

ESS 312 Geochemistry

Biogeochemistry of trace elements and stable isotopes

Why would a geochemist be interested in biology? Bones and teeth contain the common mineral hydroxyapatite (hydrated Ca phosphate). Invertebrates such as corals, land snails and plankton deposit calcium carbonate shells. Various species of bacteria utilise the energy available from oxidation-reduction reactions involving S, Fe and Mn, causing dissolution or deposition of sulfides and Fe-Mn oxide minerals. Some grasses precipitate tiny grains of silica (phytoliths) in their stems and leaves. Although the biochemistry can be quite complicated, many of the fundamental principles we've learned to apply to inorganic reactions also help us understand the chemical record contained in "fossil" materials such as bones and shell.

In this lab, we will examine trace element and stable isotope records in corals. We will discover that these simple organisms compile and archive detailed and accurate environmental information. This lab will give you a chance to explore a large and fairly complicated geochemical data set.

The data you'll work with are real, including real experimental errors and systematic problems that you will have to address. They were measured by Mike Gagan and Linda Ayliffe, at the Australian National University, on samples cut from a core drilled in mid-1994 into a living coral head (*Porites Lutea*) off Orpheus Island in the Great Barrier Reef. Mike Gagan kindly gave us access to the data. They are described in a paper he wrote in *Science* (vol. 279, pp. 1014-1018, 1998) comparing climatic conditions in the mid-Holocene (~5000 years ago) to the present day.

The coral sample was collected from a reef near Orpheus Island, at ~ 18°50' S latitude off the northeastern coast of Australia. Orpheus Island lies fairly close inshore, in the "lagoon" behind the Great Barrier Reef front. Water around the island is exchanged with the open ocean through channels and shallow openings in the reef front, but can also be affected by freshwater discharge from the Burdekin River 100 km to the south. The headwaters of the Burdekin receive monsoonal storms in the early months of the year, giving it the highest river discharge in Australia.

Before starting on the data analysis, let's consider some aspects of the chemical "system" we're working with.

Many marine organisms precipitate calcium carbonate (CaCO_3) shells. Some, such as bivalves, brachiopods and molluscs, deposit the calcite polymorph, which has a molar volume of $36.94 \text{ cm}^3/\text{mol}$. Surprisingly, other organisms such as corals deposit the polymorph aragonite, with a much smaller molar volume of $34.16 \text{ cm}^3/\text{mol}$. In the inorganic world, aragonite is found in blueschist metamorphic rocks formed at pressures greater than 4-5 kbar. Evidently organisms such as corals can use biochemical processes to manipulate the atomic arrangement of the crystalline material they deposit in their skeletons.

A related set of osmotic and enzymatic processes admit the elements these organisms need to function, and exclude other elements. However, their ability to distinguish certain trace elements from their accustomed nutrients is not perfect. Chemical analyses show that elements such as Sr, Ba and U are present in coralline aragonite in almost exactly the same proportions relative to Ca as they are in seawater. In effect, the corals' metabolic processes cannot discriminate between these elements and the Ca they use to form their carbonate skeletons. In the first part of the lab we will see that they are also hostage to the same thermodynamic principles that govern the temperature dependence of trace element substitution, and that we can use the Sr/Ca ratio in coralline aragonite as a thermometer for past ocean temperatures.

Now let's turn to the Orpheus Island data (given in the spreadsheet which you can download from the class website)

The first two columns contain a satellite-derived bi-weekly temperature record for the ocean surface in a 1° latitude x 1° longitude grid square surrounding Orpheus Island. The date (column A) assigned to each temperature measurement (column B) is in "decimal years".

(1) Make a plot of the ocean temperature variation from 1989 - 1994. Make the graph wide and not too tall and place it so you can display the chemical records beneath it.

(2) Now plot the Sr/Ca ratio (column C) on a separate graph, using the timescale in column A to assign a date to each measured sample.

The Sr/Ca ratios were measured on tiny samples cut sequentially from along the growth axis of the coral. This coral grew at 10 - 20 mm/yr. This is determined by measuring the distance between fluorescent bands in the skeleton, which result from riverine organic matter trapped in the coral skeleton. The organic matter originates from the annual floods of the Burdekin River, which usually occur during cyclone season, from about January through March. Annual growth increments are also marked by variations in skeletal density due to changes in the coral growth rate through the year. These can be counted like tree rings. However, despite these markers, our ability to assign a date to each sample cut from the coral is limited, and it is only assumed that the ~ 50 or so samples cut per annual layer correspond to successive weekly growth increments.

Scale the plot and position it beneath the sea-surface temperature (SST) record for comparison.

(3) Is Sr uptake by the coral temperature-sensitive? You can safely assume that neither the Sr or Ca concentration in seawater changes significantly through the year.

