Paleoclimate Reconstruction from Oxygen Isotopes in a Coral Skeleton from East Africa

A DATA-ENHANCED LEARNING EXPERIENCE

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PURPOSE OF ACTIVITY

One of the several benefits of data-enhanced learning experiences that expose students to the process of scientific inquiry and methods of data analysis is to prepare students to address real-world problems such as climate change (Kirk et al., 2014). Because the science behind climate and paleoclimate research is complex, these topics are typically covered in specialized or upper-level courses. Non-science majors should be exposed to climate science so they can better evaluate the world around them and how the media portrays the topic. Here, we present an activity targeting non-major, general education, introductory students that provides a data-enhanced learning experience and illustrates the basics of how paleoclimate can be reconstructed. Specifically, this activity shows how marine paleoclimate records are reconstructed from biological carbonates (corals) and also strengthens students' basic statistical and spreadsheet skills. Students use published coral isotope data downloaded from the National Oceanic and Atmospheric Administration Paleoclimate Database to develop a paleotemperature equation from oxygen isotope data paired with sea surface temperature (SST) data. They then use this equation to hindcast SST back to the beginning of the coral record in 1801. Students are exposed to isotope geochemistry (at a basic level), as well as error analysis, to better understand how paleoclimate records are generated.

AUDIENCE

This activity was developed for a non-major, general education, introductory oceanography class, but could also be used in mid-level marine science, environmental science, or geochemistry classes with minor modifications. We have used this exercise in Introduction to Oceanography, a non-major general education course, and Historical Geology, a course for majors, at two liberal arts colleges with good results.

BACKGROUND

Oxygen isotopes in carbonates provide a powerful tool for reconstructing climate or past environmental conditions. The oxygen isotopic ratio in $CaCO_3$ varies based on the water temperature at the time the carbonate precipitates (Urey, 1947; McCrea, 1950; Epstein et al., 1953). This is typically an equilibrium fractionation. When bonds are being made and broken at the surface of a growing carbonate crystal, the bonds between heavy isotopes are slightly more difficult to break than those between light isotopes; thus, more of the heavier ^{18}O accumulates in the carbonate than the lighter ^{16}O. As temperature changes, so does the difference between ^{18}O and ^{16}O dissociation energies (i.e., how easy it is for the isotope to break free). A decrease in temperature (i.e., less energy in the system) leads to a decrease in disassociation energy and therefore an increased accumulation of ^{18}O in the carbonate relative to ^{16}O. This results in a negative correlation between water temperature and $CaCO_3$ oxygen isotope ratios (i.e., the lower the water temperature, the higher the $^{18}O/^{16}O$ ratio).

A second factor affects oxygen isotope composition of carbonates: the isotopic composition of the water itself. The temperature-based fractionation discussed above is between water and $CaCO_3$ oxygen isotopes, so the oxygen isotope ratio of the water is an important factor. Evaporation and precipitation are the dominant controls on the oxygen isotope composition of water (Dansgaard, 1964). The light isotope ^{16}O evaporates faster, leaving the heavier isotope behind in the water. Thus, precipitation and freshwater in general contain relatively more of the light isotope ^{16}O when compared to marine waters. This typically results in a positive correlation between oxygen isotope values of water and salinity (i.e., the higher the salinity, the higher the $^{18}O/^{16}O$ ratio in water; e.g., Epstein and Mayeda, 1953). During glacial periods, as water is removed from the ocean through evaporation and then precipitation is trapped as ice, the ocean progressively accumulates the heavier ^{18}O isotope (Emiliani, 1955). Note that other factors affect the oxygen isotope values of carbonates, such as vital effects (i.e., biologically mediated non-equilibrium carbonate precipitation), diagenesis, and organism ecology (e.g., movement between water masses with different oxygen isotope ratios) (see review by Sharp, 2007).

