Multiple Isotopic Studies of Calcium Carbonate Growths in Concrete Structures

Danielle M. Schmitt

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MULTIPLE ISOTOPIC STUDIES OF CALCIUM CARBONATE GROWTHS IN CONCRETE STRUCTURES

by

Danielle M. Schmitt

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
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Department of Geosciences

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1999
ACKNOWLEDGMENTS

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I would like to thank Dr. Mark Baskaran for determining the $^{210}\text{Pb}$ ages of my samples, as well as Purdue's PRIME Lab for determining the $^{14}\text{C}$ activities of my samples.

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Danielle M. Schmitt
Secondary minerals, predominantly carbonates, forming under concrete structures have received attention in terms of their possible role in the degradation of their hosts. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses of several calcium carbonate growths collected from bridges in Michigan and New York were performed. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values clustered around $-24.7 \pm 1(\text{PDB})$ and $13.7 \pm 1(\text{SMOW})\%$, respectively. A positive $\delta^{18}\text{O}$-$\delta^{13}\text{C}$ correlation suggests kinetically driven precipitation involving atmospheric $\text{CO}_2$. $^{14}\text{C}$ activities determined for select samples support the theory that atmospheric $\text{CO}_2$ is involved in the formation of these deposits. The $\delta^{18}\text{O}$ values indicate that the oxygen in the deposits is in part derived from atmospheric $\text{CO}_2$. In addition, select samples were dated using the disequilibrium between $^{226}\text{Ra}$ and $^{210}\text{Pb}$, on the assumption that some amount of $^{226}\text{Ra}$ is incorporated and there was no initial $^{210}\text{Pb}$. The ages ranged from the 3.8 to 64 years, not unreasonable based on the actual age of the bridge. If true, this provides a means to date calcite minerals found in concrete structures.
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CHAPTER I
INTRODUCTION

Concrete is the most widely used construction material in the world. Per capita, concrete consumption may be used as an index of industrial development. Degradation of concrete is a worldwide concern. Great economic and safety implications are associated with the premature weakening of concrete infrastructures. Prevention of this degradation would be beneficial, by lengthening the lifespans of infrastructures, and requiring less revenue to repair or rebuild dilapidated structures. Safety of individuals who utilize the structures would be greatly increased with the restoration of the structures’ integrity.

Secondary carbonate minerals deposited on concrete structures may provide clues to some of the processes responsible for concrete degradation. The processes governing secondary mineralization is not well understood. This study describes the use of several different isotopic techniques to attempt to understand the processes responsible for the formation of these growths, the source of CO$_2$, as well as the ages of these growths. This information may be used to devise ways to prevent or, at the least, to retard the premature deterioration of concrete infrastructures worldwide.
Concrete is a mixture of mineral grains (ranging in size from fine sands to pebbles) and cement. The mineral grains act as the filler and usually account for approximately 75% of the total concrete volume, whereas the cement (cement paste), which acts as a binding agent, accounts for the remaining volume (Troxell et al., 1968). The most commonly used cement paste, Portland cement, is mainly composed of lime and silica. Through chemical reactions involving the lime, calcareous cements, such as Portland cement, attain the adhesive and cohesive properties required to produce concretes that posses the ability to withstand appreciable loads and adverse exposure conditions. Reactions that occur between the lime and silica components of the paste and water result in hydrated calcium silicates (Lea, 1970).

Production of Portland Cement

Natural calcareous deposits, such as limestone, can provide the three basic ingredients (lime, silica, and alumina) necessary to manufacture Portland cement. These raw materials are crushed and used to form a "raw mix" by grinding and blending the desired amounts of parent materials. The mix is then placed in a rotary kiln to be heated. This "burning" process heats the mixture until partial melting ("clinkering") according to the following reaction:
\[ \text{CaCO}_3 + \text{heat (900°C)} \rightarrow \text{CaO} + \text{CO}_2 \uparrow \]  

(1)

During the clinkering process \( \text{CO}_2 \) gas is driven off of the original \( \text{CaCO}_3 \) solid when a temperature of approximately 900°C is attained. Reactions similar to this one result in the formation of other oxides. Table 1 lists the approximate oxide composition limits of Portland cement (Lea, 1970).

Table 1

Oxide Composition Limits of Portland Cement

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Major oxides</strong></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>60 - 67</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>17 - 25</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>3 - 8</td>
</tr>
<tr>
<td><strong>Minor oxides</strong></td>
<td></td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>0.5 - 6.0</td>
</tr>
<tr>
<td>MgO</td>
<td>0.1 - 5.5</td>
</tr>
<tr>
<td>Na(_2)O + K(_2)O</td>
<td>0.5 - 1.3</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.1 - 0.4</td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
<td>0.1 - 0.2</td>
</tr>
<tr>
<td>SO(_3)</td>
<td>1 - 3</td>
</tr>
</tbody>
</table>
Description of Secondary Mineral Deposits

The concrete-hosted calcium carbonate deposits exist in several forms. Calcitic crusts can be found on the surfaces, walls, and undersides of structures such as bridges, roads, and parking structures. These crusts can be a thin coating or several centimeters thick. Stalactites, which form on the undersides of concrete structures such as bridges and parking structures, can reach lengths of 2 meters or more (Macleod et al., 1990). Flowstones, features that form beneath the dripping stalactites (in a manner similar to the formation of stalagmites), are dome-like. These domes can be up to 50 cm wide, or more and about 10 cm thick or higher. All of these features may possess distinguishable growth layers. Growth of these deposits is not limited seasonally. It is possible that these features grow year round, therefore making it difficult to decipher one year from the next.

As previously stated, these secondary deposits are comprised of calcium carbonate. It is thought that the formation of these deposits is a result of the reaction of the cement paste with H$_2$O from precipitation events and CO$_2$. It has been suggested that the Ca in the free lime (CaO) within the cement is the source of Ca in the secondary CaCO$_3$ precipitated from the structures during the degradation process (Lea, 1970).
Controversy exists regarding both the carbon and oxygen sources (Macleod et al., 1991).

Objectives of this study are to determine the sources of oxygen and carbon in these secondary minerals and to ascertain the "age-dates" of the deposits. The age-dates may provide information regarding the rate of formation of the minerals. This information may be useful in determining the mechanisms of degradation of concrete (Macleod et al., 1990, Pye and Schiavon, 1989).

Previous Work

To date, few studies have applied isotope geochemistry principles to the study of secondary mineralization in concrete environments. Macleod et al. (1991) performed a field study in Scotland, using stable isotopes of oxygen and carbon to attempt to determine the source of carbon and oxygen involved in the secondary mineralization. The following reactions were suggested:

\[
\text{CaO(s) + H}_2\text{O(l)} \leftrightarrow \text{Ca(OH)}_2(s) \tag{2}
\]

\[
\text{Ca(OH)}_2(s) + \text{CO}_2(g) \leftrightarrow \text{Ca}^{++}(aq) + \text{CO}_3^{--}(aq) + \text{H}_2\text{O(l)} \tag{3}
\]

\[
\text{Ca}^{++}(aq) + \text{CO}_3^{--}(aq) \leftrightarrow \text{CaCO}_3(s) \tag{4}
\]

The authors assumed that two-thirds of the \text{CaCO}_3-oxygen is provided by the \text{CO}_2 and one-third is provided by the formation waters (in this case
local meteoric water) involved in the reactions, as suggested by O'Neil and Barnes (1971). They concluded that the CO\(_2\) is of atmospheric origin.

Letolle et al. (1990) performed lab studies which analyzed the oxygen and carbon isotopes of calcium carbonates precipitated in waters with pH >12.5. The waters which pass through concrete structures are assumed to attain similar, or higher pH values and the carbonates precipitated on concrete structures are considered comparable with the carbonates that these authors analyzed. Field pH measurements obtained from the present study are comparable with the values obtained in this lab study.

The formation of these secondary minerals has been suggested to be similar to the formation of cave speleothems. A large number of isotopic studies involving speleothems have been performed. These studies have primarily focused on the use of carbon and oxygen isotopes to aid in the understanding of paleoclimates. However, the studies were mainly concerned with glacial-interglacial periods.

