

White paper on “Speleothem-based climate proxy records“

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1. Background

Speleothems, such as stalagmites, stalactites and flowstones, are a rich archive of terrestrial paleoclimate information. The full potential of these materials has come to realization only during the last decade creating a surge in speleothem-based research. This has led to focused and high-quality research that has utilised many of the more recently available state-of-the-art sampling (e.g. laser ablation mass spectrometry) and dating (e.g. multi-collector ICPMS) techniques. This wave of research has contributed to some of the more compelling paleoclimate records produced in this period and placed speleothems at the forefront of paleo-environment reconstructions. However, it perhaps also due to their relative infancy that speleothem-based reconstructions often carry greater uncertainties than other archives such as sediments and tree rings that have long been the focus of terrestrial paleoclimate research.

The more commonly examined speleothem-based paleoclimate proxies are:

1. **Growth intervals:** determined by Uranium-series age determinations and used to identify wetter vs. drier or warmer vs. cooler climate intervals (e.g., Aylliffe et al., 1998; Spötl *et al.*, 2002).
2. **Oxygen ($\delta^{18}\text{O}$) isotope ratio:** interpreted as variations in cave temperature and properties of rainfall (temperature, air mass trajectory, source and amount effects etc.) (McDermott et al., 2004).
3. **Carbon ($\delta^{13}\text{C}$) isotope ratio:** interpreted as changes in overlying vegetation (C3 versus C4 plants) and vegetation density (Dorale et al., 1998; Baldini et al., 2008). The potential corruption of this signal downstream of the source caused by equilibration of aqueous CO₂ with cave air is also recognised, and in some cases, exploited as a proxy.
4. **Annual band thickness:** used as a proxy for the amount of rainfall (Polyak et al., 2001; Fleitmann *et al.*, 2004) or mean annual temperature (Frisia *et al.*, 2003; Tan et al., 2003).
5. **Trace elements:** interpreted as proxies for rainfall, vegetation, and growth rate and increasingly measured at high resolution to resolve seasonal information and annual features (e.g., Treble *et al.*, 2003; Johnson et al., 2006).

Other, but less frequently used climate proxies are Deuterium (δD) in speleothem fluid inclusions (Fleitmann et al., 2003), pollen (McGarry et al., 2004) and lipid biomarkers (Blyth et al., 2007). However, the large sample sizes required for these techniques have limited their use in highly-resolved paleoclimate records. Further emergent research showing promise includes sulphur concentrations and its isotopes (atmospheric source, paleo-pH; Frisia et al., 2005; Wynn et al., 2008) and noble gas concentrations (paleotemperature; Kluge et al., 2008).

To date, particular strengths of speleothem records are their potential for constructing long duration (10^3 - 10^4 years) and high-resolution records with very precise chronologies. The stacked Shanbao Cave record from China, for instance, covers the last 240,000 years with a temporal resolution of around 100 years (Wang et al., 2008); other records are shorter but preserve near-annual resolution (Tan et al., 2003; Fleitmann et al., 2004). In particular, precise chronologies of speleothem records led to significant advances in identifying and dating major climatic events and transitions (e.g., Wang et al., 2001), such as Dansgaard-Oeschger events or the start of termination II (Cheng et al., 2006). A large part of speleothem studies have focused on centennial-millennial scale climate variability, whereas monthly to annually resolved speleothem proxy records (Treble et al., 2003; 2005a) are still extremely rare.

Although the number of speleothem records is increasing steadily, a considerable weakness of speleothem records is our limited understanding of the true sensitivity of measured parameters (e.g. $\delta^{18}\text{O}$, $\delta^{13}\text{C}$) to climatic variables. The reason for this is the general lack of: (1) long-term (inter-annual) and comprehensive cave monitoring data; (2) investigation of speleothem calcite that overlaps periods for which instrumental data are available; and (3) laboratory-based empirical investigation of calcite formation under conditions analogous to caves. The first objective has been identified as particularly important as there is a high degree of variability in the climatic, geologic and geomorphic environments which host caves. Indeed, the few existing detailed monitoring programs indicate that the geochemistry of cave drip waters and contemporaneously deposited stalagmites may vary considerably within a cave (e.g., Asrat and Baker, 2008). This has been attributed to the result of differences in the flow paths of seepage water and hydrological routing effects (e.g., variable proportions of “event” and “storage” water; Asrat and Baker, 2008). There is now a consensus among researchers working on stalagmites that cave monitoring programs should complement paleoclimate studies on speleothems.

