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Carbon-14: Basics of the system and its use in dating secondary mineralizations on degraded concrete

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Abstract:

Carbon 14, the radioactive isotope of carbon, provides an isotopic dating system that is very useful in determining ages for fairly recent, organic, fossilized materials. Paleoclimatic studies benefit from the use of the carbon system, because carbon 14 can provide an age for a structure and stable carbon isotope variations provide indications about past climate trends. The system can also be used to calculate ages for inorganic materials, specifically building materials partially composed of lime. The creation of the building materials involves burning fossil limestone, and allows the capture of atmospheric carbon dioxide, as the material hardens after construction. Often through degradation of such structures, secondary carbonate mineralization takes places in the form of speleothem-like formations underneath bridges. Isotopic analysis of the carbonate in such structures can provide information on sources of carbon in the structure as well as past ambient temperatures.

Introduction:

The purpose of this study is to investigate speleothem-type formations found under man-made concrete bridges, and to conduct an isotopic analysis of the formations. These speleothems are secondary deposits, forming as the concrete forming the bridge begins to degrade and minerals such as calcite and calcium carbonate dissolve from the material comprising the bridge and re-precipitate in crystalline form. Concrete degrades either physically, through mechanisms such as freeze thawing, stress cracks or salt wedging, or through chemical processes like the formation of secondary minerals. Similar to the speleothem formations found in caves, these speleothems also form in growing layers. This project is attempting to ascertain information about changes in atmospheric carbon 14 from chemical analysis of samples collected from all over the country. These changes can help determine paleoclimates and more recent climate trends, and can aid with predicting climate changes in the future.

Because dense speleothems and building materials can be considered closed systems after hardening, they can be dated using most isotopic systems. However, the most common method of dating inorganic carbonate materials is carbon dating. This is ideal because of the very recent age range of materials such as cement, mortar and plaster, and because all of these substances can be made with limestone. A summary of the carbon 14 method of dating inorganic carbonate formations, particularly building materials, is presented. The dating of ancient churches in the Aland Islands, Finland provides an example of the system's use in archaeology.

Isotope Systematics of Carbon-14 Dating:

The information in this section is summarized from the following sources; the NTD Resource Center, the University of Arizona AMS Laboratory webpage, and Wellington & Grottoli-Everett (1996). Carbon has three isotopes, ^{12}C, ^{13}C and ^{14}C. ^{14}C is formed as neutrons from cosmic radiation enter the upper atmosphere and are captured by nitrogen nuclei (Figure 1).

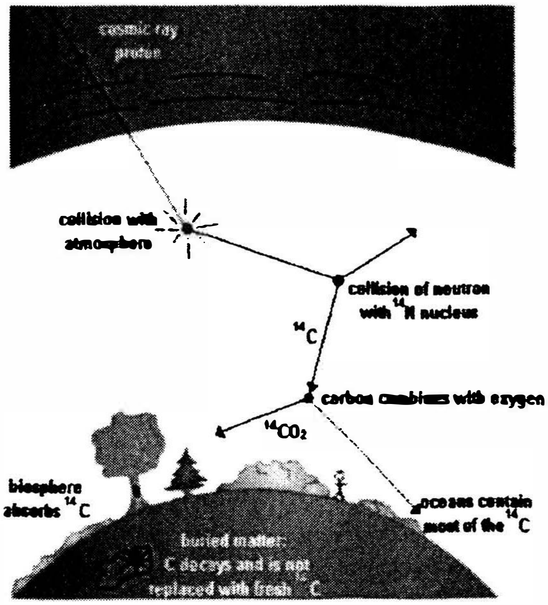


Figure 1: Formation of ^{14}C and the Carbon Cycle *(NTD Resource Center)*

^{12}C and ^{13}C are stable, while ^{14}C decays via weak beta decay to ^{14}N as shown by the following equation:

$$(1)\ {}^{14}_{6}C \rightarrow {}^{14}_{7}N + \beta^{-};$$

and has a half-life of approximately 5,730 years. Once the ^{14}C is formed, it can bond with O_2 to form $^{14}CO_2$ which then enters the Earth's carbon cycle. This carbon cycle and its properties provide the basis for the carbon isotope dating system.