Genty et al. (1998), used radiocarbon data from two cave stalagmites (one from Slovenia and the other from Belgium) to construct a \(^{14}\)C activity time series over the past 50 years and to gain a better understanding of CO\(_2\) sources and sinks. The CO\(_2\) responsible for the formation of speleothems has been linked to atmospheric CO\(_2\), either directly or indirectly (through soil CO\(_2\)). The connection between speleothem production and atmospheric CO\(_2\), coupled with the annual laminations produced during
speleothem formation, allowed these authors to model carbon cycling in soils.

Since the advent of Accelerator Mass-spectrometry (AMS) it has become possible to analyze small quantities of samples, and therefore, CO$_2$ from individual growth laminations can be analyzed by AMS. A survey of the literature suggests that no studies have used radiocarbon to elucidate the source of CO$_2$ or to determine the mechanism responsible for concrete-hosted calcium carbonate growths. Similarly, this work appears to be the first to explore the possibility of using $^{210}$Pb/$^{226}$Ra ratios as a geochronological tool in this respect.
CHAPTER II

METHODS AND PRINCIPLES

This chapter discusses sample collection procedures and the principles and methodologies involved in the various isotopic studies performed during this study.

Sample Sites

Samples utilized in this study were obtained from Nassau Community College, Garden City, New York and west of Flint, Michigan (Figure 1). Samples from the New York site were collected from the underside of a walking overpass, from walls supporting the overpass, as well as from concrete beneath the overpass which also served as a sidewalk for pedestrians. The Michigan site was a bridge over the Shiawassee River. Samples were obtained from the underside of the bridge and from the walls beneath the bridge. This particular bridge was extremely degraded.

Sample Description and Collection Procedure

The secondary calcite minerals exist in several forms; stalactites, crusts (on the surface, underside, and sides of the structures), and
Figure 1. Sample Site Locations.
flowstones. The present study analyzed stalactite and flowstone samples (Figure 2). The stalactites analyzed range in length from 6 centimeters to approximately 50 centimeters. The flowstones are large dome-like features that form beneath the stalactites, as water drips from the stalactites to the concrete below. These features range in width from approximately 6 cm to approximately 20 cm. Their heights may be 6 cm or greater.

Ordinary straight edge razor blades served as the main excavation tool during sample collection. The stalactites were removed by cutting between the structure itself and the top of the stalactites. Small stalactites were placed in septum tubes to protect them during transport. Flowstone samples were also removed with the aid of a straight edge blade, in a manner similar to the stalactites, but removal was from the ground, not the ceiling of the structure’s underside. Flowstones and stalactites larger than the septum tubes, were wrapped in tissue paper, placed in a plastic sampling bag, if their size did not exceed the size of the bag, and then placed in ordinary cardboard boxes for protection during transport.

Isotope Studies

$^{210}\text{Pb}/^{226}\text{Ra}$

The radioactive decay of uranium-238 has served as an important chronological tool during the 20th century. Figure 3 shows the decay series of $^{238}\text{U}$ to its stable daughter, $^{206}\text{Pb}$. Both $^{210}\text{Pb}$ and $^{226}\text{Ra}$ are
Figure 2. Sketch of Stalactite and Flowstone.
radioactive daughters of $^{238}\text{U}$. If the half life of a radioactive parent is much greater than those of its daughters, secular equilibrium is propagated through the entire series. Under secular equilibrium conditions the rate of decay of the parent is equal to the rate of growth of the daughters, according to Equation 5.

$$\lambda_1 N_1 = \lambda_2 N_2 \ldots \lambda_n N_n = 1 \quad (5)$$

where $\lambda_1, \lambda_2, \lambda_n$ are the decay constants of isotopes 1, 2, and n respectively. $N$ represents the number of atoms of the respective isotopes.

Figure 3. Decay Series of $^{238}\text{U}$ to Stable $^{206}\text{Pb}$ (adapted from Faure, 1986).
The half life of $^{238}\text{U}$ is much longer than those of its daughters. Table 2 provides the half lives of $^{238}\text{U}$ and of two of its radioactive daughters of interest in the present study, namely $^{226}\text{Ra}$ and $^{210}\text{Pb}$. If secular equilibrium exists between these two daughters, then

$$\lambda_1 N_1 = \lambda_2 N_2 = 1$$

where $\lambda_1$ and $\lambda_2$ represent the decay constants of $^{226}\text{Ra}$ and $^{210}\text{Pb}$, respectively, and $N_1$ and $N_2$ represent the number of $^{226}\text{Ra}$ and $^{210}\text{Pb}$ remaining atoms, respectively.

Table 2

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half life (yrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}\text{U}$</td>
<td>$4.468 \times 10^9$</td>
</tr>
<tr>
<td>$^{226}\text{Ra}$</td>
<td>1599</td>
</tr>
<tr>
<td>$^{210}\text{Pb}$</td>
<td>22</td>
</tr>
</tbody>
</table>

Nuclides are placed in one of two categories, particle-reactive-nuclides or non-particle-reactive nuclides, based on the transport pathways taken. Particle-reactive-nuclides include isotopes that adsorb onto particles within fluids. Non-particle-reactive nuclides are soluble in
water, therefore their fate is mediated by water mass movement (Baskaran, 1999). $^{210}\text{Pb}$ is a particle-reactive nuclide and therefore adsorbs to particles present in rain water as it is transported to the surface. $^{226}\text{Ra}$ is a non-particle-reactive nuclide. It dissolves in the rain water and becomes incorporated into the crystal lattices of the secondary calcites precipitated from concrete structures.

Once the $^{226}\text{Ra}$ is trapped in the lattices it begins decaying to $^{210}\text{Pb}$ via several short-lived daughters (see Figure 3). Since $t_{1/2}\text{Ra} \gg t_{1/2}\text{Pb}$ secular equilibrium can be expected to be reached in this system. The activity ratio at any given time follows the equation:

$$
(\frac{^{210}\text{Pb}}{^{226}\text{Ra}})_t = 1 - e^{\lambda_{210}t}
$$

where $\lambda_{210} = 0.0315$ yr.$^{-1}$. Since the half life of $^{210}\text{Pb}$ is only about 22 yrs., the time frame that this method of dating is applicable to is limited to approximately 200 years. Normally, once ten half lives of a radioactive isotope have passed, the number of atoms present are beyond detection limits.

The $^{210}\text{Pb}/^{226}\text{Ra}$ analyses for the present study were performed at Texas A&M University, Galveston, TX.
Radiocarbon

Since its discovery, $^{14}$C has served as a powerful geochronometer. W. F. Libby received a Noble Prize for chemistry in 1960 for developing the $^{14}$C dating method (Faure, 1986). An understanding of $^{14}$C production and distribution in nature is required to comprehend this method of dating.

Through nuclear reactions, involving cosmic rays and atmospheric constituents (N, O, and C), thermal neutrons are produced. These neutrons, in turn, react with atmospheric constituents, during “spallation reactions”. The spallation reaction between thermal neutrons and the nuclei of stable $^{14}$N is responsible for the production of $^{14}$C, as depicted in Equation 8.

\[
{^1}_0n + ^{14}_7N \rightarrow ^{14}_6C + ^1_1H
\]  

(8)

where $^1_0n$ is the thermal neutron and $^1_1H$ is the proton emitted from the N atom. The $^{14}_6$C atoms produced are incorporated into the earth’s atmosphere by reactions with gaseous $O_2$, $CO$, or $CO_2$. The $^{14}CO_2$ molecules are quickly dispersed throughout the earth’s atmosphere.

Constant levels of $^{14}$C activity are maintained throughout the atmosphere, despite the fact that the cosmic flux, which $^{14}$C production is a function of, varies with latitude. The consistency of the $^{14}$C level in the dynamic carbon cycle is a result of steady-state conditions, i.e. the
continual production and decay of $^{14}$C. Equation 9 shows the decay of $^{14}$C to stable $^{14}$N, through the emission of a beta particle.

$$^{14}_{6}C \rightarrow ^{14}_{7}N + \beta^-$$ (9)

All living things are labeled with $^{14}$C. Plants, for example, incorporate CO$_2$ into their tissues through photosynthesis. During a plant’s life, the $^{14}$C in the plant will decay, but the continuous incorporation (through photosynthesis) of atmospheric $^{14}$CO$_2$ establishes the steady-state equilibrium. At all times during its life the plant will have a level of $^{14}$C equal to that of all living things and to that of the atmosphere. Once the carbon cycle has been cut off (i.e. the plant has died and photosynthesis has ceased) the decay of $^{14}$C present in the plant’s tissue will continue, but no further $^{14}$C will be added to the system. It is this disequilibrium that allows one to obtain a $^{14}$C date.