2. Sources of uncertainty in speleothem proxies

2.1 Dating

One particular strength of speleothem is age dating. The most commonly used methods for dating speleothems are Uranium-series dating (U-Th hereinafter) and to a much lesser extent radiocarbon dating (^{14}C hereinafter). Furthermore, some stalagmites show annual lamina which can be counted, similar to tree rings (e.g., Tan et al., 2003). The strengths and limitations of both methods are described below:

Uranium-series dating is based on the decay of the parent isotopes ^{238}U , ^{234}U to ^{230}Th . Provided that the speleothem calcite contains no initial ^{230}Th (see next paragraph) U-Th ages are absolute ages and no correction is needed. Relative age uncertainties are small and typically vary between 0.5 and 2% of the absolute age, depending on the Uranium content (typically 0.05-0.5 ppm). However, obtaining precise chronologies for stalagmites younger than ~2000 years is difficult as concentration of ^{230}Th is low and close to the detection limit of TIMS (Thermal Ionisation mass spectrometer) and MC-ICPMS (Multi-Collector Inductively Coupled Plasma Mass Spectrometer). As a result, age uncertainties for young speleothems with low U can be in the range of 5 to 10% of the absolute age, which limits the ability of correlating speleothem-based time series with other records, such as instrumental time series and annually-precise tree ring records.

Large age uncertainties are associated with the presence of so-called “initial” ^{230}Th , which is incorporated with other impurities at the time of speleothem formation and leads to artificially

old U-Th ages. While it is clearly desirable to work on speleothems with very low “initial” ^{230}Th , it is not always possible to obtain such material. ^{232}Th is routinely measured as a “proxy” for ^{230}Th , and combined with estimates of the $^{230}\text{Th}/^{232}\text{Th}$ ratio of the contaminant phases to correct U-Th ages for the presence of initial ^{230}Th . Values of $^{230}\text{Th}/^{232}\text{Th}$ can be obtained using isochron techniques, or directly measured on chemically separated detrital phases (Dorale et al., 1992). However, relatively few estimates of this key ratio exist, and it is highly likely that this ratio varies from site to site and through time at a given site, such that ^{232}Th -corrected ages can be associated with extremely large errors (especially in young and/or low-U materials, where the relative contribution of initial ^{230}Th to the total ^{230}Th pool can be very high). Workers typically discard high- ^{232}Th ages from an age model, choosing only to include low- ^{232}Th ages where the ^{232}Th correction is only several times larger than the analytical error (i.e. $\pm 2\text{-}5\%$).

Hiatuses and/or non-linear growth rates can introduce significant chronological error into high-resolution speleothem proxy records, because the climate proxy of choice (e.g. $\delta^{18}\text{O}$) is typically measured at a much finer resolution than are U-Th dates (by a factor of 10-100). Therefore, undetected hiatuses and/or changes in growth rate between U-Th dating horizons can introduce appreciable error into the resulting proxy record (making the chronological error significantly larger than the analytical precision of U-Th dates, for example). In dating speleothems, it is also important to recognize that a drilled sample might contain powders from different time periods (in the extreme case where a U-Th date is drilled across an undetected hiatus), with the resulting age being a weighted average of the two periods. These problem points to the need for:

1. Closely-spaced U-Th age determinations which will reduce the impact of any individual date and indicate non-linear growth characteristics (and see Drysdale et al., 2007 for a method of modelling growth rate changes between age determinations).
2. Careful screening (both visual and geochemical) for hiatuses (including pre-scanning samples for ^{232}Th and Al to indicate regions of high ^{232}Th and hiatuses, respectively, by laser ablation ICPMS).
3. Replication of speleothem climate proxy records from multiple samples at a given site

However, U-Th-dated changes in growth rate (including hiatuses) have been applied to climate studies and interpreted in terms of climatic forcings. For example, Wang et al. (2004) found that periods of deposition in a Brazil cave correlate with North Atlantic Heinrich events. Such interpretations require a good understanding of local cave processes. For example, in some cases (particularly in arid environments), wetter periods can actually reduce the amount of moisture available in a cave by stimulating vegetation growth that intercepts soil moisture.