The actual difference in ^{18}O and ^{16}O abundance is very small, with ^{16}O dominating the natural abundance of oxygen (the average terrestrial abundance of ^{16}O in atom percent is 99.759%). Because we are discussing small variations of a small percentage of oxygen, we use the "delta notation" or $\delta^{18}O$ value when discussing these differences, which are expressed in "per mil"

units (symbol ‰). This notation is a departure from a sample $^{18}O/^{16}O$ ratio from that of a standard, multiplied by 1,000 to make it an integer value:

$$\delta^{18}O = [^{18}O/^{16}O_{sample} \,/\, ^{18}O/^{16}O_{standard} - 1] \, {}^{*}1000 \text{ (in ‰)}.$$

The standards used for $\delta^{18}O$ values are Standard Mean Ocean Water (SMOW) for waters and PDB (a belemnite from the Cretaceous Pee Dee formation of South Carolina) for calcium carbonates. Asking students to substitute these standards as the "sample" in the delta equation above (i.e., calculating the $\delta^{18}O$ values of SMOW and PDB, both of which are 0‰) typically demystifies the equation by illustrating how this initially seemingly complex equation works in a very simple manner.

The $\delta^{18}O$ value of carbonates thus reflects the $\delta^{18}O$ value of the water ($\delta^{18}O_W$) and water temperature (SST). Water $\delta^{18}O$ values vary with ocean salinity or with glacial cycles, but the region where the tropical massive coral that we are using for this exercise grew did not experience large variations in $\delta^{18}O_W$ values (Cole et al., 2000). In the tropical ocean, local rainfall $\delta^{18}O$ values are not strongly depleted from average seawater values, and salinity gradients are small far from direct river inputs, such as where this coral grew. Therefore, the skeletal $\delta^{18}O$ values in this coral should correlate well with SST. Although corals precipitate their aragonite skeletons out of isotopic equilibrium (e.g., Swart, 1983; McConnaughey, 1989), paleotemperature equations developed from serially sampled $\delta^{18}O$ values of individual coral heads robustly record SST (e.g., Linsley et al., 1999). Thus, paired $\delta^{18}O_{coral}$ and SST can be used to construct a paleotemperature equation, which can then be used to hindcast SST to the bottom of the coral core back in time.

RESEARCH QUESTION

How are paleoceanographic temperature series created and what are the associated errors?

MATERIALS

Laboratory handout (see online supplementary materials), an Internet connection, spreadsheet software (e.g., Microsoft Excel), and a word processor (e.g., Microsoft Word).

ACTIVITY

Before the laboratory, a lecture on paleotemperature proxies is required to introduce students to the basics of oxygen isotope paleothermometry (such as the information presented above and in Fry, 2007, and Sharp, 2007). Students will gain a basic understanding of the delta value (δ) and how isotopic fractionation works. For introductory classes, this discussion is kept simple by using examples that focus on evaporation. More detailed lectures can be given on fractionation in carbonates, but they are not necessary for this exercise. It is helpful to include discussion on how paleoclimate archives are sparse through time and space to illustrate why it is important to develop such records. The laboratory exercise typically takes students between two and three hours, largely depending on students' Excel and algebra skills.

Step 1. The Data

Students locate the data set and open it in the spreadsheet. The data are available on the National Oceanographic and Atmospheric Administration Paleoclimate Database and were originally published in Cole et al. (2000). This step is purposely kept vague to encourage students to understand how publicly available data can be obtained and used. Students should find the Malindi Marine Park, Kenya, Coral Data located at https://www.ncdc.noaa.gov/paleo/coral/malindi.html and use the "Malindi (2000) annual O18 Data" (these data are also available as online supplementary materials). Note that there are many other paleoclimate records that could be used for this activity. Many students have difficulty using software such as Excel and have not been exposed to features that allow importing data from a text file. Here and throughout this activity, we use the principle of "scaffolding" (providing help in small steps and allowing the students to move forward autonomously until they require help again) to move students toward successful completion of a task.

