



# Establishing paleorecords in the galapagos using hydrogen isotope ratios as a proxy for climate change

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## NONTECHNICAL SUMMARY

Global climate is heavily influenced by the hydrology of the tropical Pacific, which is characterized by a band of heavy precipitation at  $\sim 10^{\circ}\text{N}$  in summer ( $\sim 3^{\circ}\text{N}$  in winter) known as the Intertropical Convergence Zone. Characterized by warm underlying sea surface temperatures and strong convection, the seasonal migrations of the Intertropical Convergence Zone alter the precipitation patterns of the tropical Pacific, as well as global climate. Therefore, understanding what triggers its movements is crucial for predicting future climate scenarios. Previous studies suggest that the mean annual position of this band was south of its present location during the Little Ice Age (1350-1850 AD), and migrated north around 1850 AD. This northern migration would have resulted in a dryer climate in the Galapagos. To evaluate this hypothesis, this study tracked the movement of the Intertropical Convergence Zone using hydrogen isotope ratios measured from terrestrial and aquatic lipid biomarkers from sediment in Lake Escondida, Isabela Island, Galapagos. The results are consistent with previous studies, and also show evidence for a northern migration of the ITCZ after 1850 AD.

## ABSTRACT

This study examined hydrogen isotope ratios of the long chain *n*-alkanes *n*-C<sub>27</sub> and *n*-C<sub>29</sub>, along with the alcohols taraxerol, dinosterol, and brassicasterol from a sediment core obtained from saline Lake Escondida (35 ppt) Isabela Island, Galapagos. Radiocarbon dating was used to construct a model of sediment age vs. depth using four terrestrial macrofossils (bark and leaves) taken from the core, and the targeted lipids were purified from sediments for hydrogen isotope analysis. Mangroves produce taraxerol, whose  $\delta\text{D}$  values ranged from  $-194\text{‰}$  to  $-208\text{‰}$ , a difference of  $14\text{‰}$ ; leaf waxes of many higher plants are major sources of long chain *n*-alkanes in sediments, and ranged from  $-132\text{‰}$  to  $-153\text{‰}$ , a change of  $21\text{‰}$ . Dinoflagellates synthesize dinosterol, which ranged from  $-265\text{‰}$  to  $-335\text{‰}$ , a difference of  $70\text{‰}$  while brassicasterol, primarily produced by diatoms, showed values of  $-222\text{‰}$  and  $-207\text{‰}$ . The combined use of terrestrial and aquatic biomarker  $\delta\text{D}$  values present a more complete characterization of the hydrologic changes during that time than would be possible with just one biomarker source. Overall, the results show increasingly enriched  $\delta\text{D}$  values from these lipids through the end of the Little Ice Age to the present, which indicate a dryer climate on Isabela Island, Galapagos after 1850 AD and further supporting the hypothesis of the ITCZs northern migration.

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### *Importance of ITCZ on Global Climate*

Earth's climate is controlled by poleward heat and moisture transport from the tropics (Chiang 2009). Therefore, a change in tropical

hydrology would have global consequences (Chiang 2009). A major component of tropical hydrology is the band of heavy precipitation that oscillates seasonally between  $\sim 10^{\circ}$  and  $3^{\circ}\text{N}$  known as the Intertropical Convergence Zone (ITCZ)

(Figure 1) (Sachs et al., 2009). Changes in the location of the ITCZ result in drastic changes in rainfall, a result of the strong relationship between surface convergence, high sea surface temperatures, and precipitation (Conroy et al., 2008). Small oscillations of the ITCZ have even been shown to alter precipitation in West Africa and northern Brazil (Toma and Webster 2009).

Around the period known as the Little Ice Age (LIA) (~1350-1850 AD), the mean annual position of the ITCZ is hypothesized to have been substantially more south of its current location, and migrated back north after ~1850 AD (Sachs et al., 2009). Globally, reduced heat and volume transport in the North Atlantic have been linked to this movement (Lund et al., 2006). Islands in the tropical Pacific would have experienced major hydrologic shifts as well. Diatom abundance in sediment cores taken from the Galapagos suggest higher sea surface temperatures and wetter climate conditions at the end of the LIA (Conroy et al., 2008). Sachs et al., 2009 concluded a northern migration of the ITCZ resulted in the hydrology of the Galapagos shifting to a dryer climate through the interpretation of dinosterol, botryococcene, and total lipid extract  $\delta D$  values. This study also explores the concentration of hydrogen isotopes on lipids for evidence of a shift in the ITCZ, focusing on Lake Escondida, Isabela Island, Galapagos (Figure 2a and 2b).

