions prior to and following the expected elution time of dinosterol. The samples were then blown down under N_2, and 5% aliquots were taken using toluene.

iv. Gas Chromatography Instrumentation

The dinosterol was quantified and the purity of the samples assessed by running them on two gas chromatography instruments. Compound identification was achieved via gas chromatography-mass spectrometry (GC-MS) using an Agilent 6890N GC with 5975 inert mass selective detector equipped with an Agilent VF-17 ms column (Nelson and Sachs, 2013). The GC oven was held at a temperature of 90°C during injection, increased to 320°C at 5°C/min, then held at 325°C for 24 minutes during sample injection. The quantification of dinosterol was conducted using the same method on a similar instrument equipped with a flame ionization detector (FC-FID), and dinosterol content approximated based on the area of the dinosterol peak relative to that of a C_{34}-alkane standard added to each sample prior to being ran.

The $^2H/^1H$ ratio within the dinosterol was measured by gas chromatography-isotope ratio mass spectrometry (GC-IRMS) using a Thermo Delta V Plus isotope ratio mass spectrometer and Thermo Trace GC Ultra interfaced to a High Temperature Conversion interface. The GC-IRMS was equipped with an identical column to the GC-MS, and the oven held at 120°C during injection, increased to 220°C at 20°C/min, then finally increased to 325°C at 2°C/min and held there for 20 minutes. The inlet was also held at a constant 320°C with a helium carrier gas at 1.1 ml/min. Samples and external standards were injected, then initial isotopic evaluations of all peaks were performed via Isodat software using a calibrated reference gas. Dr. Wolhowe then performed corrections for the added hydrogen from the acetylation step based on a mass balance equation in order to yield a $^2H/^1H$ ratio of algal lipids.

v. Climate Model Simulations

Simulations with the isotope-enabled Community Earth System Model were forced with realistic meltwater fluxes to the Labrador Sea (Bauer et al., 2004). Due to the wide divergence of models in their response of tropical Pacific rainfall to a freshwater forcing, the reconstructed $^{2}H/^{1}H$ ratios aided in providing a benchmark for these models to constrain the mechanisms by which the tropics respond to abrupt AMOC disruptions. This in turn acted to ensure confidence in the analyzed palaeoceanographic data by addressing the caveat of natural variation within the Earth's climate system.

Results

The sediment chronology was constructed from ^{14}C dates of 10 macrofossils found within the sediment cores in the form of an age-depth model (**Fig. 1**). The x-axis represents the depth of the core, in centimeters. The calendar age is shown on the y-axis, in years before present, or the year 1950 CE in radiocarbon dating. At approximately 700 cm depth, the slope of the regression increases, indicating a greater sedimentation rate. The linear sediment accumulation rate spanning the time of the cold snap, 7-9 kyr, was approximately 13.3 cm/kyr (**Fig. 1**).

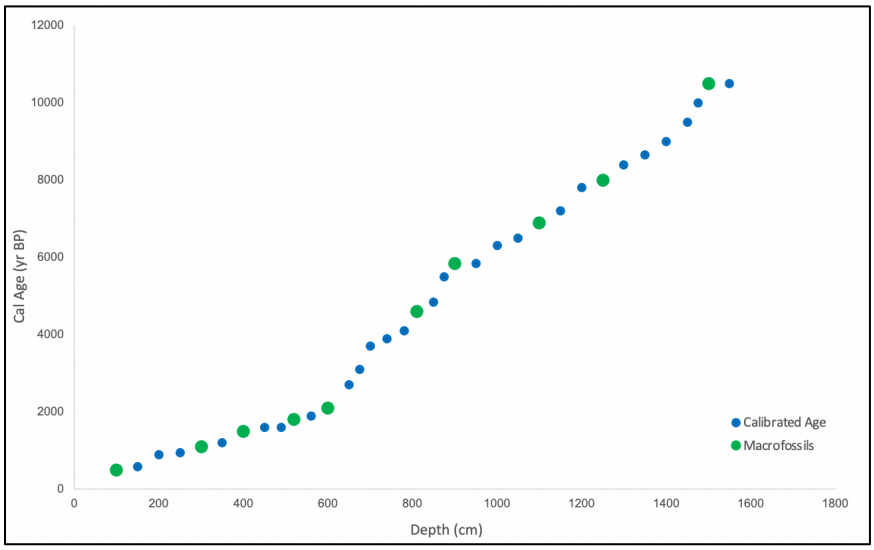

Figure 1. Age-depth model for Jellyfish Lake, Palau. The distribution of calibrated radiocarbon ages used to develop the model are shown in orange.

