

Climate of the Past - Discussions

New on-line method for water isotope analysis of speleothem fluid inclusions using laser absorption spectroscopy (WS-CRDS)

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The paper I'm reviewing is a gem! It is well written, clear, concise and contains enough detail for an experienced experimenter or analyst to replicate the method in their own laboratories. I have no hesitation in recommending it for publication with little or no modification. Below I set out some of the background to speleothem isotope measurements before considering the paper in more detail.

Speleothems (cave carbonates) have the potential to be one of the most significant climate proxies for the terrestrial environment. Specimens are available from many geological periods and most importantly from the Quaternary. Combined with high resolution dating (both radiometric and layer counting) there is the possibility to produce climate records of high temporal resolution. Witness the many exquisite records produced from Chinese caves. Decoding the speleothem record in terms of climatic variables such as temperature and rainfall amount, however, is complex. This is despite the fact that caves tend to have constant temperatures at, or very close to the annual average surface temperature above the cave.

Whilst there is a growing body of work that is concerned with trace element geochemistry, luminescence and so on by far the greatest effort has been expended on the stable isotope geochemistry of speleothems including their carbon and oxygen isotope compositions. During early research it was hoped that the oxygen isotope composition in particular could be interpreted in terms of cave temperatures. However as with all oxygen isotope thermometry determining temperatures requires that the carbonate is precipitated in isotope equilibrium with its host fluid and requires knowledge of both the carbonate and fluid oxygen isotope composition. In most cases it is not possible to measure the composition of the parent water. In the marine environment one can make an educated estimate of the marine isotope signal which only varies within limited bounds. For the freshwater environment, however, this is not possible. Our understanding of the hydrological cycle shows us that the meteoric signal can vary over large ranges as a result of temperature changes, fluctuations in evaporative fluxes and changes in seasonality. Moreover, studies of modern and fossil material shows that many speleothems grow out of isotopic equilibrium with cave drip waters.

More recently clumped isotope geochemistry methods have been applied to speleothems. Again, however, it seems that the carbonate precipitates out of isotopic equilibrium with determined D47 temperatures greater than the growth temperature of the speleothem.

Despite these caveats, almost uniquely, speleothems provide us with an opportunity of studying the complete isotope system. That is the isotopic composition of the carbonate and the water from which it grew. Most speleothems contain water in the form of inclusions in the range of 0.1 to perhaps 1 or 2 weight percent. The water, a relict of the cave drips from which the speleothem grew, can be analysed to yield important data on the isotope composition of palaeogroundwater and palaeoprecipitation. In combination with the speleothem carbonate isotope composition there remains the opportunity for those specimens that are in equilibrium to determine cave temperatures.

Since the 1970's attempts have been made to extract and analyse the isotopic composition of inclusion waters. Considerable progress has been made and the community has a good understanding of the problems inherent in the techniques that are used. These mostly centre around isotope fractionation associated with poor yields as a result of water adsorption onto the crushed carbonate surface. Perhaps our own work represented the state-of-the-art in 2001 when we reported on the dual oxygen and hydrogen isotope composition of speleothem inclusion waters using zinc reduction (hydrogen), micro-equilibration (oxygen) and dual inlet isotope ratio mass spectrometry. The work was painstaking and slow as a result of the need to eliminate all possible sources of contamination from atmospheric water vapour through to water desorbing from viton o-rings.

The more recent development of continuous flow systems (pyrolysis and mass spectrometry) and infra-red absorption spectroscopy offer the possibility of 'rapid' analysis of both hydrogen and oxygen isotopes on small (sub micro litre) water inclusion samples. Using a carrier stream of either helium or nitrogen it might be possible to eliminate many of the problems associated with water adsorption and enhance recovery yields. These methods, though, bring with them new problems. Not least of these are the large inter-sample memory effects. In routine water analysis this is not an issue. One simply runs many repeats, five or six, and uses the last few analyses as representative of the true sample composition. Another problem is the small and variable sample amounts that one expects to find with fluid inclusion analysis. Most analytical systems, both mass spectrometers and infra-red analysers have a threshold below which both accuracy and precision are seriously degraded. Many speleothems have water concentrations that are such that total liberated water is close to, and sometimes below this threshold.

