Chapter 6

BIOGENIC CARBONATES – OXYGEN

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Chapter 6

**BIOGENIC CARBONATES – OXYGEN**

### 6.1 Introduction

Carbonates are one of the most studied phases in stable isotope geochemistry. They are found at all but the oldest chronological intervals, and the information from oxygen and carbon isotopes can be used to infer paleotemperatures, paleoproductivity, circulation patterns, water depth, etc. Oxygen isotope ratios of marine carbonates most often provide information about water temperature and ice volume, while carbon isotopes provide information about biological productivity conditions. Because of the vastness of the field, and the different information obtained from each isotope, they are presented in separate chapters (6 and 7), although some overlap is unavoidable.

The potential use of biogenic carbonates as a paleoclimate indicator played a pivotal role in the development of stable isotope geochemistry. The discipline as we know it today was spawned by Harold Urey, who recognized the possibility of determining temperatures of ancient oceans from the preserved oxygen isotope ratios of biogenic carbonates deposited by marine organisms. But, for meaningful application to paleoceanography, these temperatures had to be determined to within ± 0.5°C, which required increasing the precision of the mass spectrometer analysis by an order of magnitude. Accomplishing this engineering feat not only made possible the development of the oxygen isotope paleotemperature scale, but allowed for the subtle variations in isotopic compositions of other light elements to be recognized as well.

Harold Urey was on his 1947 lecture tour sponsored annually by the Royal Society of London. He was speaking about the physical fractionation of stable isotopes between ideal gases and simple aqueous solutions. He finished his lecture at ETH Zürich and accepted a question from Paul Niggli, the renowned Alpine geologist. Niggli asked if the fractionation between carbonates and water might be large enough and sensitive enough to temperature variations so that the carbonates could be used for reconstructing ancient marine temperatures. The story goes that Urey thought a second, said that he didn’t know, but that it seemed reasonable. Later calculations led him to believe that there was promise in this avenue of research. But numerous hurdles presented themselves before he would be able to apply his paleothermometer. Urey needed a more precise mass spectrometer. He needed a method to reproducibly convert carbonates to a gaseous phase that he could analyze in the mass spectrometer. And he needed to quantify the fractionation between carbonate and water as a function of temperature. Putting together a remarkable team of young scientists, including Samuel Epstein, Charles McKinney, John McCrea, Harold Lowenstam, and Harmon Craig, he was able to work out the details in record time, and clear the hurdles necessary to bring the paleotemperature technique to fruition.

The basic idea for the carbonate paleothermometer is as follows: The fractionation between calcite and water is a function of temperature. So the difference in the δ¹⁸O values of calcite and water can be used for determining the temperatures of the ocean at the time the carbonate formed. In addition to the analytical problems mentioned above, there were several other concerns that needed to be addressed: 1) Did the marine organisms precipitate their shell material in isotopic equilibrium with the ocean water, or
is there a biological ‘vital effect’ that causes organisms to precipitate calcite out of isotopic equilibrium with water? Realize that many marine organisms precipitate aragonite shells rather than calcite, even though aragonite is not stable at the Earth’s surface. Perhaps the isotopes are out of equilibrium as well. 2) Have the carbonates preserved their oxygen isotope composition over the millions of years since their initial deposition, or have they undergone diagenesis? 3) Was the δ¹⁸O value of the ocean at the time the calcite formed the same as it is today? We only measure the δ¹⁸O value of the carbonate. The δ¹⁸O value of the water from which it formed is almost always inferred. All of these problems, noted by Urey in 1948, are addressed in the following sections.

6.2 The Phosphoric Acid Method

6.2.1 A major breakthrough

The quest for reliable methods to pretreat shells and to make precise oxygen isotope analysis of their constituent carbonate was described by Harold Urey as “the toughest chemical problem I ever faced.” The development of the phosphoric acid method of carbonate analysis by his doctoral student John McCrea (1950) was a seminal chapter in the history of stable isotope geochemistry. This method, only slightly modified in the ensuing years, involves converting carbonate to CO₂ gas by reaction with phosphoric acid. The CO₂ is then analyzed in the mass spectrometer. The technique remains the protocol for analysis of carbonates in stable isotope laboratories the world over. Carbonate analysis today is routine, but the Urey group faced major obstacles to overcome this chemical challenge in 1949.

McCrea initially tried liberating CO₂ from carbonates by thermal decomposition

\[ \text{CaCO}_3 + \text{heat} \rightarrow \text{CaO} + \text{CO}_2 \]  

Despite good chemical yields (i.e., the reaction went to completion), the extracted CO₂ had scattered δ¹⁸O values, far outside the required reproducibility of ± 0.1‰ and the approach was abandoned. McCrea next turned to acid decomposition

\[ 2\text{H}^+ + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2 \]  

The procedure involves reacting the carbonate with an acid in an evacuated vessel, purifying, collecting and finally analyzing the CO₂ gas as a measure of the δ¹⁸O value of the original carbonate. The only common acids whose vapor pressures of water and other compounds are low enough to use in a vacuum system are concentrated H₂SO₄ and H₃PO₄. It soon became apparent that 100% H₃PO₄ was the acid of choice. The early workers were concerned about contamination from organic matter present in commercial acids because fragments of organic molecules made in the source of the mass spectrometer could have masses in the 43-47 range that would interfere with determinations of 46/44 and 45/44 ratios. Thus the acid recipe (see Box 6.1) finally adopted by the Chicago group assured that no contamination arose from the specially prepared acid. The ‘100% phosphoric acid’, common in many laboratories around the world is light green (from addition of chromium oxide), very viscous and known to spontaneously crystallize at any time. Most likely, some of the procedures developed by the early workers are unnecessary or have become obsolete by the commercial
availability of pure H$_3$PO$_4$, but most researchers take the approach ‘if it ain’t broke, don’t fix it’, so the acid ritual survives. Some laboratories have found that commercially available 85% phosphoric acid can be vacuum distilled to obtain a 100% phosphoric acid, which apparently works just fine.

<table>
<thead>
<tr>
<th>Box 6.1: Preparation of 100% H$_3$PO$_4$ for stable isotope analysis of carbonates - Recipe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Pour 2.5 L (one bottle) of commercial 85% phosphoric acid into a large Pyrex beaker that is placed on a hotplate in a fume hood.</td>
</tr>
<tr>
<td>2. Slowly stir in about 1.4 kg of analytical grade P$_2$O$_5$. The ensuing reaction is exothermic and should be done with care.</td>
</tr>
<tr>
<td>3. Add a spatula-tip quantity of CrO$_3$. The solution turns pale yellow.</td>
</tr>
<tr>
<td>4. Slowly raise the temperature to 200$^\circ$C and heat for about 7 hours. The solution turns green.</td>
</tr>
<tr>
<td>5. Raise the temperature to 220$^\circ$C and heat 4-5 hours.</td>
</tr>
<tr>
<td>6. Stop heating when the density @25$^\circ$C = 1.9, the density of 100% H$_3$PO$_4$.</td>
</tr>
<tr>
<td>7. When the acid cools, stir in 3mL of H$_2$O$_2$.</td>
</tr>
<tr>
<td>8. Store in brown glass bottles with rubber seals. 500 mL is a convenient size.</td>
</tr>
<tr>
<td>9. Age for about one month before using.</td>
</tr>
</tbody>
</table>

**Notes**

1. The density must be > 1.8. [H$_3$PO$_4$] > 100% is desirable as excess P$_2$O$_5$ readily takes up water. Solutions with [H$_3$PO$_4$] > 103%, however, are more prone to crystallize, and inhibit diffusion of CO$_2$ out of the acid into the head space.
2. The acid is very corrosive and will destroy the markings on glass thermometers. Use a glass sleeve or other means of protecting these markings.
3. The acid turns green as a result of reduction of Cr(VI) to Cr(III) by organic matter present in the commercial acid.
4. H$_2$O$_2$, a reducing agent in this case, is added to reduce residual Cr(VI) to Cr(III).
5. Avoid exposing the acid to air for extended periods, as it is hygroscopic.
6. No one understands what happens during the aging period, but aging seems to be necessary. At least, it can’t hurt!