Plants absorb carbon in the form of CO_2 during photosynthesis. Herbivores then receive the carbon as they eat plants, and the cycle continues. Through the basic processes of breathing and eating, an organism's carbon supply is constantly replenished. All terrestrial plants and animals will maintain approximately the same level of ^{14}C due to metabolic processes and constant levels in the atmosphere. Oceanic organisms display the same tendency, but with a slightly different ^{14}C level than terrestrial organisms.

When an organism eventually dies and becomes a fossil, its ^{14}C decays along with its body, and is not replaced. Thus, the fossil is no longer at equilibrium with the carbon cycle, and the loss of ^{14}C can be used to attain a date for it. This is done by burning a sample to convert the carbon to CO^2 gas, and then using some type of radiation counter to measure the number of electrons given off as ^{14}C decays to ^{14}N. Older types of radiation counters allow measurements of up to approximately 50,000 years, while a newer method, accelerator mass spectrometry (AMS) (Figure 2) extends that to approximately 100,000 years. The advantage of this method is not only that it doubles the age range ^{14}C dating is useful for it also requires a much smaller sample than the traditional measurement.

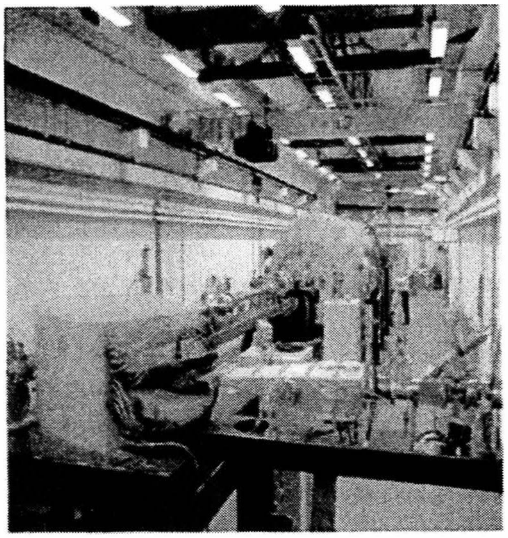


Figure 2: Proton Accelerator - *Particle accelerators such as this one at a laboratory in Aarhus, Denmark, can be used to separate carbon-14 from the more abundant isotopes of carbon (carbon-12 and carbon-13), a technique called accelerator mass spectrometry (AMS). The major advantage of AMS over conventional radiocarbon measurement (counting electrons emitted by the radioactive decay of carbon-14) is that much smaller samples are required. Whereas conventional measurement typically requires several grams of carbon, AMS demands only a milligram. (Photograph courtesy of Jan Heinemeier.) (Hale et al)*

The equation for radioactive decay of carbon from an organism that died t years ago is:

$$\textbf{(2) } A = A_0(e\text{-}\lambda t)$$

Where

- A is the measured activity due to ^{14}C in units of disintegrations per minute per gram of carbon
- A_0 is the activity of ^{14}C in the same specimen when the organism was alive
- λ is the decay constant, and
- t is time. (NTD Resource Center)

Carbon 14 dating has been most often used to date organic materials such as fossilized bone, shells, wood or peat, or carbonate deposits such as speleothems. In the 1960's, however, French scientists were able to extend the usefulness of the system to include man-made, inorganic materials such as mortar or concrete. This was possible because these building materials contain lime, from fossil limestone, and maintain a concentration of carbon that was fixed when the material hardened.

Inorganic Carbonates – Dating Mortar:

A study was conducted on ancient churches and stone towers in the Aland Islands, Finland, and in the United States by a team consisting of two archaeologists, an art historian, a geologist and a nuclear physicist (Hale et. al, 2003). The team created and refined a method for dating building materials such as mortar, cement and plaster that all have a common ingredient; lime.