Thus fluid inclusion analysis which is close to a one-shot method, with very small amounts of liberated water can be regarded as being close to the limit of what is doable in terms of isotopic analysis. This is especially so when one considers that isotopic variation with for example Holocene climate change is likely to be small. There isn't the opportunity of multiple injections to eliminate memory and improve the standard error of the mean. Thus one has to be careful to establish a method in which the memory effects are minimised and the accuracy and precision of the method is well characterised.

In the present work the authors have described a system that explicitly deals with the small and variable sample volumes of fluid inclusions and how they eliminate the memory effect. Their solution is imaginative and novel. Briefly they inject a constant background of a standard water into a dried nitrogen gas carrier stream and bleed this through their sample crushing apparatus and into the laser cavity. This establishes a background of both constant water concentration and isotope composition. When a sample is crushed the released inclusion water mixes with the standard and produces a pulse, or spike of increased water amount and a change in the measured isotope composition. By integrating across the spike in the isotope composition and the associated water concentration curve and subtracting the background signal they can recover both the isotope composition and water amount released from the speleothem.

The fact that the technique sounds intuitively obvious and simple belies the very careful experiments that the authors report in some detail. In so doing they are able to establish the optimum operating parameters for the method. Inspection of these shows that at present the technique might be best suited to samples that have relatively high water contents. For example, they show that good results can be obtained from as little as 0.5 micro litres. However, if one is working with many temperate region speleothems with water contents on the order of 0.1 weight % then this would require 500mg or more of sample material. For slow growing specimens this represents a large sample.

The data that is shown for speleothems, however, is impressive in terms of the measurement precision where repeat samples are available. Importantly they show that the measured isotope composition is robust with respect to variations in water amount released. It is harder to assess the accuracy of the reported values. The only test the authors apply for the Borneo specimens is to point out that the data lie on the Global Meteoric Water Line (GMWL). This might or might not be a good way to evaluate the data. What would be very interesting would be for the authors to include data on modern precipitation in Borneo so as to compare the data. Does precipitation in Borneo have a deuterium excess of +8? If not then either the hydrogen or oxygen isotope composition of the recovered water may have shifted. For example in the modern speleothem material from Milandre Cave (Switzerland) the oxygen isotope composition is shifted by ca. 1 per mille from that of modern drip waters. The authors suggest this might be due to post precipitation isotope exchange between the inclusion water and speleothem. This is certainly possible but there is not enough data to rule out artefacts associated with crushing this particular specimen.

In summary, this is a first class piece of work that should be published as soon as possible. I don't have any major recommendations to make that would materially improve the manuscript. As far as I am concerned it is an exemplar of a well written methodological study. My only suggestion would be to give a little more background on the natural speleothem material studied and to draw the caveat that despite the extensive testing of the method with standard waters, standard injections etc. there is only a limited data set for natural samples.

Specific points

Points 1) through 7) are just to make the prose flow more easily.

Point 6) asks what is meant by the term potentiometer in the context of the work.

Point 8) asks for clarification of the calibration procedure

Point 9) concerns Figure 8 which I don't think is referenced in the text anywhere.

1) Page 431, line 19: change **made** for **make**

2) Page 433, line 6: insert **a** between of and water

3) Page 435, line 10: replace **trough** with **through**

4) Page 435, line 16: replace **avoid that** with **prevent**

5) Page 435, line 17: replace **travel** with **travelling**

6) Page 436, line 23: what do the authors mean by **potentiometer** in this context?

7) Page 437, line 12: Insert **Whilst** at the start of the sentence "It was recommended...."

8) I didn't quite follow the calibration procedure of the CRDS system that is outlined in section 2.4.1. Is the injection of the standard via the peristaltic pump, or via the septum port prior to the crushing cell? My reading of the section is that it is via the peristaltic pump but this is not made explicitly clear in the text.

The method should be explicit because users of CRDS systems usually calibrate by injecting standard waters directly into the evaporator and may conclude that you have done something similar and not quite understand what you mean by "Injection of each standard lasts at least three hours to ensure that the system reaches an equilibrium state".

9) I think Figure 8 is an important diagram and should be referred to in section 3 - Raw data evaluation. However you only refer to Figures 9 (the water amount calibration curves) and Figure 10 which is just a schematic of the eluted sample peaks. Perhaps the best place to refer to Figure 8 is in section 3.1 where you describe how you determine the peak start and end times based on the rate of change of the water amount in the cell.