The phosphoric acid and calcite are reacted at a constant temperature. Most calcium in solution is present as calcium phosphate ion pairs (CaPO$_4$)$^-_2$ and CaHPO$_4$. The water produced is taken up by excess P$_2$O$_5$ to form H$_3$PO$_4$. During extraction of the CO$_2$, a very small amount of some other volatile compounds, mostly water vapor, is also liberated and is separated from the CO$_2$ by judicious use of cryogenic traps.

6.2.2 Acid Fractionation Factors

In both thermal and acid decompositions of carbonates, the liberated CO$_2$ contains all the carbon but only 2/3 of the oxygen in the carbonate (equations 6.1 & 6.2). As a consequence, the $\delta^{13}$C value of the evolved CO$_2$ and parent carbonates are identical, but the oxygen isotope ratios are different due to a fractionation between the CO$_2$ gas and
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Oxygen from the carbonate that remains dissolved in the acid. $^{18}\text{O}/^{16}\text{O}$ ratios are always higher in liberated $\text{CO}_2$ than in the original carbonate (related to the stronger C=O double bonds in $\text{CO}_2$ gas). The magnitude of the oxygen isotope fractionation is probably controlled by both kinetic and equilibrium effects. A so-called acid fractionation factor must be applied to the $\text{CO}_2$ analysis to obtain the oxygen isotope ratio of the carbonate. The oxygen isotope fractionation between evolved $\text{CO}_2$ and a given carbonate is given by

$$
\alpha_{\text{CO}_2-\text{carbonate}} = \frac{1000 + \delta^{18}\text{O}_{\text{CO}_2}}{1000 + \delta^{18}\text{O}_{\text{carbonate}}}$$

and is constant at a given temperature of reaction. The $\alpha$ value becomes smaller with increasing temperature. Because of the temperature effect, $\text{H}_3\text{PO}_4$-carbonate reactions must be run at a constant temperature. For many years these reactions were carried out at 25°C, but temperatures as high as 90°C are commonly used today to a) ensure that reactions are complete in the relatively short times used in automated systems and b) to reduce the solubility of $\text{CO}_2$ in the acid allowing for smaller samples to be analyzed. It makes no difference what temperature is used because the method is calibrated to

Table 6.1: Acid Fractionation Factors.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Temperature (°C)</th>
<th>Fractionation factor $\alpha$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite - $\text{CaCO}_3$</td>
<td>25</td>
<td>1.01025</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1.01049</td>
<td>4</td>
</tr>
<tr>
<td>‘sealed vessel’</td>
<td>50</td>
<td>1.009311</td>
<td>2</td>
</tr>
<tr>
<td>‘common acid bath’</td>
<td>50</td>
<td>1.009002</td>
<td>2</td>
</tr>
<tr>
<td>aragonite - $\text{CaCO}_3$</td>
<td>25</td>
<td>1.01034</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1.01107</td>
<td>4</td>
</tr>
<tr>
<td>dolomite -$\text{CaMg(CO}_3$</td>
<td>25</td>
<td>1.01109</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>50-100</td>
<td>4.23 + 6.65$\times10^5$/T$^2$</td>
<td>3</td>
</tr>
<tr>
<td>siderite - $\text{FeCO}_3$</td>
<td>50-150</td>
<td>3.85 + 6.84$\times10^5$/T$^2$</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>25, 50</td>
<td>1.01017, 1.01016</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>8.5-62</td>
<td>19670/T – 36.27</td>
<td>7</td>
</tr>
<tr>
<td>ankerite - $\text{CaFe(CO}_3$</td>
<td>50-150</td>
<td>4.15 + 6.68$\times10^5$/T$^2$</td>
<td>3</td>
</tr>
<tr>
<td>magnesite - $\text{MgCO}_3$</td>
<td>50</td>
<td>1.01160</td>
<td>5</td>
</tr>
<tr>
<td>strontianite - $\text{SrCO}_3$</td>
<td>25</td>
<td>1.01049</td>
<td>1</td>
</tr>
<tr>
<td>witherite - $\text{BaCO}_3$</td>
<td>25</td>
<td>1.01097</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1.01063</td>
<td>4</td>
</tr>
<tr>
<td>smithsonite - $\text{ZnCO}_3$</td>
<td>25</td>
<td>1.01130</td>
<td>1</td>
</tr>
<tr>
<td>otavite - $\text{CdCO}_3$</td>
<td>25</td>
<td>1.01145</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1.01124 – 1.01369</td>
<td>4</td>
</tr>
<tr>
<td>rhodocrosite - $\text{MnCO}_3$</td>
<td>25</td>
<td>1.01012</td>
<td>1</td>
</tr>
<tr>
<td>cerussite - $\text{PbCO}_3$</td>
<td>25</td>
<td>1.01013</td>
<td>1</td>
</tr>
</tbody>
</table>

1 (Sharma and Clayton, 1965); 2 (Swart et al., 1991); 3 (Rosenbaum and Sheppard, 1986); 4 (Kim and O’Neil, 1997); 5 (Perry and Tan, 1972); 6 (Carothers et al., 1988); 7 (van Dijk et al., 2018)
international reference standards reacted at the same temperature as the samples. As long as temperatures are kept constant, and an $\alpha$ value is determined based on accepted standards, measured (and corrected) $\delta^{18}O$ values of samples will be consistent with IAEA-accepted scales (SMOW or PDB), and will be comparable lab-to-lab.

For many years, the values of acid fractionation factors were unknown, because the $\delta^{18}O$ values of the carbonate themselves were unknown. All that could be measured was the $\delta^{18}O$ value of the evolved CO$_2$ gas. Sharma and Clayton (1965) and others later finally measured the $\delta^{18}O$ value of the total carbonate by the method of fluorination. Once the baseline $\delta^{18}O_{\text{carbonate}}$ value was determined, it became a trivial exercise to determine the $\alpha$ value at any temperature. Fractionation factors have values on the order of 1.010 $^{xx}$ (10 per mil) and are different for different carbonates (Table 6.1). Remember that the $\alpha$ value in equation 6.3 is not the equilibrium CO$_2$-calcite fractionation, which is closer to 1.0109‰. It is the kinetic fractionation that occurs during dissolution of the calcite. As long as the fractionation is constant, however, it does not matter if it is equilibrium or not.

6.2.3. Applicability

The H$_3$PO$_4$ method is one of the most robust used in stable isotope geochemistry and is applicable to the analysis of all carbonates. Some carbonate minerals, like magnesite and smithsonite, require relatively high reaction temperatures because they react so slowly at room temperature. Using even the most basic extraction line, $\delta^{18}O$ and $\delta^{13}C$ values of samples weighing about 1 mg or more can be measured with a precision of better than 0.1 and 0.05‰, respectively. With sophisticated extraction systems connected directly to the mass spectrometer (on-line systems), samples as small as tens-to-hundreds of micrograms can be analyzed routinely with the same precision. A few authors have reported that grain size and carbonate/acid ratio can significantly influence the isotopic analyses (Wachter and Hayes, 1985; Barrera and Savin, 1987; Al-Aasm et al., 1990; Swart et al., 1991), but these effects are generally eliminated when the reactions are carried out at relatively high temperatures. Contamination by organic matter, chlorine- and sulfur-bearing compounds, or inclusions of other carbonates pose more serious problems (Charef and Sheppard, 1984). Organic matter is a particular concern for modern samples and should be removed before analysis. This can be done a number of ways including roasting the sample in a stream of helium, treatment with mild oxidizing agents, and exposure to an oxygen plasma. The small amount of organic matter present in fossil carbonate generally has no effect on the measured $\delta^{13}C$ and $\delta^{18}O$ values of the carbonate, but the samples are routinely sent through a pretreatment step in any case. One can always analyze treated and untreated splits of a given sample to ascertain if pretreatment is necessary. Recently, continuous flow techniques have been developed for rapid analysis of small samples (see Section 2.8.3). These automated peripherals are standard additions offered by all mass spectrometer manufactures.

