Paleothermometry and Paleoclimate

Reading:
White’s lecture #35 on paleoclimate

Motivation:
One of the important questions we ask about past earth environments is, “What was the temperature?”…. in the oceans, in the atmosphere, in hydrothermal systems that formed ore deposits
...As you might imagine, finding evidence in the rock record to answer this is not easy. Isotopes give us one of the few ways to do this.

Guide Questions:
If we know the difference in some stable isotope ratio between two phases, why does this have the potential to give us paleotemperature information?
How does $\delta^{18}O$ change in calcite precipitated from water as temperature increases (assuming the $\delta^{18}O$ of the water remains the same)?
Do living organisms produce calcite with oxygen isotope fractionation equal to that measured in inorganic laboratory experiments? Which organism is most heavily used in studies of past ocean temperatures?
Foramifera $\delta^{18}O$ values from the last glacial maximum were a few per mil greater relative to those of today in the same locations. What two effects contribute to this?
Can $\delta^{18}O$ values of silica and phosphate materials produced by living organisms in the oceans and lakes be used as paleotemperature indicators? Do they work as well as carbonate materials? What controls $\delta^{18}O$ values in lacustrine carbonate material? Does it record temperature, or other factors, or both?
What controls $\delta^{18}O$ values in cave carbonate material (speleothems)? Does it record temperature, or other factors, or both?

Paleothermometer Theory

General idea:
If we have two phases in isotopic equilibrium, the fractionation between them is usually a function of temperature. Thus, if we can measure or otherwise constrain the two isotope ratios, we should be able to calculate the temperature at which the equilibrium occurred.

Usually, the equilibrium occurs during precipitation of minerals from solution. The crystals then are closed systems thereafter, and do not get reset (unless they recrystallize).

1. Calcite precipitated from water.
Equilibrium fractionation for oxygen isotopes between water and calcite during calcite precipitation is temperature dependent. The idea of using this effect to determine paleotemperatures was first published by Urey (1947). Urey, later a Nobel laureate, did this work at U. of Chicago.

Calcite-water fractionation is strongly temperature dependent:
$$\delta^{18} = 15.36 - 2.673\sqrt{(16.52 + T)} \quad \text{(Epstein et al., 1953)}$$
or
$$T \ (°C) = 17.04 - 4.34\delta^{18} + 0.16\delta^{18}^2 \quad \text{(Horibe and Oba, 1972)}$$
Similar fit equations exist for silica and phosphate. See fig. 24.12 in Faure, 1986.

Recently, it has been noticed that the biological fractionation of the P causes trouble with the paleotemperature interpretations.

Colder temperature $\rightarrow$ greater fract. $\rightarrow$ calcite is isotopically heavier. So greater delta values means colder temperature (all other things being equal)

**Marine Paleoclimate records**

What materials are present in ocean sediments to record these T changes? Most carbonate material produced in the oceans is produced biologically. The equilibrium $\delta^{18}O$ fractionation is close to that predicted by inorganic experiments, but is altered somewhat by “vital effects”. These vary, so some species producing high-quality records and other do not.

- Foraminifera: Small animals that build shells (“tests”). Used most frequently.
- Coccoliths, Corals, Molluscs: Lower quality records?

Recrystallization of the materials is a big problem. Varies from core to core and is a gerater problem with older sediment (e.g., it is very difficult to get good paleoclimate records $>50$ Ma)

What do we see in the ocean seds record?

- Figure above is the SPECMAP compilation- an average of many marine records
  - Beware, SPECMAP is a highly contrived average
    - Timing of changes adjusted to make curves fit Milankovitch theory
    - Amplitude scaled to allow “stacking” of data
  - See also fig. 24.10 in Faure or Fig. 35.3 in White.

20,000 years ago, forams about 3.2 per mil heavier than today (note that many cores show much less change, as little as 1.0‰). This could be caused by:

1. colder temperature- if it were all due to this, temp change would be 12°C!
2. more ice in the polar ice caps (removal of light water from the system)
It turns out, it is both. Recent research gives:
- 1.1‰ for the water’s $\delta^{18}O$ change in Pacific, 0.8‰ for the water’s $\delta^{18}O$ change in Atlantic
- This was worked out by looking at the $\delta^{18}O$ in the pore waters.