#### *Hydrogen Isotopes as a Proxy for Paleoclimate Reconstruction*

Deuterium is an isotope of hydrogen, with a nucleus composed of one neutron and one proton, versus hydrogen which has no neutrons. It exists naturally in the environment, in lower quantities than hydrogen. For this study, the ratio of deuterium to hydrogen will be expressed as  $\delta D$ , in terms of per mil,

$$\delta D = \left[ \left( \frac{\frac{D}{H} \text{ sample}}{\frac{D}{H} \text{ VSMOW STD}} \right) - 1 \right] * 1000\text{‰}$$

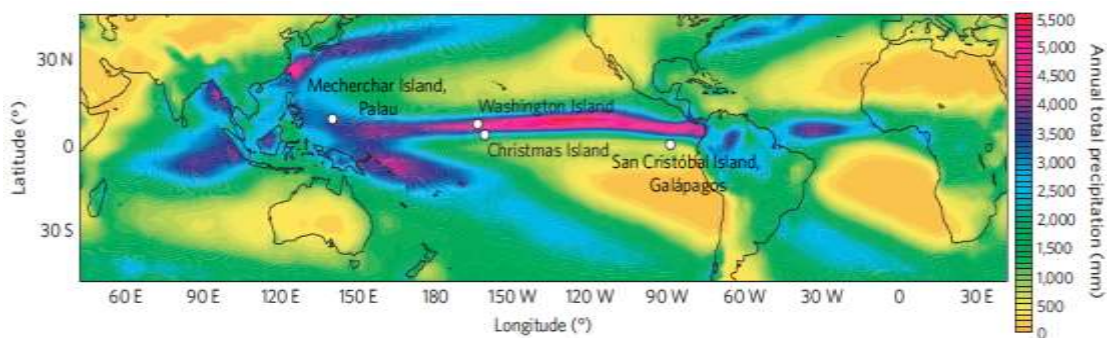
where D represents deuterium, H represents hydrogen, and VSMOW (Vienna Standard Mean Ocean Water) is a known standard. Because it is

significantly heavier than hydrogen, its abundance in source water is influenced by Rayleigh-like processes during evaporation and precipitation (Sachse et al., 2012). Two such processes are the temperature effect and the amount effect. The temperature effect has a greater impact at higher latitudes where seasonal variations in temperature result in heavy rainfall which deplete deuterium in source water (Gat 1996; Sachse et al., 2012). Lower latitudes, such as the tropics, which experience limited temperature variability are effected more profoundly by the amount effect (Sachse et al., 2012). According to the amount effect, source water  $\delta D$  is related to evaporation and precipitation where net evaporation results in an enrichment of deuterium and net precipitation results in a depletion of deuterium (Dansgaard 1964; Sachse et al., 2012). Due to the location of Lake Escondida, the  $\delta D$  trends observed should follow shifts in precipitation rather than temperature. Changing hydrology on Isabela Island would alter the ratio of deuterium and hydrogen in source water, and the resulting isotopic signature would be preserved by autotrophic organisms. During the synthesis of lipids, these organisms will use hydrogen and deuterium in a ratio that reflects the source water signal.

Strong, positive correlations between source water  $\delta D$  and terrestrial and aquatic lipid  $\delta D$  have been observed in both lab and field studies (Sachse et al., 2012). However, although the lipid  $\delta D$  ratios reflect the  $\delta D$  ratios of the source water, a discrepancy exists between these values, which can be described as the fractionation factor.

$$\alpha = \frac{[\left(\frac{D}{H}\right) \text{ lipid}]}{[\left(\frac{D}{H}\right) \text{ water}]}$$

The fractionation factor describes the magnitude of difference between the  $\delta D$  lipid and  $\delta D$  source water, and can be influenced by environmental changes (Gat 1996; Sachse et al., 2012). One such change would be salinity.