---

1 The fluorination reaction is approximated by $2\text{CaCO}_3 + 4\text{F}_2 \rightarrow 2\text{CaF}_2 + 2\text{CF}_4 + 3\text{O}_2$. All O$_2$ is extracted from the carbonate and measured for $\delta^{18}O$ value, hence the ‘total carbonate’ value.

2 With a known $\delta^{18}O$ value of the carbonate (from fluorination) and a measured $\delta^{18}O$ value of evolved CO$_2$ gas from phosphoric acid digestion, the $\alpha$ value could be determined by plugging these values into equation 6.3.
6.3 The Oxygen Isotope Paleotemperature Scale

Armed with an improved isotope ratio mass spectrometer and the phosphoric acid method of carbonate analysis, the Chicago group faced the challenge of calibrating a temperature scale based on the temperature-sensitive oxygen isotope fractionation between biogenic carbonate and ocean water. They had no established reference standards at that time nor knowledge of the fractionation factors for the analytical methods they employed: acid-carbonate reaction for carbonates (McCrea, 1950), and CO₂-H₂O equilibration for waters (Cohn and Urey, 1938). Undaunted, Samuel Epstein addressed the problem by making a simple empirical calibration. He collected shells and water from cold and warm water environments. He also cultured shells in laboratory aquariums. He then measured the difference between the oxygen isotope composition of CO₂ liberated from the carbonate by phosphoric acid at 25°C and CO₂ equilibrated with the ambient H₂O at 25°C. Fortuitously, this difference for normal marine calcite and ocean water is very small at 25°C. The point is illustrated in Fig. 6.1 using a δ¹⁸O value of water = 0‰ as an example. The α(CO₂ - H₂O) value at 25°C is 1.0412 (O’Neil et al., 1975), corresponding to a δ¹⁸O value of CO₂ equilibrated with ocean water (δ¹⁸O = 0‰).

![Fig. 6.1. Difference in the δ¹⁸O value of acid liberated CO₂ from Pee Dee belemnite (PDB) and that equilibrated with SMOW. Delta values are shown on the SMOW scale (normal) and PDB scale (italic). In either case, the difference between the CO₂ gases measured in the mass spectrometer is only on the order of 0.2‰. Note: This difference between CO₂ equilibrated with SMOW and acid liberated CO₂ from a carbonate in equilibrium with SMOW at 25°C would be almost 2 ‰.](image)

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The difference between the δ¹⁸O value of CO₂ and H₂O varies slightly in relation to the δ¹⁸O value of the phases relative to the standard, although the α value does not. For example the α(CO₂ - H₂O) value at 25°C is 1.0412. If the δ¹⁸O value of the water is 0, then the coexisting CO₂ is 41.2‰ heavier. However, if the δ¹⁸O value of the water is 20‰, for example, then the δ¹⁸O value of the CO₂ is 62.02, 42.0‰ heavier. The α value is the same in both cases.
at 25°C of 41.2‰ on the SMOW scale. The standard PDB calcite is 30.91‰ heavier than SMOW (Coplen et al., 1983). Finally, the $\alpha$(CO$_2$ – calcite) value for acid fractionation is 1.01025 at 25°C (corresponding to $\Delta^{18}$O$_{CO_2}$ of 10.57 for $\delta^{18}$O$_{cc}$ = 30.91‰ on SMOW scale (0‰ on PDB scale) or $\alpha_{CO_2}$-SMOW = 1.03091×1.01025=1.04148), so that the CO$_2$ liberated from PDB calcite has a $\delta^{18}$O value of 41.48‰. When all of these corrections are made, the difference between the $\delta^{18}$O value of CO$_2$ equilibrated with SMOW and that liberated by phosphoric acid digestion from PDB is only 0.28‰. Craig (1965) reported a value of 0.22‰ for this difference. The discrepancy is due to an earlier $\alpha$(PDB-SMOW) = 1.03086, compared to the now accepted value of 1.03091. In fact, it shouldn’t be surprising that the $\delta^{18}$O values of the CO$_2$ liberated from the calcite and the CO$_2$ equilibrated with the water are almost the same. The CO$_2$ equilibrated with the water is in equilibrium with the water at 25°C, and the acid fractionation liberates a CO$_2$ that is close to equilibrium with the calcite. So if the calcite is in equilibrium with the CO$_2$, and the water is in equilibrium with the CO$_2$, and the calcite and water are in equilibrium with each other, then both CO$_2$ samples should have the same $\delta^{18}$O value. The variation in the CO$_2$ ‘differences’ is due to the temperature of equilibration between the calcite and the water from which it forms.

To calibrate the temperature dependence of the isotopic fractionation between biogenic carbonate and water, Epstein made analyses of shell material from attached or sedentary organisms including mussels, brachiopods, red and black abalone, and limpets that were living in the cool waters off Puget Sound (lowest T = 7.4°C), in the temperate waters of Monterey Bay, and in warm waters along the coast of Baja California (highest T = 20°C). Two higher temperature calibration points at 29 and 31°C were obtained from analyses of calcite regenerated by a cultured snail and a bivalve (Pinna sp.) to repair holes that were purposely drilled into their shells. Oxygen isotope analyses of the natural and cultured carbonate samples in addition to the ambient waters provided adequate data to establish an empirical calibration for the fractionation between biogenic calcite and water over the range of temperatures found in modern oceans. After publication of the paleotemperature equation in 1951, the authors recognized that the helium roasting procedure used to remove organic matter from the shells had introduced extraneous oxygen to the system. Epstein et al. (1953) corrected the procedure and published the following revised equation which became the classic paleotemperature equation:

$$t(°C) = 16.5 - 4.3(\delta_c - \delta_w) + 0.14(\delta_c - \delta_w)^2$$  \hspace{1cm} 6.4.

In this equation, $\delta_c$ is the $\delta^{18}$O value of CO$_2$ liberated from reaction between the carbonate and phosphoric acid at 25°C, and $\delta_w$ is the $\delta^{18}$O value of CO$_2$ equilibrated with water at 25°C. Their data and polynomial fit are reproduced in Fig. 6.2. There is no theoretical basis to the form of equation 6.4; it is simply a best-fit of the data to a second order polynomial. Over the 0-30°C range of modern ocean waters, $\delta^{18}$O (PDB) values of marine carbonates range from about +3 to −3‰. The first measurements of paleotemperatures using this method are shown in Figure 6.3.

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4 Interestingly, the temperatures obtained from the Pee Dee belemnite (PDB standard) correspond to a temperature of 15.8°C, assuming a $\delta^{18}$O value of the ocean of 0 on the SMOW scale.

5 These warm water organisms were cultured in a tank in Bermuda.
Both $\delta_c$ and $\delta_w$ are the values relative to the same working standard of the mass spectrometer. CO$_2$ from PDB was the working standard used in the early days at the University of Chicago. Be aware that water analyses normalized to the SMOW scale and carbonates normalized to the PDB scale cannot be used in the classic paleotemperature equation, but the equation can be rewritten in a form appropriate for the delta values of the calcite and water relative to the PDB and SMOW scales respectively:

$$t(°C) = 15.75 - 4.3(\delta^{18}O_{c-PDB} - \delta^{18}O_{w-SMOW}) + 0.14(\delta^{18}O_{c-PDB} - \delta^{18}O_{w-SMOW})^2$$

6.5.