Mortar is made from limestone ($CaCO_3$), which is heated to 900°C (Figure 3). During the heating process, CO_2 is released and CaO is formed. The mortar then hardens by reabsorbing CO_2 and becomes $CaCO_3$ again. This means the ^{14}C ratio is fixed in the newly formed $CaCO_3$ at the exact time of construction. The material can then be considered a closed system, and radioactive decay of ^{14}C proceeds as usual. The parent and daughter isotopes are measured and used to create an isochron to determine ages.

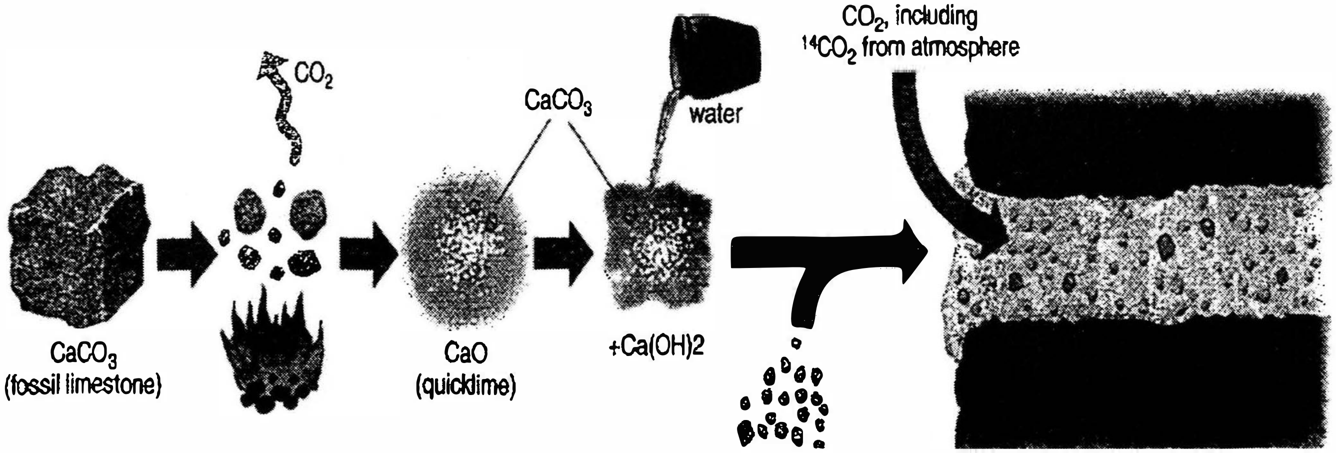


Figure 3: Creating Mortar from Fossil Limestone – Entrapment of Atmospheric CO_2 - *Mortar is made using limestone, which is primarily composed of calcium carbonate. The limestone is crushed and heated to at least 900 degrees Celsius, causing the release of carbon dioxide and the formation of calcium oxide ("quicklime"). Adding water and sand (the "aggregate") then creates mortar, a substance that hardens by absorbing carbon dioxide from the atmosphere, transforming the quicklime back into calcium carbonate. Ancient mortar thus contains a sample of atmospheric carbon, which can be subjected to radiocarbon dating. The presence of fossil carbon, however, complicates the endeavor. Particles of unburned limestone (calcium carbonate that survived the heating) constitute one source of contamination (tan). The aggregate used can also prove problematic, particularly if the sand employed to form the mortar contains shells, which are made of calcium carbonate (red). Various chemical and mechanical treatments help to identify and reduce the effects of such troublesome components. (Hale et al)*

Several sources of contamination led to problems when this type of dating was first introduced. Impurities can be introduced if the original limestone is not fully burned or if the sand added in the mortar creation process contains fossils or other carbonate material. These impurities make the method quite complicated and unreliable, because different sources of ^{14}C will give different age results. Fortunately Hale et al. found ways to minimize the sources of error. Fine meshes and dry and wet sieving help to mechanically separate the pure lime from various contaminants, and cathodoluminescence can display impurities that were missed. Using these techniques, impurities can be identified and removed to make the dating process much more reliable. Hale et al. used standard procedures to process the mortar for dating. Samples were crushed, sieved and combined with acid to yield CO_2. The CO_2 was dated via accelerator mass spectrometry (AMS).

