Archives of Climate Change in Karst

Proceedings of the symposium
Climate Change: The Karst Record (IV)

held May 26 through 29, 2006
Băile Herculane, Romania

Edited by
Bogdan P. Onac, Tudor Tămăș, Silviu Constantin, and Aurel Perșoiu
Special Publication 10

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Scărișoara Cave is situated in the Apuseni Mountains, NW Romania. At the bottom of the 48 m entrance shaft the cave hosts a glacier-like ice block. The total volume of the clearly stratified ice block is estimated to ~100,000 m³. The top ice surface area visible in the Big Room covers approximately 3000 m², and the ice thickness exceeds 22 m. Radiocarbon dating of organic material from the upper part of the exposed wall yielded ages from about 1000 to 700 cal yrs BP, but the pollen association within the bottom layers suggests the ice is at least 3,500 years old.
Foreword

This is an anniversary year for the karst paleoclimate research community and also for the Karst Waters Institute. Ten years ago, in Bergen (Norway), Stein-Erik Lauritzen launched/organized the first Climate Change: the Karst Record meeting. It was there for the first time that leading scientists, studying different types of cave sediments from various perspectives, gathered together in a large-scale, focused conference. The driving force for the critical interest in studying cave sediments was the increasing role these type of archives play in Quaternary paleoclimate and paleoenvironment reconstruction.

Until recently, the primary evidence of a close link between climate changes, sea-level rise and fall, and ice-sheet growth and decay, came from deep-sea sediments, ice cores, precisely dated coral terraces, and peat deposits. Over the last decade, major improvements in analytical facilities allowed the generation of high-resolution paleoclimate data. Thanks to many works published in leading journals, paleoclimatologists became more than ever aware that speleothem archives are the best datable continental records. Many of the papers published in this special publication address or answer complex problems that regard the relationship between speleothem geochemistry, macroclimate, ecosystem (vegetation and soil), karst aquifer, and intimate crystal growth.

“Ten years after” the Bergen meeting, the community of researchers and/or speleologists is gathering again in Băile Herculane, Romania, for the Fourth Conference “Climate Change: the Karst Record” (26–29 May, 2006) (KR4), organized by the “Emil Racoviță” Institute of Speleology and the Romanian Society for Speleology and Karstology. As organizers, we are extremely honored that our scientific community has chosen Romania as a host-country. In the last decade the studies dedicated to climate change as derived from karst deposits of Romania have significantly increased, although many of them made their way to mainstream journals only in the last years. The conference was organized as a special edition (the 19th) of the “Theoretical and Applied Karstology” (TAK) International Symposium.

This book includes the full series of abstracts and extended abstracts presented at the KR4 Conference and a few associated, off-topic, TAK papers. The papers are grouped into topical sections, with papers arranged alphabetically inside sections. The last section presents the off-topic communications. If one would compare the papers presented at the first, Bergen Conference, with current ones, both scientific and technical advances are obvious. Therefore, we won’t add any more comments about the extreme technical and scientific refinement that may currently be encountered in the studies of the karstic realm. We let the readers judge for themselves, but we are convinced that they will appreciate the broad range of methods and new results emerging from our ‘black box’.

Silviu Constantin and Bogdan P. Onac
This Karst Waters Institute Special Publication was published on the occasion of the
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Archives of Climate Change in Karst

KEYNOTES
Speleothems are regarded as valuable archives of continental paleoclimate. Their isotopic and chemical compositions depend on the vapor source, storm trajectories, air temperature, distance from sea, elevation, fractionation processes between rainfall and the unsaturated zone and soil-water-rock interactions. They are the end product of the oceanic-atmospheric-land hydrological cycle, and are the continental equivalent (“continental cores”) of marine cores. Their precise dating (at least for the last 400–450 kyr) enables to accurately determine the timing of oxygen and carbon isotopic signals of major and minor climatic events such as glacial/interglacial transitions, the Younger Dryas, Dansgaard-Oeschger and millennial-sub-millennial time-scale oscillations, offering the opportunities to assess leads and lags in the sea-atmosphere-land hydrological-climate system. Dating growth periods of speleothems, in conjunction with the isotopic record, mineralogy, petrography and trace elements, enable to derive information on the low latitude monsoon activity, high-latitude Atlantic-Mediterranean rainfall system, ITCZ, snow cover extent and melting, desert migration, and vegetation throughout the world.

We examined the transition between glacial Marine Isotopic Stage (MIS) 6 to interglacial MIS5 in order to determine the relationships between maximum insolation and the hydrological conditions. Growth periods of speleothems from caves located in high and mid latitudes show that the initiation of their growth does not always coincide with maximum summer insolation in 65°N at 128 kyr. At higher latitudes (e.g., Norway), speleothems growth initiated only at 123.5 kyr, ~5,000 years after insolation maximum (Linge et al., 2001), probably related to the timing of ice melting. This is in contrast to the timing of speleothems growth following glacial MIS6 in northern England and at the high Austrian Alps, which occurred at 133 and 135 kyr, respectively (Baker et al., 1995; Spotl et al., 2002), i.e., 5,000 to 6,000 years before maximum insolation.

In central-western Italy, speleothem growth started at the end of MIS6, at 141 kyr and the change in their δ18O to lower values occurred at ~130 kyr (Drysdale et al., 2004). In the Eastern Mediterranean (EM) region speleothems grew continuously through glacial and interglacial intervals, but the change in their δ18O values occurred in 3 steps, at 141, 134 and 129 kyr. The abrupt decreases in the δ18O values at 141 and 134 kyr indicate that the changes in the hydrological conditions pre-date the maximum insolation. The time interval between 129 and 120 kyr is characterized by minimum δ18O of EM speleothems coinciding with increased tropical-subtropical (monsoonal) precipitation driven by insolation.
as evident by the minimum $\delta^{18}O$ values of speleothems from Asia (Burns et al., 2001; Yuan et al., 2004). Thus, timing of speleothem growth and their isotopic composition on a cross section from northern Europe, through the Mediterranean into Asia demonstrate that MIS6-MIS5 transition occurred in 3 steps, at 141, 134 and 129 kyr. These steps can be identified in mid-latitudes, whereas in north and central Europe only two steps are recognized due to the timing of ice cover melting. In Asia MIS6-MIS5 transition occurs only in one step at ~129 kyr and it correlates with monsoon maxima which in turn depend directly on insolation.

Examples regarding whether the entire Sahara-Arabian desert belt was under the influence of the monsoon can be derived from the study of speleothems from caves located presently in arid regions at the north-eastern corner of the Sahara desert (the Negev Desert, southern Israel). This region is situated on the border between Mediterranean climate region and the Saharo-Arabian Desert. Accurate dating of speleothems growth and their isotopic composition show that southward migration of the desert border occurred during glacial humid intervals at 190-150 kyr, 76-42 kyr, 40-25 kyr, 23-13 kyr, and interglacial humid intervals at 200-190 kyr, 137-132 kyr, 131-123 kyr and 84-77 kyr. During these periods the north-eastern corner of the Sahara desert was wetter compared with the present arid climate and climate during intervals when speleothem deposition did not occur at 150-144 kyr, 142-138 kyr, 117-96 kyr, 92-85 kyr, 42-40 kyr, 25-23 kyr, and 13 kyr to present-day. Maximum monsoon index values at 198 kyr, 127 kyr, and 83 kyr coincide with wetter intervals whereas at 105 kyr and 11 kyr coincide with dryer conditions. During glacial, when the monsoon index was high at 176 kyr, 151 kyr, 61 kyr, and 33 kyr the region was relatively wetter, but it also was wetter during minimum monsoon index values. The similarity between the $\delta^{18}O$ values of the speleothems from the north-east corner of the Sahara Desert compared with speleothems from central and northern Israel implies that the dominant rainfall source to the north-eastern corner of the Sahara Desert was the Eastern Mediterranean Sea. However, during wetter periods when the monsoon index was maxima, it is possible that the north-eastern corner of the Sahara Desert received its moisture also from a remote southern tropical source.

References


SPELEOTHEMS AS RECORDERS OF FLOODING AND INSIGHTS INTO THE EARTH’S HYDROLOGIC CYCLE

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Shallow, dendritic cave systems in close association with the modern water table are commonly prone to flooding during high recharge events. The nature of the flooding involves numerous recharge points but few discharge points in the groundwater system, creating a condition of slow backflooding in the cave. Clays and silts may be suspended during the flooding, which then coat bedrock and speleothem surfaces that are inundated by the flood waters. After flood waters recede, the flood event may be preserved by the subsequent resumption of speleothem growth, which traps the detrital layer in calcite. Stalagmites that grow nearly continuously for long periods of time may thus preserve a detailed flood record for thousands of years.

The well-dated speleothem stable isotope record from Crevice Cave in southeastern Missouri, U.S.A. (Dorale et al., 1998) is augmented by such a flood record preserved in stalagmite calcite. The moisture source for Missouri is the subtropical Gulf of Mexico, and flooding in this region usually involves a persistent meridional circulation pattern that delivers Gulf moisture to passing storm tracks, as occurred in 1993. Interestingly at Crevice Cave, flood-deposited detrital laminae are ubiquitous to Holocene-age formations in the cave, but are absent in most, but not all, intervals from the last glacial and previous interglacial periods. Millennial-scale cycles of more frequent flooding are a dominant feature in the Holocene flood record from Crevice Cave, as is an apparent increase in the frequency of flooding in the Late Holocene versus the Middle and Early Holocene. ENSO is a possible explanation for these observations, because the long-term variability of warm ENSO (El Niño) periods as recently modeled (Clement et al., 2000) shows a close correlation to the millennial-scale flooding record in Crevice Cave. The flooding record also supports the idea that El Niño is a phenomenon unique to the Holocene and other discrete periods, as determined by a specific combination of orbital parameters (Kukla et al., 2002). The observation that flooding is most active during the Holocene and is least active during the Last Glacial is opposed to the view offered by polar ice-core based temperature records, where Holocene climate appears stable. In contrast, the Earth’s hydrologic cycle during the Holocene as viewed from North American flooding appears remarkably dynamic.

References


Caves are prone to seasonal fluctuations in physical properties (such as the supply of water and the composition of cave air) that strongly influence the formation of speleothems. The movement of matter and energy into and out of caves constitutes the physiology of the cave system (Figure 1). The speleophysiology builds on the work on cave physics that have been carried out by numerous previous researchers, but here we emphasize the connection to speleothem formation. As with other systems involving mass transfer, a box model can be set up to describe the system functioning and to draw attention to the factors that are likely to be controlling growth rate and geochemical properties of speleothems. Under suitable circumstances, models can be calibrated quantitatively.

The supply of dripwater to speleothems can be relatively constant or highly variable over time, depending on the relative supply from a seepage reservoir, fractures or conduits (Figure 2). A modelling study at Brown’s Folly Mine, Bath, UK (Fairchild et al., 2006), shows that the flows can be quantified in relation to infiltration events, but that aspects of the mixing of waters that control the geochemistry are more complex than simple conservative processes.

Whilst variations in fall height can control the lateral dispersion of the water, the driprate and the cave humidity determine the extent of evaporation, if any, of water on speleothem surfaces. The exposed surface area of the water is critical to the process of CO₂-degassing that controls the supersaturation state with respect to CaCO₃ that allows carbonate speleothem formation in the first place. Degassing may be associated with precipitation of CaCO₃ within or on the ceiling or walls of caves such that stalagmites and coneshaped stalactites show geochemical effects (e.g. enhanced
Sr/Ca and Mg/Ca) of prior calcite precipitation. Drips with a fracture-fed component will reflect seasonality if infiltrating rainfall shows seasonal variation.

The CO2 composition of cave air is a limiting factor on degassing and hence the supersaturation of karst dripwaters. Most, but not all caves show increases in CO2 in the summer season. Traditionally higher pCO2 in cave dripwaters and cave air has been interpreted as causally related to higher soil pCO2 in summer. However, at some cave sites (e.g. Ernesto, Obir), it has been established that there is a year-round constancy of the CO2 reservoir. In that case, lower pCO2 in winter might be related to higher ventilation (e.g. Obir cave), consistent with observations from other caves where radon concentrations are lower in winter. Alternatively, the filling of the aquifer by infiltration from autumnal rains could cut off the supply of air-filled fissures from the soil and epikarst to the cave. Observations can distinguish between these possibilities.

Speleothems display a number of properties by which annual cycles can be detected. Where rainfall isotopic composition shows distinct seasonal variations, and where there is a distinct fracture-fed component to dripwater, dripwater can show seasonal δ18O variations and high-resolution analyses are now demonstrating their preservation in cave calcite precipitates. Where there is a strong seasonal dryness, or seasonal variations in the pCO2 of cave air, prior calcite precipitation can vary seasonally, giving rise to annual cycles of covarying Mg and Sr. Covariation of such tracers with δ13C is an expected result of this combination of processes. The independent pH effect (related to variability of cave air pCO2) on the incorporation of trace components is currently being researched, but there are grounds for believing that sulphate exemplifies such a pattern. This is because its incorporation reflects its ratio to the carbonate ion which is pH-controlled. In the case of infiltration-control, a distinct visible and/or UV-fluorescing autumnal layer is associated with enrichments in a number of elements whose transport can be enhanced by organic colloids. In detail, some speleothems may reflect multiple events within one year, whereas others, such as all those studied at the Ernesto cave, overwhelmingly reflect the annual process scale.

Reference

UNFINISHED BUSINESS

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During a long career in any part of field-based earth sciences a researcher can expect to accumulate a stock of studies that remain incomplete and unpublished for a variety of reasons. There are many examples amongst the speleothem studies that I undertook, alone or with Henry Schwarcz and others, over the period from 1967 to 2005. This paper will discuss a selection of them, and lessons that may be learned from the problems that were encountered. The selection ranges from arctic and alpine caves through temperate and tropical sites to hot deserts. It includes conventional vadose calcite and aragonite stalagmites and flowstones, phreatic meteoric and thermal water geodes, clouds, folia, crusts and rafts. The review will cover U-series dating, $\delta^{18}O$ and $\delta^{13}C$ results, with an emphasis on the unexpected and (occasionally) inexplicable.
A key component of studies that use cave deposits as archives of past climate change is chronology. Whether studies are based on (1) presence or absence of speleothems (sea level, permafrost, rainfall or other limiting conditions for growth), (2) archival information contained within calcite deposits (such as trace elements, luminescence, $\delta D$, $\delta^{18}O$, $\delta^{13}C$, pollen and internal stratigraphy, including growth rate and hiatuses), or (3) stratigraphical relationship with evidence of human occupation, flooding, seismicity and so on, age determinations and their associated uncertainty are paramount. One could argue that the prime reason for the continued surge in interest in karst and climate change research has been the derivation of robust chronologies, which are often continuous and very high-resolution. Indeed, one could go further and also suggest that in many cases we are more confident in the timing of a shift in the archive response than the nature of environmental change associated with it. We will discuss the extent to which chronologies are robust by presenting examples from a whole range of timescales from $<10^0$ to $10^5$ years, and suggest methods we might adopt to improve upon the current situation. We will first look at the age estimates themselves and then the period of time represented by material or hiatuses between them.

A host of geochronological methods have been applied to speleothems, and include $^{14}C$, ESR, amino-acid racemization, layer-counting, and the widely used U-series disequilibrium methods (listed in order of applicable age range - $^{210}$Pb, $^{226}$Ra-excess, U-Pa, U-Th, U-Pb). We will draw principally on the latter methods and discuss first the uncertainty and limitations associated with individual age determinations by considering issues such as initial assumptions (particularly initial $^{230}$Th concentration), intercalibration, standards and half-life determinations. We will argue that an under-utilised approach within dating is the search for concordant age estimates. Closed system behaviour for both the $^{238}$U and $^{235}$U decay chains, for example, adds confidence to derived age estimates.

We then focus on the quality of temporal constraints that can be derived for any particular archival response by using interpolation or extrapolation of age determinations. In the majority of paleoclimate records derived from speleothems, the density of sub-sampling for proxy information such as stable isotopes and trace elements is much higher than that for age determination. Interpolation methods are required. We will present a suite of methods that use non-parametric smoothing splines to generate chronologies. We will also discuss the extent to which longitudinal data from a single cave or region can be compared with alternative archives such as ice cores, ocean and lake cores in a correlative sense. Can we be “wiggle-matching”? The karst and climate change community is well-placed at the current time to make statements about the external and internal forcing of climate at a wide range of temporal and spatial scales. For the most part we are adopting robust methodologies to do this, but there are opportunities for the widespread use of simple and standard protocols that would strengthen our science.
In OIS-3 times, especially in colder episodes during which the northern European plain would have been an arctic desert, the Iron Gates of the Danube were the obligatory passage across the Carpathian Mountains for access to Central and Western Europe from the Near East and the areas surrounding the Black Sea. Thus, one might predict from this geographical location alone that the Romanian karst would represent a key research area for the study of the dispersal of the first modern human populations into the European continent. That is exactly what the last five years of scientific developments have dramatically highlighted.

Rather complete but essentially undescribed human remains were already known from the sites of Cioclovina and Muierii; their relevance for modern human origins research, however, would only come to light after 2001, when their direct radiocarbon dating showed that their age fell in the ca. 29–30 ka 14C BP range. The accidental discovery, in 2002, and subsequent archaeological study, in 2004–05, of the Pеștera cu Oase cave system (Figure 1), yielded even older human fossils, belonging to two individuals, one of which directly dated to ca. 35 ka 14C BP. Unlike the previous finds, the Oase material (Figure 2) was recovered in well controlled conditions, with associated detailed stratigraphic, taphonomic, and chronometric data.

As these developments were occurring in Romania, the direct dating of other human remains that for a long time were presumed to date to the relevant time period (most notably, those from the Vogelherd cave, in Germany) showed that they were much younger, in actual fact of Holocene age. The fossil record that emerged from the weeding of this spurious evidence now presents a striking concentration of the finds in eastern Europe: the three Romanian sites plus Mladěč, in Moravia, and La Quina Aval, in France, are now the only instances where uncontroversially diagnostic modern human remains are directly dated to the period between 30 and 35 ka 14C BP (or presumed with good reason to be of that age on the basis of the stratigraphic integrity of the levels containing them).

The research carried out in the Oase cave system has provided much information on the history of the site and the nature of the bone accumulations contained therein. Above the presently active underground stream, and sharing the same general NW–SE orientation, there is a network of fossil galleries located at different elevations, comprising at least two main levels that reflect different stages in the history of the incision of the Minișdrainage. The uppermost level is at present exposed over extensive stretches as a result of collapses, originating an exokarst dotted by numerous dolines but whose connections with the deeper levels are everywhere blocked by the accumulation of sediments. Because of this cluttering, the Oase galleries, which belong to the intermediate level, situated on average ca. 40 m above the stream, cannot at present be reached from the surface. Their discovery, as well as their subsequent scientific exploration and study, resulted from the establishment, by the Timișoara-based ProAcva Group, of an access route from below, via the spring and underground stream.