The preliminary data of analyzed deuterium content in Jellyfish Lake, Palau illustrate a period of less negative delta-values during the 8.2 ka event (**Fig. 2**). The x-axis represents the years before present, as modeled by ^{14}C data shown in Fig. 1. The hydrogen isotopic composition of the biomarker dinosterol is compared to a standard as represented by the Delta notation depicting the $^{2}H/^{1}H$ ratio on the y-axis.

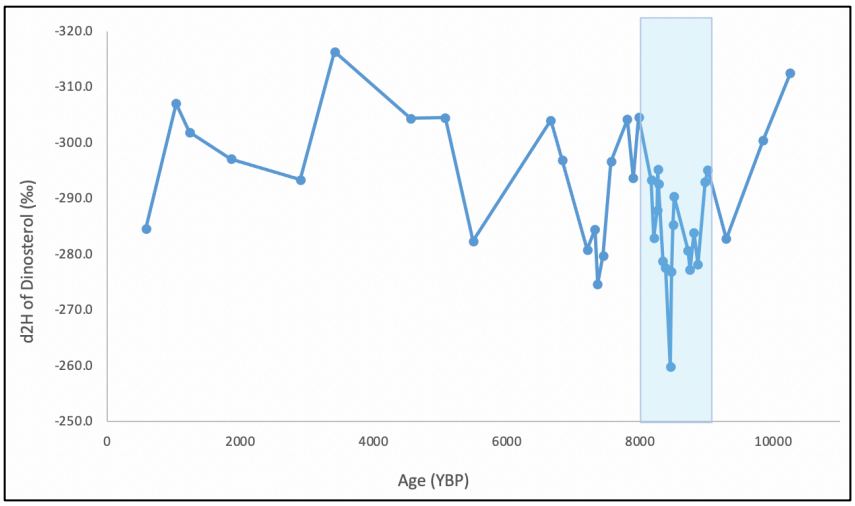

Figure 2. Relationship between the Jellyfish Lake δ^2H value of Dinosterol vs. Age, measured in years before present. The 8.2 ka period is highlighted by the blue bar.

There is no correlation in the relationship between the standard deviation of a single sample with its deuterium content (**Fig. 3**). The hydrogen isotopic composition of dinosterol in delta notation on the x-axis. Each sample was run and assessed on the GC-IRMS three times, ensuring confidence in the data via repetition. This is represented on the y-axis, with the standard deviation of the isotopic data. Since these preliminary values are independent of each other, there is no bias in the palaeoceanographic data.

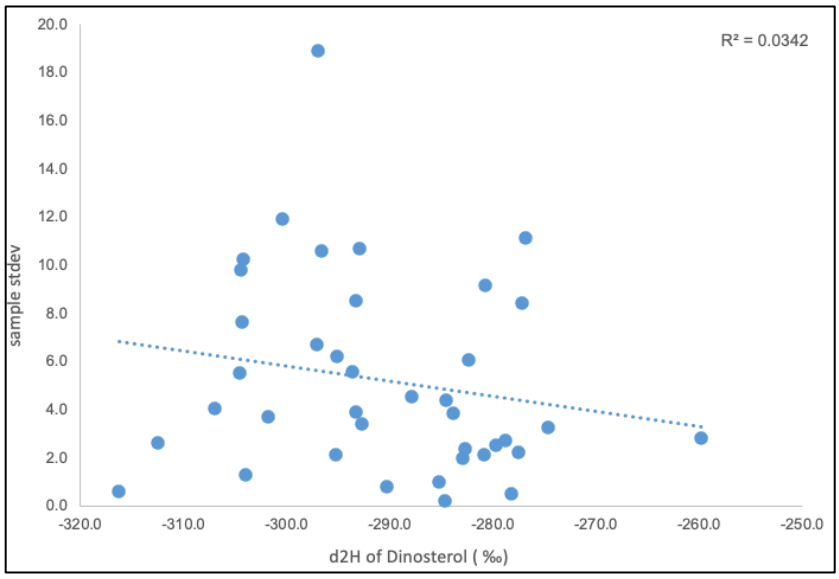

Figure 3. The relationship between the standard Deviation and δ^2H values of dinosterol in Jellyfish Lake, Palau.

