Oxygen-18, ice volume, and temperature.

Notes:

1. The calcium carbonate in a foraminifer shell were formed at 25°C in today’s ocean ($\delta^{18}O_{SMOW} = 0$ ‰), what is the $\delta^{18}O$ of the shell on the SMOW scale? Also, estimate its $\delta^{18}O$ value on the PBD scale.

Assume that the fractionation factor between carbonate and water is given by $1000*\ln(\alpha_{cc-water}) = 2.78*10^6/T^2 - 2.89$ (T in K; valid between 0 and 500 °C).

Reminder: by definition:

$$\alpha_{cc-water} = \frac{^{18}O/^{16}O}_{carbonate}/^{18}O/^{16}O_{water}$$

$$\delta^{18}O_x / 1000 = \left(\frac{^{18}O/^{16}O}{^{18}O/^{16}O}_{SMOW} - 1\right) * 1000 \text{‰}$$ (i)

$$\delta^{18}O_{water} = \left(\frac{^{18}O/^{16}O}{^{18}O/^{16}O}_{SMOW} - 1\right) * 1000 \text{‰}$$ (ii)

Rearranging (i) and (ii) we obtain:

$$^{18}O/^{16}O}_{carbonate} = \left[\delta^{18}O_{carbonate}/1000 + 1\right] * \left(\frac{^{18}O/^{16}O}{^{18}O/^{16}O}_{SMOW}\right)_{SMOW}$$ (iii)

$$^{18}O/^{16}O}_{water} = \left[\delta^{18}O_{water}/1000 + 1\right] * \left(\frac{^{18}O/^{16}O}{^{18}O/^{16}O}_{SMOW}\right)_{SMOW}$$ (iv)

Dividing iii by iv the SMOW term cancels:

$$\frac{^{18}O/^{16}O}_{carbonate} / {^{18}O/^{16}O}_{water} = \left[\delta^{18}O_{carbonate}/1000 + 1\right] / \left[\delta^{18}O_{water}/1000 + 1\right]$$ (v)

$$= \frac{\delta^{18}O_{carbonate}+1000}{\delta^{18}O_{water} + 1000}$$

$$= \alpha$$

Rearranging gives us

$$\delta^{18}O_{carbonate} = a[\delta^{18}O_{water} + 1000] - 1000$$ (vi)

$$= 1.0288*1000 - 1000 = 28.8 \text{‰}.$$}

So the $\delta^{18}O_{carbonate}$ is 28.8‰ on the SMOW scale.
Finally, if the carbonate is in equilibrium with water at 25°C, then by definition it approximately 0‰ on the PDB scale. As many of you noted, the SMOW and PDB scales are offset by roughly 24‰, as I stated in class. Why the difference? The SMOW PDB scales are based on measurements of the CO\textsubscript{2} in equilibrium with water and carbonate, respectively, rather than the absolute abundances of 18O and 16O in the water and carbonate themselves. There is a 4‰ fractionation associated with the dissolution of carbonate in phosphoric acid (to produce CO\textsubscript{2}). Hence the difference in the “expected” and “observed” answers.

2. Show that the simple mass balance equation below is valid (where \( M = \text{mass} \))

\[
(M_{\text{ice}} \ast (\delta^{18}\text{O}_{\text{ice}}+1000))_{\text{LGM}} + (M_{\text{ocean}} \ast (\delta^{18}\text{O}_{\text{ocean}}+1000))_{\text{LGM}} = (\text{Mass}_{\text{ocean}} \ast (\delta^{18}\text{O}_{\text{ocean}}+1000))_{\text{TODAY}}
\]

This is straightforward algebra with the approximations that 1) there is a negligible amount of ice present today and 2) the mass of water is approximately equal to the mass of pure H\textsubscript{2}\textsuperscript{16}O water [that is, \( M_{\text{water}} = \text{number of H}_{2}\text{H}_{2}\text{O molecules times the molecular weight of H}_{2}\text{H}_{2}\text{O (} \sim \text{18 g/mol)}\].

Solution:

2. Making the very reasonable approximation that all water on earth is either in ice or in the ocean, and that there is a negligible amount of ice on land today, then:

\[
M_{\text{ice}} + M_{\text{ocean}} = M_{\text{today}} \quad (i)
\]

Furthermore, we can replace this with a mass balance of number of \( {^{16}}\text{O} \) atoms in H\textsubscript{2}O: (call this \( N \)):

\[
N_{\text{ocean}} = N_{\text{today}} - N_{\text{ice}} \quad (ii)
\]

and recognize that the mass of water in each reservoir is directly proportional to the number of \( {^{16}}\text{O} \) atoms (call this proportionality \( x \)) if we ignore the very small contribution from \( {^{18}}\text{O} \) and \( {^2}\text{H} \) which amount to less than 1/10 of 1% of the total.

Note that this works because the ratio \( N_{i}/M_{i} \) for each reservoir is the same number. \( M = N \ast \text{atomic mass of oxygen} + 2\ast N \ast \text{atomic mass of hydrogen} \), so \( N/M = 1/(\text{atomic mass of oxygen} + 2\ast \text{atomic mass of hydrogen}) \).