Previous estimates: Ice volume was well known, but isotopic composition of the added ice during glacial was uncertain.

The two low-latitude records in Faure Fig. 24.10 show only a small temperature effect. It’s mostly driven by ice volume.

Analytical details: Very quick analysis.
1. Usually, foraminifera species are used. Common in most parts of the ocean. CaCO$_3$ “tests”, or shells/ skeletons
2. Pick individual species to minimize impact of “vital effects”
3. Maybe clean up with weak acid to reduce recrystallized calcite
4. Load into automated device (Kiel device). Reacts sample with acid, gives off CO$_2$.
5. Clean up gas (remove H$_2$O) and send to mass spec
6. In mass spec, rapid sample-standard alternation gives very good control over drift in the instrumental discrimination
7. Resulting uncertainty: about 0.1 per mil, maybe better for the best labs.
8. Automated analysis: 30 samples a day or more

Can look at benthic vs. planktonic forams: bottom water versus surface water. Sometimes, the differences are fairly great. See fig. 2-14 from Brownlow or fig. 24.11 from Faure, 1986. Bottom water in the pacific has changed by several per mil during the cenozoic. This is probably not an ice effect- too large, and the planktonic forams don’t change much

2. $\delta^{18}O$ in silica (from radiolarians and diatoms) works well also, but is more work to analyze.
   - Fig. 24.12 from Faure, 1986.
   - Too bad the slopes of silica and calcite fractionation ($\delta^{18}O$ vs. T) are the same: If they were different, we could use a mineral-mineral paleothermometer and not have to worry about the $\delta^{18}O$ of the water.

3. Phosphate:
   Same $\delta^{18}O$ vs. T temperature dependence here too. So still no min.-min. paleothermometer
   BUT, perhaps we could use the following:
   Mammal teeth or bones- no temperature effect, body temp. is constant
   Vs. fish teeth- $\delta^{18}O$ depends on the water temp.
   Problems with biological processing of phosphate cause some problems.

**Continental paleoclimate records:**

Continental paleoclimate records are perhaps more important than marine ones, because we need to know how climate change affects the places we live and grow food.
1) Carbonate precipitated as:
   a. Ostracods in lakes (much like forams)
   b. Speleothems in caves and other groundwater-related calcite
Here, the $\delta^{18}O$ of the lake or cave water is possibly widely variable. We expect the hydrologic balance to change with climate. (e.g., lakes in Nevada). Difficult to distinguish the $\delta^{18}O$ shift due to T change from that due to potentially large $\delta^{18}O$ shift in parent water resulting from hydrologic changes (in rain-out, evaporation from lake surface, etc.).

See figs. 2 and 3 from Winograd et al., Science, 258, 10/92. Calcite from wall of a spring known as Devil’s Hole in Southern Nevada, USA.

Combination of $\delta^{18}O$ measurements and U-series age dates, fig. 2
   Note that calcite is about 2‰ LIGHTER during COLD TIMES
   - This is the reverse of the normal.
   - In Nevada, glacial climates were less dry relative to today’s very dry climate. So we might expect that there was less evaporation from soils and therefore the groundwater had lower $\delta^{18}O$ values.

Importance: This record is much better dated than the ocean record.- U-series dating
   I guess forams are not amenable to good U-series dates.
Timing of the abrupt deglaciations seems to contradict the idea that changes in the earth’s orbit (Milankovitch cycles) cause glacial-interglacial oscillation. Some people used this to argue that the Milankovitch theory is incorrect. Others said that the Devil’s hole record was flawed in some way (e.g., bad U-series dates). I don’t know what the latest conclusion is.

3) Records in soil carbonate, tree rings and clays
These record changes in $\delta^{18}O$ of the soils water, among other things.
   Evaporation is an added complication.
$\delta^{18}O$ and $\delta^{D}$ together in tree cellulose may give information about source water $\delta^{18}O$ and $\delta^{D}$ and humidity at the same time- recent research, Xiaohong Feng, Dartmouth College.