Step 2. Metadata

Students are required to become familiar with the data and how they were generated. They answer questions obtained from the metadata file such as: Where did the coral sample originate? Why are some SST data missing? and How did the researchers assign dates to coral $\delta^{18}O$ values (age model development)? Corals typically produce massive annual bands, easily seen in core sections (Figure 1), and the metadata explain this.

FIGURE 1. Section of the coral core used by Cole et al. (2000). The annual bands used to date the coral (i.e., age model development) are clear (scale bar is in cm).

Step 3. The Paleotemperature Equation

Here, students develop the paleotemperature equation—the mathematical relationship between the proxy data and SST. Coral isotope data extend from 1801 to 1994, while SST cover the period from 1951 to 1989. Because there are gaps in the SST data, students need to group all coral $\delta^{18}O$ values that have corresponding SST data. For example, they can copy the data to a new tab and sort the data by SST, then delete the $\delta^{18}O$ values lacking paired SST data. Sorting again by year will rearrange the data chronologically. Next, they fit a simple linear regression model relating $\delta^{18}O$ values with SST. To do this step, they should create a scatter plot with the SSTs as the independent variable (x-axis) and coral $\delta^{18}O$ values as the dependent variable (y-axis). To add the regression line, students should use the "add trendline" feature of Excel. The equation and the R^2 value of their model should be included on their plot. (In most versions of Excel these options are included in the format trendline dialog box.) Students should insert this graph (Figure 2) into a word processor file and write an appropriate figure caption. Finally, students should solve the equation for SST (i.e., solve for x). This is the final paleotemperature equation they will use in the next step of the lab.

Step 4. Validation

To check the work done and the paleotemperature equation, the next step is to validate the paleotemperature equation. This is typically done with data not included in the original model, but we preferred to include all data in the model and validate it with the same data because more data can be used in both the model and the validation. It also results in some interesting statistics that help students understand basic regression statistics (see questions in the laboratory handout, available in the online supplementary materials). Because all of the data are part of the validation, the regression between the measured and the calculated SST results in a slope close to one and an intercept near zero. It also results in the same R^2 value as the relationship between $\delta^{18}O$ values and SST data because the $\delta^{18}O$ data are transformed to SST with a linear equation. These results allow for discussion that shows students how regression statistics work. We find these discussions illuminating for students and feel the benefits of using all of the data in the equation outweigh the negatives. However, the exercise could easily be done using data excluded from Step 3 above, which would be more correct in terms of how researchers do paleoclimate reconstruction.

Step 5. Error Analysis

The root mean square error (RMSE) is a simple way to calculate error and is used widely in paleoclimatology (e.g., Joussaume and Braconnot, 1997; Wanamaker et al., 2006; Phipps et al., 2013). Students first calculate the difference between the measured SST and the calculated SST. Next, they square this difference, then average the squared differences. Finally, the square root of the average squared differences is calculated to obtain the RMSE. They then use the RMSE to interpret their final data. In this simple and robust tool, any differences less than the RMSE should not be interpreted as statistically different.

Step 6. SST Reconstruction

Here, students use their paleotemperature equation to calculate SST for all 193 years. They are required to plot the results and include the plot in their final report (see Figure 3).

Step 7. Comparison With Other Climate Records

For this step, students are supplied with a plot of global annual-mean surface air temperature. They are asked to visually compare the two records. They can immediately see that their
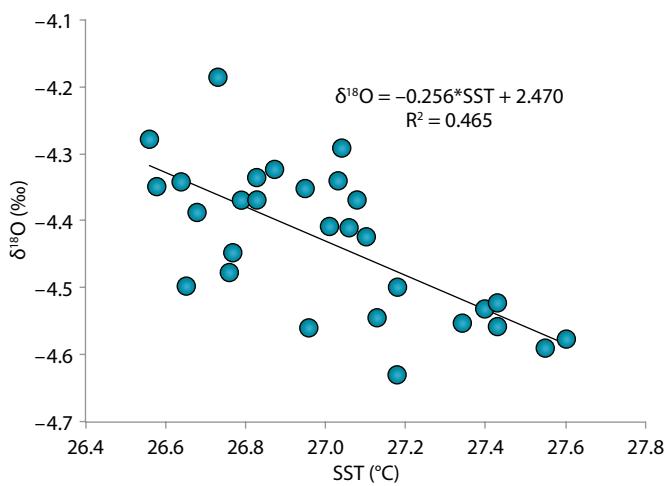

FIGURE 2. Development of the paleotemperature equation. Data from Cole et al. (2000).