**Figure 1:** Mean annual precipitation in the tropical Pacific (Wallace 1995)

Previous studies have shown that the fractionation factor between algal  $\delta D$  and source water  $\delta D$  increased with increasing salinity (Sachse and Sachs 2008; Sachs and Schwab 2011). These differences have been attributed to either limited growth at higher salinities, or restricted water exchange in high saline water resulting in enriched deuterium in the plant cells (Ladd and Sachs 2012; Sachse et al., 2012). Algal lipids observed in this study are expected react to potential salinity changes as observed by these previous studies. This is not the case, however, for the grey mangrove lipids observed by Ladd and Sachs 2012. Mangrove lipid  $\delta D$  and source water  $\delta D$  were negatively correlated with increasing salinity (the fractionation factor decreased with increasing salinity). Because taraxerol is derived from mangroves, it is expected to behave similarly to the grey mangrove lipids studied by Ladd and Sachs 2012. Lake Escondida is fringed by a mangrove forest, leading us to conclude that the *n*-alkanes in this study were produced from mangroves and will also follow a similar trend to the mangrove lipids observed by Ladd and Sachs 2012.

#### *The Significance of Multiple Biomarkers*

To form a more complete characterization of precipitation changes in the Galapagos, and to account for potential environmental changes such as those mentioned above, this study researched both aquatic and terrestrial lipids, with the theory that a global hydrologic shift would produce similar trends among a variety of biomarkers. Taraxerol concentrations are high in the leaves of *Rhizophora* mangroves (Kim et al. 2005).

Dinosterol is a sterol produced by dinoflagellates (Shimizu et al., 1976), and brassicasterol is produced by diatoms (Gladu et al., 1990). Were a shift in  $\delta D$  values observed, the broad range of lipid biomarkers would make identifying the source of  $\delta D$  changes more conclusive than with a single biomarker.

## METHODS

### *Sample Collection*

An 83 centimeter-long sediment core was collected from lake Poza Escondida on Isabela Island, Galapagos using a universal percussion corer (Aquatic Research Instruments, Hope, ID) in June 2008. Surface sediments were sectioned in the field at one centimeter intervals to 20 centimeters depth before the remaining core was capped and transported to the University Washington. Surface sediments were frozen in the field, and then stored at  $-20^{\circ}\text{C}$  while sediments remaining in the core barrel were stored at  $4^{\circ}\text{C}$  until processed in 2012. Prior to core subsampling, the core barrel was split lengthwise into working and archive halves and photographed.

### *$^{14}\text{C}$ Dating*

To calculate a rate of sediment accumulation, terrigenous organic matter, bark and leaves, were sampled from the core at 17.5, 36.5, 72.5, and 80.5 centimeters, and prepped for radiocarbon dating using the methods of Brock et al., 2012. Samples were processed by Direct AMS. Dates were calibrated with the CALIB  $^{14}\text{C}$  Calibration Program, using the Intcal 09 atmospheric calibration curve (Table 1).



**Figure 2a and b:** Location of Lake Escondida (circled in yellow in figure 2a and starred in figure 2b).

### *Lipid Extraction and Column Chromatography*

One-centimeter sections of the core (~9-12 grams dry weight) were selected every ~two to four centimeters up to 20 centimeters deep, and every ~15 centimeters between 20 and 80 centimeters core depth. Samples were freeze-dried and extracted using an Accelerated Solvent Extractor (ASE-200, Dionex Corp., Sunnyvale, CA, USA) and 9:1 combination of dichloromethane (DCM)/methanol (MeOH) at 100°C and 1500 psi. Lipids were extracted during three five-minute cycles, and the solvent was evaporated under nitrogen gas using a Turbovap system (Caliper, Hopkinton, MA, USA). Total lipid extracts (TLEs) were saponified with 1 N aqueous potassium hydroxide and methanol overnight at 70°C, and then acidified to pH 2 with hydrochloric acid to convert ester bound steroids and triterpenols to free alcohols. Three to eight liquid-liquid extraction separations with hexane were used to recover lipids from the HCl/MeOH phase. The hexane extractions were mixed with 1 mL nanopure water to reduce the acidity of the residual water dissolved in the hexane before the hexane was removed and dried over sodium sulfate. Saponified TLEs were sorted into compound class fractions using one gram of silica gel (5% deactivated by weight, EMD, 35-75  $\mu$ L). Hydrocarbons were eluted first with 10 mL hexane, followed by ketones/esters using 6 mL hexane/DCM 1:1, alcohols with 6 mL hexane/ethyl acetate 4:1, and a polar fraction with 4 mL methanol.