Current Study:

The sample analyzed for this project was a flowstone obtained from the Meridian St. Bridge over Fall Creek in Indianapolis, Indiana (Figures 4, 5).

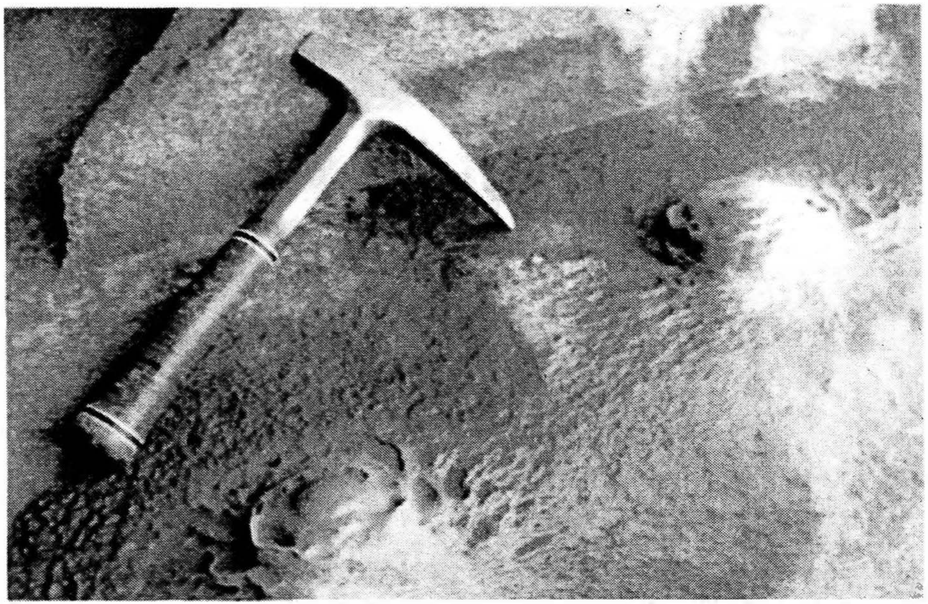


Figure 4: Flowstones under the bridge before they were removed for sampling *(Atekwana)*