Uniting these levels, a 30 m shaft (the Putul) preserves, against the walls, a rather complete profile representing fluviatile deposits that, for the most part, were removed by erosion; these deposits contain remains of cave bears for which preliminary U-series dates on bone suggest an OIS-5 age. The base of the deposits filling the Oase galleries has not been reached, but ca. 80 cm below the surface, they are radiocarbon dated to ca. 47.6 ka 14C BP. This deposit, Level 2 of the stratigraphy recognized in the excavated area of the site, corresponds to successive episodes of torrential accumulation of thousands of cave bear bones resulting from natural deaths during hibernation. This mode of accumulation ceased...
to function after ca. 43 $^{14}$C BP, after which time only low-energy processes are documented (Level 1 of the stratigraphy). In this area, a period of stabilization ensues, marked by the formation of stalagmitic crusts and the growth of stalagmites, for which preliminary U-series results indicate an age of ca. 42 ka cal BP.

The human remains lay on top of this stabilized surface, where remains of ibex have also been found; whereas the former represent an episode of accumulation dated to between 35 and 30 ka $^{14}$C BP, ibex remains continued to enter the system until the Last Glacial Maximum. Wolves denning at the site once it became inaccessible to cave bears are probably the agent of accumulation of the ibex; the same may apply to the human remains, although secondary accumulation by gravity from a primary site located in the exterior remains the most parcimonious explanation; in fact, no evidence of human frequentation of the interior of the cave was found, and no artifacts or cut-marked bones suggestive of human activity were recovered in the deposits. However, open caves containing archeological deposits exist in other parts of the Oase karst, preliminary testing having already reached Pleistocene deposits; plans exists to continue this work in the hope that a cultural context for the Oase fossils will eventually be retrieved.

The establishment of such a cultural context is all the more important because of the presence of several anatomically “archaic” features in these otherwise clearly modern human fossils. Such mosaics have also been identified in all other early modern human remains of Europe dated to within some 5000 years of the time of contact with the Neandertal populations that previously inhabited the continent. Thus, it would seem that significant levels of interbreeding resulting in extensive admixture between the two groups and the eventual disappearance of the Neandertal phenotype happened at that time, a conclusion that finds strong support in the evidence from the Romanian karst.

**Figure 2.** The Oase human remains.
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PRESENT-DAY KARST ENVIRONMENT
The stalagmites in Shihua Cave, Beijing, are characterized by visible and fluorescent laminae that correspond to annual cycles as shown by TIMS-230Th dating (Tan et al., 2000). A 2650 years long (BC665-AD1985) warm season (May to August) temperature reconstruction has been derived from a correlation between thickness variations in annual laminae of a stalagmite from Shihua Cave and instrumental meteorological records (Tan et al., 2003). In order to develop a comprehensive understanding of the relationship between the nature of stalagmite laminae and surface climate and environmental variation, five drips in Beijing Shihua Cave were chosen to analyze for discharge at 1–3 days interval and concentration of dissolved organic carbon (DOC) at 1 day to ~4 weeks interval from December 2003 to December 2005.

Results show that there are intra- and inter-annual variations in concentration of DOC in all drip waters, however with different patterns in different years (see Figure 1). In 2004, high DOC concentrations are synchronously introduced after a threshold of rainfall during rain periods. This suggests that higher abundances of organic substances are flushed from the soil by critical rainfall, which results in the formation of organic substances laminae in the stalagmites. During the rain period of 2005 however, peak of DOC concentration is lower than in the former year in all drip water, and different drip sites showed different variation of DOC. Only one drip water (drip site JG) responded to precipitation rapidly showing a high DOC peak in August 2005. Other drip waters show lower or lag peaks of DOC concentration.

**Figure 1.** The intra- and inter-annual variation of dissolved organic carbon (DOC, unit: mg/L) of cave water for five sites in Beijing Shihua Cave and the amount of rainfall during the time period October 2003–January 2006.

**Figure 2.** Comparison of drip rate (unit: drops/min) of five sites in Beijing Shihua Cave and amount of rainfall for the time period October 2003–January 2006. Arrows show continuous flow of water.
These variations may be caused by several factors that can be inferred as follows.

First, the type of rain is the most important factor. There was almost the same amount of rainfall (about 580 mm) in both years. But frequent and continuous rain that makes rainwater more permeable into the soil and karst fissures occurred from the middle of June to July in 2004, while less frequent but stronger storm events happened during July and August 2005. The latter tends to form surface flow that leads to a decrease of water infiltration. Second, the condition of hydrological forcing is another switching. Dripping at all the sites continues all year long. The drip rate of the five drip sites shows marked spatial changes with different lag times controlled by soil and karst micro-fissure/porosity network recharge (see Figure 2). Higher concentration of DOC occurred in drip sites responding to precipitation more rapidly. For the type of drip with thinner bedrock, discharge increases rapidly after a critical rainfall, which suggests that they can be mainly provided through short path and macro-fissure flow during the rain period. In comparison, some drip waters provided by longer and complex flow route cannot respond to change in precipitation so rapidly. Thus they could only take less DOC into cave, or maybe water with high DOC come into cave after a long time and then a damped peak of DOC is produced (e.g. drip site PL2, see Figure 1). Therefore the potential soil and aquifer zone flow pathways and conditions may control karst water evolution and affect the type of discharge and the character of geochemistry of drip water. Third, the amount of DOC source in soil, which is controlled by climate, may be different between the two years. More detailed research on the cycle of dissolved organic matter (DOM) in soil must be done to evaluate this factor.

Similar experiments measuring drip water luminescence over a hydrological year at Lower Cave, Bristol (Baker et al., 1997) and the Brown’s Folly Mine site (Baker et al., 1999) in England also revealed an increase in luminescence of DOC during the period of hydrologically effective precipitation in late fall or early winter. However, at Marengo Cave, Indiana in America (Toth, 1998; van Beynen et al., 2000) high fluorescent intensity and DOC enter the cave during the spring, when rain melt the snow and thaw the soil, generating a flush of organics from the soil to the cave. These observations confirm that seasonal dry/wet and cold/warm shifts in climate zones as diverse as those in China, England and America can produce clear growth-layers.

In conclusion, fluorescent laminae of stalagmites in which the fluorescing components are organic acids may be formed during the rain period in some drip sites in Shihua Cave, and have therefore the potential to record the change in past climate. However, as different sites in the cave show different variations of DOC, we must be cautious in selecting stalagmites to reconstruct paleoclimate. Such variability between samples is maybe related to the heterogeneity of karst groundwater flows. It is possible that concentration of DOC in drip water is an indicator of complex response to water flow route and climate. Stalagmites formed by drip waters that respond rapidly to climate could better form perfect annual laminae and are more suitable as the archive of paleoclimate.

References


GEOCHEMISTRY OF WARM SPRING WATER IN NORTH SPRINGS OF CHONGQING: WATER SOURCE AND ITS RELATION TO TRAVERTINE FORMATION IN THE PAST

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North Springs, a famous state park in Chongqing, China, contains eight warm springs for public use. An 80-m long travertine cave whose formation remains unclear was estimated to be about 90 ka old. In order to understand the formation of the travertine cave as well as the source and quality of the warm springs, we investigated the physical and chemical features of the spring water between June and December of 2005. Measurements of temperature, pH, conductivity, dissolved O2, salinity, Cl–, HCO3–, SO42–, K+, Na+, Ca2+ and Mg2+ of the eight springs have been conducted every month since June 2005. Figure 1 shows the average values with standard deviations of the major parameters in each spring. Our measurements indicate that (1) the major anions are HCO3– and SO42–; (2) the cations are mainly Ca2+ and Mg2+ with small amounts of K+ and Na+; (3) water temperature remains relatively constant regardless of air temperature changes; (4) Spring No.3 exhibits low values in almost every parameter; and (5) pH is elevated in Springs No. 7 and 8.

From the above observations, we conclude that the warm springs of North Springs belong to Ca–SO4 type which is quite different from the spring type of Na–HCO3 that is probably a deep source thermal spring in eastern Tibetan Plateau. According to the chemical features of the warm springs, the source of North Springs may come from recharge of meteoritic water into deep earth where dissolution of limestone rocks (Jialingjiang and Leikoupo formations; the latter formation is younger and contains gypsum layers) would occur. This hypothesis is supported by positive correlations among conductivity, SO42–, Ca2+ and Mg2+ (e.g., Figure 2). During the past when the travertine cave formed, the recharge water might penetrate further deep into the limestone of Jialingjiang formation to dissolve abundant Ca2+ and CO32– concentrations. The saturated CaCO3 in the spring water would provide conditions for the formation of the travertine carbonates around 90 ka. Since then, the recharge water might have had shallower penetration and mainly dissolved limestone and gypsum in the Leikoupo formation. The high content of SO42– might prevent CaCO3 precipitation. Further investigation on the depth of penetration of recharge water is needed.

The elevation of pH in Spring No. 7 which is located inside the cave and in Spring No. 8 is probably due to mixing of groundwater because of their lower elevations and proximity to the river. The low measured values of Spring No. 3 are attributed to mixing of an external, fresh and cold water source. In Figure 3, the relatively conservative proxies, SO42– and Ca2+ in Spring No. 3 show two-end member mixing between the original spring water and river water. It seems that the amount of freshwater contribution to the spring water is related to rainfall. Based on a simple mass balance model of SO42– concentration and current measurements, the contributions of the external water source to Spring No. 3 are
about 40–50% in the rainy season and about 15–20% in the dry season.

Figure 1. The average values with standard deviations of the major parameters in springs from the studied area.

Figure 2. Correlations among $\text{SO}_4^{2-}$, $\text{Ca}^{2+}$, and $\text{Mg}^{2+}$ concentrations in the springs, indicating the same source of the parameters.

Figure 3. The mixing trends of $\text{SO}_4^{2-}$ and $\text{Ca}^{2+}$ concentrations between the spring water and river water in Spring No. 3.
We present a continuous high-resolution (monthly) record of stable isotopes (δ¹³C and δ¹⁸O) in a well laminated freshwater travertine deposited at Baishuitai, SW China from May 1998 to November 2001. The travertine exhibits clear annual bands with coupled brown/white color laminations.

Throughout field investigation, it was found that the thin (1.5–2.2 mm), brown porous lamina was formed in the monsoonal rainy season from April to September, whereas the thick (5–8 mm), dense white lamina was formed in the dry season from October to March. The comparisons of lamina thickness and stable isotope signals in the travertine with the meteorological records allow us to constrain the relevant geochemical processes in the travertine formation under different climate conditions and to relate climate variables to their physico-chemical proxies in the travertine record.

Sympathetic variations in lamina thickness, δ¹³C and δ¹⁸O along the sampled profile reflect changes in hydrogeochemistry, showing that thin lamina and low δ¹³C and δ¹⁸O values occur in warm and rainy seasons. The decreased amount of calcite precipitation and low δ¹³C values during the warm and rainy seasons are caused by dilution of overland flow after rainfall. The low δ¹⁸O values are believed to be related to the rainfall amount effect in subtropical monsoonal regions. This process is thought to be markedly subdued whenever the amount of rainfall is lower than a given threshold. Accordingly, distinct minima in lamina thickness, δ¹³C and δ¹⁸O are interpreted to reflect events with above-average rainfall, possibly heavy floods, and vice versa. This study demonstrates the potential of freshwater travertine to provide valuable information on seasonal or even monthly rainfall variations.
THE INFLUENCE OF BEDROCK DEPTH ON THE HYDROCHEMISTRY OF CAVE DRIP WATERS FROM A KARST SYSTEM IN SOUTHEASTERN AUSTRALIA

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Introduction

Karst aquifers respond to variations in surface recharge via shifts in drip water discharge and chemistry (Fairchild et al., 1996; Fairchild et al., 2000). Since these shifts are subsequently encoded in speleothem calcite, it is possible to extract palaeohydrological information from measurements of speleothem geochemistry (Baker et al., 2000; Fairchild et al., 2001; Huang et al., 2001). However, improved understanding of how speleothems record palaeoclimatic information requires study of how cave drip waters respond to individual recharge events and their ability to record a site’s hydrology (Fairchild et al., 2005). Here we present the results of a four-year study of cave hydrochemistry-climate relationships from two caves at Wombeyan, eastern Australia. The region’s rainfall is highly variable and seasonal recharge patterns are regularly disrupted by ENSO (McDonald et al., 2004). The discharge of 10 drip sites located beneath bedrock thicknesses of 12, 22 and 45 metres was monitored either continuously (using automated infrared sensors) or at discrete ~monthly intervals (Table 1) and compared with site rainfall, water balance and geochemical data (major cations and anions, and organic fluorescence).

Discharge

Mean hydroclimatic data indicate that a strong seasonal drip discharge pattern should occur at Wombeyan Caves. As expected, drip discharge generally decreased during the summer months at most sites, except during periods of thunderstorms. However, winter recharge was disrupted severely by the 2002/2003 El Niño and the 2004 drought, when a persistent negative water balance prevailed. This resulted in a steady decline in discharge at the shallowest two sites (12 m and 22 m). At these sites, drip response was almost simultaneous with recharge events, although the lag at the individual event scale varied according to the volume of pre-event storage (Figure 1). Overall, increases in drip discharge slightly lagged increases in site water balance, with a steady decline in discharge occurring through the moisture-deficit period, and increased flows during phases of positive water balance (McDonald et al., 2004). Hydrographs for these depths showed different recession limb characteristics, in-

Figure 1. The response of drips K1, K2, W1 and W2 at 6 hourly intervals to two rainfall episodes between 16 November and 12 December, 2003. Two responses were recorded by the drips: A = response 1 (November) and B = response 2 (December). Note the difference in the shape of the recession limbs between each drip. The lag-times for episode B were ~40% faster than for episode A indicating the importance of vadose-zone storage in controlling response times. The arrows indicate a minimal response to 20 mm rainfall on 16 November, which was preceded by hot, windy conditions and nil recharge for 17 days.
indicative of differences in their respective flow paths and delivery mechanisms. The hydrographs for the shallowest drips (K1 and K2) have sharp crests and steep recession limbs, indicating rapid delivery through well-developed fractures with minimal input from storage flow (Figure 1). On the other hand, the gradual recession of W1 and W2 (22 m depth) suggests tortuosity in delivery due to higher resistance of less-developed fissures at the greater depth (Williams, 1983) and reduced inter-connectivity (Tooth and Fairchild, 2003).

Three drips within 1.5 m of one another at 45 m depth did not respond consistently to individual recharge events and displayed unique hydrological behaviour. None of the recharge/discharge coupling patterns observed at higher-level drips was evident at this depth (Figure 2). W5A is generally in-phase with the water balance, but its short-term behaviour is highly erratic, with large abrupt excursions in discharge suggestive of access to several reservoirs. W6C shows only a muted response to site water balance, and no response to individual rainfall events. W6A shows little short-term variability with no apparent response to individual recharge episodes. The results from these three deep drips highlight the need for the careful consideration of speleothem sampling depths, especially if high-resolution palaeohydrological reconstructions are sought (McDonald and Drysdale, 2005, submitted).

**Mg/Ca and Sr/Ca relationships with discharge**

For drip water chemistry to be meaningful in palaeoclimate studies, a link between hydrology and one or more geochemical parameters is necessary (Baker and Brundson, 2003). Periods of aridity enhance degassing and calcite precipitation in ventilated voids, leading to elevated Mg/Ca and Sr/Ca (Fairchild et al., 2000). Thus, emphasis is placed on these ratios in the following discussion since prior calcite precipitation (PCP) has been demonstrably linked to dewatering of fractures and fissures in the Wombeyan karst during

<table>
<thead>
<tr>
<th>Site</th>
<th>Depth (m)</th>
<th>Qmean (drips s⁻¹)</th>
<th>Q CV (%)</th>
<th>Mg/Ca vs Sr/Ca (r)</th>
<th>Mg/Ca vs Q (r)</th>
<th>Mg/Ca vs Ca (r)</th>
<th>Mg/Ca mean</th>
<th>Mg/Ca range</th>
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<tr>
<td>K1*</td>
<td>12</td>
<td>0.012</td>
<td>44.7</td>
<td>0.91</td>
<td>-0.71</td>
<td>-0.82</td>
<td>33.45</td>
<td>40.24</td>
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<tr>
<td>K2*</td>
<td>12</td>
<td>0.0032</td>
<td>39.7</td>
<td>0.87</td>
<td>-0.81</td>
<td>-0.65</td>
<td>50.73</td>
<td>64.83</td>
</tr>
<tr>
<td>K3</td>
<td>12</td>
<td>0.0051</td>
<td>33.1</td>
<td>0.81</td>
<td>&lt;-0.10</td>
<td>-0.56</td>
<td>22.57</td>
<td>19.45</td>
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<tr>
<td>W1*</td>
<td>22</td>
<td>0.0023</td>
<td>15.1</td>
<td>0.89</td>
<td>&lt;-0.10</td>
<td>-0.35</td>
<td>16.90</td>
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<td>W2*</td>
<td>22</td>
<td>0.0017</td>
<td>13.2</td>
<td>0.94</td>
<td>&lt;-0.10</td>
<td>-0.56</td>
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<td>W2A</td>
<td>22</td>
<td>0.024</td>
<td>102.8</td>
<td>0.80</td>
<td>&lt;-0.10</td>
<td>-0.73</td>
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<td>12.46</td>
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<td>22</td>
<td>0.002</td>
<td>27.4</td>
<td>0.94</td>
<td>-0.18</td>
<td>-0.76</td>
<td>12.39</td>
<td>10.99</td>
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<td>W5A*</td>
<td>45</td>
<td>0.129</td>
<td>51.4</td>
<td>0.90</td>
<td>&lt;-0.10</td>
<td>-0.76</td>
<td>22.88</td>
<td>25.58</td>
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<tr>
<td>W6A</td>
<td>45</td>
<td>0.158</td>
<td>13.5</td>
<td>0.81</td>
<td>&lt;-0.10</td>
<td>-0.81</td>
<td>15.55</td>
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<tr>
<td>W6C*</td>
<td>45</td>
<td>0.018</td>
<td>72.2</td>
<td>0.85</td>
<td>&lt;-0.10</td>
<td>-0.82</td>
<td>14.95</td>
<td>9.10</td>
</tr>
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</table>

**Figure 2.** Discharge at sites W5A, W6C (daily) and W6A (monthly) for the period February 2003 – August 2003. The squares are the corresponding manual readings. W6A was not monitored continuously. Notable is the inability of less frequent manual sampling to resolve the highly erratic behaviour of W5A.