Keep in mind that $\delta_c$ on the PDB scale is about 30 per mil lower than $\delta_c$ on the SMOW scale. In the first case (eq. 6.4), one uses the isotopic composition of CO$_2$ released from the carbonate by acid decomposition and, in the second case (eq. 6.5), the isotopic composition of total oxygen in the solid carbonate is reported (relative to PDB). To emphasize this important point that is frequently misunderstood, recall that $\delta^{18}O$ of the PDB carbonate standard is 0‰ on the PDB scale and 30.91‰ on the SMOW scale (Eq. 2.21). This difference seldom poses a problem in the practical world because the PDB scale for oxygen isotope analyses is restricted to analyses of carbonates only. The SMOW scale is used to report oxygen isotope analyses of every other substance including water.

The temperature dependence of the calcite-water system was revisited when O’Neil et al. (1969) measured the equilibrium oxygen isotope fractionation between inorganic calcite and water from 0 to 500°C using precipitation methods at low temperatures and recrystallization methods at high temperatures. The results of these
experiments were fit to an equation\(^6\) whose form has a basis in statistical mechanics:

\[
1000 \ln \alpha_{\text{calcite-water}} = \frac{2.78 \times 10^6}{T^2} - 2.89
\]

where \(T\) is in Kelvins. Note that the \(\delta\) values of calcite and water must be on the same scale (either PDB or SMOW) for this equation. The results are virtually indistinguishable from Epstein’s earlier work. Kim and O’Neil (1997) synthesized carbonates at low temperature and developed a similar, though slightly different fractionation equation:

\[
1000 \ln \alpha_{\text{calcite-water}} = \frac{18.03 \times 10^3}{T} - 32.42
\]

The additive term originally published was \(-3.39\). This number was later corrected to \(-2.89\) after recognition that an error was made in a mass spectrometer correction factor.

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\(^6\) The additive term originally published was \(-3.39\). This number was later corrected to \(-2.89\) after recognition that an error was made in a mass spectrometer correction factor.
(Tarutani et al. (1969) obtained identical fractionations as Kim and O’Neil at 0 and 25°C). The difference between the O’Neil ’69 vs Kim and O’Neil ‘97 results was explained by Kim and O’Neil as a result of kinetic factors that occur during synthesis. Their data result in a smaller fractionation that the earlier O’Neil et al. work. In contrast, Coplen (2007) came to the opposite conclusion. He measured the δ18O values of vein calcite and water from Devils Hole, Nevada. His empirical estimate gives a 1000lnα value of 28.09±0.13 at 33.7°C, significantly larger than the experimental data. He argued that kinetic effects result in laboratory fractionations that are smaller than equilibrium, a conclusion supported by a more recent work by Watkins et al. (2015). It their study, Watkins et al. synthesized calcite in the presence of dissolved bovine carbonic anhydrase, a catalyst that minimized isotopic disequilibrium between all the dissolved species CO2, H2CO3, HCO3− and CO32−.

Fig. 6.4. Comparison of the calcite (aragonite)-water fractionation curves from various authors. Each has the same temperature dependence, but the absolute values are slightly different. Data sources: (Epstein et al., 1953; O’Neil et al., 1969; Grossman and Ku, 1986; Kim and O’Neil, 1997; Coplen, 2007). (The Kim and O’Neil and O’Neil et al. curves are only strictly valid for δ18Owater = 0‰.)

What is clear from Fig. 6.4 is that the precision of an oxygen isotope temperature estimate can be as high as ±0.5°C but, given the uncertainties in the calibration and also the standardization, the accuracy is considerably lower. The empirical calibration of Epstein et al. seems to work for natural samples. Slowly precipitated cave calcites appear to have larger fractionations that biogenically-formed samples. It may be fortuitous that the empirical and experimental calibrations give reasonable temperatures for natural assemblages. What is clear is that relative temperature differences are accurate, and reliable estimates of temperature change are generally what is desired in palaeoclimate studies.

Many organisms deposit aragonite in their shells, so it is important to know if different polymorphs of CaCO3 have significantly different oxygen isotope properties.
From limited experimental data, Tarutani et al. (1969) determined an inorganic aragonite-calcite fractionation of 0.6‰ at 25°C. While this fractionation is relatively small, as expected for two such similar minerals, it is significant in terms of paleotemperature determinations. That is, the paleotemperature equation developed for calcite is not appropriate for shells made of aragonite. Grossman and Ku (1986) empirically determined the aragonite-water fractionation between living organisms and seawater over a temperature range of 4-20°C (Fig. 6.4). Their equation, presented in terms of δ¹⁸O aragonite on the PDB scale and δ¹⁸O water on the SMOW scale for mollusks is given by

\[ T(°C) = 21.8 - 4.69(\delta^{18}O_{\text{aragonite}} - \delta^{18}O_{\text{water}}) \]

Equilibrium dolomite-water fractionations are larger than those for calcite-water. At 25°C, the Δ¹⁸O dolomite-calcite value is ~4‰, decreasing with increasing temperature. The dolomite-water equilibria is given by (Horita, 2014)

\[ 1000ln\alpha = 3.14(±0.02) \times 10^6/T^2 - 3.14 (±0.11) \]

### 6.4 Factors Affecting Oxygen Isotope Paleotemperatures

The carbonate paleotemperature equation has three variables; δ¹⁸O_carbonate, δ¹⁸O_water and temperature (t). We estimate t from the measured δ¹⁸O_carbonate value and an assumed δ¹⁸O_water value. The validity of the t estimate depends on a number of factors, already recognized by Urey early on (1948): 1) The δ¹⁸O_water value at the time of calcite growth: The δ¹⁸O values of the ocean have undoubtedly changed in the past due to glacial – interglacial periods. Over the long term, the δ¹⁸O values of the oceans appear to be buffered by hydrothermal interaction with the seafloor (Chapter 5), but the level of fluctuation is not known. Isolated basins, or shallow seas could be perturbed from the normal marine value by evaporation or influx of fresh water. We know that ancient carbonates have low δ¹⁸O values, supporting (but in no way proving) that the δ¹⁸O value of the ancient ocean was lower than today. 2) The degree to which the δ¹⁸O values of carbonates have been altered: Even low temperature diagenesis can alter the δ¹⁸O value of a carbonate due to the ease of dissolution in fresh waters. Great care is taken to avoid the effects of diagenesis, but no foolproof method exists to prove a lack of diagenesis. The low δ¹⁸O values of ancient carbonates are equally explained by diagenesis as by changing ocean composition. 3) The degree to which the carbonates precipitated in equilibrium with water: It is known that some organisms (e.g., corals) secrete carbonate that is not in isotopic equilibrium with water. This so-called ‘vital’ effect must be also be considered.

#### 6.4.1 Variations in δ¹⁸O of ocean water in space and time

We have seen that variations in oxygen isotope compositions of surface waters in modern oceans arise from both evaporation and influx of fresh water. These processes must be taken into consideration when working with the carbonates formed in the near-surface environment, or planktic organisms, especially in samples from shallow epicontinental seas or restricted marine basins where influx of fresh water and evaporation could have caused large isotopic shifts. The problem can be at least partly
addressed because oxygen isotope values and salinity are generally correlated (Chapter 5). For fossil materials, therefore, it is sometimes possible to estimate the $\delta^{18}O$ value of the ocean if an independent estimate of salinity can be made from salinity-dependent cation ratios in the carbonate (Carpenter and Lohmann, 1992), from Sr/Ca ratios (Beck et al., 1992; DeVilliers et al., 1994) or by some other means.