$^{14}$C Dating

The $^{14}$C date obtained during routine dating is determined via the following Equation:

$$t = \frac{1}{\lambda} \ln\left(\frac{A}{A_0}\right)$$ (10)

where $t$ is the amount of time elapsed since exchange with the carbon
reservoir ceased, \( \lambda \) is the decay constant of \(^{14}\text{C} \) (1.209 \times 10^{-4}, based on a half life of 5730 yrs.), \( A \) is the measured specific activity of the sample, and \( A_0 \) is the specific activity of the plant or animal when it was alive. Specific activity is reported as disintergrations per minute per gram of carbon. For the purpose of routine applications of this technique, \( A_0 \) is considered to be a constant that has not varied in the past 70,000 years.

\(^{14}\text{C} \) activity is reported with respect to an international standard. This reference value is 95% of the activity of NBS oxalic acid in AD 1950 normalized to \( \delta^{13}\text{C} = -19\%_\circ \) with respect to PDB. Equation 11 defines this value.

\[
A_{\text{ON}} = 0.95A_{\text{OX}}\left(1 - \frac{2(19 + \delta^{13}\text{C})}{1000}\right) \quad (11)
\]

The \( \delta^{13}\text{C} \) value is a result of the fractionation associated with the production of \( \text{CO}_2 \) from oxalic acid. The activity \( A_{\text{ON}} \) is dependent upon the year of measurement (y) and must be corrected for decay that occurred between 1950 and y. This correction is made via Equation 12 and results in the “absolute international standard activity”, \( A_{\text{abs}} \).

\[
A_{\text{abs}} = A_{\text{ON}}e^{\lambda(y-1950)} \quad (12)
\]

where \( \lambda = 1/8267 \text{ yr}^{-1} \).
The $^{14}$C activity of a sample can be given as:

$$A_{SN} = 0.95A_s \left(1 - \frac{2(25 + \delta^{13}C)}{1000}\right)$$  \hspace{1cm} (13)

where $A_s$ is the measured sample activity. This equation also includes the fractionation of $^{14}$C that occurs during photosynthesis. The mass difference between $^{14}$C and $^{12}$C is twice that of between $^{13}$C and $^{12}$C, hence, the $^{14}$C fractionation is taken to be twice that due to $^{13}$C. The fractionation due to $^{13}$C is assumed to be -25‰, the value observed in natural plants. In addition, there may be additional fractionation involved during the analytical procedures of sample preparation. Thus, it is desirable to determine the fractionation due to $^{13}$C in each sample that is being analyzed for $^{14}$C activity. Equation 13 incorporates this factor. Using the measured $^{14}$C activity of the oxalic acid standard and of the sample, the $^{14}$C date can be written as:

$$t = -8033 \ln \left(\frac{A_{SN}}{A_{ON}}\right)$$  \hspace{1cm} (14)

This equation assumes that, among other conditions, the year 1950 is the reference year. Hence, the age is given as “years B. P.” (B. P. being 1950 AD). Such dates are referred to as “conventional radiocarbon ages”.
Reporting of $^{14}$C Data

Since $^{14}$C is used as both a dating tool and as a tracer there are several ways in which $^{14}$C data are reported in literature (Stuiver and Polach, 1977). $\delta^{14}$C, $\Delta^{14}$C, and pM are commonly used for tracer studies.

$\delta^{14}$C is defined as the relative difference in $^{14}$C activity between the absolute international standard and the sample, corrected for age but not corrected for $\delta^{13}$C. It may also be used when age correction is not possible. Equations 15 and 16 define age-corrected and non-age-corrected $\delta^{14}$C, respectively.

$$\delta^{14}C \% = \left( \frac{A_s e^{\lambda(y-x)}}{A_{abs}} - 1 \right) 1000$$  \hspace{1cm} (15)

where $y$ is the year of measurement and $x$ is the year of growth,

$$\delta^{14}C \% = (A_s / A_{abs} - 1) 1000$$  \hspace{1cm} (16)

$\Delta^{14}$C is used to report $^{14}$C data that has been corrected for age and normalized with respect to $\delta^{13}$C. It is defined as:

$$\Delta^{14}C = \delta^{14}C - 2(\delta^{13}C + 25) (1 + (\delta^{14}C/1000))$$  \hspace{1cm} (17)
Percent Modern is the desired notation used to report $^{14}$C measurements for geochemical and $^{14}$C equilibria (the distribution of $^{14}$C in nature) studies (Stuiver, 1977). Percent Modern is defined by Equation 18.

$$pM = \left( \frac{A_{SN}}{A_{abs}} \right) \times 100$$

(18)

where $A_{SN}$ is the activity of a sample corrected for $\delta^{13}$C (Equation 13) and $A_{abs}$ is the reference value with respect to oxalic acid in 1950 AD normalized to $\delta^{13}$C=-19%o and corrected for decay which occurred between the year of measurement and 1950 (Equation 12).

Finally the relationship between $pM$ and conventional $^{14}$C age is given by:

$$t + ((y-1950)/1.03) = -8033 \ln \left( \frac{pM}{100} \right)$$

(19)

when $y =$ the year of measurement of the sample and oxalic acid.

Although for routine dating the atmospheric value of $^{14}$C activity is considered to be constant, this value has varied in the past. The level of $^{14}$C in the atmosphere during the first half of the 20th century decreased. This reduction was a consequence of the addition of dead carbon (old enough that virtually all of the original $^{14}$C had decayed) into the atmosphere as a consequence of the burning of fossil fuels. This dilution
of $^{14}$C is known as the Suess effect (Genty et al., 1998). In the 1960's atmospheric $^{14}$C activity practically doubled as a result of the addition of artificially produced radiocarbon. This artificial $^{14}$C was introduced into the atmosphere from thermonuclear reactions. The excess $^{14}$C is referred to as "bomb-carbon".

The discovery of the Suess effect and bomb-carbon has created difficulties in reporting $^{14}$C dates accurately. It has, however, made $^{14}$C a useful tracer in geochemical studies. The use of dendochronology has aided in the determination of atmospheric $^{14}$C concentrations during the past 8,000 years. From this information corrections have been developed to account for the $^{14}$C level variations.

Studies that have used the U/Th method for the dating of corals have also been useful in determining variations of $^{14}$C production in the past. The ages of corals obtained by this method are considered to be "absolute ages" since U/Th ratios are not affected by variations in cosmic flux, as $^{14}$C production is, and therefore, conventional $^{14}$C ages are. Plotting U/Th absolute ages of corals against conventional $^{14}$C ages of the corals provides information regarding variations of $^{14}$C production (Bard et al., 1990). If the plot results in a 1:1 ratio then the $^{14}$C production had not varied during the time frame in which the selection of corals lived.

In recent years the use of $^{14}$C as a tracer in geochemical studies has gained popularity. With this method, one is not concerned with the age of
the material being analyzed but with the processes that affect carbon transfer in many reservoirs. The use of \(^{14}\)C as a tracer has provided great insight into the sources and sinks of the dynamic carbon cycle. The study involving cave stalagmites, which was described in the Chapter I, is an example of how \(^{14}\)C may be used as a tracer.

Radiocarbon analyses were performed via Accelerator Mass-spectrometry (AMS) at Purdue University's PRIME Lab, Lafayette, IN.

**Stable Isotopes**

Isotopes are placed in two categories, stable and radioactive. Of the nearly 1700 existing nuclides, only approximately 260 are stable. Table 3 shows the natural abundances of carbon and oxygen, the two isotopes used in the present study. Unlike radioactive isotopes, stable isotopes do not undergo radioactive decay, and therefore do not lose energy by emitting \(\alpha\), \(\beta\), or \(\gamma\) particles. A difference in mass exists between isotopes. This difference results from the differing number of neutrons present within the nuclei of atoms with the same atomic number. It is this mass difference that results in the fractionation of isotopes during physical and chemical changes.
Table 3
Abundances of Stable Carbon and Oxygen Isotopes

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}\text{C}$</td>
<td>98.89</td>
</tr>
<tr>
<td>$^{13}\text{C}$</td>
<td>1.11</td>
</tr>
<tr>
<td>$^{16}\text{O}$</td>
<td>99.759</td>
</tr>
<tr>
<td>$^{17}\text{O}$</td>
<td>0.037</td>
</tr>
<tr>
<td>$^{18}\text{O}$</td>
<td>0.204</td>
</tr>
</tbody>
</table>

Fractionation

Fractionation is a mass dependent phenomenon, in which the lighter isotopes are separated from their heavier counterparts during physical and/or chemical processes. There are two main types of isotopic fractionation processes: (1) equilibrium fractionation and (2) kinetic fractionation.