**Table 1.** Discharge statistics from monthly manual measurements (mean discharge \[Q\], coefficient of variation (CV)), selected chemical data and correlation coefficients (\(r\)), and site depths. Sites marked * were continuously monitored. NB: Mg/Ca is \(\times 1000\).

While all sites show a negative correlation between discharge and Mg/Ca, these are only statistically significant for sites K1 and K2 (12 m depth) \( r = -0.67 \) and \( -0.71 \) \( [p < 0.01] \) respectively) (Table 1). Similarly, Sr/Ca and discharge are significantly correlated only at K1 and K2 \( (r = -0.58 \) and \(-0.57, \) \( [p < 0.01] \) respectively). Mg/Ca is significantly inversely related to Ca at all sites except at W1. There is significant correlation between Mg/Ca and Sr/Ca at all sites \( (r \geq 0.80; \) \( p < 0.01) \). At a bedrock depth of 12 m, Ca and discharge at two sites show strong covariation, which suggests a hydrochemical link via the occurrence of PCP (Fairchild et al., 2000) and thus strong coupling of climate to drip hydrochemistry. K1 and K2 each display higher mean and range in Mg/Ca when compared to the deeper sites, reflecting the geochemical differences between “new water” and water modified by PCP processes (the higher mean and range exhibited by W5A in all probability reflects the dissimilar ages and chemistry of its source reservoirs (Baker and Brunsdon, 2003). Overall, the results can be summarised:

At 12 m:
— Q tracks short-term changes in potential evapotranspiration (PE);
— sharp recession limbs indicate throughput and rapid exhaustion “new water” (i.e. dilution flow);
— Mg/Ca (and Sr/Ca) significantly negatively covariant with Q;
— PCP proven; large range in Mg/Ca; high mean Mg/Ca.

At 22 m:
— Q traces short-term changes in PE; gradual recession limb (storage access only – i.e. no dilution);
— PCP proven but low Mg (Sr) source suggests dissolution of secondary calcite above the cave;
— small range in Mg/Ca; low mean Mg/Ca; Mg/Ca (and Sr/Ca) not covariant with Q.

At 45 m:
— Q does not trace short-term changes in PE (may trace longer-term variation in vadose storage);
— no interpretable recession curves;
— PCP - possibly at W6A and W6C (sourcing ventilated reservoirs);
— W5A – No; small range in Mg/Ca; low mean Mg/Ca (except W5A).

Conclusions

While PCP is observed both qualitatively and quantitatively at shallow sites, the site water balance or PE is recorded via a quasi-linear relationship between Mg/Ca, Sr/Ca, Ca and discharge at only three near-surface sites. Thus, only at these sites can geochemical changes be used confidently as proxies of past aridity/high rainfall. With increasing depth, the complexity in interpretation increases, as not all drip waters record an interpretable, short-term palaeohydrological signal due to decreasing fissuring, increased proportion of matrix flow to the drip, and the length of time for PCP-affected water to reach the drip. This has implications for the site of sampling and the interpretation of speleothem geochemistry at varying bedrock depths. Importantly, the significance of understanding the site hydrology and drip response at various depths is confirmed. In addition, the hydrological patterns have implications for palaeohydrological histories from speleothems since at this and similar sites water balance deficits inferred from speleothem geochemical variations may reflect drought (an aseasonal phenomenon) rather than the ‘dry’ summer season (McDonald and Drysdale submitted). Furthermore, speleothems from these caves will lack a consistent annual geochemical marker, making it impossible to establish a true calendrical chronology (McDonald and Drysdale, submitted).

References


McDonald, J. and Drysdale, R., Hydrology of cave drip waters at varying bedrock depths from a karst system in southeastern Australia: Hydrological Processes (submitted).


LONG-TERM DRIP-RATE MONITORING AT GROTTA DI ERNESTO (TRENTINO, NE ITALY): HYDROLOGICAL ASPECTS

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Introduction

Monitoring of the hydrology at Grotta di Ernesto cave (Trentino, NE-Italy) has been discontinuously carried out since 1995. The data for the period 1995 to 1996 were published by Borsato (1997). Here we present the results of the monitoring programme which started in 2002 with the AQUAPAST project and finished in 2005. Monitoring is still ongoing in the framework of the “Dated Speleothems Archives of the Paleoenvironment” DFG-Forschergruppe.

Results

Grotta di Ernesto cave develops in partially dolomitized limestone and opens on the N-slope of a wide karst plateau in the Trento Province (NE Italy) at the elevation of 1167 m above sea level. It is a very shallow cave consisting in a single, 65 m long, downdipping gallery, and with a maximum rock cover of c. 30 m (Figure 1). All the cave is decorated with active speleothems and hosts small pools.

The climate in the area is sub continental, with a mean annual precipitation ranging from c. 1000 to c. 1500 mm. From December to early March, mean monthly surface air temperature is near or below zero and results in snow precipitations. The recharge of the aquifer has a bimodal distribution with a maximum in Autumn and a secondary maximum in Spring, during snowmelt (Borsato, 1997; Fairchild, 2000). Strongest autumnal recharge episodes mobilize soil-derived trace elements and micro-particles which are carried into the cave and are incorporated into the cave calcite (Huang et al., 2001; Frisia et al., 2003).

During the period from January 2002 to January 2005 ten stalactites from Sala Grande chamber (sites “G”) and Ramo Terminale (sites “T”, the deepest part of the cave) were monitored on a monthly basis (Figure 1). Most of this dripping actually fed annually laminated stalagmites, as described by Huang et al. (2001) and by Frisia et al. (2003).

In Figure 2, the variability of the discharges is compared with precipitation and temperature data. A first group of fast drip stalactites (G1, G6) shows the larger discharge variability throughout the year (up to four order of magnitude): these act seasonally as overflow systems. A second group of very stable drip-sites (T3, T5, T8, T9, and G7 stalactites), shows responses only to major recharge events, and dry periods which last for more than 4 months. In particular, following the 2003 dry period, drip rates for T8, T9 and T5 decreased to ½ of their mean discharge. By contrast, G1 and G6 drip rates decreased of 3 to 5 order of magnitude. A third group of stalactites (G2, T4 and T6) show intermediate behaviour.

These observations are confirmed by statistical analysis: T3, T5, T8, T9, and G7 stalactites (group 2) are characterized by a coefficient of variation (CV) commonly < 40, within the “seepage flow” field; G1 and G6 (group 1) stalactites have a CV commonly > 80, within the “seasonal drip” field (cf. Smart and Friedrich, 1987; Baker et al., 1997).

Figure 1. Cross-section of Grotta di Ernesto with the position of the monitored stalactites.
By considering the inter-annual variability we observed a good power-function correlation between discharge and the inter-annual discharge standard deviation (IaDSD) (Figure 3). The stalactites in the Sala Grande, which have a shallower rock overburden, commonly show higher discharge and IaDSD. By contrast, in Ramo Terminale the drips are characterized by lower discharge and IaDSD. Furthermore, G2, T4 and T6 (group 3) stalactites are aligned below the regression line, i.e. they systematically show higher IaDSD with respect to group 2 stalactites (Figure 3). The different discharges influence the shape of actively forming speleothems. The faster drips feed flowstones (G1) or large dome-shape stalagmites (G6), intermediate discharges (G2) correspond to cone-shaped stalagmites, and lower and constant drip-rates usually feed cylindrical stalagmites.

Figure 2. Results from three-year monitoring of stalactite discharges at Grotta di Ernesto compared with precipitation and external temperature records (Vezzena meteostation, Istituto Agrario di S. Michele all’Adige network).
In three annually-laminated stalagmites (ER76 = G2, ER77 = T3 and ER78 = T6; cfr. Frisia et al., 2003) the annual growth rate calculated on a multi-decadal basis shows no correlation with the mean annual discharge, but seems to be inversely correlated with the CV. The lower growth rates are associated with higher CV (and higher discharge variability). These data suggest that the discharge dynamics and variability is an important process on speleothem growth and, therefore, has to be considered in the palaeoclimatic interpretation of stalagmite laminae thickness data.

References


DRIP WATER MONITORING RESULTS FROM A CAVE IN PERUVIAN AMAZONIA

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Introduction

Paleoclimatic studies on speleothems are based on two fundamental principles: 1) The cave temperature represents the mean annual temperature outside the cave; and 2) the oxygen isotopic composition of the cave drip water is approximately equal to the mean annual precipitation outside the cave (Schwarcz et al., 1976; Yonge et al., 1985; Linge et al., 2001).

Changes in the $\delta^{18}O$ of the speleothem carbonate can be caused by changes in the temperature and in the isotopic composition of seepage water. To use $\delta^{18}O$ from speleothem carbonate for long-term climate reconstruction it is necessary to record whether the cave drip water is isotopically constant over the year and whether it represents the mean annual composition of the precipitation. If so, the oxygen isotope signal in the speleothem carbonate will change due to temperature fluctuations as carbonate deposition in the cave environment generally occurs in isotopic equilibrium with seepage water from which they are formed (Hendy, 1971).

However, the climate signal captured by $\delta^{18}O$ of stalagmites can also be influenced by changes in the isotopic ratios of the meteoric water, which feeds these formations (Cruz et al., 2005). To investigate the influence of rainwater variation on the drip rate and, therefore, on the isotopic composition, we have set up a 1-year monitoring project in Cueva de las Lechuzas.

Local settings

The study was carried out in a karstic cave (Cueva de las Lechuzas) in Peru. This cave, located close to the town of Tingo Maria (700 m a.s.l.; S 09° 19’ 44.4”, W 76° 01’ 37.5”) on the foothills of the Andes, is one of the wettest parts of the Amazon basin with up to 3800 mm of annual rainfall. The cave has developed within the Late Triassic limestone of the Grupo Pucará of Norian age which dips to the southeast at 45° to 50°. The environment has a very steep cliff face developed by down cutting of the rivers Río Monzón and Río Huallaga. Above the cave a typical tropical soil has developed. The climate is tropical, with a mean annual temperature of 24.7°C. The migration of the ITCZ over the area results in a strong seasonal contrast, with maximum rainfall (~400 mm) in January and minimum rainfall (~120 mm) in August. Average isotope composition of rain water differs significantly between wet and dry season.

Cueva de las Lechuzas falls under control of the National Parc Tingo Maria of INRENA and the entrance hall is open for public visits. The main entrance is ~25 meters high and a new part was discovered in 2003. The monitoring equipment was installed in this newly discovered part.

Methods

Water samples of seepage water were taken between September 2003 and October 2004. Precipitation and stalactite drip rates were measured using an automatic tipping bucket system coupled to a logger for 5248 events. This tipping-bucket system collects 5.5 ml before it tips. The drip rate was continuously measured at two different locations in the cave over a period of 12 and 8 months respectively. One tipping-bucket system was placed outside near the entrance to the cave and measured the amount of precipitation close to the cave for 1.5 month. These data were compared with the data of the local meteoric station in the town of Tingo Maria, 8 km southeast of the cave. As these data sets fitted very well, it was decided to use the data of the meteoric station. Temperature and humidity were measured for one year with a Junior escort temperature and humidity recorder with 0.3 °C accuracy and 0.3 °C resolution for temperature and +/– 3% accuracy and 0.5% resolution for humidity. A Hugrun temperature logger with 0.1°C precision was installed in the entrance hall.

Results

Loggers

The Hugrun temperature recorder in the entrance hall showed an average temperature of 23.3 °C with a maximum variation of 1.4 °C over one year. This was the maximum temperature variation recorded in the cave as this logger was installed in the entrance hall which was influenced by outside conditions through the 25 meter-high entrance. Deeper in the cave the average temperature was 21.3 °C and fluctuated 0.6 °C over a 1-year period. The humidity was close to a 100% +/- 3% as our sensor was completely saturated after a month and gave a 100% readout for the rest of the period. The drip rate was monitored to investigate the influence of rainfall. Figure 1 shows the tipping-bucket record of logger A.
versus the amount of rainfall. No clear correlations can be detected between those two. The drip rate remains fairly constant over the year and is not influenced by changes in the amount of rainfall. Figure 2 shows the drip rate at a deeper location in the cave. This drip shows the overall pattern of the seasonal variation of the dry and wet season. During the wet season, December to May, the drip rate is highest at about 1:45 hour between each registration. This looks like the maximum drip rate possible; more rainfall will not increase the drip rate. The drip rate is lower during the dry season (June-November) with more than 6 hours between each registration. The oscillations in the drip rate seen in the dry period might be responses of the drip rate to individual rain showers.

Figure 1. Logger A, installed at the monitoring location shows (black dots) the time in hours between each registration (5.5 ml). The bars indicate the daily amount of precipitation in mm during the monitored period (~1 year).

Figure 2. Logger B, installed deeper in the cave, shows (black dots) the time in hours between each registration (5.5 ml). The bars indicate the daily amount of precipitation in mm during the monitored period (~8 months).

Water samples

Figure 3 shows the isotope values of water samples collected between September 2003 and October 2004. Most of the samples give an isotope ratio for hydrogen and oxygen which is close to the meteoric waterline. The heaviest and lightest isotope ratios come from rainwater samples during the two different seasons. The cluster in the middle gives the typical isotope ratio for different drips in the cave. This spread in isotope values is small compared to the isotopic range of the rainwater. The drip water values outside the cluster are samples from very rapid drips; these are probably directly influenced by surface water. During the sampling period in the dry season they are affected by the positive isotope ratio of the rainwater.

Conclusion/discussion

Comparison of the two sites in the Cueva de las Lechuzas shows that the hydrological circumstances can vary enormously at different locations in the same cave. At the monitoring location the drip remains stable whereas at the location of the deeper hall the drip is highly influenced by the rainfall pattern above the cave. This means that the drip in this deeper hall will have a drip-water composition that is seasonally influenced by the isotope signal of the rainwater. This is supported by the samples of the fast drips which are shifted to heavier values during the dry season. In Figure 2 a direct response of an increasing drip rate to periods of extensive rainfall and even to individual tropical showers is evident. The maximum drip rate is reached a couple of days

Figure 3. The δ18O and δD composition of the dripwater and rainwater from the Cueva de las Lechuzas (2003–2004).
after the maximum rainfall. This lag implies that the maximum hydraulic conductivity is reached a few days after the precipitation event. This means that there is a direct connection from the stalactite to the surface, with just a very small hydrological reservoir. It implies that a seasonal and even a local shower will disturb the mean annual precipitation oxygen isotope signal at that location.

The data from logger A, the monitoring location, has a reservoir large enough to provide a continuous and stable drip. The residence time in this reservoir will probably be sufficient to mix the rainwater isotopically, and therefore shows potential for a paleoclimatic study on speleothems.

Further research

Our preparation device to measure speleothem fluid inclusions online for $\delta^{18}$O and $\delta^{2}H$ using continuous-flow stable isotope technique (Vonhof et al., 2005) makes it possible to measure fluid inclusions of ~0.2 microliters. These measurements on fluid inclusions in speleothems make it possible to reconstruct the isotope composition of the paleo-drip water. The original oxygen isotope value of the drip water can be used for paleo-temperature reconstruction and provides information about the isotopic composition in the past. Using this technique one can distinguish if a speleothem is recording temperature changes or changes in the drip-water signal.

References


THE CONTRAST IN ISOTOPIC COMPOSITION OF CAVE ICE ACROSS THE DIVIDE IN WESTERN NORTH AMERICA

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Introduction

Caves containing perennial ice (ice caves) exist in many high-latitude mountainous regions of the world (see Yonge, 2004 and Ford and Williams, 1989 for summaries). That perennial ice in caves may yield past climatic information has been the subject of a number of studies (Marshall and Brown, 1974; Wigley and Brown, 1976; Silvestru, 1999; Yonge and MacDonald, 1999; Holmlund et al., 2005) and is the focus of the study here.

A number of ice caves exist in the western cordillera of North America on both sides of the Divide (Halliday, 1954; MacDonald and Yonge, 1997 — see also Figure 1). Coupled isotopic measurements of the ice ($\delta^2$H and $\delta^{18}$O) on four caves east of the divide suggest that the climatic interpretation may be very different to that of similar proxy climate indicators (polar ice and cordilleran glacier cores; Jouzel and Merlivat, 1984). Typically, the major effect in the depletion of $\delta^2$H and $\delta^{18}$O has been associated with a cooling climate, whereas in three of the caves found in permafrost zones, the effect was found to be opposite (Yonge and MacDonald, 1999).

We have measured the $\delta^2$H and $\delta^{18}$O of cave ice from 20 ice caves in Western North America, from latitudes 35–65°N, focusing on differences in the stable isotope composition of the ice on either side of the cordilleran divide. Broadly the caves can be separated across the divide as those < 250 km from the ocean (west) and those > 750 km from the ocean (east). In addition we have examined the isotopic evolution of cave vapour, sequestered as hoar ice, as it was exhaled into winter air. The vapour to ice condensation is shown to be a dynamic Raleigh distillation process that contributes a wide range of isotope values to cave ice.

Results and discussion

The coupled measurements of $\delta^2$H and $\delta^{18}$O in cave ice yield distinctive signatures on the east and west sides of the Divide. The east side of the Divide is characterized by lower $\delta$-values falling beneath the Global Meteoric Water Line ($\delta^2$H = 8 $\delta^{18}$O + 10; Craig 1961; Dansgaard, 1964), while $\delta$-values on the west side are higher and fall close the GMWL (Figure 2). The data can be summarized by the following equations:

\[ \delta^2\text{H} = 7.8 \, \delta^{18}\text{O} + 8.4 \]  

for samples from 7 caves west of the divide,

\[ \delta^2\text{H} = 8.0 \, \delta^{18}\text{O} + 4.0 \]  

for samples from 13 caves east of the divide.

The principal difference between the east and west divide zones appears to be due to the mode of ice deposition. Whereas east of the divide the climate is cooler (Continen-
tal >750 km from the Pacific Ocean) and the caves tend to be found in permafrost, in the west (Temperate/Maritime climate < 250 km from the Pacific Ocean), cave ice is mainly derived from the accumulation of snow in cold traps or blown into cold zones horizontally. The two distinctive mechanisms tend toward a summer accumulation of ice in caves east of the divide and a winter accumulation in caves west of the divide.

For the caves studied by Yonge and MacDonald (1999) on the east side of the divide, summer moisture is forced to freeze at around 0 °C as it enters the cave. This yields δ-values for the ice higher than would be found for winter precipitation, both because of the relatively warm source of vapour and the large fractionation induced by the freezing of the vapour. The hoar ice formed then falls to the floor adding to the mass of ice there. While there may be other sources of moisture (e.g. seepage), the summer moisture component tends to raise the overall δ-value of the ice. In winter where the outside temperatures are lower than inside the cave - and entrances often blocked by snow - little or no hoar accumulates on the cave surfaces. The Meteoric Water Line east of the divide with the low intercept (low δ-excess - equation 2 and Figure 2) reflects both the vapour-ice fractionation effect in the cave as well as the summer seasonal continental evapotranspiration of precipitated moisture along a relatively long travel trajectory (Rozanski et al., 1993).