### *Leaf Wax $\delta$ D Measurements*

The hydrocarbon fractions from silica gel chromatography, primarily composed of *n*-alkanes *n*-C<sub>25-31</sub> (leaf waxes), were re-suspended in toluene and analyzed by gas-chromatography-mass spectrometry (GC-MS) (Agilent, Santa Clara, CA, USA). Samples were injected in splitless mode at 300°C with helium carrier gas at 1.5 mL min<sup>-1</sup> using a VF-17ms column (60m X 0.32mm X 0.25 $\mu$ m). Initial oven temperature of 110°C was increased to 170°C at 15°C min<sup>-1</sup>, then ramped to 325°C at 5°C min<sup>-1</sup> where it was held for 24 minutes. MS was operated in full scan mode (*m/z* 50-700). Fractions were then analyzed by gas chromatography-flame ionization detector (GC-FID). An Agilent 6890N gas chromatograph equipped with an Agilent 7683 autosampler, a programmable temperature vaporization inlet (PTV) operated in splitless mode, and an Agilent DB-5 ms capillary column (60 m x 0.32 mm x 0.25  $\mu$ m) was used with helium as a carrier gas (2.4 mL min<sup>-1</sup>). The oven temperature increased from 60°C to 150°C at 15°C min<sup>-1</sup>, then at 6°C min<sup>-1</sup> to 320°C, where it was held for 28 minutes. Lipids were quantified by comparing integrated peak areas against external 5 $\alpha$ -Cholestane standards. Samples were re-suspended in toluene to achieve a minimum 300 nanogram peak for the least abundant leaf wax present per sample.  $\delta$ D values were measured using a Thermo DELTA V PLUS gas chromatograph isotope ratio mass spectrometer (GC-IRMS) (Thermo Scientific, Waltham, MA, USA). Two standards with known alkane concentrations and  $\delta$ D values (*n*-C<sub>21</sub>, *n*-C<sub>23</sub>, *n*-C<sub>26</sub>, *n*-C<sub>28</sub>, *n*-C<sub>32</sub>, *n*-C<sub>34</sub>, *n*-C<sub>38</sub>, and *n*-C<sub>41</sub>), which spanned a wide range of isotope ratios (-49‰ to

-231.8‰), were used to correct the measured  $\delta D$  values. The  $H_3+$  factor was calculated prior to each sample sequence, and was stable and lower than 4. Each sample was measured in triplicate. Small shoulder peaks appeared for two  $n$ -C<sub>29</sub> samples, at 72.5 and 80.5 centimeters, and for taraxerol at 30.5 centimeters. For taraxerol, the shouldering did not appear in one of the runs, and because the single  $\delta D$  value calculated matched the overall trend, it was included in the results for reference. Manual integration was used to determine  $\delta D$   $n$ -C<sub>29</sub>, however this resulted in a large standard deviation for these two samples. Similar to the taraxerol, the data points matched the overall trend of  $n$ -C<sub>29</sub> and were therefore included for reference.

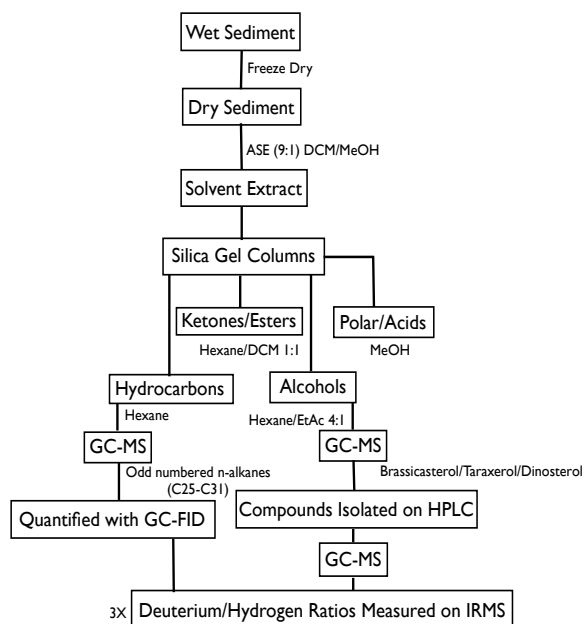
#### Alcohol $\delta D$ measurements

Alcohol fractions were acetylated in 20  $\mu$ L acetic anhydride and 20  $\mu$ L of pyridine at 70°C for 30 minutes. Aliquots were analyzed by GC-MS following the same procedure as the hydrocarbons to identify samples containing taraxerol, dinosterol, and brassicasterol. These samples were then purified by High Performance Liquid Chromatography (HPLC). Samples were dissolved in 25  $\mu$ L DCM/MeOH (2:1) and processed on an Agilent 1100 HPLC equipped with Zorbax XDB C18 column (250mm x 4.6mm x 0.5 $\mu$ L) and matching guard column. Initial mobile phase was 5% MeOH in acetonitrile at a rate of two mL min<sup>-1</sup>. Fractions were run again on the GC-MS to confirm their presence and purity before being placed on the GC-FID and GC-IRMS. Methods are summarized in figure 3.