Equilibrium fractionation results from reactions which do not involve change of the chemical species involved in the reaction, but do involve exchange of isotopic species between the reactants and the products. Equation 20 is an example of an equilibrium fractionation process.
In this process the $^{18}\text{O}$ of the liquid water exchanged with the $^{16}\text{O}$ of the gaseous $\text{CO}_2$, yet no change of chemical species resulted.

The definition of fractionation refers to the ratio of heavy isotopes to light isotopes of either a substance in two different phases or of two different substances. This ratio is referred to as the fractionation factor and is defined as: $\alpha = \frac{R_A}{R_B}$ where $R_A$ and $R_B$ are the ratios of the heavy isotopes to the light isotopes ($^{13}\text{C}/^{12}\text{C},^{18}\text{O}/^{16}\text{O}$) of phases (or substances) A and B, respectively.

Harold Urey founded the concept of applying stable isotope geochemistry principles to paleoclimate studies. He realized that the degree of fractionation in equilibrium isotope exchange processes is temperature dependent and provides a means to calculate paleotemperatures based on the $\delta^{18}\text{O}$ of $\text{CaCO}_3$ secreted by marine organisms. Calcium carbonates are enriched in $^{18}\text{O}$ by 28.6‰ relative to the water they form in, @25°C. Equation 21 is a commonly used paleotemperature equation. This relationship was determined experimentally by Epstein and Mayeda (1953) and later modified by Craig (1965):
where $\delta_c$ is the $\delta^{18}$O value of the CO$_2$ produced from the reaction of the calcite and 100% phosphoric acid at 25°C and $\delta_w$ is the $\delta$ value of the water involved in the calcite formation. The $\delta$ notation is discussed below.

Prior to this discovery, estimated paleoclimate temperatures were based on fossil and faunal information. The use of stable isotopes potentially suggests a means of estimating paleotemperatures more precisely and accurately.

Unlike processes that result in equilibrium fractionation, processes that result in kinetic fractionation are irreversible. These reactions are primarily the result of a difference in reaction rates of isotopic molecules. These reaction rates are dependent on mass. A lighter isotope reacts more quickly than its heavier counterpart due to the lighter isotope’s greater vibrational energy. Evaporation is a good example of a process that produces kinetic fractionation effects. For example, during evaporation of H$_2$O, H$_2^{16}$O will preferentially evaporate, as compared with H$_2^{18}$O, due to the lower mass of H$_2^{16}$O.

**Reporting of Stable Isotope Data**

Ratios determined for samples of interest are compared to the ratios of international standards and reported in the standard $\delta$-notation where

$$t^\circ C = 16.9 - 4.2 (\delta_c - \delta_w) + 0.13 (\delta_c - \delta_w)^2$$

(21)
\[
\delta (\text{‰}) = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 10^3
\]  
(22).

Pee Dee Belemnite (PDB) is the international standard for carbon isotopes. Although $\delta^{18}$O can be reported with respect to PDB, it is common practice to report it with respect to Standard Mean Ocean Water (SMOW). The $\delta^{18}$O\textsubscript{PDB} values can be converted to $\delta^{18}$O\textsubscript{SMOW} via the following equation:

\[
\delta^{18}\text{O}_{\text{SMOW}} = 1.03086 \times \delta^{18}\text{O}_{\text{PDB}} + 30.86
\]  
(23)

The standard practice in routine isotope analyses is to prepare internal standards that are calibrated with respect to the international standards. Inter-relationships of $\delta$ values between two standards are obtained via the following equation:

\[
\delta_{\text{sample-International}} = \delta_1 + \delta_2 + (\delta_1 \delta_2 \times 10^3)
\]  
(24)

where $\delta_1$ is $\delta$ of the sample with respect to the internal lab standard and $\delta_2$ is $\delta$ of the internal standard with respect to the international standard.

Sample Preparation and Extraction of Carbonate Samples for Stable Isotope Analysis

All stable isotope analyses were performed at Western Michigan University’s Isotope Laboratory. The carbonate samples were powdered
with a mortar and pestle. A known amount of sample (ranging from 5 to 20 mg) was placed at the bottom of a 16 x 100 mm septum tube (Vacutainer Septum Tubes, Becton Dickson & Co., Franklin Lakes, NJ 07417). A Pyrex boat (9 mm diameter, ~6 cm long) was glued to the inside of the tube and filled with approximately 2 ml of 100% phosphoric acid. The adhesive used, Elmer's Wonderplus Super Glue (Borden Inc. HPPG, Columbus, OH 43215), was determined, by Krishnamurthy and Atekwana (1997), to be chemically inert. After replacement of the septum, the tubes were evacuated with a 26 gauge needle, to a vacuum pressure of $10^{-3}$ Torr.

Once the required vacuum condition was established the tubes were placed in a water bath for half an hour, to attain thermal equilibrium at 25°C. The tubes were then tilted at such an angle to allow the $\text{H}_3\text{PO}_4$ to flow to the bottom, while the sample within remained at the tubes bottom. Great care was taken to tilt the septum tubes at this angle for two reasons: (1) to ensure that the sample remained at the bottom of the tube during contact with the acid, therefore minimizing the possibility of the effervescing action forcing any portion of the sample to be pushed towards the top of the tube and not react completely; and (2) to ensure the tubes were not taken out of the water causing the reaction to proceed at a temperature other than the desired 25°C.
The $\text{CO}_2$ gas produced by the reaction was extracted from the septum tubes, following the procedure detailed by Krishnamurthy and Atekwana (1997) and measured manometrically. The gas was collected and introduced into a Mass Spectrometer to determine the samples’ $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values with respect to PDB using NBS-19 as the main calibration standard.

Mass-spectrometry

The Mass Spectrometer

The relative difference in the ratios of the heavy isotopes to light isotopes of a sample and a standard is physically determined by a Mass Spectrometer. This machine is essentially comprised of a curved tube that is kept under high vacuum ($10^{-6}$ Torr), an ion source, a magnetic field, and ion collectors. The magnetic field is normal to the tube. The gas of interest is introduced into the ion source, where it is partially transformed into positive ions by electrons emitted from a tungsten or rhenium plate. Upon exiting the ion source the ions acquire a kinetic energy equal to:

$$1/2 \ m \ v^2 = n e V$$

(25)

where $m$ is the mass of the ions, $v$ is the velocity, $V$ is the voltage of the ionization chamber (the accelerating voltage), $e$ is the electrical charge of the electron, and $n$ is the number of electrons lost by the gas molecules.
The ions enter the tube at the same velocity. As they proceed their velocities change and they are deflected, according to their masses, due to the magnetic field that the tube is subjected to. Within the tube the ions are subjected to a force equal to $H\text{nev}$, where $H$ is the magnetic field strength.

As the ions exit the tube they are collected, according to mass, in the ion collectors. The lighter ions are collected by the first collector, the heavier ions collected in the second collector.

A double inlet Mass spectrometer allows measurements of the isotope ratios of the sample and of the reference under identical conditions. This type of Mass spectrometer possesses two gas reservoirs, one for the sample gas and one for the reference gas, each individually connected to the ion source.

**Isotopic Species of CO$_2$**

Table 4 lists the weights of different isotopic species of CO$_2$ and their relative abundance with respect to other CO$_2$ species of the same mass.