The situation west of the divide is quite different. Ice principally evolves from snow masses precipitated vertically into open caves (snow trap type) or by snow blown more or less horizontally into cave cold zones (Yonge, 2004). In this situation ice accumulation takes place in winter and the accumulated layers are similar to glacial cores where temperature is the dominant effect on δ-value. (It is of course recognized that snow trap accumulation occurs east of the divide too, but here we are examining overall trends.) The ice layers in snow trap caves will be subject to greater homogenization through melting and refreezing as the snow evolves into massive ice. In addition summer rainfall will modify the ice, as will the cave vapour exhaling from the cave in winter. Both effects are very hard to estimate and would require a detailed study at given cave sites, such as is currently underway at Scarisoara Cave in Romania (Holmlund et al., 2005). Nonetheless, considering all moisture sources contributing to the ice, there are no dominant mechanisms that would lead to points migrating off the Global Meteoric Water Line. As a result, the local meteoric water line is not significantly different from the GMWL (Figure 2).

In an attempt to estimate the effect of the evolution of cave vapour as it is sequestered as ice as it is exhaled into winter air, we measured hoar ice formed at Rats Nest Cave, Alberta. Warm cave air at 4.7 °C, with a starting δ²H composition of around -147‰ was frozen on the outside wall above the cave at around -25 °C on two occasions (Figure 3). Rayleigh distillation (vapour-ice fractionation) is seen as the vapour is frozen at increasing distances from the entrance; the lowest (and furthest from source) δ²H reaching around −180‰. With the range being more than 30‰, this could have a profound effect on the composition of cave ice if added to it (The maximum variation found in the studied caves — Canyon Creek Ice Cave — is 40%). Furthermore, the Rayleigh effect while depleting both the δ²H and δ¹⁸O will generate a straight line of slope of 8 with values lying along the local meteoric water line, thus making it difficult to distinguish this component from others.

### Conclusion

In respect of climate studies of the ice in these caves, it is important to understand the very distinctive mechanisms leading to its deposition. As a result, the interpretation of the records will be cave-specific — and of note here — will be quite different in caves from the east to the west of the Divide. Our studies therefore suggest that for stratified cave ice to be useful as an isotopic proxy climate indicator, careful monitoring of individual caves would be necessary. Thus the ongoing study of Holmlund et al. (2005) at Scarisoara Ice Cave is a very important contribution to this understanding. We would agree with them that the detailed study of local climate with the isotopic measurement of precipitation and temperature over a one-year period at the cave entrance should be done. In addition, the study of the ice stratigraphy along with an estimate of the moisture transport and heat budget at the cave ice surface should be undertaken.

### References


Archives of Climate Change in Karst

KARST EVOLUTION, KARST MODELING, PALEOKARST
Katerloch, situated in the Styrian Karst province several kilometers north of Graz, is one of the most beautiful and most abundantly decorated dripstone caves of Austria. For many years access to Katerloch was virtually impossible. It recently opened again as a show cave and is now part of our ongoing research project on (peri)alpine dripstone caves. The speleothem decoration in Katerloch is dominated by stalagmites, the majority of which is of the candlestick type. Most of them appear inactive today suggesting a change in conditions of speleothem formation. Four inactive stalagmites were recovered and U/Th dated. Two of the stalagmites (K1 and K3) yielded early Holocene ages, whereas the other two stalagmites (K2 and K4) proved to be of Eemian age.

All stalagmites are composed of low-Mg calcite only and are macroscopically laminated. Thin-section petrography reveals that this lamination results from changes in the crystal fabric: milky-white laminae with frequent intercrystalline pores alternate with dense, translucent laminae. The thickness of the individual laminae varies widely. Milky-white laminae are typically up to 1 mm thick, whereas the compact laminae are mostly only a few tenths of millimetres thick. The distribution of the milky-white laminae reflects preferential calcite precipitation near the stalagmite’s axial zone giving rise to the candle-stick morphology.

Preliminary stable isotope studies show a high variability in the C isotopic composition of the stalagmite calcite, while the O isotope values vary only within a small range. Holocene and Eemian stalagmites show rather similar overall values (e.g. stalagmite K3: $\delta^{13}$C ca. –11 to –4 ‰, $\delta^{18}$O ca. –7 to –5.5 ‰; stalagmite K2: $\delta^{13}$C ca. –11.5 to –6.5 ‰, $\delta^{18}$O ca. –8 to –6 ‰ VPDB, respectively). Micromill-sampling revealed a clear relationship between the C isotope composition and petrography: high $\delta^{13}$C values coincide with compact, translucent laminae whereas milky-white laminae are characterized by lower values.

These observations suggest a seasonally (?) changing regime of calcite deposition under equilibrium (milky-white laminae) and nonequilibrium conditions (translucent laminae), respectively. In contrast, the O isotope values change very little and indicate that drip waters are sourced from a well-mixed karst aquifer. Growth dynamics of stalagmites in Katerloch are probably controlled by a combination of seasonally varying drip rate (lower during winter) and ventilation (resulting in lower $p$CO₂ during winter) and an ongoing program of water and air monitoring in the cave is designed to quantify these relationships.
GROWTH PATTERN AND DEPOSITIONAL FEATURE OF STALAGMITES IN THE KARST REGION OF CHONGQING, SW CHINA: CLIMATIC IMPLICATIONS

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We have attempted to collect Holocene stalagmites in caves around Chongqing for paleoclimate reconstructions over the past few years. These caves are Liangtianwan (LT), Furong (FR), Xueyu (XYD), Shuiming (SM) and Xinyan (XY). The caves are located in the karst region of southeastern Chongqing and are largely mirroring the depositional conditions of cave speleothems in the area. Up to date, 63 ICP-MS $^{230}$Th/U dates were obtained in the Isotope Lab at the University of Minnesota from 14 stalagmites showing that most of the stalagmites stopped to growth during the Holocene (Figure 1). With the current set of ages and stable isotope profiles, here we discuss the growth pattern and depositional feature of these stalagmites and their paleoclimatic significance. In summary, our observations from the preliminary results indicate: (1) slow or no deposition during the Holocene Optimum; (2) abundant and fast growth of the stalagmites during

Figure 1. The ages of stalagmites in Chongqing area compared with the SPECMAP record.
The growth of stalagmites in caves is mainly controlled by the saturation of calcium carbonate, CO₂ degassing and evaporation of cave dripping water. The CaCO₃ saturation of the dripping water is a function of surface precipitation, temperature, vegetation coverage, soil pCO₂, pH of seepage water, and bedrock dissolution, etc. Numerous previous studies in China found slow or no stalagmite growth during glacial intervals due to strongly cold and dry climates, and fast growth of stalagmites during interglacial times under warm and wet summer monsoons especially in northern China. However, we find that the growth of stalagmites in Chongqing area was significantly abundant and fast during glacial intervals. Our hypothesis on this phenomenon is that the monsoon boundary in China was shifted southeastward during glacial times and the rainy front zone was probably above the Chongqing area. On the other hand, the temperature was not low enough to generate mountain glaciers to cover the surface above the caves. Therefore, higher CaCO₃ saturation under cooler temperature and continuous flow of cave drip water would make the stalagmites to grow intensively. In contrast, if temperature was higher and seepage water flow was too fast such as during the Holocene Optimum and MOIS 5e, the conditions might have been not in favor of stalagmite growth.

The reason of increase in the δ¹⁸O values when the deposited calcite becomes dirty remains unclear. In general, when surface temperature is high, decomposition of organic matters and dissolution of chemical components from soil should increase. In this case, the detritus in stalagmites could have been high, which means that the heavier δ¹⁸O in stalagmite reflects warmer surface temperatures. However, according to previous studies that heavier δ¹⁸O values in stalagmites represent weak summer monsoon strength under cold episodes, hence, increase in the δ¹⁸O values might chiefly indicate dry conditions. Based on such an interpretation, the increase in impurity of calcite stalagmites could not be caused by surface temperature increase. Rather, it might have been caused by dust input into seepage and dripping water under relatively cold and dry climates. Therefore, it is very important to understand whether the stalagmite δ¹⁸O here reflect mostly temperature or precipitation.
DAMAGED SPELEOTHEMS RECORD 200,000 YEARS OF EARTHQUAKE ACTIVITY: DEAD SEA TRANSFORM REGION

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The study of rockfalls and damaged deposits in caves provides an alternative and underutilized method for paleoseismic reconstruction. Dating of damaged speleothems and deposits overgrowing rockfalls constrains the dates of earthquakes. We have compiled a long (200 ka) paleoseismic record at the Soreq and Har-Tuv caves, near Jerusalem, Israel. The studied caves, located 60 km west of the Dead Sea Transform, contain a record of earthquake damage from Dead Sea Transform ruptures and, possibly, smaller local intraplate events.

Non-seismic sources of collapse, such as ice-movements, ground subsidence, and cave-bears, problematic elsewhere, were investigated and refuted. Neither ice cover, nor permafrost, have occurred in this region during the investigated period. Ground subsidence is not likely since the cave floors are solid carbonate rock. The caves have only non-natural openings, and therefore cave-bears have not entered. The studied caves offer an excellent opportunity for paleoseismic research as they contain a large amount of fallen cave deposits of all types and sizes, such as stalactites, stalagmites, soda-straws, and pillars, and other damage (Figure 1). The two studied caves present the opportunity to correlate between two nearby sites.

Comprehensive maps of the Soreq and Har-Tuv caves were prepared and demonstrate dominant EW and NW-SE orientation of fractures, and dominant EW and NS orientation of collapsed speleothems. The prevailing orientations of collapsed speleothems are consistent with Dead Sea Transform earthquake motion directions. These preferential orientations of collapse strongly support a seismic source of collapse. We identified “new generations” of speleothem growth on top of collapses. This post-collapse precipitation constrains the minimum age of collapse. The unconformities between the collapses and the in-situ regrowth were recognized, and termed paleoseismic “contacts” or “horizons”. Laminae above and below the unconformity were separated and dated by the $^{230}$Th/$^{234}$U mass spectrometry method. The pre-seismic and post-seismic dates of a collapse give a bracket period within which the earthquake occurred. The closer in age the pre-seismic and post-seismic deposits are, the better
constrained is the earthquake’s age. When dating post-seismic regrowth on collapsed bedrock (and not collapsed speleothem), only the post-seismic age is available. We also drilled cores into the flowstone floor and discovered laminae that embed fallen small stalactites (soda-straw formations). We dated the laminae that embeds the fallen stalactites, which gives the age of the seismic event. We also compared the oxygen stable isotopic record ($\delta^{18}O$) of the laminae adjacent to the tectonic unconformities with the extensive well-dated stable isotope record of Soreq Cave speleothems, as was reconstructed for the last 185 ka by Bar-Matthews et al. (2000) and Ayalon et al. (2002), for paleoclimate purposes. This stable isotope technique comparison improves and corroborates the U/Th ages.

Thirty-eight collapses were sampled and dated. The dates suggest that at least 13 (up to 18) individual seismic events have been identified. The one Holocene event observed in the cave correlates with lacustrine seismites dated in cores from the Dead Sea and with an archeologically recorded earthquake. An event dated to ~13 ka is recorded by two collapses, for which there is no independently dated paleoseismic event in the region to which we can correlate our 13 ka event. Most Dead Sea sediments recovered so far show a prominent “Younger Dryas” hiatus, however salt deposits from this period may reveal deformation. For the period between 75 to 20 ka, we identified 3 events. Two of these (at 51–52 and 35.5–40.5 ka) correlate with seismites in the Lisan record (at 52 and 39 ka). Another event (at 46.5–46.7 ka) coincides with a hiatus in the lacustrine sections from 49 to 44 ka. An event at 70.2–72.8 ka correlates with a cluster of seismites in the pre-Lisan section. Twelve cave events older than 71 ka are at present the only dated paleoseismic record for this period in the region. Future work on the middle to lower Pleistocene Amora formation will reveal if there is correlation with the cave record.

The karstic paleoseismic record supports the lacustrine seismit evidence, and the long dating range of calcite cave deposits and their potential for recording seismic events can vastly increase the length of the seismic record. The long Late Pleistocene record is useful for correlation with other records and for substantiation of the method, while the Holocene events are valuable for seismic hazard assessment. The unique opportunity to compare the stable isotope profiles of the speleothem seismites with the extensive paleoclimate record of the caves improves the accuracy of the seismite ages.
Speleothems in Central European caves display a wide variety of natural damage. Different processes have been discussed in the literature to explain the causes of such damage. Rock falls (inkasion), mass wasting, compaction of sediments, undercutting by erosion, frost shattering near entrances, inundation of the cave, or desiccation of sediments can account locally for some of this damage. Earthquakes are the leading hypothesized cause of observed, widespread damage.

Historically, broken and leaning stalagmites were first depicted by Schaffrenrath from Postojnska jama in the 1820’s and discussed by Hohenwart in 1832, clearly excluding rock fall or earthquakes as a cause. Evidence collected from four caves (Postojnska jama/Slovenia, Geisloch/Frankonian Alb, Baumannshöhle/Harz Mountains, and Adventshöhle/Rhenish Massif) during speleothem inventories suggests, however, that earthquakes cannot readily explain much of the observed speleothem damage. Instead, the most likely explanation for these damage-patterns appears to be the formation and thawing of cave ice during onset and termination of glacial periods. Specific examples such as broken and leaning stalagmites, missing older stalactite generations, precariously placed sinter fragments, speleothem piles along the sides of passages, speleothem fragments misplaced away from the line of fall, and flowstone pieces fixed on steeply sloping surfaces can best be explained by the action of ice which filled the caves during Glacial times. In addition, precipitation of calcite in ice pools (cryogenic speleothems) may have left a puzzling “sand” consisting of mm-sized calcite rafts or linings observed, for example, in newly discovered parts of the Adventshöhle. These rafts are now U/Th dated to 29,170 ± 480 years B.P., placing them into the Dansgaard/Oschger Cycle 2, a short lived warming phase.

In detail, consequences of thawing and freezing cave ice and of the advance and retreat of permafrost remain an unexplored process highly important for the preservation of the older speleothem generations. To the extent its timing can be accurately constrained, speleothem damage caused by cave ice may form a marker facies for the extent of the 0°C isotherm during past glacial periods.
Introduction

The seismicity of Bulgaria is documented by instrumental records and fragmentary historical archives that covered a period up to 2000 years ago. The seismic hazard assessment is primarily based on the estimation of the return period of the large earthquakes. For this purpose, it is necessary to search additional data about catastrophic seismotectonic events during prehistoric time.

Caves represent an environment relatively well protected from most of the exogenic geomorphologic processes: erosion, denudation, deflation, etc. In this context, the cave deposits are a medium favorable to the recording and preservation of damages caused by earthquakes. The broken and deformed speleothems in caves are accepted by many researchers as a good tool for palaeoseismic reconstructions. The “seismothems” (speleothems potentially broken by a seismic event — sensu Quinif, 1999) can be dated (U/Th, 14C, etc.) and offer the possibility to obtain the age of the palaeoevent that caused the collapsing (Forti, 1998; Forti & Postpischl, 1984; Gilli, 1995; Quinif, 1996; Camelbeeck, 1998; Delaby, 2000, etc.). However, recently performed seismologic investigations on speleothems (Lacave et al., 2004), modeling of speleothem ruptures (Cadorin et al., 2000), and field observations after strong earthquakes (Gilli et al., 1999; Gilli, 2005) showed that most of the speleothems are stable to the impact of seismic waves. The aim of this paper is to report the results from observations of the deformed speleothems in three caves in Rhodopes Mts., Southern Bulgaria.

Description of the studied caves

Shepran Cave is located on the southern slope of the Dobrostan karst plateau (Central Rhodopes Mts., South Bulgaria) at an elevation of 840 m. a.s.l. This dry fossil cave consists of a gallery having a length of 260 m ending in an 18 m pit. The total relief of the cave is 39 m and the volume ~ 3010 m³. The cave is rich in various concretions, mostly of them perturbed (fallen stalagmites, recovered with new speleothems). Yamata Cave is situated in the middle of the plateau, in a deep river valley. The cave entrance is at 860 m. a.s.l. The length of the cave is 183 m. Ahmetyova Doupka Cave is the highest one; the entrance of this pothole is at 1360 m.a.s.l. and situated on the plateau. The cave begins with a 12 m pit followed by a hall (42 x 20 x 12 m). All the caves are developed in the Proterozoic marbles of the Dobrostan formation. From a structural point of view, the three caves are situated in different tectonic blocks, separated by a series of parallel normal faults that strike east-west and dip to the south.

Methodology

Two techniques were used in this investigation. The first technique measured the preferred directions of the deformed speleothems, described in the works of Gilli (1995), Delaby (2001), and Dublyansky (1995). This method is based on the premise that the availability of clearly expressed maxima in the spatial orientation of the broken and deformed speleothems ( stalagmites, stalactones) is an indicator about the seismotectonic origin of the deformations. For this purpose, the studied caves must be well protected against anthropogenic impact (recent vandalism or availability of prehistoric artifacts). There are no traces of glaciation during the Quaternary in the Rhodopes Mountains. Gilli (2005) accepts the movement of ice as a reason for destruction of speleothems in this region. The caves are dry, having no underground streams and dynamic fluvial deposits that are necessary conditions for this type of seismotectonic study.

The second technique measures the natural frequencies on speleothems (Lacave et al., 2004). The natural frequency measurements of speleothems are made with a laser interferometer or accelerograph. The speleothem can be excited with a light held by one’s hand. The frequency of vibration velocity of the studied speleothem is recorded as a function of time with calculated average Fourier spectrum. This technique is described in detail in Lacave et al. (2004).

Results

From the comparatively wide range of seismotectonic speleoindicators described in previous works (Bini et al., 1992; Dublyansky, 1995; Quinif, 1996; 2000; Delaby, 2000; Gilli, 1995; 2005) the following elements are established in the studied caves:

*Fallen stalagmites.* The fallen stalagmites are the most expressive seismothems. The “stalagmite cemeteries” (sensu Quinif, 2000) in some caves represents the best evidence for
seismotectonic or neotectonic activity. In the three studied
caves the direction of broken stalagmites were measured. In
Shepran Cave 46 directions were measured; in Yamata Cave
50 were measured and 16 measurements were taken in
Ahmetyova Doupka Cave (Figure 1). The maximal size of
the studied speleothems is up to 1 m in height and 40 cm in
diameter. All of the samples are covered with speleothems
re-growth. The statistical analysis of the deformations gives
clear directions in the first two caves with three almost iden-
tical maxima in the rose-diagrams.