## RESULTS

#### <sup>14</sup>C dating

Calibrated <sup>14</sup>C dates were plotted versus depth to find a linear regression, with an  $r^2$  value of 0.990 (Table 1, Figure 4). The 2-sigma age range and most probable age for each radiocarbon-dated sample was plotted, and a linear slope was forced



**Figure 3:** Summary of methods

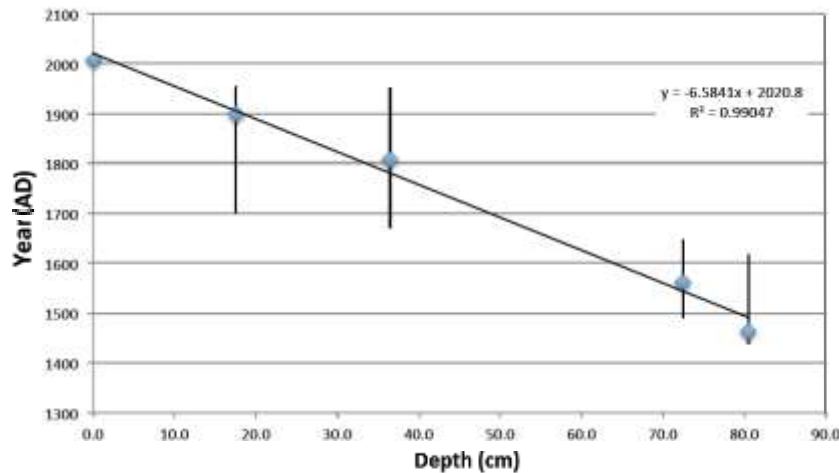
through these points and the point (0 cm, 2008 AD), implying the top layer of sediment dated to 2008, the year the core was collected. This correlation indicates the shallowest sample at 2.5 centimeters depth dates to ~2004 AD and the deepest sample at 80.5 centimeters dates to ~1491 AD, with a sediment accumulation rate of ~1.5 mm year<sup>-1</sup>.

#### Leaf Wax $\delta D$

Of the  $n$ -alkane leaf waxes targeted ( $n$ -C<sub>25-31</sub> alkanes) only  $n$ -C<sub>27</sub> and  $n$ -C<sub>29</sub> were resolved with adequate chromatography for  $\delta D$  analysis. Other  $n$ -alkanes either existed in quantities too low to be measured, or coeluted on the GC with unknown hydrocarbons. In the surface sediments, even analyses of the  $n$ -C<sub>27</sub> and  $n$ -C<sub>29</sub> alkanes were prevented by the presence of GC co-eluting compounds, and only  $\delta D$  measurements from 13 centimeters and deeper were possible. Measured  $\delta D$  values for  $n$ -C<sub>27</sub> ranged from -148‰ to -153‰, a range of 8‰, while  $\delta D$  values for  $n$ -C<sub>29</sub> ranged from -132‰ to -144‰, a range of 12‰. (Figure 5)

Sample	Depth (cm)	Radiocarbon Age (BP)	Deviation (years)	Calibrated Age (AD)	2-Sigma Age Range (AD)
GIPE217.5	17.5	24	25	1901	1880-1915
????????			????????	????????	
GIPE236.5	36.5	141	25	1807	1798-1828
????????			????????	????????	
GIPE272.5	72.5	310	28	1562	1489-1603
????????			????????	????????	
GIPE280.5	80.5	409	25	1463	1436-1513

**Table 1:** Radiocarbon ages, deviation, calibrated age (AD), and 2-sigma age range (AD).



**Figure 4:** Age Model and radiocarbon dating results for Lake Escondida. Linear slope fit to a depth of 0 cm and 2008 AD.