Discussion

The decaying biomass and sediment from the surface of Jellyfish Lake sink to the anoxic bottom zone of the lake with a sediment accumulation rate of 13.3 cm/kyr (**Fig. 1**), creating a layered sequence of the local, and likely regional, environmental history. The cores used in this project have extensive ^{14}C age control and are therefore able to provide decadally-resolved rainfall reconstructions for the 8.2 ka event; lending confidence to the isotopic trends.

The preliminary results of the meltwater-induced overturning of the AMOC demonstrate a trend toward a drier climate in Palau at the time of the glacial meltwater pulse into the North Atlantic 8,200 years ago (**Fig.2**). Lake sediment data collected from Brown's Lake, located in Ohio, depict a cooling event occurring around 8,200 cal yr BP, and an increase in the sediment thickness due to an abrupt change in climate during that time (Lutz et al., 2007). This variation in the sediment core during the cold snap is similar to what was observed in the preliminary data of this project.

Dinosterol is isotopically lighter than the water it was grown from, resulting in overall negative delta values when compared to seawater, which is near zero. This is due to isotopic fractionations during biosynthesis. Because atmospheric water vapor and precipitation are deuterium depleted, heightened precipitation and an increasingly humid climate lead to even more negative delta values. Combined with the heightened mixing of freshwater and saltwater, increased precipitation leads to a decrease in the $^{2}H/^{1}H$ ratio of Jellyfish Lake (Sachs et al. 2018).

However, dinosterol produced by dinoflagellates that grew in isotopically heavier water will be more enriched in deuterium and thus less negative. If a greater quantity of deuterium is seen in lakes that deviates from the average hydrogen isotope ratio, then that area is receiving less precipitation and experiencing a drier climate than normal. A higher percentage of seawater in the lake, and thus less precipitation and drier climate, as seen around 8000-8,5000 years before present, is demonstrated with less negative values closer to 0 (**Fig. 2**).

In order to test whether less negative $\delta^{2}H$ values would result in decreased data precision, I compared the $\delta^{2}H$ values measured to the standard deviation of their replicate injections. A positive correlation would be produced where increasingly negative delta values

would be more trustworthy than data points closer to zero. However, this was not the case as no trend was observed in the data (**Fig. 3**). The lack thereof of this relationship reaffirms the magnitude of significance in all data points and no bias throughout the sample. Thus, the preliminary data of analyzed deuterium content of dinosterol in Jellyfish Lake, Palau depicts a period of dryness during the 8.2 ka event, with confidence enhanced by the location of study and replication of measurements.

Conclusion

One glacier drastically altered global climate 8,200 years ago. Presently, glacial melting worldwide is occurring at an exponential rate due to fossil fuel emissions. With mountain glaciers and ice sheets, such as the Greenland ice sheet, melting rapidly due to anthropogenically induced climate change, it is possible a similar disruption might occur in the future. This paleoclimatic data has important implications in furthering our understanding of how drastic alterations in ocean circulation could affect climate on a global scale, as Palau is located ~12,000 km from the North Atlantic Ocean regions where the ocean circulation disruption occurred.

Future paleoclimatic research on lake sediment data from El Junco, Galápagos, would aid in evaluating a southward shift of the Pacific ITCZ in response to the glacial meltwater pulse in the North Atlantic (Sachs and Nelson, 2016). Located 1°S of the equator on the opposite side of the globe, if the Galápagos got wetter as Palau got drier, this would lend further confidence in the null hypothesis that a multi-century hydroclimate anomaly occurred in the Tropical Pacific 9-8 ka. Additional data taken from Socorro island, located within the Revillagigedo island chain 18°N of the equator, would provide aid in determining the global span of the climatic impacts of a southward shifted ITCZ.