The presence of different isotopic species with the same mass causes interference during analysis. Corrections specific to CO$_2$ must be made to counteract the effects of this interference. Table 4 shows that although the mass 45 is primarily due to $^{13}\text{C}^{16}\text{O}_2$, approximately 6% of CO$_2$ with this mass is due to the $^{13}\text{C}^{16}\text{O}^{17}\text{O}$ species. The correction is obtained via the
Table 4
Distribution of Isotopic Species of CO₂ (Gat and Gonfiantini, 1981)

<table>
<thead>
<tr>
<th>Isotopic Species</th>
<th>Molecular weight</th>
<th>Relative abundance wrt all isotopic species with the same mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}\text{C}^{16}\text{O}_2$</td>
<td>44</td>
<td>100</td>
</tr>
<tr>
<td>$^{13}\text{C}^{16}\text{O}_2$</td>
<td>45</td>
<td>93.67</td>
</tr>
<tr>
<td>$^{12}\text{C}^{16}\text{O}^{17}\text{O}$</td>
<td>45</td>
<td>6.33</td>
</tr>
<tr>
<td>$^{12}\text{C}^{16}\text{O}^{18}\text{O}$</td>
<td>46</td>
<td>99.79</td>
</tr>
<tr>
<td>$^{13}\text{C}^{16}\text{O}^{17}\text{O}$</td>
<td>46</td>
<td>0.205</td>
</tr>
<tr>
<td>$^{12}\text{C}^{17}\text{O}_2$</td>
<td>46</td>
<td>0.003</td>
</tr>
<tr>
<td>$^{13}\text{C}^{16}\text{O}^{18}\text{O}$</td>
<td>47</td>
<td>negligible</td>
</tr>
<tr>
<td>$^{12}\text{C}^{17}\text{O}^{18}\text{O}$</td>
<td>47</td>
<td>negligible</td>
</tr>
<tr>
<td>$^{13}\text{C}^{17}\text{O}_2$</td>
<td>47</td>
<td>negligible</td>
</tr>
<tr>
<td>$^{12}\text{C}^{18}\text{O}_2$</td>
<td>48</td>
<td>negligible</td>
</tr>
<tr>
<td>$^{13}\text{C}^{17}\text{O}^{18}\text{O}$</td>
<td>48</td>
<td>negligible</td>
</tr>
<tr>
<td>$^{13}\text{C}^{18}\text{O}_2$</td>
<td>49</td>
<td>negligible</td>
</tr>
</tbody>
</table>

following equation:

$$\delta^{13}\text{C} = \left(1 + \frac{2R_{12}}{R_{13}}\right)\delta_{45}^{13} - \frac{R_{17}}{R_{13}}\delta^{18}\text{O}$$  \hspace{1cm} (26)
where $R_{13} = ^{13}\text{C}/^{12}\text{C}$, $R_{17} = ^{17}\text{O}/^{16}\text{O}$, and $\delta_{45}$ is the value provided by the Mass Spectrometer. A similar correction can be made for the interference from the species that comprise 0.2% of the 46 mass. This correction is obtained via Equation 26.

$$\delta^{16}\text{O} = \frac{[R_{18}(1 + R_{13} + 2R_{17}) + R_{13}R_{17}]\delta_{46} + (R_{18} - R_{17})R_{13}\delta^{13}\text{C}}{R_{18}(1 + R_{13} + R_{17}) + R_{13}R_{17}/2}$$

(27)

where $R_{18} = ^{18}\text{O}/^{16}\text{O}$ and $\delta_{46}$ is the value obtained from the Mass spectrometer.
CHAPTER III

RESULTS AND DISCUSSION

All data obtained by the present study are listed in Tables 5 and 6.

\(^{210}\text{Pb}\) Ages

\(^{210}\text{Pb}\) ages determined for 5 samples from the Shiawassee River Bridge are shown in Table 5. The samples analyzed include a composite stalactite and a flowstone. These results are also displayed in Figure 4. The purpose of the \(^{210}\text{Pb}\) dating was twofold: (1) to examine whether or not this technique is applicable to dating these types of minerals and (2) to determine the timing of the process of degradation of the bridge.

Results from the composite stalactite gives ages of 64 and 18 yrs for the longer and the shorter stalactites, respectively. Since the sample analyzed for these dates was a composite age of several layers, the date obtained is an average, or composite, age of the stalactite, and thus can be considered a minimum age. Based on the nature of the growth of stalactites, the age of the longer stalactite suggests that degradation of the bridge started at least 64 years ago. This is consistent with the fact that the bridge was constructed in 1931, which means that it was 67 yrs old at the
### Table 5
Isotopic Results for MI Samples

<table>
<thead>
<tr>
<th>Sample#</th>
<th>Description</th>
<th>%carbonate</th>
<th>$\delta^{13}$C</th>
<th>$\delta^{18}$O</th>
<th>$^{210}$Pb-age</th>
<th>$^{14}$C (pM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s1</td>
<td>flowstone</td>
<td>58.8</td>
<td>-24.9</td>
<td>+12.8</td>
<td></td>
<td>110.9%</td>
</tr>
<tr>
<td>s2</td>
<td>bottom layers (s1A)</td>
<td>57.8</td>
<td>-23.4</td>
<td>+12.8</td>
<td>4.8yrs</td>
<td>111.4%</td>
</tr>
<tr>
<td>s3</td>
<td>middle layers (s1B)</td>
<td></td>
<td>-23.7</td>
<td>+13.3</td>
<td>3.8yrs</td>
<td>108.2%</td>
</tr>
<tr>
<td>s4</td>
<td>top layers (s1C)</td>
<td>63.8</td>
<td>-25.2</td>
<td>+12.5</td>
<td>5.9yrs</td>
<td></td>
</tr>
<tr>
<td>s5</td>
<td>bottom</td>
<td>64.0</td>
<td>-27.9</td>
<td>+13.0</td>
<td>64yrs</td>
<td>110.0%</td>
</tr>
<tr>
<td>s6</td>
<td>bottom</td>
<td></td>
<td></td>
<td></td>
<td>18yrs</td>
<td></td>
</tr>
<tr>
<td>s7</td>
<td>intralayer (1)</td>
<td></td>
<td>-23.5</td>
<td>+15.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s8</td>
<td>intralayer (1)</td>
<td></td>
<td>-23.6</td>
<td>+14.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s9</td>
<td>intralayer (1)</td>
<td></td>
<td>-22.8</td>
<td>+14.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s10</td>
<td>intralayer (1)</td>
<td></td>
<td>-24.0</td>
<td>+13.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s11</td>
<td>intralayer (1)</td>
<td></td>
<td>-24.2</td>
<td>+13.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s13</td>
<td>intralayer (5)</td>
<td></td>
<td>-25.8</td>
<td>+12.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s14</td>
<td>intralayer (5)</td>
<td></td>
<td>-28.9</td>
<td>+12.9</td>
<td></td>
<td>106.4%</td>
</tr>
<tr>
<td>s15</td>
<td>intralayer (5)</td>
<td></td>
<td>-24.7</td>
<td>+13.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s16</td>
<td>intralayer (5)</td>
<td></td>
<td>-24.6</td>
<td>+13.3</td>
<td></td>
<td>108.3%</td>
</tr>
<tr>
<td>s17</td>
<td>intralayer (5)</td>
<td></td>
<td>-25.5</td>
<td>+13.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s18</td>
<td>intralayer (5)</td>
<td></td>
<td>-24.8</td>
<td>+14.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s19</td>
<td>intralayer (5)</td>
<td></td>
<td>-25.1</td>
<td>+12.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s20</td>
<td>intralayer (5)</td>
<td></td>
<td>-22.8</td>
<td>+15.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s21</td>
<td>intralayer (5)</td>
<td></td>
<td>-22.3</td>
<td>+15.0</td>
<td></td>
<td>110.2%</td>
</tr>
</tbody>
</table>

s14+s17:

s20+s21:
<table>
<thead>
<tr>
<th>Sample#</th>
<th>Description</th>
<th>%carbonate</th>
<th>δ¹³C</th>
<th>δ¹⁸O</th>
<th>δ¹⁴C (pM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ncc1</td>
<td>12cm long stalactite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>top portion</td>
<td>61.9</td>
<td>-27.4</td>
<td>+13.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>middle</td>
<td>58.3</td>
<td>-30.7</td>
<td>+12.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>bottom</td>
<td>65.2</td>
<td>-29.2</td>
<td>+12.8</td>
<td></td>
</tr>
<tr>
<td>ncc2</td>
<td>8cm long stalactite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>top</td>
<td>76.8</td>
<td>-27.3</td>
<td>+13.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>middle</td>
<td>72.3</td>
<td>-27.8</td>
<td>+12.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>bottom</td>
<td>75.0</td>
<td>-29.2</td>
<td>+12.0</td>
<td></td>
</tr>
<tr>
<td>ncc3</td>
<td>6cm long stalactite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>top</td>
<td>56.7</td>
<td>-24.9</td>
<td>+14.6</td>
<td>104.8%</td>
</tr>
<tr>
<td></td>
<td>bottom</td>
<td>47.2</td>
<td>-26.4</td>
<td>+13.3</td>
<td></td>
</tr>
<tr>
<td>ncc4</td>
<td>10cm long stalactite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>top</td>
<td>45.5</td>
<td>-29.9</td>
<td>+13.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>bottom</td>
<td>46.1</td>
<td>-31.4</td>
<td>+12.4</td>
<td>106.4%</td>
</tr>
<tr>
<td>ncc5</td>
<td>8cm long stalactite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>top</td>
<td>71.2</td>
<td>-21.6</td>
<td>+15.2</td>
<td>102.9%</td>
</tr>
<tr>
<td></td>
<td>middle</td>
<td>78.8</td>
<td>-28.8</td>
<td>+13.4</td>
<td></td>
</tr>
<tr>
<td>ncc6</td>
<td>10cm long stalactite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>top</td>
<td>55.5</td>
<td>-29.5</td>
<td>+12.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>bottom</td>
<td>74.0</td>
<td>-29.1</td>
<td>+13.4</td>
<td></td>
</tr>
<tr>
<td>ncc7</td>
<td>middle-5cm long stal.</td>
<td>72.4</td>
<td>-30.3</td>
<td>+11.8</td>
<td></td>
</tr>
<tr>
<td>ncc8</td>
<td>middle-8cm long stal.</td>
<td>80.0</td>
<td>-29.0</td>
<td>+13.5</td>
<td></td>
</tr>
<tr>
<td>ncc9</td>
<td>middle-8cm long stal.</td>
<td>80.3</td>
<td>-30.4</td>
<td>+11.8</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4. $^{210}\text{Pb}$ Ages of Stalactites and Flowstone.
time of sample collection and analysis. The smaller stalactite records an age of 18 yrs. This young age is consistent with the manner suggested for the formation of these stalactites, as they are expected to grow in breadth and length with time (Macleod et al., 1991).

The $^{210}$Pb dates may serve another intriguing purpose. If several samples are dated with respect to their position below a bridge, then information on the onset and progression of degradation spatially may be obtained.

$^{210}$Pb dates for the flowstone from the same bridge are shown in Figure 4. The ages range from 4.8 yrs at the feature’s top to 5.9 yrs at the its base. The data obtained suggest that the flowstone is much younger than the stalactites. The distribution of the ages suggests that the formation process associated with flowstones is rather rapid. The data represents 2 cm growth in just 2 years. The fact that the ages obtained for the flowstone are much younger than those of the stalactites also suggests that the flowstone was formed much later in the degradation process.

The results from these analyses also demonstrate the potential this method of using $^{210}$Pb ages as a useful chronological tool has to study the formation of the secondary carbonate minerals responsible for concrete degradation.
Stable Isotopes

Carbon

Equations 28 through 31 represent the reactions that occur when solid calcium carbonate is precipitated as a consequence of the dissolution of gaseous CO$_2$ in water. (Note that CO$_2$(aq) and H$_2$CO$_3$(aq) are used interchangeably.)

\[
\begin{align*}
\text{CO}_2(g) + H_2O(l) & \leftrightarrow H_2CO_3(aq) \quad (28) \\
H_2CO_3(aq) & \leftrightarrow H^+(aq) + HCO_3^-(aq) \quad (29) \\
HCO_3^-(aq) & \leftrightarrow H^+(aq) + CO_3^{2-}(aq) \quad (30) \\
Ca^{2+}(aq) + CO_3^{2-}(aq) & \leftrightarrow CaCO_3(s) \quad (31)
\end{align*}
\]

A distinctive mass dependent fractionation accompanies each of these reactions. In open systems, where there is a sufficient amount of CO$_2$ available to continuously supply the system with CO$_2$, the $\delta^{13}$C of the dissolved inorganic carbon (DIC) is controlled by the $\delta^{13}$C value of the gaseous CO$_2$ source. Under these conditions, the degrees of fractionation between the source CO$_2$ and CO$_2$(aq), HCO$_3^-$ (aq), CO$_3^{2-}$ (aq), and CaCO$_3$(s) are determined by the following equations:

\[10^3 \ln \alpha^{13}C_{\text{CO}_2(aq)} - \text{CO}_2(g) = -0.373(10^3 \ T^{-1}) + 0.19 \] (32)
where $\alpha^{13}C$ is the fractionation factor of the respective species with respect to the CO$_2$ gas, and T is the absolute temperature at which the reactions proceed (Vogel et al., 1970, Mook et al., 1974, Deines et al., 1974, Bottinga, 1968).

With respect to the $\delta^{13}C$ of the source CO$_2$ (g), aqueous CO$_2$ is depleted by 1.1‰ when CO$_2$ gas is hydrated (Equation 28) at 25°C. A large enrichment in HCO$_3$(aq) accompanies the dissociation of H$_2$CO$_3$(aq) (Equation 29). At 25°C, this enrichment, with respect to the source CO$_2$(g), is 7.9‰. Similarly, the dissociation of the bicarbonate ion (HCO$_3$(aq)) results in enrichment of 7.6‰ in the carbonate ion (CO$_3^{2-}$(aq)) with respect to the CO$_2$ gas. The precipitation of solid CaCO$_3$ from this system will result in a carbonate enriched by 10.4‰ with respect to the $\delta^{13}C$ of the source CO$_2$(g).

The ocean system can be considered an open system for this model. Atmospheric CO$_2$ is in chemical and isotopic equilibrium with the ocean surface. The $\delta^{13}C$ value of atmospheric CO$_2$ is approximately -8‰. If a
temperature of 25°C is assumed, application of the enrichment factor discussed above (+10‰) would result in expected δ¹³C values DIC in the ocean to be close to 0‰.

Another example of an open system is the soil zone. In this environment soil CO₂ is continuously produced by root respiration within the soil. The majority of natural plants produce CO₂ with a δ¹³C value of approximately -25‰. In this environment the δ¹³C of the inorganic carbon will be governed by Equations 32 through 35. At 25°C, for example, applying the 10‰ enrichment, the δ¹³C of DIC in the soil zone will be ~-15‰.

It was previously stated that the majority of plants respire CO₂ with a δ¹³C value of ~-25‰. These plants are referred to as C₃ plants. Another category of plants, namely C₄ plants, exists. CO₂ produced by the respiration of C₄ plants has a δ¹³C value of ~-12‰. For open system dissolution of CaCO₃, the δ¹³C_DIC in a region dominated by C₄ plants will be -2‰.

As opposed to open system dissolution, under closed system conditions the δ¹³C values of DIC is not controlled exclusively by the gaseous CO₂ source. An example of a closed system results when water from the soil zone infiltrates below this zone. When the water leaves the soil zone, CO₂ is no longer supplied by plant respiration. The H⁺ ions
provided by the CO$_2$ (Equation 30), which originate in the soil zone, are utilized for the dissolution of aquifer carbonates. This results in variations of $\delta^{13}$C values associated with carbonates precipitated under such conditions.

The carbon supplied from the dissolution of aquifer carbonates is expected to have a value of approximately 0‰. As stated above, the carbon from the soil zone is expected to have $\delta^{13}$C values close to -25‰, if the region is dominated by C$_3$ plants. Since a portion of the CO$_3^{--}$ ions are supplied by the soil CO$_2$ (~ -25‰), and the remainder is supplied by the soil carbonates (~ 0‰), the $\delta^{13}$C value of the DIC will be within the range of -25 to 0‰. Ultimately, 50% of the CO$_3^{--}$ ions will be provided by the soil CO$_2$ and the other 50% by the soil carbonates. Hence, the expected $\delta^{13}$C of the DIC is $\sim$ -12.5‰.

For a closed system, in which soil CO$_2$ is primarily produced by C$_4$ plants, the $\delta^{13}$C value of carbonates is expected to be $\sim$ -6‰ (if 50% of the carbon is derived from soil CO$_2$ and the remainder is from limestone dissolution).

Table 7 gives theoretical $\delta^{13}$C values of DIC dependent on the dominant vegetation type for both open and closed systems.
Table 7
Calculated $\delta^{13}C$ Values of DIC in Soil Zones (@25°C)

<table>
<thead>
<tr>
<th>Vegetation type</th>
<th>Initial $\delta^{13}C_{CO_2}$</th>
<th>Final $\delta^{13}C_{DIC}$ for Open Systems</th>
<th>Final $\delta^{13}C_{DIC}$ for Closed Systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_3$</td>
<td>-25‰</td>
<td>-15‰</td>
<td>-12.5‰</td>
</tr>
<tr>
<td>$C_4$</td>
<td>-12‰</td>
<td>-2‰</td>
<td>-6‰</td>
</tr>
</tbody>
</table>

An enrichment of ~2‰ in CaCO$_3$ with respect to the $\delta^{13}C_{DIC}$ accompanies the precipitation of solid calcium carbonate from a solution. If this precipitation occurs within an open system dominated by $C_3$ plants, the expected $\delta^{13}C$ value of the solid calcium carbonate is equal to -15‰ + 2‰, or -13‰.