The overall trends of both leaf wax  $\delta D$  records covary, which supports the assumption that they are derived from similar biological sources.  $n-C_{27}$   $\delta D$  values appear linear, however  $n-C_{29}$   $\delta D$  values become progressively more enriched moving forward in time, specifically after ~1810 AD.

#### Alcohol $\delta D$

$\delta D$  values for taraxerol ranged between -194‰ to -208‰, a range of 14‰; dinosterol  $\delta D$  values ranged from -265‰ to -335‰, a difference of 70‰. Due to coeluting, only two brassicasterol points were recovered, at 2.5 and 5.5 centimeters with values of -222‰ and -207‰. Despite limited data, all alcohols exhibit similar trends over the entire period of overlap (Figure 6). Of the three alcohols, taraxerol shows the clearest trend towards enriched  $\delta D$  values. No taraxerol, dinosterol, or brassicasterol was recovered below 30.5 centimeters.

#### DISCUSSION

Overall, the results support the hypothesis that the ITCZ migrated north after ~1850 AD, which resulted in a major hydrologic shift towards a dryer climate on Isabela, Island, Galapagos. This shift towards a dryer climate is supported by increasingly enriched  $\delta D$  values on algal and mangrove-derived biomarkers. However, because the observed isotopic signatures of lipids could be attributed to changing source water  $\delta D$  due to precipitation or evaporation (amount effect) or alternative environmental factors, the results considered a gamut of potential influences for  $\delta D$  lipids variation before concluding the  $\delta D$  values observed were indeed a result of a global hydrologic shift.

Arguably, these changing  $\delta D$  values may have occurred due to a salinity change in Lake Escondida. However, this is unlikely due to the covariance of the lipids trends. Increasing salinity

would result in decreased  $\delta D$  fractionation during algal lipid synthesis (Sachse et al., 2012), and increased fractionation of leaf waxes and taraxerol (Ladd and Sachs 2012). Had salinity changes been the primary cause of changing lipid  $\delta D$  values in Escondida, the mangrove-derived taraxerol and leaf wax data and the algae-derived dinosterol and brassicasterol data would display opposite trends. However, the data for these aquatic and terrestrial biomarkers show nearly identical trends over the short period of overlap between these lipids (Figure 6). This suggests that the  $\delta D$  ratios were driven by changes in the isotopic composition of the source water over the past 100 years. Furthermore, if salinity were responsible for the pre-20<sup>th</sup> century mangrove trends, it would require that the system were saltier in the past, and this is inconsistent with other paleoclimate data (Sachs et al., 2009).

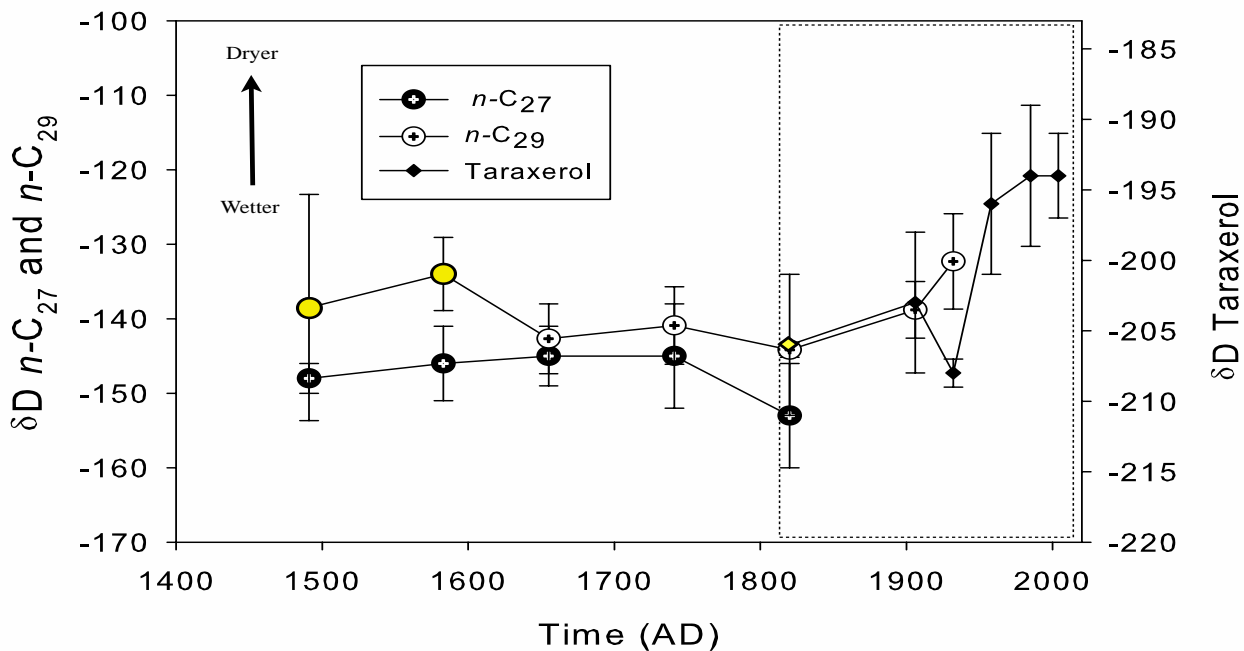
Temperature is closely related to rainfall  $\delta D$  values in areas of high temperature variability in mid and high latitudes (Sachse et al., 2012). In these regions, increasing temperature correlates to a decreasing equilibrium isotope fractionation between water vapor and condensation (Gat 1996; Sachse et al., 2012). However, Isabela Island is located in the tropical Pacific, a region characterized by limited temperature variability. Therefore it is reasonable to assume the temperature variation would be nearly insignificant.

