THE TRIPLE THREAT: STABLE ISOTOPE STUDIES OF FLUID INCLUSIONS, CARBONATE AND CLUMPED ISOTOPES

Monica M. Arienzo, Peter K. Swart, and Sean Murray

PROJECT OBJECTIVES

- Applying multiple geochemical proxies to stalagmites from the Bahamas offers the opportunity to better understand the paleoclimate of the region.
- Initial results support the idea that cold periods in the North Atlantic during the last glacial period (Heinrich events) are intervals of aridity followed by a shift to a much wetter climate in the sub-tropics. Additionally, these periods were extremely dusty, a phenomenon which could have actually induced climate change.
- The methods proposed here are additionally applicable for a range of studies including diagenetic histories in all types of carbonates.

PROJECT RATIONALE

During the last glacial period there is substantial evidence for global variability in climate dominated by Heinrich events. Heinrich events are categorized in the North Atlantic by the deposition of ice rafted debris (IRD) and have been shown to correlate with rapid climate change such as cooling in the North Atlantic, precipitation decrease in Africa and Asia and warming in Antarctica. While a comprehensive picture of climate patterns is emerging, the climate in the tropical Atlantic is still not as well understood.

In order to better understand the paleoclimate of the Bahamas during the last glacial period, a variety of geochemical proxies from stalagmites collected from flooded caves will be utilized (Figure 1). In the subtropics, it has been demonstrated that higher volume rainfall events generally leads to a depleted $\delta^{18}O$ and $\delta^{13}C$ signal, whereas heavier $\delta^{18}O$ and $\delta^{13}C$ values are attributed to lower amounts of rainfall. However, oxygen isotopes of the carbonate are not only reflective of the $\delta^{18}O$ of the water, the $\delta^{18}O$ is also influenced by the temperature at the time of formation of the carbonate mineral, therefore making it difficult to elucidate between these competing influences. These problems can be overcome by combining the $\delta^{18}O$ analyses of fluid inclusions with clumped isotopes.

Fluid inclusions are small voids within the calcite crystal that trap water at the time of formation. The trapped water can then be extracted and the water is measured for oxygen and hydrogen isotopes. This allows for the direct measurement of the isotopic composition of the fluid from which the calcite precipitates. This information combined with the $\delta^{18}O$ of the carbonate allows us to calculate the formation temperature.

The temperature at the time of formation can also be determined through the analysis of multiply substituted 'clumped' isotopologues since temperature and the proportion of clumped isotopologues are directly related (Ghosh et al., 2006). At low temperatures, the carbonate mineral is more stable and therefore an increased number of rare isotopes are multiply substituted into a single molecule. As the temperature increases, there is a decrease in the number of clumped isotopes. To measure clumped isotopes, the proportion of doubly substituted isotopologues (predominately $^{13}C^{18}O^{16}O$) of the sample gas is compared to CO_2 gas that has a stochastic isotopic value (Eiler, 2007; Ghosh et al., 2006). This relationship is expressed as the Δ47 value of the sample gas. The linear relationship between temperature and Δ47 has been demonstrated by Ghosh et al. (2006) and Dennis and Schrag (2010). Clumped isotopes have been utilized for a wide range of paleoclimate and paleotemperature studies (Eiler, 2011). In one study conducted on speleothems from Soreq cave it was demonstrated that the derived temperatures were similar to those in the literature, however, there was an observed offset in the modern temperature values (Affek et al., 2008). This suggests that there is a need for a separate calibration line for speleothems. The observed offset is thought to be due to the mechanism of calcite precipitation in a speleothem. Calcite precipitation occurs through the rapid degassing of CO_2 from a thin film of solution. During this process, the DIC does not undergo full oxygen isotope exchange with the water leading to an additional fractionation and a calcite which is enriched in Δ_{47} (Affek *et al.*, 2008, 2010). Through the application of stable isotope analysis of calcite, fluid inclusions and clumped isotopes, we can develop a better understanding of the paleoclimate in the Bahamas.