Displaced and inclined stalactones. One of the attractive
features of Shepran Cave and Yamata Cave are the anom-
alties established on massive columns having heights up to 4
m and diameters of 1 m.

Broken soda-straws. Being in the initial stage of the stalac-
tites development, soda-straws are the speleothems that are
the most amenable to seismic effects. In all the three caves,
there are areas were the broken thin stalactites are attached
with calcite onto the floor.

In Ahmetyova Doupka Cave the natural frequency of two
speleothems – a stalactite with length of 75 cm and a thin
240 cm high stalactone with a minimal diameter of 7 cm
were measured. The measurements were made with a strong-
motion digital accelerograph SMACH - 2 (Szeidovitz et al.,
unpublished data under processing). The preliminary results
showed that the measured frequencies of the two speleothems
are much higher than the upper range of a seismic excitation
— between 0.1 and 30 Hz (Lacave et al., 2000).

Discussion and conclusion

The results of the investigations in the Rhodopes Moun-
tains give an argument that the seismic waves cannot de-
stroy the speleothems. The argument against destruction from
to seismic waves is based on the difference between their
dynamic characteristics, especially their predominant fre-
quencies and the self-resonance characteristics of the
speleothems. Furthermore, in most of the cases, observa-
tions have shown the deformations or the destruction of the
speleothems are not due to the deformation of their base.
The only possible explanation of the sudden loss of equilib-
rium and destruction of the stalagmites is the impact of some
horizontal acceleration, creating a shear stress exceeding the
strength of the material. This type of effect can be expected
if the tectonic block, with the concerned cave is suddenly
displaced along a seismically activated tectonic fault. In this
part of the Rhodopes Mts., significant quantities of broken
speleothems have been discovered in caves situated inside
subsided and horizontally displaced blocks near clearly ex-
pressed active faults (Shepran Cave and Yamata Cave). The
rose-diagrams of the fallen stalagmites can indicate the hori-
zontal component of the predominant direction of displace-
ment (the opposite direction of the maximums) of the hang-
ing wall of the fault.

This investigation showed the important role of the tectonic
block movement during the process of rupturing and dis-
placement along the active fault. The impact of the seismic
waves can be considered only for speleothems such as soda-
straws and very tall and thin cylindrical stalagmites (Lacave
et al., 2000; Szeidovits et al., unpublished data).

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U-PB DATED LAMINATED SPELEOTHEMS FROM THE WESTERN AUSTRIAN ALPS: CONSTRAINTS ON PLIOCENE TO EARLY PLEISTOCENE CLIMATE VARIABILITY AND UPLIFT

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In the European Alps there are only a few, poorly dated records spanning the Pliocene-Pleistocene transition, a time interval characterized by the onset of significant glaciations in the Northern Hemisphere (Haug et al., 2005). Studies in the northern alpine foreland suggest that ice reached the northern foothills of the Alps already between 2.5 and 1.8 Ma (Bolliger et al., 1996; Ellwanger et al., 1994), whereas sedimentological and palaeomagnetic evidence from the Po Plain argues for a much later start of the extensive (south) alpine glaciation sometime after 0.87 Ma (Muttoni et al., 2003). We present one of the first absolute-dated, high-resolution climate records from two alpine cave sites that help to shed light on this important time interval.

Located at 2400 m a.s.l. in the Allgäu Alps close to the Austrian-German border, these caves are currently in a state of destruction by surface erosion and collapse. We examined flowstones and stalagmites, both composed of dense low-Mg calcite. No macroscopic nor microscopic evidence of diageneric alteration was observed in these samples, which is in agreement with the preservation of microscopic lamination visible under UV illumination. High U contents (4-43 ppm) coupled with low nonradiogenic Pb levels allowed to date three samples from these sites using U-Pb isochron techniques. Two samples from one cave site yielded an age of 2.1 to 2.2 Ma – confirmed by two U-Pb isotope systems - and the third sample from the second site gave a slightly younger age of 1.7 Ma. Oxygen isotope values of two stalagmites record fairly stable environmental conditions lasting for several thousands of years. Isotope values of a thick flowstone are more variable (-12 to -9 permil VPDB) and probably reflect significant climate change on orbital time scales.

A software tool for lamina analysis was developed (Meyer et al., 2006) to investigate the duration and growth variability of long laminated sequences in our speleothem samples. Assuming annual origin for these highly regular and well preserved micron-scaled growth layers, we developed an oxygen isotope record tied to a lamina-counting chronology.

The abundance of these large speleothems requires a well developed soil horizon and vegetation in the recharge area of the former karst fissure aquifer; conditions that are vastly different from today’s barren, high-alpine landscape in this region. Assuming a conservative mean annual uplift rate of 0.5-0.7 mm/a during the past 2 Ma for this part of the Alps, these speleothems could have developed at elevations between 1000 and 1400 m, i.e. well below the timberline.

References


**Introduction**

Caves are environments where continental deposition produces sediments different from surface ones. Although many facies of cave deposits have surface analogues, they show specific features due to deposition in limited space and in more constant microclimate. Genesis of separate units in a sequence of cave sediments assists the ascertaining of changes in Quaternary climate. Knowledge about climatic variations during the Quaternary is very important for the recognition of oscillations within modern climate conditions. In addition, caves are ones of the most suitable continental sites for preserving records of climate variation.

This study attempts to reconstruct the palaeoclimatic and paleoenvironment in which the sediments from the Orlova Chuka Cave (NE Bulgaria) originated, based on physical parameters of lithologic units and on their paleontological content. The physical parameters of subaerial lithologic units depend on local climatic conditions during deposition. Complex origins and post-sedimentologic processes complicate the proximate paleoclimatic interpretation. The stratigraphic sequence in Orlova Chuka Cave could be informative for studying continuous, long-term palaeoclimatic records because it reaches a thickness up to 12 m.

**Cave morphology and genesis**

Orlova Chuka Cave is a network maze composed of subhorizontal passages with total surveyed length of more than 13 km. Morphological features of the cave galleries suggest a phreatic origin. The elevation of the cave system lies just below an old river terrace at about 60 m above the present floodplain of Cherny Lom River, a tributary of the Danube River. Terraces at 60 m correspond to an erosion surface formed in the southern margin of so-called Dacian Basin during the Pliocene and Early Pleistocene. The erosional surface formed around 2.59 Ma BP, and the alluvium deposits over it extend to the beginning of loess formation in NE Bulgaria during MIS 20 (Evlogiev, 2000) or MIS 22. Therefore, the main phreatic stage of cave formation should assign to a similar time span. The Brunhes/Matuyama geomagnetic boundary (0.78 Ma BP) has been found at 1.20 m below the top of a sedimentary sequence within an excavation in the cave (Evlogiev et al., 1997).

The average height of cave passages is 10-20 m, approximately two-thirds of which are filled with clastic deposits intercalated in rare instances by speleothem. Although the large volume of cave passages further equalizes sedimentary conditions, lithologic units show lateral discontinuity.

**Methods**

Sediment facies have been defined on the basis of structure, texture, and color. Lithologic features, magnetic susceptibility, organic carbon content, and fossil fauna from sedimentary units in a pit situated 20 m away from the cave entrance are applied for the purposes of paleoclimate reconstruction. The location of the pit was chosen next to the entrance to guarantee the presence of animal remains. The closeness to the entrance supposes more influence of surface climatic conditions while the sediments were being deposited. In the studied cross-section there are no speleothems. Relationships between different speleothem generations and clastic sediments have been observed in other excavations within the cave.

Variations of grain size, carbonate content, and magnetic susceptibility along the profile show clear distinctions between different layers (Figure 1), which means that the chosen physical parameters can be used as dependable criteria. Organic carbon content in the profile is less variable than the other parameters. Sedimentologic agents are complex, but usually only some of them dominate during formation of an individual layer. Grain size content and other lithological features (e.g. color, structure) are used as tools to establish the relative proportions of mechanical and chemical weathering of the bedrock, and the aeolian transport factor. Large grains coming from bedrock are very important as paleoclimate indicators because they have thermoclastic origin, and a large amount of these sediments in a layer suggests a severe cold climate. Magnetic susceptibility variations are mainly controlled by the concentration of ferromagnetic grains. Variations of magnetic content of the cave sediments may reflect (1) sedimentation of finer material during warm climatic periods, which contain a significant amount of superparamagnetic grains due to an enhancement of pedogenesis on the adjacent open areas, would cause an increase of the magnetic signal; (2) higher concentrations of large detrital magnetite particles resulting from intensification of mechanical weathering and higher wind potential.
during cold climatic periods is another way of magnetic enhancement; and (3) lower susceptibility values could be obtained in layers formed during warm climatic periods, if geochemical conditions (e.g. very low pH, saturated, reducing conditions) during and after sedimentation are unfavorable for survival of Fe oxides (Radulov and Jordanova, 1999).

The organic carbon content in a cave deposit depends on the intensity of pedological processes and plant growth on the surface. Light organic particles are very mobile, which facilitates their transportation into a cave by air, animals and water. In addition, organic debris contributes to the enrichment of organic carbon.

Small mammal remnants from studied sequence represent at least 35 species of Insectivora, Rodentia, Lagomorpha and Chiroptera (analysis by V. Popov, Institute of Zoology, Bulgarian Academy of Science). Animal habitat gives important additional information for paleoenvironmental conditions. Remnants found in the cave sediments have been distributed in five units, A, B, C, D, and E (Figure 1). Fauna in each unit indicate paleoenvironment during deposition of several layers.
Sediment sequence

The upper part of terrigenous sediments next to the entrance consists of four main genetic types: weathering detritus, aeolian silts, thermoclastic fragments and speleothems. On the base of structure and color, fourteen lithologic units (layers) are sequestered in the studied site (Figure 1).

Layer 1 (light brownish gravelly-silty sand) and layer 2 (yellowish gray sandy silt) contain lenses of thermoclastic bedrock particles, most of which consist of cobble-size grains. In these deposits, allochthonous silt transported by air dominates. Carbonate content and magnetic susceptibility are of low values. The layers most likely originate in cold and arid conditions.

Layer 3 (dark brown laminated silt) has a much lower carbonate content (2%), very high magnetic susceptibility and the highest organic carbon content (1.66%). Its most probable zoogenetic origin suggests a temporary break in aeolian deposition and warmer climate.

Layer 4 consists of yellowish to gray silt. Calcium carbonate varies from 7% to 28%, and its magnetic susceptibility has a low value. There are six very thin beds of laminated silt and some very thin beds of sandy silt (the sand content is approximately 30%). The sandy component in coarser beds is calcareous and derived from the bedrock. Higher values observed in these beds imply more active mechanical weathering of limestone bedrock. As a result, detrital fractions contain a limited quantity of ferromagnetic grains, which determines the observed low values of magnetic susceptibility. Aeolian deposits and weathering detritus in layer 4 suggest sedimentation during typical glacial conditions.

Layer 5a consists of gray brown pebbly-gravelly calcareous sand. Pebbles and gravels are angular. The calcium carbonate content of sandy matrix is 32%; magnetic susceptibility and organic carbon have exceptionally low values. Weathering detritus of thermoclastic origin suggests a severe cold climate during deposition. Lower carbonate content (7%), the highest magnetic susceptibility and higher organic carbon content characterize layer 5b (dark brown silt). Chemical weathering of bedrock prevails. Layer 5b probably originated in a warmer and wet climate.

Layer 6 is a thermoclastic scree that is composed of angular cobble-size limestone particles (particle sizes from 10 cm to 30 cm are common). A thin layer within the scree was sampled. All measured parameters show values similar to typical aeolian deposits. These features likely imply a severe cold climate.

Layer 7 (reddish sandy silt), layer 8 (brownish sandy silt) and layer 9 (yellowish brown sandy silt) are characterized by weakly variable carbonates, magnetic susceptibility and organic carbon. A lot of animal remnants occur at the bottom of layer 7. The loam of these series mainly consists of chemically weathered detritus, but mechanically weathered particles also occur. In general, the characteristics suggest a mild climate.

Layer 10 consists of dark brown sandy silt. The layer is very rich in animal remnants including those of bear skeleton. Chemical weathering of bedrock again prevails.

Layer 11 consists of fifteen similar pairs of very thin beds. The boundaries between individual pairs are wavy parallel due to dripping water, which is typical for deposition under subaerial conditions. Each pair is composed of lower brown lamina of sandy-clayey silt and upper yellow lamina of gravely-silty calcareous sand. The transitions between laminae are gradual. The brown laminae are formed due to more active chemical weathering, while yellow laminae are due to more active mechanical weathering. The climate during deposition was changeable; probably frequent cooling occurred. In contrast to the other layers, which originated in a cold climate, layer 11 does not contain aeolian silts.

Layer 12 (reddish sandy-clayey silt) and layer 13 (silty clay, partially indurated) are substantially different from the other layers in the site. In this part of the sequence there is a significant lack of variability in measured parameters. The almost complete absence of calcium carbonate can be explained by the low pH. The lower susceptibility values could imply dissolution of Fe oxides due to the presence of very low pH, saturated, and/or reducing conditions. Limestone and bone particles are rounded due to intensive chemical influence. Based on these features two origins can be assumed: (1) deposition of autochthonous material in subaqueous environment but without any significant turbulent flow (traces from phreatic stage of cave development) and (2) postsedimentological flooding that caused diagenetic changes in both layers. The high clayey content can support infiltrating water at this level. The water source can be erosional streams cut in layer 11 (which caused the hiatus between layer 10 and layer 11) or higher dripping water from the cave roof during later wet periods. The lack of changes in layer 11 (excepting the lowermost part) is due to its high permeability. The presence of bones supports the second assumption about its origin, mentioned above. At this stage of our investigation, the diagenetic changes in these layers do not allow palaeoclimatic reconstruction.

Climatic records and age

Proportions between different ecologic groups of fauna remnants in separate units reflect paleoenvironment. Remnants from each unit reflect average paleoenvironment during deposition of several layers building an unit. Fauna poorly differ
in units (Figure 1). Species and quantitative proportions between species indicate relatively cold, continental and arid climate; and open area dominates. Unit B distinguishes from others because of prevalence of high mountain and boreal species. Unit D also contains boreal representatives. Unit A contains largest variety of species. They indicate deposition in cold to mild, and relatively arid climate. Fauna in unit C is similar to that of unit A but steppe mammals prevail.

In deposits of the studied sequence, evidence for four periods of severe cold climate (layer 2, layer 5a, layer 6 and layer 11), two periods of aeolian deposition (layers 2 and 1 and layer 4) and three mild periods (layer 3, layer 5b and layers 10 - 7) are preserved.

A bear skeleton is found in layers 8, 9 and 10. The remnants could be defined as Ursus deningeri romeiensis known in Mindel-Riss and Riss or transitional form between Ursus deningeri and Ursus spalaeus.

A continuous speleothem level below aeolian deposits represented by layer 4 is well developed in the cave. A similar stratigraphic position of that speleothem layer has been observed in several excavations in the cave. One of the stalagmites has been dated. U-series date of the base is 137±6 Ka BP and the active growth occurred in MIS 5 (Hercman and Nowicki, pers. comm., 1999). Taking into account position of the bear skeleton and dated stalagmite units A and B should be younger than MIS 5, and most of unit C should be older than 137±6 Ka BP.

**Conclusion**

Parent material in the upper 1.50 m section of cave sediments close to the entrance derives mainly by mechanical weathering of bedrock and aeolian transport of outer material. Both processes occur more likely in glacial periods. Thus depositional rate during glacial periods is much higher than during interglacial periods. Speleothem growth and deposition of chemical weathered detritus are typical for interglacial periods.

**References**


UNDERGROUND GLACIERS AND CLIMATE CHANGE:
VELIKA LEDENA JAMA IN PARADANA NATURE RESERVE

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Introduction

The Velika ledena jama (Big Ice Cave) is one of the most important parts of the Paradana Nature Reserve, covering an area of 18 ha (1230–1099 m above sea level at the surface, 565 m above sea level, 45°59'17" N, 13°50'57" E). The cave derives its name from the area where fog often appears under Golaki (1495 m–1480 m), the highest summits of the Trnovski gozd karst massif.

The Paradana Nature Reserve

The reserve is famous for the intermingling of superficial and underground karst with glacial features, and for its notable temperature and vegetation inversions. At an altitude difference of around 100 meters, the following belts occur (first described in 1906 by V. M. Beck): fir-beech (Abieti - Fagetum dinaricum), spruce (Piceetum subalpinum dinaricum), willow-tree (Salicetum appendiculatae), dwarf-trees, mountainous grasses, mosses, snow and glaciers in the entrance to the cave system. Deeper inside the cave system the ice is no longer present; approximately every 100 meters the temperature rises by 1 °C.

The Paradana cave system

The Paradana cave system consists of three caves: Velika Ledena jama (650 m deep, more than 4 km long; (Figure 1 and 2, by P. Kunaver, 1917) Mala Ledena jama (Small Ice Cave, 65 m deep and 125 m long) and the so-called Jama pri Mali Ledeni jam (Cave near Small Ice Cave, 25 m deep and 235 m long, all data from Nagode, 2002a, b). The connection among the caves has not yet been discovered. Moreover, cavers have not discovered yet the bottom of the cave system. The variety of the different passages: some covered by ice (in the topmost part), others iceless, shafts, ox-bow passages and sharply turning channels with strong draughts, is very interesting. The ice table fluctuation is large, sometimes the passages in the iceless parts of the system are completely blocked.

The underground glacier

The surface part of the glacier in the Vhodna dvorana—Entrance Hall of the Velika ledena jama, lowered about 1 m in the last five years. Also a pothole opened in the eastern part below the Grlo—Throat [low passage and step between Vhodna and the Velika ledena dvorana—Entrance and Big Ice Hall in 2002 (Figure 3)].

From the second half of the 19th century up to 1963, thousands of cubic meters of the cave ice were extracted and exported (even to Egypt!), but the ice renewed regularly. The natural ice level fluctuation is considerable in the last four decades; sometimes the passage from Vhodna and Velika ledena dvorana is even closed.


Conservation of nature

Glaciokarst depressions and caves in Paradana were declared natural monuments and the area around them a nature reserve by the old commune of Nova Gorica in 1985. The entrance part of Big Ice Cave was opened to the public by

Figure 1. Groundplan of the Velika ledena jama entrance part by Pavel Kunaver, 1917.
Turistično društvo Lokve—a local tourist club, in 1987. Members of the club have built a new path across the belts of mountainous grasses, mosses and snow to the glacier. The new path including a staircase was completed in 1988 after negotiations between the club and the Institute for Conservation of Cultural and Natural Heritage. A significant concern is erosion within the vegetation belts caused by thousand of visitors, because there is only one path through the steep, rocky scree. The scree is not consolidated, so stones and rocks periodically and dangerously fall. A small rockfall in the autumn of 2004, and regular avalanches in the winter of 2004/2005 destroyed the staircase at the entrance. A new project where the length to the entrance hall is around 150 m and the height is 30 m is the best solution for discontinuation of the erosion across the scree.