Radiocarbon dating: ^{14}C -dating of speleothems is difficult due to the highly variable dead carbon proportion inherited from limestone carbon, which makes it virtually impossible to date speleothems by this method without assuming the dead carbon contribution. However, radiocarbon measurements have been used to identify the 1964 “bomb testing” peak in modern stalagmites (Genty et al., 2001). Obtaining a precise chronology for the youngest section is, particularly if annual layers are absent, a prerequisite to calibrate measured proxies against instrumental data

Annual lamina: If annual laminae are present throughout the entire stalagmite, chronologies can be established by counting the layers. Most stalagmites, however, do not show such annual lamination at all or only over fairly short sections in the stalagmite (e.g., Genty et al., 1996). However, many speleothems with annual growth rates above 50 μm have detectable seasonal variation in trace elements (often referred to as “annual trace element cycles”; Fairchild et al., 2001). These “cycles” similarly offer a tool for resolving annual chronological markers. Importantly, U-Th ages are needed to confirm any chronology based on annual laminae or trace element cycles. However, such layer counted time series can have still age uncertainties due to the presence of sub-annual laminae (Tan et al., 2006), missing laminae or double-peak trace element cycles (Treble et al., 2005b). Again, replication of annual lamina time series is critical, as it has been demonstrated that multiple speleothems from the same site have markedly different growth rates during the same time period, and different distributions of hiatuses (Partin et al., 2007).

2.2 Stable isotope ratios of speleothem calcite ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$):

The interpretation $\delta^{18}\text{O}$ in speleothems is complicated by the fact that various and usually competing factors influence $\delta^{18}\text{O}$ in speleothem calcite. An early objective was to use $\delta^{18}\text{O}$ in speleothems to reconstruct absolute changes in mean annual air temperature, as the fractionation of $\delta^{18}\text{O}$ during calcite precipitation is dependent on temperature. However, $\delta^{18}\text{O}$ of speleothem calcite in most caves is primarily controlled by isotopic composition of the cave seepage waters and meteoric precipitation, whereas $\delta^{18}\text{O}$ of precipitation is climatically controlled. On seasonal time scales variations of $\delta^{18}\text{O}$ in precipitation arises from variations in the source of rainfall and its characteristics (e.g., frequency, duration, intensity) and surface air temperature. On decadal to millennial timescales, additional factors such as changes in the $\delta^{18}\text{O}$ of the ocean (“ice volume” effect), changes in the seasonality of precipitation (e.g., change in the proportion of winter and summer precipitation) and shifts in the source of moisture and/or storm tracks must be taken into account (e.g., Bar-Matthews *et al.*, 1999, Fleitmann *et al.*, 2003). Despite these complications, $\delta^{18}\text{O}$ of speleothem calcite is currently the most frequently used speleothem-based proxy as it can provide information on $\delta^{18}\text{O}$ of precipitation on time scales ranging from annual to millennial. Ultimately, data from on-site rainfall and dripwater $\delta^{18}\text{O}$ monitoring programs must be combined with atmospheric general circulation models equipped with water isotopes to begin to unravel the complexities surrounding the interpretation of speleothem $\delta^{18}\text{O}$ records. This process is still in its infancy.