The Quaternary period presents a unique problem in that we have to deal with fluctuating $\delta^{18}O_{\text{ocean}}$ values related to glacial-interglacial cycles. On a time scale of tens of thousands of years, the $\delta^{18}O$ value of the entire ocean mass changed when isotopically light water was transferred from the ocean to continental ice sheets. Numerous isotopic studies have shown that during periods of advance and retreat of continental glaciers, $\delta^{18}O$ values of marine carbonate changed repeatedly and in a regular manner. Are the isotopic shifts due to changing ocean temperature or changing composition of the ocean related to growth of ice sheets? When the temperature of seawater decreases, the fractionation between carbonate and water increases (lower temperature, larger fractionation), so that organisms should precipitate carbonate with higher $\delta^{18}O$ values. At the same time, however, when temperatures decrease, ice caps grow, removing light water from the ocean and increasing the $\delta^{18}O_{\text{ocean}}$ value. Both effects – lowering temperature and raising the $\delta^{18}O$ value of the ocean – will cause the $\delta^{18}O$ values of carbonates to increase. We cannot tell *a priori* if high $\delta^{18}O$ values in glacial times are due to lower ocean temperatures or larger ice caps. Emiliani (1955, 1966) attempted to deconvolute this problem by analyzing carbonates that were precipitated in warm-water regions of the Caribbean and equatorial Atlantic (Fig. 6.5). He reasoned that temperatures would be relatively constant in the Central Atlantic, so that changes in the secular isotope record would be related to changes in the $\delta^{18}O$ values of the oceans and not temperature. He therefore, interpreted the regular variations in oxygen isotope ratios of the carbonates as a record of changing ice volumes.

This conclusion was reaffirmed in a later series of works by Shackleton and Oddyke (1973; 1976) using $\delta^{18}O$ values of benthic and planktic foraminifera from the western tropical Pacific. Following Emiliani’s reasoning, they assumed that deep waters – generated at high latitudes and buffered by the presence of ice – have relatively constant, near-freezing temperatures. Variations in the $\delta^{18}O$ values of deep (benthic) foraminifera should therefore track the isotopic composition of the ocean. They found that deep (benthic) and shallow (planktic) foraminifera had the same secular isotopic patterns, offset only by a constant amount related to their relative temperature differences. The magnitude of the isotopic variations were therefore related to changes in the ocean’s isotopic composition and not temperature.
The usefulness of measuring coeval benthic and planktic foraminifera is illustrated in a comparative chemostratigraphic study of the Central and Intermediate Pacific ocean over a much longer time interval (Fig. 6.6). The similarity and gradual increase in δ¹⁸O values of benthic and planktic foraminifera from intermediate latitudes over the past 80 million years shows that temperatures have decreased during this mostly ice-free time. In contrast, planktic foraminifera from the Central Pacific have a nearly constant δ¹⁸O value, suggesting that the surface temperatures at the more tropical latitudes have remained constant as have the δ¹⁸O values of the oceans.

6.4.2 Vital effects

Epstein’s early calibration of the paleotemperature scale was made using mollusks. Fortunately, mollusks, especially belemnites and brachiopods, tend to precipitate their carbonate shells in oxygen isotope equilibrium with ambient waters (Lowenstam, 1961) – see Carpenter and Lohmann (1995) for additional details. Some organisms secrete shells out of equilibrium with ambient water, leading to the so-called vital effect. For purposes of thermometry, it is critical to identify those organisms whose life processes always introduce an oxygen isotope offset by the vital effect and to recognize the conditions under which vital effects operate only sometimes for other organisms (e.g. foraminifera).

The commonly used planktic foraminifera often, but not always, secrete their tests in oxygen isotope equilibrium. Divergence from equilibrium is related to environmental factors including intensity of sunlight, temperature stress, nutrient supplies and the like. Thus planktic foraminifera can secrete carbonate out of equilibrium with ocean water, especially at tropical temperatures. Most benthic foraminifera, on the other hand, live in a
more uniform environment and are isotopically much better behaved. In fact, the extremely uniform temporal variations in data for certain benthic foraminifera (and corrected planktic data) allow precise correlations to be made between cores that are thousands of kilometers apart (Prell et al., 1986).

Coccoliths (single celled algae) not only deposit their calcium carbonate plates out of oxygen isotope equilibrium with environmental waters, but the magnitude of the vital effect for this class of organisms varies irregularly with both temperature and taxa. Echinoderms, corals, red algae, and certain benthic foraminifera notoriously precipitate their carbonate out of equilibrium with ambient waters (Fig. 6.7).

Over the course of 50 years or more, we have learned which species to use in oxygen isotope studies of paleoclimate and also to make sensible corrections to isotopic analysis that are predictably offset by a vital effect. Biogeochemists have even used disequilibrium deposition of carbonate to study details of life processes of modern and extinct marine organisms. Proposed explanations of the vital effect, particularly for carbon are discussed in more detail in Section 7.4.3.

6.4.3. Diagenesis

Original isotopic ratios must be preserved in carbonate shells for meaningful studies of palaeotemperature to be conducted. Reactions between biogenic carbonate and diagenetic fluids can easily erase the original isotopic record if fluid/carbonate ratios are large. During carbonate diagenesis, little or no direct isotopic exchange takes place between solid carbonates and aqueous fluids, because the rates of solid state diffusion of carbon and oxygen in carbonates at low temperatures are inconsequential (O'Neil, 1977). Carbon and oxygen isotope ratios of biogenic carbonate can be changed by two diagenetic processes: (1) addition of new carbonate by cementation, and (2) dissolution of unstable carbonate and reprecipitation of a stable mineral, normally low magnesium calcite.

Cementation is the most common diagenetic process leading to a change in the isotopic composition of a marine carbonate. Isotopic measurements of a cemented biogenic carbonate reflect mixtures of original (unaltered) and new carbonate rather than original carbonate alone. Cementation of marine carbonates commonly occurs where sediments are exposed to high-energy conditions. Because carbonate cements are abiotic, there can be no vital effect and they are likely to be deposited in both carbon and oxygen isotope equilibrium with their parent fluids. The pore waters in equilibrium with the
earliest-formed cements often are the same as marine water, so that these early cements will be in isotopic equilibrium with ocean water. Unlike many biogenic carbonates, which are often unstable aragonite or high-Mg calcite (see below), cements are generally thermodynamically stable low-Mg calcite (although this varies between ice age and greenhouse conditions due to changing ocean chemistry) and therefore not prone to recrystallization at some later time. Clearly then, cements have a high potential for providing information relating to the original isotopic composition of seawater and/or temperature.

Unfortunately, not all cements give primary information. The cementing fluid may be locally confined and not in rapid communication with the major aqueous oceanic reservoir. In such cases, breakdown of organic matter can lead to formation of cements with very low δ13C values. Secondary cements are often coarse-grained, but reflect equilibration with meteoric water. Carbonate cements are frequently large enough to sample cleanly, but infilling cements, particularly in shells of small organisms, can be analyzed separately only with very high spatial resolutions techniques, such as sophisticated micro-sampling or in situ ion probe analysis.

**Solution and reprecipitation** is a combined process that is thermodynamically driven towards a lower free energy state. For example, calcite is stable relative to aragonite, and low Mg-calcite is stable relative to high-Mg calcite. During the thermodynamically-driven chemical reactions to more stable phases, isotopic exchange will occur. Recrystallization can take place on a very fine scale (e.g. replacement reactions) such that original textures are retained despite chemical and isotopic changes. Recrystallization or neomorphism are terms used to describe the process of solution and redeposition and strictly used to describe the isochemical process of grain coarsening.

The magnitude of change in isotopic compositions of carbon and oxygen in biogenic carbonate that undergoes recrystallization depends on four factors: (1) temperature, (2) isotopic compositions of H2O and HCO3− in the fluid, (3) fluid/solid (or fluid/rock) ratio, (4) the susceptibility of the carbonate to recrystallization to a more stable phase. As an end-member case, consider a biogenic marine carbonate that recrystallizes with a tiny amount of pore water of marine composition at a temperature close to the original deposition temperature. This process cannot significantly alter the isotopic ratios of the original carbonate and indeed such recrystallization occurs in marine sediments directly after deposition. On the other hand, isotopic ratios of the same biogenic carbonate would change dramatically if it underwent neomorphism bathed in a diagenetic fluid containing a component of low δ18O fresh water that carried low δ13C soil-derived bicarbonate. In general, open-system diagenesis (high water/rock ratios) leads to loss of primary isotopic information but, if diagenetic trends in isotopic ratios are regular, it may be possible to extrapolate back to original compositions (Fig. 6.8).