Conclusions

In the Paradana nature reserve there is an extremely rich natural heritage. The tourist club does not have adequate resources to cover the expenses of design and construction of new staircase, which is urgently needed.

Much work should be done for the regulation of human impact in the entrance part of the Velika ledena jama. For example, a contract could be formed between the Republic of Slovenia, which owns the land of the reserve and the caves, and managing organization of adequate financial backing. Remote monitoring of human impact and natural processes will be challenging and expensive, as the closest electricity source is 5 km away and the mountainous landscape challenges GSM or FM transmissions of data from sensors and cameras at the reserve to the receivers at Nova Gorica or Lokve, the nearest town and village.

An issue which will need further debates is: is the oscillation of ice on the top of the cave glacier only a natural phenomenon or the underground glaciers are natural indicators of climate change?

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THE ORIGIN OF THE CALCITE SPELEOTHEMS IN YONGCHEON AND DANGCHEOMUL LAVA TUBES, JEJU ISLAND, KOREA: THEIR SEDIMENTOLOGICAL SIGNIFICANCE AND POTENTIAL FOR THE WORLD HERITAGE NOMINATION

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The Jeju Island in Korea is essentially made of one shield volcano with more than 200 hundred parasitic cones around it. Among more than 120 lava tubes, the lava tubes in low elevation areas sometimes contain calcareous speleothems. Especially, the Yongchoen and Dangcheomul Caves are famous for its superlative beauty of these speleothems, and becomes potential sites for the World Heritage Nomination. The cave includes calcite speleothems such as soda straws, stalactites, stalagmites, columns, cave corals, curtains, flowstone, limestone, and cave pearls as well as lava speleothems. Wind-blown sediments, forming carbonate sand dunes, transported from beaches nearby are present over the tubes. Dissolution of the carbonate sediments by meteoric water and the supply of calcium carbonate through plant roots and cracks are responsible for the formation of carbonate speleothems.

Textural and geochemical of the column in Dangcheomul Cave revealed that the column is mostly composed of columnar calcite, and numerous growth laminae are present. The growth laminae were produced by coating of clay minerals from the soil zone above. Zones of spaced growth laminae (SGL) exhibit continuous growth of the calcite crystals, whereas zones of dense growth laminae (DGL) are characterized by instantaneous cessation. DGL is commonly associated with corroded surfaces. This suggests that the growth of the column was hindered and calcite crystals were corroded due to the increased supply of meteoric water that was undersaturated with respect to calcite. Carbon isotopic compositions are more enriched in SGL (ca –2‰, PDB) than DGL (ca –10 ~ –8‰). This indicates that the carbon in SGL was mostly supplied from the overlying carbonate sediments. Also, more depleted carbon isotopic values in DGL should reflect more influence by organic carbon within the overlying soil. This opposite trend should be closed related to vegetation density, soil development, and ultimately the amount of rainfall in this region. Growth of the DGL may well reflect more vegetation, better soil development and higher precipitation rate.
NEW TECHNIQUES AND INSTRUMENTAL ADVANCES
VISUALIZATION OF ELEMENTAL DISTRIBUTIONS USING HIGH-SPATIAL RESOLUTION, LARGE-AREA X-RAY MAPS OF A STALAGMITE

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Introduction

A number of in situ measurements techniques can provide chemical data at high spatial resolution. The chemical records provided by these techniques can be used for speleothem growth rate measurements, chronology, and, although often (generally?) equivocal, as proxies for paleoclimate conditions (see Fairchild et al., 2005, for a review). As noted by Treble et al. (2005), such geochemical records usually are based on one or two linear analysis transects orthogonal to speleothem growth direction. Recognizing the importance of intra-layer variation some workers have attempted to map element variation in two dimensions. By rastering the ion beam Roberts et al. (1998) obtained a SIMS image of Sr/Ca of a 0.15 x 0.15 mm area; Finch et al. (2003) constructed a Sr map of a 0.3 x 0.3 mm area from SIMS data; and Treble et al. (2005) constructed a number of element maps of a 0.5 x 1.4 mm area using adjacent SIMS transects. All of these studies noted element variability both orthogonal to and roughly parallel with stalagmite banding. However, only very small areas, about 0.02, 0.09, and 0.7 sq. mm respectively, were investigated in these studies.

To better understand stalagmite growth and associated element spatial distributions we have obtained X-ray element maps of large areas of a stalagmite, ASM-1, from Niue Island, South Pacific. The stalagmite is approximately 6 cm high and 4.5 cm wide at the base, and shows numerous well defined light-dark band couplets. X-ray maps of 3 mm wide swath (Swath Maps) along the entire central axis of the stalagmite have been constructed for Mg, Ca, Na, P, and S. In addition, maps of these elements and Sr, Si, Ba, Fe, and Mn have been obtained from other large (>10 sq. mm) off axis areas.

Procedure

X-ray maps were obtained on a polished slab using a JEOL-8600 electron microprobe equipped with five wavelength dispersive spectrometers. Thus, five elements were mapped in a single pass. Individual X-ray maps were obtained using a beam current of 400 nA, 15kV beam accelerating voltage, 5 µm beam diameter, sample pixel size of 7.25 µm, and 150 ms dwell time per pixel. It takes approximately 40 hours plus setup time to map a five element 5 x 3 mm area. Swath maps of the entire stalagmite were constructed by combining individual 5 x 3 mm area images in Adobe Photoshop™. All maps have been contrast/brightness adjusted but no other image processing has been applied.

Figure 1. Niue Stalagmite ASM-1 with Mg and S X-ray swath maps. a) ASM-1 showing start – end location of X-ray swath maps. Central arrows point to a crack in the stalagmite which is visible on the X-ray maps. b) Mg-swath map - dark bands in the stalagmite are more Mg rich than light bands. c) S-swath map; numbers on right side correspond to S-spikes, relatively large sudden increases in S. Width of swath maps is 3 mm (Brighter areas on all X-ray maps in Figures 1-3 correspond to higher concentration of the element mapped.)
**Results**

X-ray maps show that chemical variability is qualitatively correlative with light – dark layering observed optically but chemical concentrations and optical intensities are not correlative. For example, Mg concentrations are higher in the dark band of couplets than in the light band, but the concentration of Mg does not necessarily correspond to the darkness of the band (Figure 1a, b; see also Murguleţ et al., this volume).

Contrast enhanced large area X-ray maps show subtle variations between large sections of the stalagmite that might otherwise be difficult to discern. For example, Figure 1b and 1c show the bottom 2.5 cm are slightly enriched in Mg and S versus most of the rest of the stalagmite. In addition, swath maps reveal relatively large episodic inputs in trace elements throughout stalagmite growth. For example, there are six bands where sulfur shows a relatively large increase (spike) compared to preceding layers, Figure 1c. Some of these bands, S-spike 1 and 6, show corresponding increases in Na, P, and Mg. In other cases, e.g., S-spikes 2 and 5, Na, P, and Mg may decrease or show no detected change.

Perhaps better than any other technique, including optical microscopy, X-ray maps show that banding in the stalagmite is not a smooth onion shell type, rather the 2-D morphology of the bands, especially well outlined by Mg, is very complex (akin to ammonite sutures) with the boundary between some bands having a corroded appearance with numerous peninsulas and occasional islands of the lower layer within the more Mg, S, P, and Na-rich upper layer. This morphology may indicate dissolution of stalagmite calcite followed by calcite precipitation from a more trace-element rich solution.

**Figure 2.** X-ray maps of the top 5 mm of ASM-1 (growth direction and top of stalagmite is toward top of page). Boundaries between bands, best defined by Mg distribution, are morphologically complex. The spike in all elements at about 4 mm from the top is S-spike number 6 in Figure 1c, and shows peninsulas and islands of the lower layer within the more Mg, S, P, and Na-rich upper layer. This morphology may indicate dissolution of stalagmite calcite followed by calcite precipitation from a more trace-element rich solution.

**Figure 3.** X-ray image from off axis of stalagmite, growth direction to the left. Mg shows complex distribution along bands with band thickness highly variable. Sr shows discontinuous enrichment along some bands, especially visible in the lower right of Sr X-ray map.
of small areas, i.e., a few square millimeters or less, may be inadequate to properly characterize element distribution in most speleothems. Microprobes are readily available, and the time to obtain X-ray maps of large areas is not excessive. We suggest that the starting point for most chemical investigations of speleothems – and subsequent paleoclimate interpretations – should be mapping element distributions by this method. Such X-ray maps should be useful as both map and compass to locate and guide other speleothem investigations.

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VARIATION OF DROP VOLUME WITH STALACTITE GEOMETRY AND DRIP RATE: INVESTIGATIONS USING A NEW ACOUSTIC DROP COUNTER

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Introduction
Stable isotope records in speleothem provide one of the most promising means of reconstructing precipitation and temperature variations back into the past. The interpretation of speleothem oxygen isotope records in terms of a climate signal is not straightforward and much progress has been made through cave monitoring programs, where knowledge of the response of cave seepage rates to rain input on the surface provides vital information on aquifer processes and speleothem deposition. Continuous monitoring of drip rates at sites of active speleothem growth provides important constraints on processes that cause chemical and isotopic change in precipitation during its passage through the aquifer and into the cave environment.

Drip rate monitoring is usually carried out using a tipping bucket system, a device which reaches a point of unstable equilibrium when its contents reach a pre-defined level. It then tips and empties itself, triggering a reed switch for recording a single event. Mechanical counting devices are sometimes unreliable in cave environments owing to condensation and carbonate precipitation interfering with the mechanism and unattended long term monitoring may be problematic. Another drawback of the tipping bucket is that the time base is defined by the volume of the bucket and time series cannot be recorded at high resolution particularly at low drip rates.

Data collection
Acoustic drip counting is an attractive alternative means of measuring water flow and we have used a simple integrated acoustic drip counter/logger (the Stalagmate, www.driptych.com) which counts the number of drips falling on the lid of the device over a user-defined time interval. The Stalagmate is a box 65 mm x 60 mm x 40 mm counts and logs every drip which falls onto its lid by means of an acoustic impulse. The data logger is programmed via a PC and can be transported in its pre-programmed state to the cave site and started by bridging a pair of external pins with a wet finger. Data can be downloaded at any time, without interrupting logging, on to a PC laptop or Palm PDA. It is desirable to have the option to leave the drop counter unattended for periods of months to years, so all the enclosed electronic circuitry is therefore of ultra low current consumption, and powered by a single 1/2 AA 1000mAh Lithium cell, which is more than able to fulfill this criterion. The integral data logger (www.geminidataloggers.com) counts in 216-1 (65,535) “buckets” of maximum capacity 28-1 (255) events, or an absolute maximum of 16.7 million drops. The time interval is set by the user via an RS232 interface, and would generally be chosen so that no more than, say, 200 drops would occur during the interval. This frequently requires some judgment and knowledge of the history of the sampling site in order not to exceed the 255 limit within the chosen time interval.

Relationship between drop volume and stalactite tip dimensions
The Stalagmate measures the frequency of drop events and knowledge of drop volume is required to estimate flow quantities. Although water drops are often assumed have a volume of approximately 0.15 ml (e.g. Genty et al., 1998) water may be collected from a variety of drip sources e.g. tubes (soda straws) or massive stalactites with a wide range of dimensions and we have used the Stalagmate drip logger to investigate the relationship between drop size and the diameter of roof straws and massive stalactites over statistically significant drop counts (between 1000 and 5000 drops per run). For these experiments either brass tubes or machined aluminium rods having different tip radii were used. In the latter case, it is assumed that the curvature of the stalactite
is constant over the width of the drop during its formation (typically four times the diameter of the pendant drop) – in other words, the tip is spherical over this limited region.

**Roof straws: drop diameter versus tube diameter**

Rayleigh predicted a linear relationship (1) between drop volume \( V \) and tube diameter \( d \), the controlling parameters being the density of the fluid \( r \), its surface tension \( s \), and \( g \) (Neda et al., 1996):

\[
V = 1.9 \frac{sd}{rg} \tag{1}
\]

The Stalagmate was first used to verify this relationship assuming that the drop diameter would be independent of drip rate, provided it was neither too fast (>1 drop/sec => inertial effects) or too slow (<1 drop/hr => evaporation), and that a mean drip rate of between 1 and 10 drops/min would be sufficiently slow to avoid inertial effects in the drop detachment. Hence no special arrangements were made to ensure a constant drip rate, and water passed to the tubes through the nozzle of a vertically mounted 100 ml syringe, the flow being restricted by a cotton wool plug in the tube. The Reynolds number is sufficiently low to be able to assume viscous Poiseuille flow, so the rate of change of volume is proportional to the height of the fluid above the tube and results in an exponential decay in the drip rate. Several runs were completed for each size of tube, ranging from 0.8 mm to 8.0 mm at temperatures between 16 °C and 21°C (Surface tensions for water vary by just 1% over this temperature range and no temperature correction was made). The relationship between drop size and tube diameter is shown in Figure 1 which shows a close correspondence with the Rayleigh model.

**Massive stalactites: drop diameter versus tip diameter**

The majority of the “stalactites” were designed be fed by a film of water running down the outside of the hemisphere. Each stalactite was wrapped in a 2 mm thick layer of absorbent paper, which was then covered with waterproof tape. Water introduced into a small reservoir at the top of the stalactite was then uniformly absorbed by the paper, and emerged from the lower end as a continuous film which coated the hemisphere before forming a pendant drop. To assist with adhesion to the surface, each hemisphere was slightly roughened with 240 grit abrasive paper.

As with the tube experiment, a constant drip rate was not thought necessary, and the water supply was a small (250 ml) reservoir approximately 300 mm above the top of the stalactite. Flow was controlled by a small thumbscrew compressing the silicone rubber tube. Four experiments were run in tandem, with stalactites of different sizes dripping onto four different Stalagmates. In each case, the time interval was set to 5 minutes, setting an upper limit of 51 drops/min within the 255 count limit. Average drip rates were generally between 3 and 10 drops/min. A TriPour 800 ml polypropylene beaker was found to be the ideal size for a Stalagmate, and a tube attached to the bottom of each one allowed the water to drain away into a 250 ml beaker, where it could be accurately measured.

The total number of drops counted for each run was between 1000 and 5000. With such a large count, it was initially assumed that the variance in drop size would be small, necessitating few measurements at each diameter. In reality, considerable variance was found between one run and the next, even though conditions were nominally identical, or certainly very similar. This surprising result leads to the conclusion that either the experimental technique needs to be improved (possibly) or that this variability is natural and that drop formation is not wholly deterministic.

Several runs were made for each stalactite, and volume plotted against diameter in Figure 2. It is clear, within the limits of experimental error, that volume is an increasing, and probably monotonic, function of tip radius which finds approximate expression when plotted on log-log axes. With volume and diameter both transformed into logs, a good least-squares fit is an exponential of the form \( y = a + b \cdot 10^{-kx} \), where \( y = \log_{10}(\text{volume/ml}) \) and \( x = \log_{10}(\text{diameter/mm}) \).
This then resolves into a power law in log(volume) of the form

$$\log_{10}(\text{volume}) = -0.557 - 2.312 \times (\text{diameter})^{-0.554}$$  \hspace{1cm} (2)

This result predicts that a drop falling from a flat plate (i.e. infinite radius of curvature) will have a maximum volume of 0.28 ml but more experimental data are needed to define this limit with greater precision. The results of this and ongoing work on the variance of drip volume as a function of drip rate will be presented.

### Figure 2.
Plot of drop volume versus diameter of stalactite tip. The best fit curve is represented by Equation (2).

Conclusions

1) Acoustic drip counting provides high resolution drop count data for fast and slow dripping sources and is ideal for using in remote sites which may not be revisited for months or years.

2) Logging capacity is approximately 60 days at 2 minute intervals (fast drips) and over 3 years at 30 minute intervals (slow drips)

2) Volume flow rates require knowledge of the average drop size and this work confirms that drop size approximately follows the Rayleigh model for tubes (soda straws) and varies with tip radius of massive stalactites

3) For massive stalactites the volume may be predicted from the tip diameter:

$$\log_{10}(\text{volume}) = -0.557 - 2.312 \times (\text{tip diam})^{-0.554}$$

4) Drop volumes are easily cross-checked in the field by collecting the water which falls onto the Stalagmite placed in a suitable container such as a TriPour 800ml beaker, modified to take a drainage tube at its base.

### References


LONG-TERM REPRODUCTIBILITY AND ACCURACY OF MC-ICP-MS SPELEOTHEM DATING

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Arguably the greatest strength of speleothem records as paleoclimatic proxies is that they may be dated in precise, absolute terms using the U-Th disequilibrium method. This should allow unambiguous high-resolution cross-comparison of speleothem records produced by different groups from different sources but has not completely lived up to this promise through some combination of inadequate dating resolution, inconsistent U-series data presentation and processing, and almost non-existent inter-laboratory standardisation. It is thus becoming increasingly important that laboratories carefully document their speleothem dating procedures, and that we find and agree on one or more solid standards for routine, widespread inter-comparison.

Here I will present multi-collector inductively-coupled plasma U-Th dating techniques in use at the University of Melbourne and discuss their long-term performance against in-house solid speleothem standards. Factors affecting long-term reproducibility relative to in-run analytical precision can be broken down into those specific to ICP-MS (sample memory, ion-beam “flicker” and general instrument stability) and those shared with thermal ionisation mass spectrometry (sample-spike equilibration, ion-counter linearity, mass tailing and Faraday amplifier lag). I will then contrast the effectiveness of solid speleothem standards with the solution standards in widespread use, and discuss some of the attributes of an ideal solid speleothem standard.

Using a MC-ICP-MS equipped with parallel ion counters, U and Th isotope ratios may be measured simultaneously within a single solution, while also internally correcting for mass bias, collector gain and elemental fractionation. Sample throughput is several times that possible with TIMS, and analytical precision is controlled by the total system counting efficiency on Th-230 of ca. 0.2%. This means 95% age uncertainties of less than two per cent are routinely obtained for samples containing only 1 ng of U, equivalent to 10 mg of a typical 100 ppb U speleothem. Speleothems containing more than a few ppm U can be dated by directly dissolving and spiking ca. 0.1 mg of sample before introduction to the ICP-MS, avoiding a chemical separation step and further improving sample throughput.