In tropical regions, such as the Galapagos, strong seasonal changes in rainfall are the main source of variation of the isotopic composition of source water. This is known as the “amount effect”. The amount effect describes the empirical relationship where increased evaporation is associated with enriched  $\delta D$  values (Dansgaard 1964; Sachse et al., 2012). Because the  $\delta D$  ratios of taraxerol, and  $n-C_{29}$ , for example, become more enriched in younger samples this study concludes that the overall hydrology of Isabela Island became dryer through time. Although this study cannot rule out the possibility that the shift towards more enriched  $\delta D$  values in the mangrove-derived lipids might be due to a decrease in salinity between the 1800s and 1900s without a complimentary algal lipid  $\delta D$  record, the covariance of the mangrove and algal lipid  $\delta D$  values over the 20<sup>th</sup> century at least

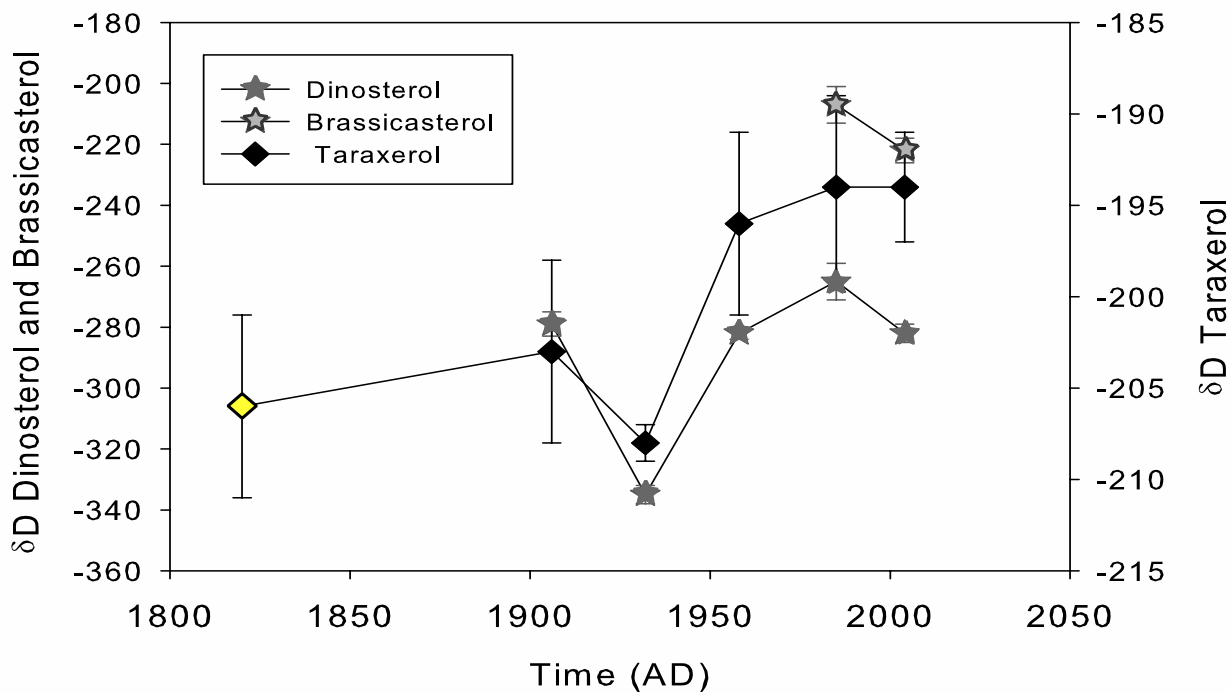
partially supports the interpretation that changes in this lake are driven by source water.