If the CO$_2$ source is atmospheric in origin, with a $\delta^{13}C$ value of -8‰, application of the +10‰ enrichment of DIC with respect to the CO$_2$ source results in $\delta^{13}C_{DIC}$ values equal to +2‰. Incorporating the +2‰ enrichment in CaCO$_3$, with respect to the DIC, the expected $\delta^{13}C$ value of carbonates precipitated under open system conditions with atmospheric CO$_2$ is +4‰. Table 8 shows theoretical $\delta^{13}C$ values of calcium carbonates deposited in open and closed systems, with respect to the $\delta^{13}C$ of the source CO$_2(g)$. 
Table 8

Theoretical $\delta^{13}\text{C}_{\text{CaCO}_3}$ With Respect to $\delta^{13}\text{C}$ of Source CO$_2$

<table>
<thead>
<tr>
<th>$\delta^{13}\text{C}$ of Source CO$_2$</th>
<th>Open System</th>
<th></th>
<th>Closed System</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta^{13}\text{C}_{\text{DIC}}$</td>
<td>$\delta^{13}\text{C}_{\text{CaCO}_3}$</td>
<td>$\delta^{13}\text{C}_{\text{DIC}}$</td>
</tr>
<tr>
<td>C$_3$ plants (-25‰)</td>
<td>-15</td>
<td>-13</td>
<td>-12.5</td>
</tr>
<tr>
<td>C$_4$ plants (-12‰)</td>
<td>-2</td>
<td>0</td>
<td>-6</td>
</tr>
<tr>
<td>Atmosphere (-8‰)</td>
<td>+2</td>
<td>+4</td>
<td></td>
</tr>
</tbody>
</table>

Values of $\delta^{13}\text{C}_{\text{CaCO}_3}$ observed in the present study (Figure 5) are all more negative than would be expected if precipitation occurred under isotopic equilibrium conditions with atmospheric or soil respiration CO$_2$ as the source CO$_2$ gas. The $\delta^{13}\text{C}$ values of the NY stalactites range from -31.4 to -21.6‰, with a mean value of -28.4‰. The range for $\delta^{13}\text{C}$ of the Michigan samples analyzed is -28.9 to -22.3‰, with a mean value of -24.6‰. Hence, it may be concluded that either the precipitation of these carbonates did not occur under isotopic equilibrium conditions, or, if isotopic equilibrium conditions prevailed, it can be concluded that the source CO$_2$ for the system must not have been of atmospheric, or soil respired, origin.
Figure 5. Stable Carbon and Oxygen Data for MI Flowstones.
If the precipitation did not occur under isotopic equilibrium conditions the fractionations observed must be a result of some kinetic process(es). A kinetic fractionation, with values ranging from -11.3 to -10‰, accompanies the production of freshwater travertines by interaction of CO$_2$ with hyper-alkaline waters (O’Neil and Barnes, 1971). This fractionation results as CO$_2$ molecules cross the gas-liquid interface. Macleod et al. (1991) suggested that the fractionations associated with this hyper-alkaline system are comparable with those associated with carbonate precipitation in concrete environments. Assuming that atmospheric CO$_2$ has a δ$^{13}$C value of -8‰, the δ$^{13}$C of the carbonates would be between -19.3 and -18‰.

Other studies suggest this fractionation is a result of 4 different kinetic fractionation processes, namely (1) the invasion of the liquid phase by gaseous CO$_2$, (2) the diffusion of CO$_2$ in the liquid phase, (3) the reaction of CO$_2$(aq) with OH$^-$ ions, and (4) the kinetic effects resulting from CaCO$_3$ precipitation (Letolle et al., 1990). The total maximum fractionation suggested by this model is -15.5 ± 1.5‰.

Observed δ$^{13}$C values of carbonates deposited in other concrete environments (Macleod et al., 1991), as well as that of the present study, are more negative than can be explained by fractionations associated with (a) CO$_2$ molecules crossing the gas liquid-interface in hyper-alkaline waters
or (b) the four kinetic fractionation processes described by Letolle et al. (1990). An additional fractionation process must occur to account for the more negative values observed.

It has been suggested that the additional fractionation may be a consequence of a secondary diffusive process that results from the passing of $\text{CO}_2(\text{aq})$ molecules through calcitic crusts that rapidly precipitate at the base of concrete structures upon contact with atmospheric $\text{CO}_2$ (Macleod et al., 1991). This fractionation is suggested to be pH dependent (Siegenthaler and Munnich, 1981). The proposed fractionation resulting from the diffusion through calcitic crusts is $-7\%$, assuming pH 10.

It has also been suggested that the diffusive fractionation processes may be enhanced by pH $>12.5$. Carbonates precipitated from solutions with such pH values are suggested to be more depleted in $^{13}\text{C}$ than those precipitated from solutions with lower pH (Letolle et al., 1990).

As can be seen by plotting the $\delta^{13}\text{C}$ values of stalactites from the New York site and flowstones from the Michigan site in the form of a histogram (Figure 6), there are two strong groupings of the $\delta^{13}\text{C}$ values. The $-29\%$ mean grouping belongs to the stalactites obtained from the New York site, and the $-24\%$ grouping belongs to the flowstone samples obtained from the Michigan site.

The model attributing this fractionation to diffusion through
calcitic crusts is based on δ¹³C values observed for stalactites. The majority of those stalactites had δ¹³C values of -26‰. The majority of δ¹³C values observed for the stalactites in the present study are more negative (-29‰) than can be explained by this model.

The maximum fractionation suggested by the 4 fractionation processes model cannot account for the values observed in the present study. If atmospheric CO₂ (-8‰) is subjected to the maximum fractionation suggested by this model, -15.5 ± 1.5‰, the most negative δ¹³C value would be -25‰. The majority of the values observed in the present study are more negative than -25‰. Thus, this model does not
sufficiently explain the δ¹³C values observed in the present study.

Consideration of the enhanced fractionation above pH 12.5 model is intriguing. The values observed in the present study become more negative as one measures from the top of a stalactite towards its bottom. This can be seen for sample "ncc2", where the δ¹³C values of the stalactite’s top, middle, and bottom are -27.3‰, -27.8‰, and -29.2‰, respectively. If the additional fractionation is pH controlled, our data suggests that the pH of the solution must vary from one portion of the stalactite to another. Another interesting observation is that the flowstones are consistently heavier than the stalactites. This can be seen in Figure 6. The flowstones form a strong grouping near -24‰, whereas the stalactites form the grouping near -29‰. Although the flowstones were collected in Michigan and the stalactites were collected in New York they can be treated as if they were collected from the same site because the δ¹³C of atmospheric CO₂ (the proposed CO₂ source) does not vary. The δ¹³C value of the one stalactite analyzed from the Michigan site ("s5") is consistent with the observed trend of flowstones having less negative δ¹³C values than the stalactites. If the fractionation is pH dependent, this trend implies that solutions responsible for flowstone formation have lower pH than those responsible for stalactite formation.

Considering atmospheric CO₂ as the source CO₂, the proposed
models of carbonate precipitation cannot account for the $\delta^{13}C$ values observed in the present study. $^{14}C$ data, which is discussed later in this chapter, may be used to lend support to the theory that atmospheric $CO_2$ is the source of carbon in the secondary mineralization of carbonates within concrete structures. It may be mentioned that, in previous works, microbial $CO_2$ has been indicated as the carbon source (Letolle et al., 1988). However the data obtained in the present study does not support this.

Oxygen

If the $CaCO_3$ precipitation occurred under isotopic equilibrium conditions the $\delta^{18}O$ value of the carbonates would be determined by that of the water involved in the reactions and the temperature at which precipitation occurred. Under carbonate-water equilibrium conditions the temperature of carbonate formation is governed by:

$$1000 \ln \left( \frac{1000 + \delta^{18}O_{CaCO_3}}{1000 + \delta^{18}O_{water}} \right) = 2.78 \left( \frac{10^6}{T^2} \right) - 2.89$$

(36)

where $T$ is in Kelvin.