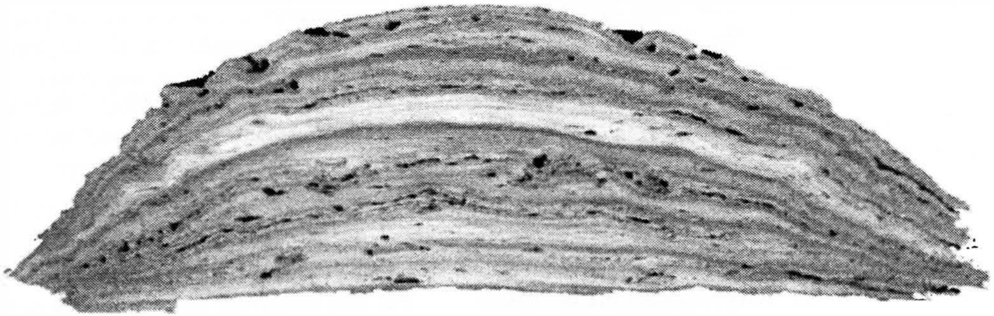
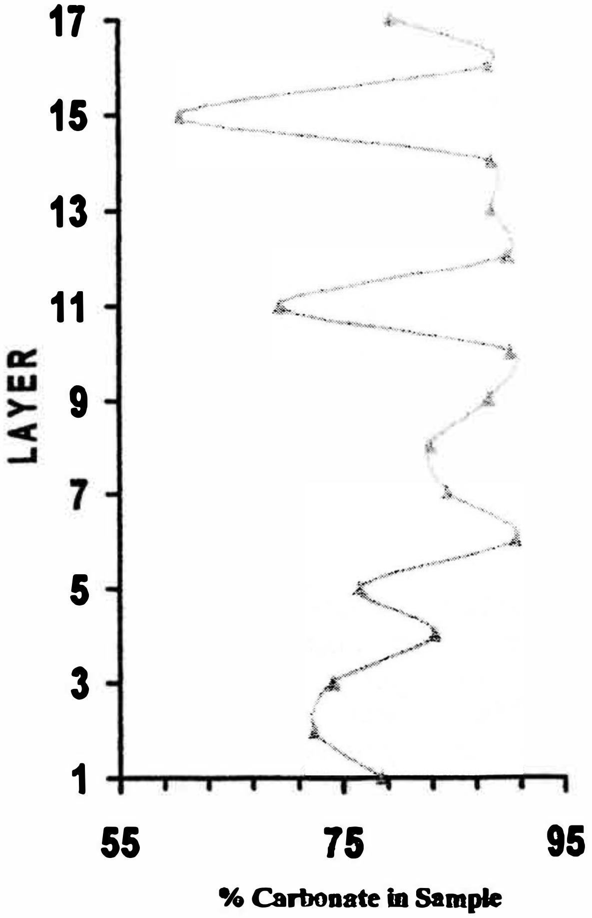


Figure 5: Cross section of a sample flowstone measuring 3.5 cm by 13 cm – note growth layers are visible. *(Atekwana)*

The sample was divided into seventeen layers for analysis, with layer one, the oldest, at the bottom and layer seventeen, the youngest, at the top. These divisions were made in an attempt to represent different growth layers of the sample. It was analyzed isotopically by reacting $CaCO_3$ with 100% phosophoric acid (Krishnamurthy et al., 1997). This provided data on the $\delta^{13}C$ $CaCO_3$ and $\delta^{18}O$ $CaCO_3$ (Figure 6) levels present.