We must also have mass balance for \( {^{18}}\text{O} \). Let “\( n \)” the number of \( {^{18}}\text{O} \) atoms in each reservoir:

\[
n_{\text{ocean}} = n_{\text{today}} - n_{\text{ice}} \quad (iii)
\]

Obviously if (c) if valid, then so is:

\[
n_{\text{ocean}}/N_{\text{ocean}} = n_{\text{today}}/N_{\text{today}} \ast N_{\text{today}} - n_{\text{ice}}/N_{\text{ice}} \ast N_{\text{ice}} \quad (iv)
\]

and since \( N/M \) is a constant for each reservoir, then:

\[
n_{\text{ocean}}/N_{\text{ocean}} = n_{\text{today}}/N_{\text{today}} \ast M_{\text{today}} - n_{\text{ice}}/N_{\text{ice}} \ast M_{\text{ice}} \quad (v)
\]
But $n_{ocean}/N_{ocean}$ is just the $^{18}O/^{16}O$ ratio in the ocean, and similarly for “today” and “ice”.

So:

$$(^{18}O/^{16}O)_{Ocean} * M_{ocean} = (^{18}O/^{16}O)_{today} * M_{today} - (^{18}O/^{16}O)_{ice} * M_{ice} \quad (vi)$$

Now divide everything by

$$(^{18}O/^{16}O)_{SMOW}$$

and note (from question 1 above) that we can replace the ratio

$$(^{18}O/^{16}O)_{SMOW} \text{ with } [\delta^{18}O_{SMOW} + 1000]/[\delta^{18}O_{SMOW} + 1000] \quad (vii)$$

But $\delta^{18}O_{SMOW} = 0$, so

$$(^{18}O/^{16}O)_{SMOW} = \delta^{18}O_{SMOW}/1000 + 1 \quad (viii)$$

$$(\delta^{18}O_{today}/1000 + 1) * M_{ocean} = (\delta^{18}O_{today}/1000 + 1) * M_{today} - (\delta^{18}O_{ice}/1000 + 1) * M_{ice} \quad (ix)$$

and finally multiplying by 1000 give us:

$$(\delta^{18}O_{today} + 1000) * M_{ocean} = (\delta^{18}O_{today} + 1000) * M_{today} - (\delta^{18}O_{ice} + 1000) * M_{ice} \quad (x)$$

3. Adkins et al. (2000) used pore water measurements from marine sediments to determine that the last glacial maximum (LGM ~the time of the most recent high $\delta^{18}O$ value in the benthic forams), the $\delta^{18}O$ of the deep ocean was +1‰ compared with today. Assuming that this value is representative of the entire ocean at the LGM:

a) calculate the deep ocean temperature change at the LGM compared with today, if the $\delta^{18}O$ of benthic forams was 1.13 ‰ greater than today.

b) use this to calculate the average $\delta^{18}O$ of the ice sheets at the LGM, assuming average ocean depth is 4000 m and that sea level at the LGM was 150 m lower.

c) use this information to estimate and plot the sea level variation and surface ocean temperature throughout the last 780,000 years, using the data in forams.txt on the class web site (under “assignments”). For simplicity, assume that the relative contributions of sea level and temperature to the benthic $\delta^{18}O$ value remain constant.

**Solution:**

a) If the $\delta^{18}O$ of the deep ocean was 1‰ greater than today, and that of benthic forams was 1.13‰ greater, then this corresponds to a change due-to-temperature of 0.13 ‰. Using the equation give in question (1) for the relationship between $a$ and temperature, one can easily show that the sensitivity of $\delta^{18}O$ of calcium carbonate to temperature is $-0.25‰/°C$. Therefore a change of 0.13‰ corresponds to 0.13/0.25 = -0.52°C. That is, it was approximately 0.5° colder in the glacial deep ocean.

b) From question (2) above, we have

$$(\delta^{18}O_{ice} + 1000) * M_{ice} = (\delta^{18}O_{today} + 1000) * M_{today} - (\delta^{18}O_{ocean} + 1000) * M_{ocean} \quad (i)$$

$$\delta^{18}O_{ice} = ((0 + 1000) * M_{today} - ((1 + 1000) * M_{ocean})/M_{ice} - 1000 \quad (ii)$$
The mass must scale approximately with the depth so

\[ \frac{M_{\text{ocean}}}{M_{\text{ice}}} = \frac{3850}{150} \text{ if sea level was 150 m lower, and } \frac{M_{\text{today}}}{M_{\text{ice}}} = \frac{4000}{150} \] (iii)

Therefore

\[
\delta^{18}O_{\text{ice}} = (1000 \times 4000/150) - 1001 \times 3850/150 - 1000 \]

(vi)

\[ = -25.7 \text{%} \]

\[c) \text{ Given the stated assumption that the fractional contribution of temperature to } \delta^{18}O_{\text{benthic}} \text{ is also constant (I will use } 0.32/1.32 = 0.24 \text{ from (a) above), then:}
\]

\[ \delta^{18}O_{\text{deepocean}} = (1 - 0.24) \times \delta^{18}O_{\text{benthic}} \text{ and} \]

we can calculate sea level from (b, equation ii), replacing “\(M_{\text{ice}}\) with sea level.

\[ \delta^{18}O_{\text{ice}} = ((0 + 1000) \times 4000 - ((\delta^{18}O_{\text{deepocean}} + 1000) \times (4000 - \text{sea level}))/\text{sea level} - 1000 \]

If we further assume that \(\delta^{18}O_{\text{ice}}\) is constant then this can be rearranged to obtain

Relative Sea level = (4000 \times \delta^{18}O_{\text{deepocean}})(\delta^{18}O_{\text{ice}} - \delta^{18}O_{\text{deepocean}})

And for surface temperature, we have simply:

Surface temperature change = 4 \times (\delta^{18}O_{\text{deepocean}} - \delta^{18}O_{\text{planktonic}})

The graph below shows the results for the last 150,000 years.