The **diagenetic potential** of a mineral in a given system can be described as the tendency of that mineral to undergo reaction with a given diagenetic fluid. The greater the departure from chemical (not isotopic) equilibrium between mineral and fluid, the greater is the diagenetic potential. Several factors control the diagenetic potential of biogenic calcium carbonate, and the strongest of these is chemical composition, specifically the Mg/Ca ratio. Low-magnesium calcite is *stable* and thus relatively insoluble and nonreactive in diagenetic fluids, whereas high-magnesium calcite is *metastable* relative to pure calcite and thus is more soluble and reactive. Crystal size is
also an important parameter because small particles have relatively high surface areas and can lower the free energy of the system by dissolving and recrystallizing to larger grains. The polymorphic form of CaCO$_3$ is another important factor that controls diagenetic potential. Aragonite and vaterite$^7$ are metastable in surface environments and are highly prone to dissolution and reprecipitation to more stable calcite, particularly when exposed to fluids with a fresh water component.

Fresh water or seawater containing a meteoric component is undersaturated with respect to marine carbonates and the disequilibrium promotes dissolution. Fresh rainwater is a particularly corrosive agent to carbonates as it is slightly acidic as well. Marine carbonates exposed to such fluids, either in shallow coastal waters or on land undergo meteoric diagenesis. Aragonite and high-magnesium calcite are common metastable constituents of biogenic carbonate and react with diageneric fluids to form more stable low-magnesium calcite and a different isotopic composition.

Meteoric diagenesis almost always lowers both carbon and oxygen isotope ratios of carbonates because $\delta^{18}O$ values of meteoric waters are normally lower than those of seawater and $\delta^{13}C$ of soil bicarbonate is lower than that of seawater bicarbonate$^8$. In arid regions where evaporation is intense, meteoric waters can have positive $\delta^{18}O$ values such that meteoric diagenesis of marine carbonate could shift $\delta^{18}O$ values to higher values, although this process is rare.

Alteration patterns on $\delta^{18}O$-$\delta^{13}C$ diagrams have characteristic shapes depending on the magnitude of the various diagenetic parameters. At the onset of diagenesis in a given region, a tiny amount of water enters the system and dissolves some carbonate. The fluid/rock ratio is perforce very low at this stage and the system is rock-dominated. The bicarbonate in solution generated by

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$^7$ Measurements are made only of calcite and aragonite. Vaterite, a rare naturally occurring polymorph of CaCO$_3$, has been studied only under laboratory-controlled conditions.

$^8$ The $\delta^{13}C$ value of atmospheric CO$_2$ is -6 to -7‰ and is in near-equilibrium with marine dissolved inorganic carbon (see Chap. 7).
dissolution of solid carbonate will exchange oxygen isotopes with the water, mix with the soil bicarbonate already present in the fluid, and reprecipitate as a cement or replacement carbonate. Under rock-dominated conditions that prevail initially, newly precipitated carbonate will have isotopic ratios that are similar to those of the original carbonate. With ever increasing water/rock (W/R) ratios, both $\delta^{18}O$ and $\delta^{13}C$ values of the carbonate will decrease. But they will not change at the same rate. Oxygen is a major component of water, while dissolved carbon is only a trace component. Therefore, early diagenesis will affect the carbonate isotope ratios of oxygen far more than carbon (Brand and Veizer, 1981; Lohmann, 1988; Marshall, 1992). In effect, the W/R ratio are higher for oxygen than for carbon for the same amount of water. As diagenesis proceeds and fluid/rock ratios increase, $\delta^{18}O$ values of successively deposited carbonate (cement) become increasingly more negative while $\delta^{13}C$ values remain nearly constant. The $\delta^{18}O$ values reach a final limiting value that is controlled by the isotopic compositions of the diagenetic fluid and effective water/rock ratios. With still increasing fluid/rock ratios, $\delta^{13}C$ of ensuing cements become more negative, once again approaching a final, limiting value defined by the $\delta^{13}C$ value of the infiltrating fluid. In the context of a time sequence, a rotated J pattern develops on a $\delta^{13}C$-$\delta^{18}O$ diagram (Fig. 6.8). The data points on the upper right limb of the curve represent unaltered material. In combination with careful petrographic examination and chemical analysis, these stable isotope patterns can provide a detailed diagenetic history in a given carbonate terrane.

During diagenesis, a number of chemical changes occur and these changes can be used to identify altered and primitive portions of the carbonates. Most commonly, the concentrations of trace elements, Mn (promotes cathodoluminescence) and Fe (diminishes cathodoluminescence) of the cement increase during diagenesis under reducing conditions, and concentrations of Sr and Mg decrease. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can increase or decrease depending on the source of strontium in the local meteoric water. All these changes are specific to the conditions of diagenesis and sources of fluids, so no one geochemical tracer is completely diagnostic.

A number of strategies can be employed to circumvent and even exploit the effects of diagenesis, particularly for older material. Thick, nonluminescent portions of brachiopods and marine cements are likely to have preserved their original mineralogy, as well as chemical and isotopic compositions (Figure 6.9). Certain portions of brachiopods can and frequently do precipitate stable, low-magnesium calcite in equilibrium with seawater and, in addition, this carbonate is relatively massive and coarse grained. Analyses of nonluminescent portions of these shells can be used to determine original isotopic composition and analyses of altered portions are used to study diagenesis.

Another strategy involves specifically searching out the metastable phases. While it may seem counterintuitive, the thinking goes that if an unstable primary phase is still present, then it most likely hasn’t undergone diagenesis. Aragonite is a metastable polymorph of CaCO$_3$ at surface conditions. It is easily altered to more stable calcite. Therefore, if aragonite can be found, its very preservation implies that diagenesis has been minimal. We have two seemingly diametrically opposed philosophies at our disposal. One is to search for metastable material, such as aragonite. The reasoning is simply that if it had been altered, it would have recrystallized as stable low-Mg calcite. The other approach is to find the most stable primary material, samples that were
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precipitated as stable low-Mg calcite. Because it is already stable, it is less likely to undergo recrystallization. Obviously, this strategy is only valid if we can be sure that the carbonate originally was low-Mg calcite. A simplified schematic of acceptable samples and strategies to use in studies of the stable isotope composition of marine biogenic carbonate is given in Figure 6.10.

For samples from marine cores of Cenozoic age, both diagenesis and ambiguities in the isotopic composition of ocean water are negligible. Consequently numerous isotopic studies have been made of pristine fossils of Cenozoic age in undisturbed cores from the deep sea. In Mesozoic or older sediments, isotopic measurements are mostly limited to shelf deposits where preservation is generally poor (and the oxygen isotope composition of the water is suspect).

Early workers active in oxygen isotope paleothermometry established guidelines to assess diagenesis of their carbonates, and these guidelines are still valid today. If any of the following are true, the carbonate is more likely (though not certain) to have retained its original $\delta^{18}O$ value:

1. The skeletal material or cement is made of unstable minerals like aragonite or high-Mg calcite. They would not survive exposure to diagenetic fluids. Their survival indicates that interaction with diagenetic fluids has been minimal.
2. The skeletal material secreted by the organism is stable low-Mg calcite. Stable minerals have a low diagenetic potential.
3. There are seasonal variations in isotopic ratios along the growth direction. Recrystallization would obliterate these signals. (This point has been challenged).
4. The material has the highest $\delta^{18}O$ value in the population. Diagenesis normally lowers the $\delta^{18}O$ value.
5. The material is not luminescent. Diagenesis often introduces cathodoluminescent Mn to neoformed carbonate.