Cross-section of Flowstone



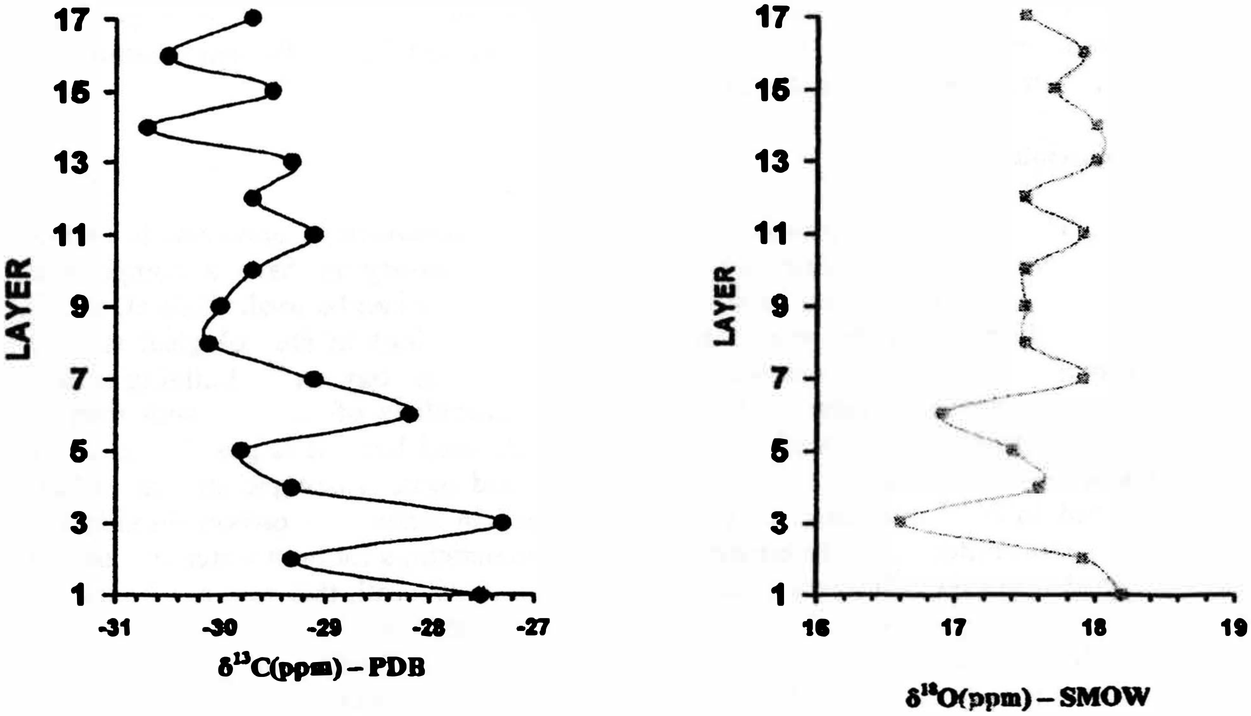


Figure 6: A cross-section of sample against % carbonate, $\delta^{13}C$(ppm) and $\delta^{18}O$(ppm) *(Atekwana, 2005)*

This isotope abundances found in this sample are reported here as compared to the international standards, i.e. Pee Dee Belemnite for the carbon isotopes and Standard Mean Ocean Water (SMOW) for the oxygen isotopes (Atekwana, 2005).

Isotope Analysis Data:

As can be seen from the graph, the amount of carbonate found in the sample fluctuates quite a bit, and the range of fluctuation increases with time. The carbon isotopes range from -27 to -31 parts per million (ppm) and show a negative trend over time. The oxygen isotopes do not noticeable trend negatively or positively, but begin to have a smaller range of variation over time.

Implications/Discussion:

The fluctuations found in the percentage of carbonate found in the sample could be due to several different occurrences. A change in climate or weather patterns such as a large storm event or pollution changes could cause changes in the amount of carbonate precipitated. The negative trend of the carbon isotope data is consistent with the addition of light CO^2 (-7 ppm) or fossil fuel CO^2 (-25 to -35 ppm) to the atmospheric reservoir. The addition of either of these two types of CO^2 increases the negativity of the $\delta^{13}C_{PDB}$ measured. The oxygen isotope data, under equilibrium conditions, is related to water temperature via the following equation:

$$\textbf{(3)}\ 1000 \ln \{(1000 + \delta^{18}O_{carbonate}) / (1000 + \delta^{18}O_{water})\} = 2.78 * 10^6/T^2 - 2.89$$

where T is in degrees Kelvin (Atekwana). This equation can be used to estimate the temperature of the water the carbonate formed in and hence the temperature of the ambient air at the time of formation.

Conclusion:

The goal of this project was to look at the variations of atmospheric carbon in recent carbonate formations. To do that, it is necessary to have a comprehensive understanding of the carbon 14 dating system and how it can be used. Hale et. al (2003) successfully clarified the role of historical stone buildings in archeological studies by determining the date of construction using ^{14}C geochronology on the building materials. Their study provided valuable insight into the difficulties of working with man-made carbonate materials. In working with the sample used here, it is possible to come to several conclusions about the nature of carbon and oxygen isotopic studies. Changes observed in $\delta^{13}C$ over time may reflect changes in where the carbon dioxide in the atmosphere comes from. Information on paleotemperatures for both water and air can be obtained using the $\delta^{18}O$ data obtained in this study. Overall, this data can be used as a proxy to obtain environmental information about the very recent past that may be difficult to obtain otherwise. The importance of this study is that it explores the processes governing degradation of concrete, and their environmental implications.

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