$\delta^{13}\text{C}$ in speleothem calcite is an additional and important environmental proxy, although $\delta^{13}\text{C}$ is more difficult to interpret in climatic terms (e.g., Baker *et al.*, 1997). Non-climatic effects, such as isotopic fractionation due to CO_2 degassing or soil water residence times, can significantly affect calcite $\delta^{13}\text{C}$, and thus blur the climatic signal. Furthermore, many studies have linked speleothem $\delta^{13}\text{C}$ variability to so-called “prior precipitation” of carbonate upstream of the speleothem formation site, a process that enriches the dripwater in $\delta^{13}\text{C}$ (Fairchild et al., 2001; Johnson et al., 2006). Nevertheless, numerous studies on stalagmites from areas with different climatic settings suggest that $\delta^{13}\text{C}$ often reflects the degree of biogenic activity above the cave and/or the ratio of C3 (trees and shrubs) to C4 (drought-adapted grasses) vegetation. Generally, higher biogenic activity and/or higher proportion of C3 vegetation (higher precipitation) results in more negative $\delta^{13}\text{C}$ calcite values. In this case $\delta^{13}\text{C}$ values could provide additional information about the hydroclimatic conditions. More recently, speleothem $\delta^{13}\text{C}$ has been linked to kinetic fractionation associated with the degassing of CO_2 from the cave dripwater, which in turn varies in response to ambient cave CO_2 levels (Matthey et al., 2008). Very few cave ventilation studies have been conducted (Baldini et al., 2008), and these must become a priority to determine whether speleothem $\delta^{13}\text{C}$ in a particular cave represents a robust climate proxy.

2.3 Annual laminae

Annual laminae (whose thickness typically varies between 50 and 500 μm) are in most cases the result of a strong seasonality in the amount of surface precipitation and drip water supply. The thickness of annual laminae can relate either to the amount of surface rainfall (e.g., Polyak and Asmeron, 2001) or cave air temperature (e.g., Tan et al., 2003). Furthermore, by counting annual bands, radiometric chronologies can be significantly improved (Fleitmann *et al.*, 2004). However, published stalagmite laminae records are almost entirely based on single stalagmites and not on replicated samples. It is therefore difficult to assign uncertainties. Betancourt et al. (2002) suggested that stalagmite-based laminated records should be held to the same standards as annually resolved tree rings, particularly in term of chronology building and climatic inference.

2.4 Trace elements

Trace elements are still an under utilized climate proxy in speleothem-based paleoclimate reconstructions, mainly due to analytical limitations which prohibited rapid acquisition of data. However, by using recently developed laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), trace elements such as Mg, P, U, Sr, Ba and Na can be measured at sub-annual resolution with scan rates of 1-2 mm/min resulting in collection of millennia to multi-millennia time series within one day. Recently published studies performed on speleothems from different environmental settings reveal that both hydrological (e.g., amount of precipitation, groundwater residence time, rock-water interaction) and/or growth-related processes can affect trace element concentrations (e.g., Treble *et al.*, 2003). Although more research in this field is certainly needed, Mg, P, U, Sr and Na appear to be the most effective and promising paleohydrological indicators (Fairchild *et al.*, 2001; Treble *et al.*, 2003). However, the relationship between trace element content in speleothems and climatic/environmental conditions can vary between caves due to differences in their general settings, such as thickness and chemical composition of bedrock, groundwater movement, soil thickness and climatic conditions. Consequently, a thorough comparison between instrumental data and a modern speleothem is important to test the proxy qualities of each trace element (e.g., Treble *et al.*, 2003). In addition, drip-water should be continuously collected and analyzed. Despite these difficulties there is fast growing interest in speleothem-based trace element time-series, as they make a monthly to annual resolution possible.

3. Make recommendations for how to better represent proxy error to non-specialists

Developing quantitative and highly resolved paleoclimate records from stalagmites is still a challenge. To date there is only a very limited number of stalagmite-based quantitative time series of temperature (Mangini et al., 2005; Tan et al., 2003) or precipitation (Hu et al., 2008), and some of them are the subject of controversial discussions. Cave monitoring data are a prerequisite to develop speleothem-based climate transfer functions which can then be applied on long speleothem time series.

Our understanding of the most frequently used speleothem climate proxies ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$, laminae thickness, trace elements) still remains limited due to the general lack of extended cave monitoring data. This makes it also difficult to assign uncertainties to an individual proxy. The speleothem community is now well aware of this problem and cave monitoring programs were launched in many caves around the world.

Multi-proxy and multi-sample approaches are a first step to ascribe uncertainties to individual speleothem proxies. However, such an approach requires substantial analytical efforts to include samples from (ideally) several caves.

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