Taraxerol displays the most obvious trend towards enriched  $\delta D$  values, especially after ~1850 AD. This trend is also seen in the  $n$ -alkane  $n-C_{29}$  after this time (Figure 5). As mentioned above, these enriched values support the hypothesis that the climate in the Galapagos was wetter than current conditions prior to 1850 AD, corresponding to cores processed from proximal lakes in the Galapagos (Nelson et al., *in prep*; Sachs et al., 2009).

Dinosterol also experienced a major shift towards deuterium enrichment, most noticeably after 1930 AD. This shift was also observed by Sachs et al., 2009, which examined dinosterol  $\delta D$  values in Spooky Lake on Palau, another island in the tropical Pacific. Due to its latitude, compared to Isabela Island, the trend in Spooky Lake is opposite of the trend in this study. Nevertheless, those values, which ranged from -320‰ and -270‰, are a similar range as the results of this study. Both dinosterol and taraxerol, however, include a depleted  $\delta D$  value at ~1930 AD. It is not observed in  $n-C_{29}$ . Brassicasterol and  $n-C_{27}$  data are not available at that time. As mentioned above, this depletion is not perceived to be the result of a change of salinity in Lake Escondida due to the isotopic fractionation observed in algal and mangrove-derived lipids. Also, both taraxerol and  $n-C_{29}$  are presumably derived from the same source, eliminating the possibility the depletion is a result of algae lipid production differentiating from mangrove lipid production. Possibly, the depletion is due to the way the  $n$ -alkanes were synthesized compared to the alcohols, so while a major hydrologic shift may have occurred, it was not reflected in these lipids. Without data from brassicasterol this is difficult to confirm. Another explanation would be a laboratory handling error, although because both taraxerol and dinosterol show the same depletion, this is less likely. However, because the data before and after these points show a trend towards more enriched  $\delta D$  values, especially evident with taraxerol and  $n-C_{29}$ , it is reasonable to conclude that the dryer climate began after ~1850 AD.



**Figure 5:**  $\delta D$  values of terrestrial biomarkers  $n$ -alkanes and taraxerol. Boxed points indicate the drying trend indicative of the northern migration of the ITCZ. Yellow indicates a point of questionable chromatography.



**Figure 6:**  $\delta D$  values for algal biomarkers dinosterol and brassicasterol and the terrestrial lipid taraxerol. Terrestrial biomarkers are black, and algal biomarkers are grey. Yellow indicates data point of questionable chromatography.

Overall, the isotopic compositions of the observed lipids become enriched in deuterium, most noticeably from lipids that extend into the 20<sup>th</sup> century. This supports the hypothesis that Isabela Island, Galapagos became dryer through the present and this change can be attributed to the northern migration of the ITCZ.

fellow classmates, the Senior Oceans Class of 2013.

## CONCLUSION

The hydrogen isotope composition of precipitation and surface water is indicative of changing hydrology, and compounds that preserve this information can be used as a proxy for climate change. This study in Lake Escondida, Isabela Island, Galapagos, used the isotopic composition of aquatic and terrestrial biomarkers in sediments to reconstruct paleoclimates in the Galapagos. Deuterium enriched 20<sup>th</sup> century samples compared to older samples, along with the covariance of algal and mangrove-derived lipid  $\delta D$  trends, suggest a change in the isotopic composition of the source water driven by a hydrologic shift towards a dryer climate over the time period observed. These findings, along with previous studies which exhibit similar observations (Nelson et al., *in prep*; Sachs et al., 2009), are attributed to the northern migration of the ITCZ after ~1850 AD. It is important to note that these alterations in hydrology in the Pacific would have resulted in global climate changes. Therefore, further research is needed to confirm these results. Future research will seek to purify co-eluting alkanes, which will provide leaf wax data through the present, providing a more complete picture of  $\delta D$  variation.

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