The well-recognised principal obstacle to accurate laser-ablation MC-ICP-MS U/Th dating is the difficulty of correcting for elemental fractionation between U and Th during analysis. The Nu Plasma – HelEx system in use at the University of Melbourne combines extremely stable ablation and plasma conditions with a static collector array allowing simultaneous measurement of all isotopes of interest. In this case, U/Th elemental fractionation can be controlled to ca. 1% by external bracketing to any other speleothem of known age. Alternatively, solution-mode analyses can be used to anchor each end of an apparent age-distance traverse, as samples containing enough U to be analysed by laser ablation can also be rapidly dated by direct dissolution as noted above. Speleothems containing 1 ppm U typically produce 95% age uncertainties of 5%, falling to 1% for samples containing 20 ppm U.
HYPERSPECTRAL IMAGING OF STALAGMITES

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Introduction
Proxy records from speleothems are increasingly used in palaeoclimatic reconstructions, as the factors controlling their growth rate and the nature of the internal structure and chemical composition of speleothems respond to changes in surface climate. Formed as part of the meteoric water cycle, speleothems are capable of recording a climatic signal smoothed by the mixing of event and stored water in the karst aquifer above the cave (Barr-Matthews et al., 1991). As such, they are capable of recording changes in climate parameters such as mean annual temperature, precipitation, or atmospheric circulation changes, and vegetation responses, back through time via a number of available proxies (McDermott, 2004). These include stable isotope ratios (Rozanski et al., 1992; McDermott, 2004), inter-annual thickness variations of growth laminae, growth rate changes (Genty et al., 2001), variations in trace element ratios (Ayalon et al., 1999; Fairchild, 2002; Roberts et al., 1999), organic acid content (White and Brennan, 1989; Rousseau et al., 1993) and trapped pollen grains (McGarry and Caseldine, 2004). An area where published research is perhaps rarer is petrographical studies of stalagmites; for example Kendall and Broughton (1978), Genty (1993), Bar-Mathews et al. (1991) and Frisia et al. (2000); despite the valuable information that can be obtained from such studies concerned with examining the visual characteristics e.g colour and the internal structure of a stalagmite (i.e. nature of the annual/sub-annual lamina and changes in crystalline fabric and porosity), as these can give important information on the environmental conditions under which the speleothem formed (Xiaoguang et al., 1998; Perrette et al., 1997).

Current use of optical analyses in speleothem research
Optical analyses of stalagmites have up until now included visual observation of stalagmite images obtained from flatbed scanners or digital cameras. Although these can provide good quality images, microscopy (under both visible and fluorescent illumination) has been required to identify finer resolved features. Subsequent digital image processing has identified such things as grey-level changes throughout individual stalagmite lamina and within a group of laminae captured under polarised visible light (Xiaoguang et al., 1998), luminescence properties under UV-light (Baker et al., 1993; Ribes et al., 2000), and crystalline fabric and calcite porosity (Kendall and Broughton, 1978; Frisia et al., 2000; Genty, 1993). Such studies have aided the recognition of sub-annual lamina made up of White Porous Calcite Lamina (WPL) and Dark Compact Calcite Lamina (DCL) which together make up an annual lamination (Genty, 1993), as well as the identification of organic acid layers (humic and fulvic acids) which may be used to determine variations in the annual growth rate (Baker et al., 1993) as well as an indicator of paleoprecipitation (Proctor et al., 2002).

Current applications of reflectance spectra in speleothem research
Reflectance spectra have been used to identify the dominant source of colour in a collection of stalagmites (White, 1981) and it is reported by Perrette et al. (1997) in their comparison of the use of reflectance spectra with the other optical analyses mentioned above. Colour is not a tangible object, merely a perception of the human eye caused by the reflection or absorption of particular wavelengths of incident light on an object. The human eye is only sensitive to the wavelengths of light reflected from an object in the region of 400 to 650 nm which provide the brain with three signals in the red, green and blue (RGB) range. The colour of an object is reconstructed by the brain according to the combination of the relative intensities of these three wavelength bands (RGB) and is affected by the wavelength of the illuminating light source as well as the reflectance/absorption properties of the object being viewed which are in-turn a reflection of their chemical composition and internal structure. By capturing an
image of the object under different light conditions it is possible to present a graphical representation of the absorption/reflection spectra of an object of a certain colour.

Absorption spectra for different coloured stalagmites have been obtained previously (Figure 1, White, 1981) showing the absorption spectra typical of common stalagmite colours. Reflective spectra of the same samples demonstrated that the location of reflectance bands of common stalagmite colours of milky yellow, orange, tan and brown were not related to those spectra obtained for oxides and hydroxides of iron, suggesting for the first time that iron oxides are not the dominant source of colour, indirectly suggesting that organic pigments were responsible for the common colours of these stalagmites, this was later supported by Perrette et al. (1997), and the subsequent identification of fluorescence organic matter and other biomarkers in stalagmites. Such studies have been limited to only being able to capture reflectance spectra of stalagmites over a particular band of wavelengths in the visible part of the spectrum and so potentially missing a large amount of detail which if available may better aid the identification of fine sub-mm lamina and crystalline features, as well as the identification of the type of organic acids, iron oxides or inclusions and whether or not similar looking features are in fact the same in terms of their reflective spectra. Similarly, an image captured on a standard digital camera-microscope set up or flat bed scanner will produce spectra in the red, blue and green bands and so similarly mask any subtle variations that may occur within these bands or outside of these bands, i.e. beyond the visual part of the spectrum. Other limitations are the destructive nature of creating thin-sections of stalagmite often used for imaging work which may use up large portions of samples, the time it takes to capture images by microscopy when working with field of views in the order of mm or less, (especially if multiple transects are taken), the process of moving the sample in order to take the next image and subsequently tiling images which can cause non-uniformity between images and discontinuities (Ribes et al., 2000). Ribes et al. (2000) describe the setup of a confocal scanning laser microscope to take photoluminescence images of speleothem micro-banding. The confocal lens eliminates light from outside the focal plane which may blur any captured image, whilst the microscope setup allows for a much larger field of view up to 7.5 × 7.5 cm (or down to 200 × 200 mm), without losing image resolution. However this setup still only really allows a qualitative analysis of luminescent lamina and suffers the same lack of detail of obtained spectra as described earlier.

Hyperspectral imaging

Hyperspectral imaging is a technique never before used in stalagmite research, but potentially has many advantages over standard optical imaging techniques in terms of the detail of information that can be obtained from a single image capture process.

An image captured by a standard scanner or digital camera is constructed by combining 3 images taken in the visible range RGB bands widths, and thus can only say whether or not there is a peak in these bands, it can’t resolve spectra finer than these 3 broad bands. In hyperspectral imaging, the final image is constructed from many image “slices” taken at whatever wavelength interval is selected. This means that spectra can be resolved in much greater detail, and may show many more reflectance peaks and troughs that standard imaging could not resolve. This offers a more accurate way of classifying certain features captured by an image. Further, hyperspectral imaging can extend beyond the visible range of the spectrum, identifying features that may not be picked up by standard imaging techniques at any magnification.

In order to demonstrate these applications, hyperspectral images of a set of stalagmites have been obtained using a high sensitivity 12-bit monochrome digital camera (QImaging Retiga Exi) and a LCD programmable interference filter (Cambridge Research Instruments). The filter can be configured to implement any narrow (approx. 7 nm) Gaussian bandpass filter in the range 400–720 nm. The camera quantum efficiency and the filter transmittance vary as a function of wavelength, resulting in total sensitivity of the system of 2% at 400 nm, 6% at 450 nm, 30% at 550 nm and 40% at 700 nm. To ensure that a sufficient number of photons reflected from the sample are collected by the camera, the acquisition times were varied as a function of wavelength, from 2.5 sec to 17 ms per image. The filter and the camera were controlled using a standard notebook computer running custom software. The samples were illuminated using a halogen light source diffused by a half-sphere coated with

Figure 1. Schematic spectra showing some relations between absorption curves and perceived colours (taken from White, 1981).
Spectralon™. Following the acquisition the spectral data was processed to remove the effects of the light source, the imaging system and the acquisition time. Black and white images have been obtained at 5nm spectral intervals. Our results highlight the following implications for this technique in terms of stalagmite research:

(1) It allows the user to define what spectral band of reflected light the stalagmite image will be viewed in. This may allow certain features to become more or less identifiable. For example, lamina in certain samples may be best picked out in one spectral band (e.g. 550 to 650 nm) whereas water inclusions may be better viewed at >1000 nm (into the infra-red part of the spectrum).

(2) Classification of certain features according to their spectra within a single sample and between a set of samples. These data may then be mapped as you can isolate an image of particular spectra and show the features that are best defined in this wavelength. Features can then be identified as being the same or different according to their optical properties. It then becomes possible to create essentially, a mini-GIS of a stalagmite containing whatever information you set.

(3) It is possible to view the emitted luminescence properties (400-450 nm) of a stalagmite without the need for UV-microscopy.

(4) There is a great reduction in the time taken to acquire images, and less need to stitch images together as field of views can be up to 5 × 5 cm.

Conclusions

The applications of hyper spectral imaging to speleothem research are potentially extensive and may go a long way to aid in the identification of annual lamina (and sub-annual features) that may be difficult to view otherwise, and identify other features that may not be observed outside the visible light spectrum. It offers advantages in terms of the speed and the detail in which spectra can be resolved and mapped on a stalagmite’s surface, and the classification (both qualitatively and quantitatively) of features as being optically similar/different which may then aid paleoenvironmental reconstructions by offering clearer understanding of the conditions under which the stalagmite formed.

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Microstratigraphic Logs: A Method for Improving Time Correlation of Speleothems for Paleoclimatic Studies

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Introduction

In calcitic stalagmites used for paleoclimatic studies, growth laminae located between absolute dated horizons are usually dated by means of linear interpolation. This approach is subjected to potentially large errors, especially if the number of absolute dates available for a given speleothem is limited. Here, we propose a method to improve the accuracy of such interpolations based on the microstratigraphic correlation of at least two coeval speleothems for which a limited number of absolute dates are available. In addition, this method highlights variations in growth rates that are potentially useful in paleoenvironmental studies. We have applied this interpolation method to three Holocene speleothems from Cueva del Cobre (Palencia, Spain).

Materials and methods

Three calcitic stalagmites (C7, C7S and C12) were collected at different levels within the same cave (Cueva del Cobre, N Spain; Rossi et al., 1997) under active drips. Two of them (C7 and C7S) are “twin” stalagmites, i.e. they grew together forming a composite (double) stalagmite: as a result, many of their growth layers can be visually traced from one stalagmite to the other. Eight subsamples of the stalagmites were dated by means of U-Th (TIMS and ICPMS; McMaster University) according to the procedure described by Li et al. (1989). The results are shown in Table 1. Subsample C7m was duplicate and analyzed by means of both TIMS and ICPMS. Finally, three ages were available for both stalagmites C7 and C12 (base, middle and top) and only one for stalagmite C7S, located at its base. U-Th dating showed

<table>
<thead>
<tr>
<th>Sample</th>
<th>total U (ppm)</th>
<th>$^{230}$Th/$^{232}$Th +/-</th>
<th>$^{230}$Th/$^{234}$U +/-</th>
<th>$^{234}$U/$^{238}$U +/-</th>
<th>Age (yr BP) +/-</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7t</td>
<td>0.4243</td>
<td>6.32 2.33</td>
<td>0.0046 0.0017</td>
<td>1.0737 0.0025</td>
<td>386 187</td>
</tr>
<tr>
<td>C7m ICP</td>
<td>0.3662</td>
<td>93.90 3.63</td>
<td>0.0279 0.0011</td>
<td>0.9974 0.0020</td>
<td>3077 123</td>
</tr>
<tr>
<td>C7m TIMS</td>
<td>0.3623</td>
<td>79.30 2.28</td>
<td>0.0289 0.0008</td>
<td>1.0155 0.0018</td>
<td>3130 92</td>
</tr>
<tr>
<td>C7b</td>
<td>0.5430</td>
<td>278.65 5.40</td>
<td>0.0474 0.0009</td>
<td>0.9982 0.0011</td>
<td>5281 103</td>
</tr>
<tr>
<td>C7S-A</td>
<td>0.3626</td>
<td>38.74 2.24</td>
<td>0.0443 0.0026</td>
<td>1.0138 0.0017</td>
<td>4932 292</td>
</tr>
<tr>
<td>C12-F</td>
<td>0.3423</td>
<td>69.07 6.41</td>
<td>0.0234 0.0022</td>
<td>1.6686 0.0193</td>
<td>2567 243</td>
</tr>
<tr>
<td>C12-C</td>
<td>0.4594</td>
<td>296.44 14.09</td>
<td>0.0341 0.0016</td>
<td>1.3514 0.0020</td>
<td>3771 182</td>
</tr>
<tr>
<td>C12-A</td>
<td>0.3975</td>
<td>187.38 3.14</td>
<td>0.0547 0.0009</td>
<td>1.3405 0.0021</td>
<td>6106 102</td>
</tr>
</tbody>
</table>

Table 1: Analytical results of the $^{230}$Th/U datings for the three stalagmites from Cueva del Cobre. Uncertainties correspond to 2σ for all samples.
that the three samples were coeval, at least in part, ranging in age from ~6200 to ~50 yr BP.

Proposed method of correlation

We propose a method of correlation of the stalagmites in order to use all the “control” dated points in each of them. To this purpose, a microstratigraphic log of each stalagmite was drawn to a 1:0.5 scale using the petrographic microscope and transparent double-polished sections with thickness varying between ~150 and ~500 µm. The transparency of the sections was optimal at that thickness. As many features as possible were recorded: 1) color of the calcite de visu, 2) kind, number, thickness, and lateral continuity of layers, 3) shape and size of the pores, and 4) nucleation of new crystals in the axial part of the stalagmite. Initially, the stalagmite

Figure 1. First chronological correlation (black dashed lines) and final correlation of the microstratigraphic logs of the three stalagmites based on intervals (grey solid lines, see text). Scale to the left of each log is in millimeters. Brackets correspond to U-Th ages. Correlation table (upper left) indicates the temporal equivalences according to the intervals-based correlation (solid lines).
records were dated through linear interpolation between the U-Th ages and a first chronological correlation was attempted (dashed lines in Figure 1). However, this former correlation is subjected to potentially large errors since there are very few U-Th dates in each stalagmite but it is very helpful in order to compare the coeval parts of each stalagmite. The texture of calcite precipitated in a single speleothem depends on many factors. In this case, coeval drips precipitated different types of calcite (Figure 1). Therefore the calcite texture is not a correlative feature for these stalagmites. However, major changes in the behaviour of the drips (and consequently, major changes in calcite texture) should be contemporaneous in all of them since they should reflect major paleoenvironmental changes. In the case of the three studied stalagmites, this correlation seems possible (Figure 1). The three sections are divided into intervals showing similar features (trend or cyclicity) and limited by paleosurfaces of the stalagmite which were clearly preserved (layers with high lateral continuity and/or thickness). The composite stalagmite permitted to check this correlation through direct observation of the layers (Figure 2). Since we assume that the textural changes in the calcite of the stalagmites are induced by paleoenvironmental changes (i.e., major textural changes are contemporaneous), then these correlation lines drawn after intervals of the logs should be considered chronostratigraphic lines. Therefore, the ages obtained in each stalagmite could be situated in the others in parallel to the correlation lines. Figure 1 shows the interval-based correlation of the three stalagmites and the correlation table.

**Results**

Thanks to this correlation it is now possible to obtain 13 control dated points for stalagmite C7, 11 dates for C7S and 10 for C12 (Table in Figure 1). New growth rates were calculated using the correlation method (Figure 3). The graphs

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**Figure 2.** Correlation of stalagmites C7 and C7S through direct observation of the common growth layers. A) Collage of ~100 photographs from the upper part of C7 and C7S. B) Schematic view of both stalagmites with their correlation elements. The line in mm 212 (C7) corresponds to the first continuous common layer of the two stalagmites. The rest of the lines were drawn using the collage to the left (A).
represent these new growth rates (solid lines) and those calculated through simple linear interpolation (dashed lines). As can be seen, the correlation method not only improves the dating of intermediate parts of the stalagmites, but also yields interesting new information about variations in growth rates for each speleothem.

**Acknowledgements**

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**References**


**Figure 3.** Growth rates of stalagmites C7, C7S and C12 calculated through simple linear interpolation (dashed lines) and with the method of interval-correlation with the other stalagmites (solid lines).
MEASUREMENT OF STABLE ISOTOPE IN SPELEOTHEM FLUID INCLUSIONS BY CONTINUOUS FLOW MASS SPECTROMETRY

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Speleothem fluid inclusions constitute the most ubiquitous and the best temporally resolved archive of Pleistocene fossil groundwater outside the main icecaps. Since the water in the inclusions derives ultimately from local rainfall, speleothems carry within them an important record of spatial and temporal changes in the isotopic composition of precipitation. Determining the stable isotope composition of such inclusions has been attempted in several laboratories over the past few decades and has proved to be technically very challenging, especially for oxygen. It is difficult to totally eliminate isotopic fractionation during sample recovery and manipulation. Presently, the relatively large sample sizes required for dual inlet mass spectrometric measurements (typically >0.5 μl of water, requiring 0.5–2.0 gms of calcite) restricts the temporal resolution of such measurements to a few hundred years.

The technique of continuous flow (CF) mass spectrometry allows (1) the measurement of much smaller samples (by 1-2 orders of magnitude) than previously possible; (2) the direct measurement of isotopic composition, following online pyrolysis reduction, without the necessity for time-consuming offline equilibration or water reduction steps; (3) the potential ability, using peak switching, to measure both oxygen and hydrogen isotope ratios in rapid succession on the same sample.

Routine measurement of δ²H for 0.02–0.1 μL groundwater samples following pyrolysis in a high temperature reduction furnace attached to a PDZ Europa GEO continuous flow mass spectrometer has demonstrated the feasibility of (1) and (2) above. Connection to the furnace of a crushing chamber and a cryo-focussing trap with flash-heating capability now allows us to crush calcite samples in a He stream. Experimentation with crushing chamber design is currently in progress to optimise water recovery efficiency. The design of the CF apparatus and instrumentation will be discussed and δ²H results of inclusion analyses from European and Middle Eastern speleothems will be presented.
INVESTIGATION OF THE FRACTIONATION OF STABLE ISOTOPES IN SPELEOTHEMS WITH LABORATORY EXPERIMENTS

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Most published speleothem stable isotope records show a positive correlation between $\delta^{13}C$ and $\delta^{18}O$ values (Mickler et al., 2006). This indicates significant influence of kinetic isotope effects (Hendy, 1971), and temperature-controlled equilibrium fractionation alone cannot explain the observed variations in these records. To use speleothem stable isotope records for quantitative paleoclimate reconstructions, an understanding of the extent of the influence of the kinetic processes is needed.