Acknowledgments

I would like to acknowledge my mentors, Dr. Julian Sachs and Dr. Rick Keil, for supervising this project and providing valuable insight. Thanks to Dr. Matthew Wolhowe for performing the $^{2}H/^{1}H$ data corrections. A special thank you to Sachs' Lab and also to Dr. Rick Keil for our cruise aboard the R/V Rachel Carson. With appreciation, to the NSF, the UW Quaternary Research Center, and all of my funding partners for supporting this research.

References

Bauer, E., Ganopolski, A., Montoya, M. 2004. Simulation of the cold climate event 8200 years ago by meltwater outburst from Lake Agassiz. *Paleoceanogr.* 19(3)

Clark, U. P., Alley, B. R., Keigwin, D. L., Licciardi, M. J., Johnsen, J. S., Wang, H. 2018. Origin of the first global meltwater pulse following the last glacial maximum. *Quat. Sci. Rev.* 34.

Elizabeth, R. T., Eric, W. W., Robert, M., Jorgen, P. S., Sigfus, J., Carol, A., James, C. W., Bruce, V., Trevor, P. 2006. The 8.2 ka event from Greenland ice cores. *Quat. Sci. Rev*. 26(1-2): 70-81.

Keigwin, L.D., Sachs, J.P., Rosenthal, Y. Boyle, E. A. 2005. The 8200 year BP event in the slope water system, western subpolar North Atlantic. *Paleoceanogr*. 20(2).

Lee, J. E., Fung, I. 2007 "Amount effect" of water isotopes and quantitative analysis of post-condensation processes. *Hydrol. Process.* 22(1).

Lutz B., Wiles, G., Lowell, T., Michaels, J. 2007. The 8.2-ka abrupt climate change event in Brown's lake, northeast Ohio. *Quat. Res.* 67(2): 292-296.

Moore, M., Kuang, Z., Blossey, P. N. 2013. A moisture budget perspective of the amount effect. *Geophys. Res. Lett.* 41(4).

Nelson, D. B., Sachs, J. P. 2013. "Concurrent purification of sterols, triterpenols and alkenones from sediments for hydrogen isotope analysis using high performance liquid chromatography." *Organic Geochemistry* 64: 19-28.

Orem, H. W., Burnett, C. W., Landing M. W., Lyons B. W., Showers, W. 1991. Jellyfish Lake, Palau: Early diagenesis of organic matter in sediments of an anoxic marine lake. *Limnol. and Oceanogr*. 36(3).

Sachs, J. P., Blois, J. L. McGee, T., Wolhowe, M., Haberle, S., Clark, G., and Atahan, P. 2018. Southward shift of the Pacific ITCZ during the Holocene. *Paleoceanogr*. 33: 1383-1395.

Sachs, J.P., Nelson, D.B. 2016. Galápagos hydroclimate of the common era from paired microalgal and mangrove biomarker $^{2}H/^{1}H$ values. *PNAS*. 113(13).

Schneider, T., Bischoff, T., Haug H. G. 2014. Migrations and dynamics of the intertropical convergence zone. *Nature.* 513: 45-53.

Thomas, R., Frederick, E., Krabill, W., Manizade, S., Martin, C. 2006. Progressive increase in ice loss from Greenland. *Geophys. Res. Lett*. 33.

Wiberg, B. K. 1955. The deuterium isotope effect. *Chem. Rev.* 55(4): 713-743.

Withers, W. N., Tuttle, C. R., Goad, J., Goodwin, W. T. 2001. Dinosterol side chain biosynthesis in a marine dinoflagellate, cryptheocodinium cohnii. *Phytochem*. 18(1).

Wolf, A., Roberts, H. G. W., Ersek, V., Johnson, R. K., Griffiths, L. M. 2020. Rainwater isotopes in central Vietnam controlled by two oceanic moisture sources and rainout effects. *Sci Rep.* 10.