(4) Does the Sr/Ca ratio increase or decrease as temperature increases?

To understand this, write the equilibrium constant for exchange of Sr^{2+} between seawater and aragonite:



Be sure you understand that the Sr term on the right-hand side can have variable activity. It corresponds to the concentration of Sr that enters the carbonate structure for a given concentration of Sr in the surrounding seawater.

(5) By equating $a_{\text{SrCO}_3(\text{arag})}/a_{\text{CaCO}_3(\text{arag})}$ with the Sr/Ca ratio of aragonite (i.e. assuming ideal solution of Sr in aragonite), show that this equilibrium constant is analogous to the trace element distribution coefficient $K_D = (\text{Sr}/\text{Ca})_{\text{coral}} / (\text{Sr}/\text{Ca})_{\text{seawater}}$.

Now let's calibrate the Sr/Ca thermometer from the data and estimate how accurately we can measure SST.

(6) Make a "scatter plot" of SST vs the coral Sr/Ca ratio, with Sr/Ca on the x axis, from mid-1991 to mid-1994. Further back in time, the age scale assigned to the coral samples begins to get out of step with the satellite temperature observations. Including this "phase-lagged" data from the earlier part of the record would destroy the coherence between Sr/Ca and temperature.

(7) Fit a regression line through the data and obtain an expression that predicts T as a function of Sr/Ca ratio. Now apply this equation to the empty column labelled "Coral Sr/Ca temperature" to calculate a T value from each Sr/Ca measurement.

How accurate is our thermometer? Overlay the sequence of "coral temperature" estimates on your original plot of sea-surface temperature. Compare the two curves.

(8) Considering only the last three years of coral growth where the dates assigned to the samples are well-aligned with the satellite temperatures, how much of the fine-scale temperature variation does the coral record? What is the approximate sensitivity and accuracy of the Sr/Ca thermometer? Can you suggest some reasons why there may be a difference between the Sr/Ca and satellite records?

Now let's move on to the oxygen isotopic record:

Column G of your spreadsheet contains $\delta^{18}\text{O}_{\text{PDB}}$ measurements for the coral samples. Before we look at the data, let's review notation. Recall the definition of the stable isotopic delta value:

$$\delta^{18}\text{O}_{\text{sample-PDB}} = 1000 \times \left(\frac{{}^{18}\text{O}/{}^{16}\text{O}_{\text{sample}}}{{}^{18}\text{O}/{}^{16}\text{O}_{\text{PDB std}}} - 1 \right) \quad (2)$$

Remember that the " δ " value is used merely for convenience in comparing very small differences between isotope ratios. Samples with isotope ratios slightly lower than the standard give negative delta values. Samples with isotope ratios slightly higher than the standard give positive delta values.

(9) Rearrange the formula above to give the ${}^{18}\text{O}/{}^{16}\text{O}$ ratio of a sample in terms of its δ value.

(10) Now apply your formula to column H, giving the ${}^{18}\text{O}/{}^{16}\text{O}$ ratio of each sample. Your formula will contain the isotopic ratio of the PDB standard, which is given on the sheet. Notice the minuscule range of isotopic compositions and the number of digits that you need to show the isotopic differences between samples!

(11) Adapt equation (2) to derive $\delta^{18}\text{O}_{\text{SMOW}}$ values for the samples, as though they had been measured with respect to the SMOW (Standard Mean Ocean Water) standard.

The last three years of the record correspond to a period of severe El Niño drought in northeastern Australia. During this period we can safely assume that the coral was growing in seawater with the "standard" isotopic composition ($\delta^{18}\text{O}_{\text{SMOW}} = 0.0 \text{ ‰}$). Can we develop an oxygen isotope thermometer that predicts water temperatures during this period?

We start with an equation calibrated by O'Neill et al. (1969) for the equilibrium constant of the inorganic isotope exchange reaction between calcite and water:



$$1000 \ln \alpha_{\text{cc-water}} = 2.78 (10^6 / T^2) - 3.39 \quad (3)$$

Recalling from lectures that we can write $1000 \ln \alpha_{\text{cc-water}} = \delta^{18}\text{O}_{\text{cc-SMOW}} - \delta^{18}\text{O}_{\text{water-SMOW}}$, and that the δ value of the water in this case = 0.0, we can re-write equation (3) as:

$$\delta^{18}\text{O}_{\text{coral-SMOW}} = 2.78 (10^6 / T^2) - 3.39 \quad (4)$$

hence ...

$$T = \frac{1}{\sqrt{(\delta^{18}\text{O}_{\text{coral-SMOW}} + 3.39)/(2.78 \times 10^6)}} \quad (5)$$

Apply this equation to one or two of the $\delta^{18}\text{O}_{\text{coral-SMOW}}$ values and confirm that it gives results which are $\sim 10^\circ\text{C}$ too high. Don't forget that equations (3) - (5) will give you T in K, whereas the SST record is in $^\circ\text{C}$!