Fig. 6.9. North American Brachiopods (solid symbols) and coexisting cements (grey circles) from Carboniferous sediments. The $\delta^{18}O$ and $\delta^{13}C$ values of cements are lower than coexisting brachiopods, indicating diagenesis with meteoric water. The thick non-luminescent samples (colored symbols) tend to be the least modified by diagenesis. Modified from Mii et al. (1999)
6.4.4 Ecology of the organism

Carbon and oxygen isotope compositions of shells reflect local conditions of productivity and temperature at the time of deposition. Some organisms spend one part of their lives in one environment and other parts of their lives in different environments that can be, for example, darker, more saline, or colder. Even among the same species, larger and more robust individuals tend to build their shells in deeper, colder waters and therefore have higher $^{18}O/^{16}O$ ratios than their more fragile juvenile counterparts. Researchers must be aware of the ecology of the organisms they use if they are to interpret the stable isotope data properly. It was precisely for these reasons that the Chicago group analyzed shells of attached or sessile organisms to establish the paleotemperature scale.

![Flowchart](image_url)

**Fig. 6.10.** Schematic flowchart of common procedures for identifying diagenesis. For further information, see (Carpenter et al., 1991; Marshall, 1992; Grossman, 1994).

6.5 Applications of Oxygen Isotope Paleothermometry

Taking into account all the factors that can affect $\delta^{18}O$ values of biogenic carbonate, including the application of appropriate correction factors, it is possible to address many
important issues of oceanography and paleoclimatology using the method of oxygen isotope paleothermometry. The principles employed are generally the same, so only a few examples of applications will be given here.

6.5.1 The Quaternary

The Quaternary record is very well preserved both in terms of complete detailed stratigraphy and minimal amount of diagenesis. The glacial periods (Ice House conditions) in the Quaternary pose a complication that is nearly unique in chemostratigraphic reconstruction. Most other times in history are free of extensive glacial ice, and the $\delta^{18}O$ values of the oceans can be considered to be constant in the short term. In the Quaternary period, the $\delta^{18}O$ values of marine carbonates are affected by changes in the isotopic composition of the ocean as much as changes in temperature as already discussed in section 6.4.1.

Arguably the most important discovery made through oxygen isotope analyses of biogenic carbonate was the delineation of important details of Pleistocene glaciation. The oxygen isotope curve originally presented by Emiliani (1966) and modified in (1978) is shown in Figure 6.6. Emiliani worked on shells of pelagic foraminifera from the perennially warm waters of the Caribbean in order to avoid the problem of temperature variations as the cause of changes in $\delta^{18}O$ of the shells. Several important features of glaciation over the last 700,000 years are apparent from Fig. 6.5:

1. The patterns are saw-toothed, implying that glaciation is a slow process and that deglaciation occurs much more rapidly.
2. A periodicity of ~100,000 years in the patterns can be reasonably linked to one of the Milankovich periodicities in orbital forcing.
3. There are many more glacial/interglacial stages in the Pleistocene than previously thought.

An extremely useful method of correlating stratigraphic sections can be made from the regularities observed in the oxygen isotope record in Quaternary foraminiferal tests from all over the world oceans. The uniformity in the record stems from two facts: (1) the effect measured is primarily a change in $\delta^{18}O$ of the oceans that resulted from changes in ice volumes on land, and (2) the mixing time of the oceans is very short (~10$^3$ years). Since the early work of Emiliani, synchronous oxygen isotope stages, termed marine isotope stages (MIS) have been recognized by many workers. Odd numbers are assigned to warmer, interglacial times and even numbers to colder, glacial times. We are presently in MIS 1. There are five recognized oxygen isotope stages in the isotopic record of the last 130,000 years and substages are recognized as well, particularly in well-studied stage 5. MIS extends back over 100 cycles.

Age assignments are critical in stratigraphic work and are frequently the subject of considerable debate. A novel approach to age assignment is to assume that astronomically driven changes in climate (orbital forcing) are responsible for the waning and growth of ice sheets. Using this approach to tune several oxygen isotope records, Imbrie et al. (1984) established a reference chronostratigraphy for the late Quaternary called the SPECMAP (Spectral Mapping Project). In this work, they took the average of multiple deep sea cores tuned to the orbital forcing parameters to generate a ‘generic’
oxygen isotope record for the past 750,000 years (Fig. 6.10). The SPECMAP composite chronology is frequently used to adjust oxygen isotope records when no reliable ages are available. It is now common parlance to speak of events that occurred in a particular stage as oxygen isotope stage 2 or 5.

6.5.2 The Paleogene and Neogene (Cenozoic)

From an historical point of view, our state of knowledge of oceanographic features in the Paleogene-Neogene was greatly enhanced by oxygen isotope analyses of benthic and planktic foraminifera made in the early 1970s from marine cores. At that time sampling techniques were primitive by today’s standards, but clear patterns were nevertheless evident in the data obtained. As a point of reference, the large difference in $\delta^{18}O$ between planktic and benthic shells forming in modern oceans from low latitudes reflect the large differences in temperature between surface and bottom waters. Bottom water temperatures are established by the sinking of cold, saline waters in the Antarctic and North Atlantic Seas. But ice volumes and ocean circulation patterns change with time, and these changes are reflected in the oxygen isotope data. Few such changes are as dramatic as those that occurred in Paleogene-Neogene time.

Data for planktic and benthic foraminiferal shells separated from cores collected at several sites in the North Pacific Ocean are shown in Figure 6.6. Differences in $\delta^{18}O$ between planktic and benthic shells were relatively small in the early Paleogene reflecting a relatively small differences in surface and bottom water temperatures. The cooling at the late Eocene to Oligocene and divergence of planktic and benthic foraminifera in Central Pacific samples suggests the beginning of cold downwelling waters originating at high latitudes. The dramatic cooling in the middle Miocene are related to the circumpolar Antarctic circulation and the formation of Antarctic ice sheets.
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The huge number of analyses of Paleogene-Neogene ocean core samples results in an extremely high-resolution record for the past 50-60 million years. Zachos et al. (2001) presents a detailed compilation of Paleogene to Present stable isotope variations (Fig. 6.12). Variations on the $10^4$ to $10^5$ y time scale are related to orbital parameters, while longer-scale, irreversible variations are related to tectonic processes. Spectral fitting of the data shows a strong periodicity at 100 ky and 41 ky for samples 0 to 4 Ma, with a loss of intensity of the 100 ky band in older samples.

6.5.3. Older samples

Well-preserved deep sea cores for Cretaceous samples exist, so that the foraminifera-based record extends back that far. Most Mesozoic and all Paleozoic samples are limited to shelf deposits. These lithologies have often undergone diagenesis, and great care must be taken to retrieve unaltered samples. In addition, the $\delta^{18}O$ value of the water in a shallow shelf setting may have been affected by a large meteoric contribution, lowering the apparent ‘seawater’ value. Workers in the field have been

![Fig. 6.12. High resolution $\delta^{18}O$ curve compiled from 40 ocean core samples. Most of the data are from the benthic foraminifera taxa Cibicidoides and Nuttallides corrected for vital effect. Absolute ages are corrected to the paleomagnetic time scale. Major events are correlated with $\delta^{18}O$ values, such as the E. Eocene climatic optimum and the timing and intensity of ice sheet formation. From Zachos et al. (2001).](image-url)
careful to alleviate these problems by analyzing diagenetic-resistant material and by correlating salinity and $\delta^{18}O$ values of seawater using a temperature-salinity-density model or salinity-dependent cation ratios in the carbonate. As the age of samples increases, the uncertainties regarding diagenesis and $\delta^{18}O$ values of the ocean increase as well. Precambrian carbonates invariably have low $\delta^{18}O$ values, which can be correlated with one or more of three variables: diagenesis, low marine $\delta^{18}O$ values or warm ocean temperatures. Other stable isotope sedimentary proxies support the low $\delta^{18}O$ values of carbonates (cherts, iron formations), although the significance of the low values is still in debate.