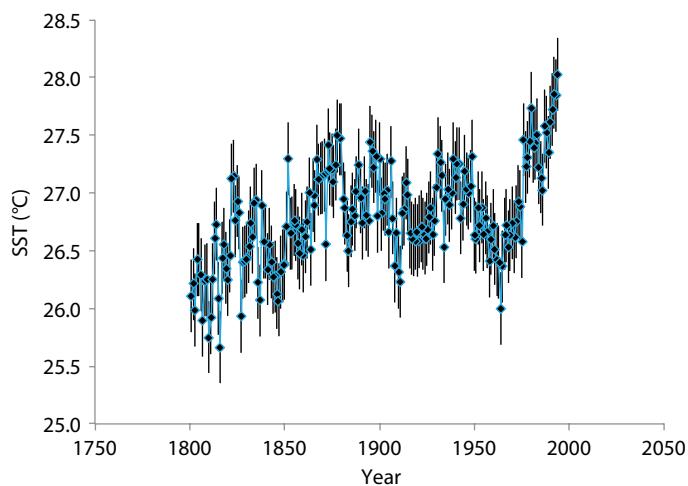$\delta^{18}O = -0.256 \cdot SST + 2.470$
$R^2 = 0.465$

FIGURE 3. Reconstructed sea surface temperature (SST) from the Malindi coral with error bars representing the root mean square error. The data show the post-industrial rise in SST, followed by stasis in the 1940s to the 1950s, and then a sharp rise in the 1970s. The profile is very similar to the global annual-mean surface air temperature available from NASA.

reconstructed data cover a longer time period than the instrumental record, and that the reconstructed SST data are similar to the global air temperature data. They are also required to interpret the variability they see in the reconstructed SST data with the error analysis in mind. This short write-up also allows the instructor to assess student understanding of the activity.

CONCLUSIONS, POTENTIAL MODIFICATIONS, AND REMARKS

This laboratory exercise illustrates that climate data can be messy, but that error analysis allows us to interpret the data in a meaningful way. In addition to working through the process for using paleoclimate proxy data, the exercise also exposes students to basic statistical approaches and forces them to use spreadsheet software, both of which are important for non-science and beginning science majors. Although aspects of this activity are simplified, it is important to leave students with an appreciation of what can be accomplished using this method. The final step, which illustrates that the coral record matches measured global annual-mean surface air temperature is simplistic, but ends the activity on a positive note, which is critical especially for non-majors. The complexities and caveats of this type of research are better covered in upper-level classes where students have a deeper understanding of the science. This activity could be enhanced for upper-level courses by, for example, including spectral analysis of the data, discussions on additional errors (e.g., analytical, sampling, time averaging), or by making this the first part of several more advanced exercises. Additionally, upper-level, or subsequent, activities could address salinity effects or biological effects. For example, students could find salinity data, convert them to $\delta^{18}O_W$, and with SST construct a model coral $\delta^{18}O$ record using aragonite paleotemperature equations (e.g., Grossman and Ku, 1986; Kim et al., 2007). They could then discuss the biological or vital effects seen in coral aragonite. Conducting this activity in the programming language R (https://www.r-project.org) would also enhance this activity. ⓒ

SUPPLEMENTARY MATERIALS
A lab handout and the Malindi (2000) Annual O18 Data are available at https://doi.org/10.5670/oceanog.2017.104.

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