The $\delta^{18}O$ values of the carbonates analyzed from the Shiawassee River Bridge range from 12.5 to 15.7‰, with a mean value of 13.7‰. The $\delta^{18}O$ values of the NY samples range from 11.8 to 15.2‰, with a mean value of 13.1‰. Assuming that local meteoric water in Michigan has a
mean annual $\delta^{18}O$ value of $-8\%_o$ (Machavaram and Krishnamurthy, 1994), and that it is involved in the carbonate precipitation, temperatures of carbonate formation obtained by incorporating the $\delta^{18}O_{CaCO_3}$ from this study into Equation 36 range from 63.7 to 67.8°C, with a mean temperature value of 65.7°C. These temperatures are unreasonably high. Thus, it can be concluded that either (a) this precipitation does not take place under isotopic equilibrium conditions with meteoric water, or (b) if equilibrium conditions do exist during carbonate precipitation, then the oxygen in the carbonates must not be provided exclusively by meteoric water.

It has been suggested that the $\delta^{18}O$ of freshwater travertines is derived from both the local meteoric waters and from atmospheric $CO_2$ (O’Neil and Barnes, 1971). Two-thirds of the oxygen atoms in the calcium carbonates are suggested to be contributed by atmospheric $CO_2$, with the remaining one-third coming from the local meteoric water. Atmospheric $CO_2$ has a $\delta^{18}O$ value of $+41\%_o$ (Bottinga and Craig, 1969). If two-thirds of the oxygen is derived from atmospheric $CO_2$ ($\delta^{18}O$ value of $+41\%_o$) and one-third is derived from local meteoric water ($\delta^{18}O$ value of $-8\%_o$), the expected $\delta^{18}O$ value of the carbonates would be 24.7%. The fact that the samples in the present study do not possess such values implies that some re-equilibration process involving the $CO_2$ and the carbonate solution...
must take place during the precipitation of these secondary minerals.

$\delta^{18}$O values of meteoric waters vary for different locations. $\delta^{18}$O values of atmospheric $\text{CO}_2$, however, are not dependent on location. Thus, the similarity between the $\delta^{18}$O values of the NY and MI samples suggests that the local meteoric waters contribute little, if any, of the oxygen atoms to the carbonates. Atmospheric $\text{CO}_2$ is the most likely candidate responsible for contribution of oxygen to form the carbonates in concrete environments. However, $\text{CaO}$ needs to be investigated, as it may be partially responsible for contributing oxygen atoms to the carbonates.

$\delta^{13}$C vs. $\delta^{18}$O

From the $\delta^{18}$O values obtained in this study it is evident that the precipitation of calcium carbonates in the concrete environment does not occur under isotopic equilibrium conditions. Hence, kinetic processes must be responsible for the fractionation of oxygen isotopes during secondary mineralization of $\text{CaCO}_3$ in such environments.

Plotting $\delta^{13}$C vs. $\delta^{18}$O values of the carbonates precipitated at the sites in the present study shows a positive correlation (Figure 7). Such a correlation is consistent with kinetically controlled precipitation of these carbonates, resulting in a co-variation of $\delta^{13}$C and $\delta^{18}$O.
Figure 7. $\delta^{13}C$ vs. $\delta^{18}O$. 
Radiocarbon ($^{14}$C)

The $^{14}$C activity range of the samples analyzed in the present study is 102.9 to 111.4 pM. The $^{14}$C activities are displayed in Figure 8. Figure 9 is an atmospheric $^{14}$C activity time series (Genty, 1999) covering the lifespan of the Shiawassee River Bridge.

A carbonate deposition system similar to the one used in this study is the cave stalagmite study described by Genty et al. (1998). These authors used cave stalagmites to construct a $^{14}$C activity time series. The speleothems were dated by counting of annual growth laminations and by the determination of $^{14}$C activities. The radiocarbon activities observed were less than those of atmospheric $^{14}$C activities of the corresponding years. Also observed was a lag in the $^{14}$C record, by approximately 10 yrs, with the stalagmite $^{14}$C data lagging behind atmospheric $^{14}$C data.

Three carbon sources were suggested for the formation of the speleothems: (1) limestone (dead carbon), (2) organic carbon with a fast turnover rate, and (3) organic carbon with a slow turnover rate. Organic carbon that has a fast turnover rate (decays rapidly) will have a $^{14}$C activity equal to that of the atmospheric activity of when it was alive. Organic carbon with a slow turnover rate will have a composite $^{14}$C activity of
organic carbon of different ages (and different $^{14}$C activities). The lag time and dampening of $^{14}$C activities was primarily attributed to the contribution of the carbon from the organic carbon with a slow turnover rate. This effect (up to 80%) was more pronounced in caves that were in forested areas. A small contribution to the dampening may be supplied by
dead carbon (limestone) which has a $^{14}$C activity of zero.

$^{14}$C data (Figure 8) observed in the present study can be interpreted in a similar manner. Firstly, we assume that contribution from dead carbon is zero. Secondly, we assume that no, or very little, organic carbon is expected to contribute to this system, due to the lack of a soil zone above bridges. Thirdly, we assume that atmospheric CO$_2$ is the primary source of carbon for the formation of these stalactites and flowstones.

The stalactite and flowstone samples analyzed in this study are composites of several layers of carbonates that were formed at different times. The portions of the samples analyzed for $^{14}$C were not individual layers, and therefore provide minimum ages. For example, the $^{14}$C activity of sample “s5”, dated 64 years by the $^{210}$Pb method, is actually given by:

$$a^{14}\text{C} = \frac{\sum_{i=1}^{64} a^{14}C_{atmi}}{64}$$

(37)

where $a^{14}$C is atmospheric radiocarbon activity and $i$ is number of years the stalactite has been growing. The total $^{14}$C activity will thus depend upon a weighted contribution from the activities of the years during which the stalactite was deposited.

Based on the available atmospheric $^{14}$C data (Figure 9) and assuming that sample s5 grew uniformly during the history of the bridge, the
expected $^{14}$C activity is 127 pM. It is interesting that such a value was not observed for any of the samples analyzed in the present study. One explanation for this may be that the growth rates are not uniform. Periods of rapid carbonate growth may exist. Variations in the growth rates of these minerals may have implications in terms of the rate of concrete degradation.

![Figure 9. Atmospheric $^{14}$C Activity Time Series.](image)

The fact that all of the $^{14}$C activities observed in this study are in excess of 100 pM suggests that the carbon in these carbonates is derived from atmospheric $\text{CO}_2$. 
CHAPTER IV

CONCLUSIONS

Objectives of this study were to determine the carbon and oxygen source(s) involved in the precipitation of calcium carbonates in concrete environments and to determine whether or not the $^{210}\text{Pb}/^{226}\text{Ra}$ method of dating is applicable to age-dating secondary minerals that form in concrete environments.

Conclusions are as follows:

1. The $^{210}\text{Pb}/^{226}\text{Ra}$ method of dating is useful as a chronological tool for secondary mineral deposits in concrete environments. The fact that the ages obtained in this study seem reasonable, with respect to the age of the concrete structure, supports this conclusion. This dating technique will be useful in identifying periods of rapid formation of the secondary carbonates.

2. The fractionation of carbon and oxygen isotopes as a consequence of the precipitation of carbonates in concrete structures is the result of some kinetically controlled processes. The use of stable isotope geochemistry principles, in this study, provided the basis for the determination of the carbon and oxygen sources in the carbonates. Both the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, obtained in the present study, elucidate that the
precipitation of the carbonates does not take place under isotopic equilibrium conditions and that the fractionations that occur during the precipitation of these minerals must be kinetically controlled.

3. $\delta^{13}C$ values and radiocarbon activities, observed in the present study, indicate that the carbon in these secondary minerals are derived primarily from atmospheric $CO_2$.

4. $\delta^{18}O$ values, observed in this study, indicate that oxygen in these carbonates is also derived primarily from atmospheric $CO_2$. These values also indicate that the re-equilibration between atmospheric $CO_2$ and the carbonate solution takes place during the secondary mineralization process.

5. The present study provides valuable information regarding the secondary mineralization of calcium carbonates in concrete environments. However, future works should incorporate the use of isotopic methods utilized in this study, as well as isotopic analyses and field measurements, such as pH, of drip-waters collected from the stalactites.
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