Although extraction of the $\delta^{18}O$ value of unaltered carbonates is complicated by the effects of diagenesis, and the relationship between the $\delta^{18}O$ values of carbonates and ocean temperature is complicated by uncertainties about the oxygen isotope composition of the ocean through time, there have been a number of attempts to determine a secular curve for $\delta^{18}O$ values of marine carbonates. Figure 6.13 shows the extraordinary compilation of Veizer et al. (1999) for low magnesium calcite shells, mainly brachiopods and belemnites. High $\delta^{18}O$ values correspond to times of glaciation and generally cold conditions, and there is a diminution in $\delta^{18}O$ values of Ordovician and older samples.

![Fig. 6.13. Variations in the oxygen isotope ratio of shell carbonates. 1σ uncertainties are shown as the shaded region around the central line. Cold periods with evidence for glaciation are indicated by the shaded boxes above the curve, with ice ages illustrated with filled black boxes. Modified from Veizer et al. (1999).](image)
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6.5.4 Application to continental carbonates

Carbonates form in equilibrium with meteoric water in a number of different environments. Climatic information can be retrieved from these samples, but interpretation of the data is often complicated by the uncertainties in the δ18O values of the water forming the carbonate. The δ18O values of terrestrial (or continental) carbonates often are used to estimate the δ18O value of the meteoric water, as opposed to the temperature of formation. Samples analyzed include speleothems, lake sediments, vein calcite, travertines and soil carbonates.

Interpretations of δ18O values from terrestrial carbonates differ from those in the marine setting (Grootes, 1993). In Quaternary marine samples, high δ18O values are caused by either increasing δ18O values of the ocean due to glacial deposition on continents or lower ocean temperatures, or a combination of the two. In contrast, the δ18O values of water from lakes are primarily a function of the δ18O value of meteoric water. In the continental setting, low temperatures increase the δ18O value of carbonates. In the continental setting, cold causes the δ18O values of meteoric water to decrease (see Section 4.7.1), which in turn lowers the δ18O value of the precipitating carbonate. The effect is essentially the reverse of that seen in the marine environment.

As an example, McKenzie and Hollander (1993) measured the oxygen isotope profile in a sedimentary sequence from a varved lake in Switzerland. There is a regular decrease in the δ18O values of the lacustrine chalk from −8‰ prior to 1887 to values of close to -11‰ in modern sediments. McKenzie and Hollander attribute the lower δ18O values in the young sediments to changes in atmospheric circulation in Central Europe. Pre-1887 meteoric waters were source primarily from cold prevailing northwesterly winds with low δ18O values. The moisture source changed to one dominated by warmer westerly to southwesterly winds in modern times.

Cave deposits provide another important archive for terrestrial paleoclimate. There are dozens of magnificent oxygen isotope records of speleothem deposits. The National Climate Data Center lists over 100 isotope cave studies from all over the world (https://www.ncdc.noaa.gov/cdo/f?p=535:6:0:::::). Deep caves with poor air circulation have nearly constant year-round temperatures. Drip waters entering a cave are often at or near carbonate saturation. Two processes contribute to the precipitation of calcite inside a cave: 1) outgassing of CO2 from the drip water, and 2: evaporation, which increases the Ca2+ concentration of the fluid (Schwarcz, 2007). If CO2 loss is slow, equilibrium between the dissolved species HCO3-, CO32- and CO2 is maintained, and carbonates precipitate in carbon and oxygen isotope equilibrium with formation waters (Hendy, 1971; Schwarcz, 1986). Combined with accurate mass spectrometric uranium-series dates of the carbonates, detailed records of terrestrial climates can be obtained.

Cave records provide a long term record in a specific location. Wang et al. (2017) measured the δ18O values of the well-dated Paraíso Cave in eastern Amazonia and concluded that rainfall in the Amazon basin was lower by 58% in the last Glacial Maximum and higher by 142% in the warmest period in the Holocene 6000 years ago. These kinds of data provide continental records of paleoclimate that are unmatched by other records. The long term climatic data extractable from speleothems are illustrated by the remarkable Hulu cave in China (Fig. 6.14) which covers a time interval in excess of 70,000 years (Wang et al., 2001). The cave record follows the Greenland Ice core...
(GISP2) closely in some regards and, significantly, diverges in others. The comparison between the Greenland record and the Monsoon-driven China record allow for climatic conditions to be compared over very different regions, and demonstrate a global insolation-driven system (Cheng et al., 2006)

Fig. 6.14. Oxygen isotope record of the Hulu cave sequence (top) compared with the Greenland GISP2 ice core (bottom in blue). The Hulu cave is the combination of three stalagmites shown in different colors. Each analysis covers a period of ~ 130 y. 59 ²³⁰Th analyses were made to date the core. The Younger Dryas (YD) and Heinrich events (H1-H6) are shown by yellow bands. The glacial/interglacial and sub-glacial events are clearly evident (numbers). Similarities as well as differences between the two records allow for global climate information to be retrieved. See Wang et al. (2001) for further details.

6.6 Clumped isotope thermometry

Clumped isotope thermometry is certainly one of the most exciting developments in paleothermometry over the last decade. The thermometer is based on the fact that the non-stochastic distribution of $^{13}$C and $^{18}$O in CO$_2$ is temperature dependent (Ghosh et al., 2006) and does not require an independent estimate of the isotopic composition of the water. It is truly a ‘single mineral thermometer’. Unfortunately, during the acid digestion of the carbonate, only 2/3 of the oxygen in a carbonate is released to CO$_2$. Fortunately, any fractionation accompanying this decarbonation reaction appears to be mostly reproducible, so that the non-stochastic isotope distribution of the evolved CO$_2$ can still be used to estimate the temperature of last equilibration (Müller et al., 2017). The analytical technique is difficult and differences between laboratories and calibrations are still being worked out (e.g., Daëron et al., 2016). The theory of clumped isotope thermometry is introduced in section 3.7.

The exchange reaction governing the clumped isotope thermometer for carbonate can be expressed as (Schauble et al., 2006)
In essence, the above reaction describes the preference for $^{13}$C and $^{18}$O to ‘clump’ together (right side of reaction) relative to the randomly distributed configuration on the left side of reaction 6.8. Because the preference for the clumped configuration (~0.4% excess at room temperature) decreases with increasing temperature due to the increased entropy contribution, the excess clumped configuration varies with temperature. Results are presented in the $\Delta_{47}$ notation, where $\Delta_{47}$ is equal to the difference in the measured abundance of mass 47 ($^{13}$C$^{18}$O$^{16}$O$_2$) from that expected from a pure random (stochastic) distribution (see Eiler 2007 for details).

Applications of clumped isotope thermometry are numerous (Eiler, 2011). They have been used for climate reconstruction from cave carbonates (Affek et al., 2008), paleoaltitude reconstruction using soil carbonates (Quade et al., 2007), fluid sources along faults (Luetkemeyer et al., 2016), paleothermometry (Cummins et al., 2014) and even for martian meteorites (Halevy et al., 2011). As with any isotopic system, clumped isotopes are subject to alteration during diagenesis. In contrast to the oxygen and carbon isotope compositions, which are altered by exchange with large amounts of meteoric water, clumped isotopes can undergo simple scrambling during recrystallization (Dennis and Schrag, 2010; Winkelstern and Lohmann, 2016). In a closed system, resetting of calcite clumped isotopes occurs in excess of 100°C (Henkes et al., 2014) and dolomite resets only at significantly higher temperatures (Lloyd et al., 2017). Vital and kinetic effects must also be considered (e.g., Spooner et al., 2016). While numerous questions remain about the details of clumped isotopes, the technique has been used successfully in numerous applications and will certainly continue to grow.

The above discussion is really only half the picture. The information from carbon isotopes is complimentary to oxygen. Together, they provide far more information than either isotope alone. Chapter 7 continues with the carbon isotope story.
References


Chapter 6. Biogenic Carbonates - Oxygen


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