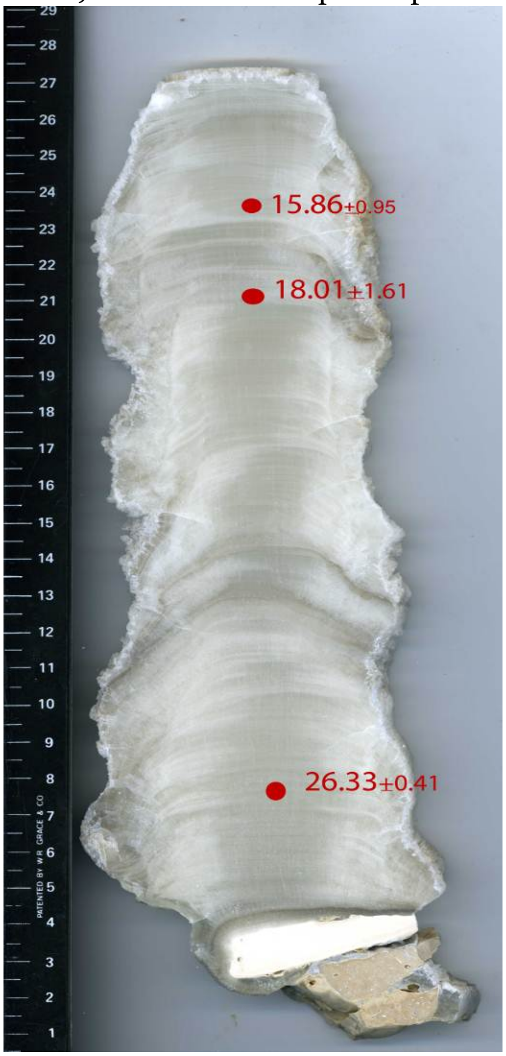

Figure 1. Cross section of stalagmite from the Bahamas showing the position of U-Th dates (kyrs). This stalagmite samples Heinrich event 1-3.

SCOPE OF WORK

Preliminary results support a significant shift in the stable carbon and oxygen isotopes of the calcite across Heinrich events. These changes were initially interpreted as a drier climate leading into the events followed by a shift to wetter climates after. However, in the summer of 2011, fluid inclusion isotopes were analyzed at Vrije Universiteit, Amsterdam, utilizing the "Amsterdam Device", an instrument built specifically for crushing carbonates in order to extract water from fluid inclusions (Vonhof *et al.*, 2006). These results support the idea that most Heinrich events are associated with cooler temperatures and a more arid climate. Initial clumped isotope results also show a decrease in temperatures across Heinrich events, however, there is an observed offset similar to other caves (Affek et al., 2008).

Recently acquired at the University of Miami Stable Isotope Laboratory is a new Picarro Cavity Ring-Down Spectrometer. The Picarro will allow for measurement of oxygen and hydrogen isotopes of water at a much higher precision than previous studies. Future plans are to construct a fluid inclusion extraction device to work in conjunction with the Picarro to conduct fluid inclusion isotopic analyses in house. Additional future work will include a cave analogue precipitation experiment where calcite will be precipitated in environments reflective of cave conditions. The experimental design will allow for various cave environments where calcite can be precipitated. For example, calcite will be precipitated in varying humidity, precipitation rates, and pCO_2 environments to better understand how these factors influence isotopic ratios. This work will help develop a clumped isotope calibration equation for speleothems.

EXPECTED RESULTS

The results of this project have important implications both for the study of speleothems and climates as well as for the study of diagenetic carbonates. The paleoenvironment of the Bahamas over the last glacial period is unknown and important for better understanding the climate system. As regards diagenetic carbonates, the fluid inclusion and clumped isotope methods are both applicable to a wide range of geochemical problems, such as understanding the paragenetic sequence of hydrocarbon bearing reservoirs.

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