The reason that O'Neill's "geothermometer" doesn't work in this case is that additional steps in the biochemical pathway the coral uses to deposit calcium carbonate are also isotopically selective. In general, the final aragonite (or calcite) precipitated by an animal is offset from the expected inorganic value by a few parts per thousand ("per mil"). The offset is called a "vital effect" and differs from one organism to another. To allow for this effect, we can modify equation (5) to read:

$$T = \frac{1}{\sqrt{(\delta^{18}\text{O}_{\text{coral-SMOW}} + 3.39 + V)/(2.78 \times 10^6)}} \quad (6)$$

where V is the offset in the coral δ value, or "vital effect" in ‰.

(12) Apply equation (6) to column J on your sheet, referring (as a fixed cell) to the "vital effect" in cell J3. This will allow you to experiment with the fit between your data and the other temperature estimates as you assign different values to the "vital effect".

(13) To calibrate the coral thermometer and determine the appropriate vital effect offset, make a graph of the $\delta^{18}\text{O}$ -based temperature estimate vs the Sr-Ca temperature estimate from 1994 back to mid-1991. We will look at the pre-mid-1991 O isotope data next. (Note that comparison with the Sr/Ca record avoids the problem of registration between the coral measurements and the satellite-based temperature record).

(14) Fit a line to the data (using the regression option in the "Chart" menu) and adjust the value of the "vital effect" to obtain a slope of 1. (Set the regression intercept to zero). By obtaining a slope of ~ 1 , you have found the vital effect that gives the best match between the Sr/Ca and $\delta^{18}\text{O}$ thermometers. You should be able to get a slope between 0.99 and 1.01, giving a near-perfect match between the temperature estimates!

(15) Now make a plot showing your Sr/Ca and $\delta^{18}\text{O}$ temperature estimates for the whole record.

(16) How well does the ^{18}O thermometer work during the drought years 1992-1994?

Notice that in the years before and after 1991 the summertime water temperature is fairly consistent at $\sim 28^\circ\text{C}$, and agrees well with the satellite data and the Sr/Ca thermometer. However, in the summer of 1991 the oxygen isotope thermometer reports that seawater temperatures rocketed to an extremely high value of 34°C . Neither the satellite data nor the Sr/Ca thermometer agree – they both report a normal 28° summer. It looks like something went wrong with the oxygen isotopes that year.

(17) Explain why the oxygen isotope thermometer gives too high a temperature in 1991. Hint – to explain this you will have to re-examine a fundamental assumption we made in order to get from equation (3) to equation (4) above, and remember that rainwater usually has a lower $\delta^{18}\text{O}$ value than seawater.

(18) Compare the $\delta^{18}\text{O}$ values of the coral from the warmest weeks in 1990 and 1992 (these will be the lowest $\delta^{18}\text{O}$ values) with the minimum $\delta^{18}\text{O}$ value in 1991. What is the approximate difference in $\delta^{18}\text{O}$?

The obvious source of ^{18}O -depleted water capable of causing such a shift is monsoonal rainfall discharged by the Burdekin River. Monsoon rainfall is generally isotopically "light" - in this case with a $\delta^{18}\text{O}$ value of approximately -8‰ relative to SMOW.

(19) Assuming the flood plume affected the $\delta^{18}\text{O}$ value of a volume of seawater $\sim 100\text{ km} \times 20\text{ km} \times 30\text{ m}$ deep, calculate how many liters of Burdekin river runoff would have been required to shift the $\delta^{18}\text{O}$ value of this water by -1‰ .

(20) Assume that the flood responsible lasted for a week. What was the average daily discharge?

Concluding note: There are two more columns of data (columns V and W on your sheet). Column V shows the $\delta^{13}\text{C}$ measurements of the coral samples. Column W is a corrected timescale for the coral samples which all but eliminates the misfit with the satellite temperature record. This timescale was derived by an ingenious method which allows a few specific points on the $\delta^{13}\text{C}$ record to be assigned a calendar date with an accuracy better than ± 1 week, and also pegs the coldest week in each record at mid-August. The record is then interpolated between these tie points. You can read about the method in the article from *Geology* cited on the spreadsheet.

Optional: You may be interested to look at the $\delta^{13}\text{C}$ record (off to the right in the spreadsheet) and compare it to the $\delta^{18}\text{O}$ record you've been working with. Does it look as though $\delta^{13}\text{C}$ is strongly controlled by temperature? What would be the major drawback of trying to develop a $\delta^{13}\text{C}$ "thermometer". Can you suggest some other factors that might influence the $\delta^{13}\text{C}$ of coral skeletal carbonate?