We studied the fractionation of oxygen and carbon isotopes in several laboratory experiments with synthetic carbonates. Synthetic carbonates were precipitated both from a body of standing water (representing a stalagmite growing in contact with a body of stagnant water) and from a solution flowing along a rod (representing conditions where the solution flows along the sides of the stalagmite, Figure 1). The complete experiment is located in a fridge, and various parameters influencing isotope fractionation (e.g. temperature, relative humidity, flow rate) can be independently, precisely regulated (Figure 1).

Slow degassing of $CO_2$ from the beakers produces carbonates with $\delta^{18}O$ values in equilibrium with the solution but

Figure 1. Schematic drawing of the setup that was used to precipitate synthetic carbonates under controlled conditions in the laboratory. The figure shows the rod experiment.
with a significant enrichment of $\delta^{13}C$, inversely proportional to the height of the solution in the beakers (Figure 2). Consequently, the resulting slope in a $\delta^{18}O$ vs. $\delta^{13}C$ plot is zero.

Fast degassing of CO$_2$ in the rod experiments at a relative humidity of 100% (70%) showed a significant enrichment of both oxygen and carbon isotopes (Figure 3). $\delta^{18}O$ and $\delta^{13}C$ were linearly correlated with a slope of $\Delta\delta^{18}O/\Delta\delta^{13}C$ of 0.7 ± 0.3 (0.9 ± 0.2). These results represent the first experimental evidence for the Hendy (1971) effect. Total evaporation of the solution from the beakers resulted in a slope of $\Delta\delta^{18}O/\Delta\delta^{13}C$ of 2.5 ± 0.2.

In summary, the slopes of $\Delta\delta^{18}O/\Delta\delta^{13}C$ in our experiments range from 0 to 1 and are within the range of slopes observed in natural speleothems which are generally deposited at rather high relative humidity.

**Figure 2.** $\delta^{18}O$ and $\delta^{13}C$ plotted against the reciprocal height of the solution in the beakers. The light blue line shows the calculated equilibrium value for $\delta^{18}O$ (Kim and O’Neil, 1997).

**Figure 3.** $\delta^{18}O$ and $\delta^{13}C$ plotted against the path length on the rod. The light blue line shows the calculated equilibrium value for $\delta^{18}O$ (Kim and O’Neil, 1997). Both $\delta^{18}O$ and $\delta^{13}C$ show a linear relationship with the path length. The correlation coefficients are R=0.95 and R=0.89, respectively.

**References**


We present a study of variations in the periodicity of climatic cycles through time from paleoluminescence records in speleothems from Savi Cave near Trieste, Northern Italy. We dated a speleothem from the cave with 15 ICP-MS and TIMS U/Th ages, ranging from 1.33 to 16.8 kyr B.P. with \( \sigma \) error ranging from \( \pm 100 \) to \( \pm 430 \) years. Three paleoluminescence records (Stoykova et al., 2003) have been measured from this stalagmite.

A very high resolution composite record covers the last 2028 \( \pm 100 \) years (2\( \sigma \)) (the upper 20 mm of the sample) with several hiatuses. This composite record of the intensity of luminescence consists of 40106 data points and is composed of 16 overlapping scans of 4800 data points each. It has a temporal resolution ranging from 15.6 days to 19.9 days. It allows also precise measurements of the annual growth rate of the speleothem, which varies from 2.2 to 45.4 \( \pm 0.5 \) microns/year with a mean value of 6.36 microns/year. The record of the annual growth rate covers 2028 years taking into account the hiatuses. This record represents mainly the annual rainfall at the cave site.

We used the special evolutive real-space periodogramme analysis algorithm described in Shopov et al. (2002) to calculate the intensity of cycles of annual precipitation at the cave site. The resulting periodogramme demonstrates that the strongest cycles of the annual rainfall in the region are with durations of about 300, 130 and 55 years. A precipitation cycle with duration of 300 years has been detected also by other authors, but its origin is still unclear. We studied variations of the length of these cycles with time by evolutive power spectral analysis. Their duration and intensity exhibit some variation with time.

We used the same digital analysis to calculate the intensity of the cycles of the speleothem luminescence (representing cycles of solar radiation or air temperature). The power spectra demonstrate that the strongest cycles of soil temperature in the region have duration of about 11, 22 and 70 years. These are well known solar cycles, which drive temperature changes in some climatic regions. We studied variations in the length of these cycles with time by evolutive power spectral analysis in 12 consequent part of the record.

References


A CONTINUOUS-FLOW CRUSHING DEVICE FOR ON-LINE $\delta^2$H AND $\delta^{18}$O ANALYSIS OF FLUID INCLUSION WATER

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We present a new design continuous-flow preparation device for on-line $\delta^2$H and $\delta^{18}$O analysis of fluid inclusions in speleothem carbonate. The design is based on a relatively low-cost adaptation to a Thermo Finnigan TC-EA pyrolysis furnace. Standard specifications of the Thermo Finnigan TC-EA allow for simultaneous $\delta^2$H and $\delta^{18}$O analysis of 0.2 microliter of water, reproducible within 2‰ for $\delta^2$H and 0.5‰ for $\delta^{18}$O (1SD).

The fluid inclusion extraction line that we have connected to the inlet of the TC-EA contains an adapted vacuum valve that serves as a hand-operated crusher, and a cold trap operating at liquid nitrogen temperature. In contrast with most existing devices, crushing and cryogenic capture of fluid inclusion water take place under a helium atmosphere, rather than in vacuum. Subsequent flash heating of the cold trap releases the frozen water sample into a helium flow, which carries the sample to the TC-EA.

First experiments with this system focused on $\delta^2$H only, and involved direct injection of sub-microliter amounts of standard waters via a septum-port attached to the crusher. Repeated analyses resulted in accurate standard water isotope values, reproducible within the standard specifications of the TC-EA. This may be interpreted to confirm the proper functioning of the cryogenic trap and sample transfer to the TC-EA.

A second set of experiments then focused on the analysis of speleothem calcite from a cave in the Peruvian Amazonian lowlands, with known modern drip water composition. Crushing and analysing a set of sample cut from a single sub-recent stalagmite growth interval gave $\delta^2$H values that compare remarkably well to drip waters from that cave, at a reproducibility well within the TC-EA specs. We further analysed a set of samples cut from speleothem calcite from a cave in the Peruvian highlands with much more depleted drip water $\delta^2$H values. Here too, we found fluid inclusion $\delta^2$H data to be in good agreement with seepage water.

The method presented is quick and requires only small (<0.5 g.) cubes of speleothem calcite. The peak-jump routine provided in the standard TC-EA software even allows for combined $\delta^2$H and $\delta^{18}$O analysis from a single extraction.
U-PB GEOCHRONOLOGY OF SPELEOTHEMS BY MC-ICPMS

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Introduction

Building upon the work of Richards et al. (1998), we have developed a method for precise dating of speleothems beyond the range of the U-Th technique using the U-Pb decay scheme. By coupling low-blank sample preparation procedures and MC-ICPMS analytical methodologies developed for low-level Pb-isotope analysis, we find that, under ideal circumstances, U-Pb dating of speleothems is not only possible but also produces excellent age resolution—often comparable to or better than U-series studies. Corrections for initial isotopic disequilibrium are necessary in most analytical situations and exert a strong control on the achievable age uncertainty.

The technique will be of immediate benefit in extending speleothem-based climate proxy records beyond ~550 ka and will also find other uses, such as the dating of associated sub-fossil remains, and providing constraints on rates of landscape evolution and neo-tectonic processes. Preliminary results will be presented for speleothems from the Nullarbor Plain, Western Australia, and the Alpi Apuane, Italy.

Results and discussion

Samples studied

Preliminary data have been obtained for several different speleothems from two regions. The first samples studied come from caves beneath the Nullarbor Plain of Western Australia. Despite an arid to semi-arid climate, lack of surface streams and little relief, satellite-derived digital terrain data show clear evidence of ancient river channels and other landforms indicative of significantly higher rainfall at periods in the past. Large, organic-rich speleothems interpreted as having formed beneath forest and/or swamp vegetation are widespread in caves beneath the plain, and until now have only been shown to be older than the ca. 350 ka maximum age limit of alpha spectrometric U/Th dating (Goede et al., 1990). Unpublished MC-ICPMS analyses (Hellstrom, 2003) from our laboratory have found some limited calcite deposition in the period 350 to ~550 ka, but confirmed that the majority of Nullarbor speleothems are significantly beyond the limit of mass spectrometric U/Th dating. The palaeoclimatic importance of these samples lies in their potential to provide insights into the timing of the onset of Australian aridity during the late Tertiary and early Quaternary. Additional samples were analysed from Antro del Corchia, a large cave system situated in the Alpi Apuane massif of northern Tuscany, Italy. A wide variety of stalagmites have been collected from Corchia, ranging in age from 0.5 ka to beyond 550 ka. Initial research has shown the cave (present-day mean annual temperature 7.5 °C) to be sensitive to the severity of Pleistocene glaciations. Variations in speleothem δ¹⁸O show a close structural similarity to the Vostok ice-core palaeotemperature record (Drysdale et al., 2005). This may stem from the site’s sensitivity to North Atlantic climate, which is linked to Southern Ocean circulation via the global oceanic conveyor belt.

Isochron formalisations

Richards and Dorale (2003) demonstrated the use of the three-dimensional variant of the Tera-Wasserburg plot developed by Wendt and Carl (1985). In the case of MC-ICPMS-generated data, however, when ²⁰⁶Pb data are of questionable accuracy such an approach is compromised. For most of our data we have therefore used the conventional Tera-Wasserburg diagram (Tera and Wasserburg, 1972), renamed the...
Accurate U-Pb geochronology relies on initial secular equilibrium in the U-series decay chains. Ludwig (1977) was the first to consider the possible errors introduced arising from violations of this assumption, and this issue has been re-iterated by Richards et al. (1998). The problem is particularly relevant to speleothem studies since it is well known that cave carbonates are precipitated out of U-series secular equilibrium (this in fact forms the basis of U-series dating). A wealth of data on both modern and Late Quaternary speleothems indicates a wide range of initial $^{234}$U/$^{238}$U, reflecting the even wider range observed in contemporary groundwaters. In addition, the time required for $^{230}$Th ingrowth (clean speleothems are precipitated with essentially no Th) in the $^{238}$U-$^{206}$Pb decay chain must also be taken into account, in addition to a number of other more minor effects.

While a correction for initial isotopic disequilibrium is performed relatively easily, the accuracy of such corrections is rather strongly dependent upon the choice of appropriate input parameters, in particular the initial $^{234}$U/$^{238}$U ratio. As an example, consider the sample from Antro del Corchia which has an uncorrected, but extremely well determined, ‘apparent age’ of 0.890±0.002 Ma. The corrected U-Pb age is some 150 ka older than the uncorrected age but the age uncertainty, while still small in relative terms (1.8%) is now increased by a factor of ~8. Corrections using the measured $^{234}$U/$^{238}$U ratio will only be accurate for samples <1.5 Ma in age, due to error magnification as this ratio approaches unity. For older samples the $^{234}$U/$^{238}$U initial must be estimated and, realistically, this estimate should be assigned relatively large errors. Such a procedure has two important consequences. Firstly, although it is commonly assumed that disequilibrium effects become negligible after several Ma, in fact such calculations should be performed routinely, irrespective of age, since they often have a significant effect on not just the age estimate itself but, equally importantly, on the error estimate. Secondly, this constraint means that, ironically, the best age precision may be obtained by U-Pb methods on samples in the age range ~250–750 ka, where $^{234}$U/$^{238}$U can best be directly measured.

**Concluding remarks**

Our pilot studies have produced a number of speleothem U-Pb ages of high quality, significantly increasing the known database. As a result, we are confident that this technique has the potential to drive significant advances in continental-based palaeoclimate research, in addition to studies of landscape evolution and palaeo-seismicity.

In terms of sampling, the key factor to obtaining high-quality isochrons is the requirement for generating a spread in U/Pb ratios while avoiding significant common Pb. While speleothems growing in isolated or remote areas of caves may ultimately prove optimal for this purpose, preliminary sample screening can be accomplished using either trace element analysis by quad-ICPMS or rapid determination of detrital Th content (as a proxy for Pb) using MC-ICPMS U-series analysis.

As with U-series geochronology, MC-ICPMS analysis has much to commend its use in the study of U-Pb systematics in speleothems. In addition to relatively rapid throughput, MC-ICPMS is much less sensitive to sample impurities and allows processing of relatively large samples with low blank chemistry. The only disadvantage - an inability to measure $^{204}$Pb accurately - is easily circumvented by using alternative isochron constructs, such as the ‘semi-total Pb/U isochron’. Using this methodology age estimates can be obtained with a precision which is comparable to that obtained from U-series analyses. A correction for initial isotopic disequilibrium, however, remains essential and contributes significantly to overall analytical uncertainty.

Preliminary ages have been obtained for speleothems from the Nullarbor Plain of Western Australia and, with additional data, promise new constraints on the critical question of increasing aridity in Australia during the late Tertiary, while new ages on samples from Antro del Corchia in Italy offer the prospect of a more detailed understanding of the landscape, tectonic and climatic evolution of the region.

**References**


USE OF HELIUM FLOW IN RETRIEVING FLUID INCLUSIONS FROM SPELEOTHEMS

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Introduction

Carbonate speleothems, especially calcite stalagmites, can be used as paleoclimate indicators when precipitated under isotopic equilibrium conditions (Hendy, 1971). Since 1970’s, speleothems have been widely applied to local or regional paleoclimate reconstruction as well as global paleoclimatic model/events correlation and refinement (Schwarcz, 1986; McDermott, 2004). In general, there are two different ways to extract paleoclimatic information from speleothems. The conventional way is to analyze variations in stable isotopic compositions of calcite along the growth axis, usually carbon and oxygen isotopes; and general paleoclimate variation trends in the study area could be obtained by comparing analyzed results with other isotopic records such as deep-sea cores, ice cores, etc. However, this method can only yield relative climatic data. The second method, involving stable isotope study of fluid inclusions, can not only provide us with direct information about paleoprecipitation but also offer a great opportunity to calculate absolute paleotemperatures based on fractionation between speleothem calcite and cave drip water. Therefore, fluid inclusion study is the major concern in this paper.

It has been shown that carbonate speleothem usually contain 0.05~1.0 wt.% of fluid inclusions, which are trapped cave drip water samples derived from local precipitation (Schwarcz et al., 1976; Harmon et al., 1978; Schwarcz & Yonge, 1983; Yonge et al., 1985). These fluid inclusions are trapped in voids of varying sizes, usually between tens and hundreds micrometers in width; but macro cavities up to several millimeter scale and nano pores as small as 200-500nm in diameter have also been reported (Schwarcz et al., 1976; Genty et al., 2002; Zhang et al., 2005). Recent petrographic studies of stalagmite caps at McMaster University showed that these voids are mostly formed along growth layer or the c-axis of CaCO₃ crystals due to incomplete coalescence and that there are great spatial and temporal variations in trapping fluid inclusions. Incipient fluid inclusions could be observed on growth surfaces in some cases, but not in others; and trapping of drip water could be sometimes continuous along the growth axis, or intermittent in other times (Zhang et al., 2005).

As there might be post-depositional oxygen isotope exchange between the trapped dripwater and the host calcite over time, δ¹⁸O of the inclusion water might differ from that of ancient drip water. On the other hand, δD of the fluid inclusions should be well preserved because hydrogen isotopes could not exchange between the inclusions and the surrounding calcite (Schwarcz et al., 1976). Two different techniques have been developed so far to liberate these trapped microscopic paleodripwaters from speleothems for δ¹⁸O analyses: one is decrepitation at high temperatures (~700-900°C), and the other is crushing at low temperature under high vacuum. However, some uncertainties still exist in both methods, i.e. thermal decomposition always gives a mysterious but consistent offset of –20 to –30‰ between modern speleothem fluid inclusions and their parent cave waters, whereas crushing may also yield unacceptable isotopic data due to incomplete extraction and recovery of the trapped fluid inclusions (Schwarcz et al., 1976, 1983; Matthews et al., 2000; Dennis et al., 2001; Fleitmann et al., 2003; Serefiddin et al., 2005). Currently, crushing method requires relatively larger size samples (~1 g, Serefiddin et al., 2005) in order to obtain sufficient inclusion water for analysis (>0.5 μl), which reduces time resolution in comparison with δ¹⁸O records.

This study mainly adopts the crushing technique originated at the University of East Anglia and earlier work in this lab (Dennis et al., 2001; Serefiddin et al., 2005), but introduces He flow at the end of crushing of the speleothem sample to help recovery of the trapped paleowaters.

Methods

The line for extraction of speleothem fluid inclusions is shown in Figure 1. Ultra-high purity He first passes through a cold trap (CT1) to remove traces of moisture, then flows through an electromagnetically driven crushing cell, and is finally pumped away slowly through the vacuum line or exits to the atmosphere. A downstream spiral trap (CT2) is cooled with liquid nitrogen to trap water samples liberated during crushing process.

Speleothem samples, weighing about 1~2 g, are loaded into the crushing chamber, then evacuated and heated at 105 °C for 15 minutes. With the vacuum leads closed, the samples are crushed initially under vacuum, and most of the liberated inclusion water is then trapped in the spiral trap. He is then admitted at a flow rate of ~5 ml/min and carries remaining
water vapour to the spiral trap. Transfer occurs in c. 30 min. After that, CO₂ and other non-condensable gases are pumped away by replacing liquid nitrogen with dry ice slush. Then the spiral trap is heated with a high-T hot-air gun and water is transferred to a Pyrex ampule with 50~100 mg Indiana Zinc.

The ampule is heated at 500°C for one hour to reduce water to hydrogen gas, which is analysed on a SIRA II mass spectrometer. Reproducibility of standard water samples is ±1‰. δD is reported with respect to VSMOW, calibrated using samples of VSLAP and VSMOW. The amount of extracted water is determined using the intensity of the M/e = 2 ion beam, calibrated against known volumes of capillary water ($r^2=0.996$).

δ¹⁸O of the homogenized crushed speleothem sample powders is determined on an OPTIMA mass spectrometer attached with an Autocarb analyser. δD of the cave water samples is converted to δ¹⁸O assuming a relationship between δD and δ¹⁸O (Craig, 1961; Dansgaard, 1964). Paleotemperature can thus calculated by:

$$10^3 \ln a_{cw} = 2.78 \times 10^6 \times T^{-2} - 2.89$$  \hspace{1cm} (1)  
\hspace{1cm} (O’Neil et al., 1969)

**Results**

**Calibration**

Blank tests showed that the moisture background of the line was close to the background signal of the mass spectrometer. The accuracy of extraction was tested by following procedures of Dennis et al. (2001) and Serefiddin et al. (2005). Known amounts of standard (DTAP) water loaded in capillaries were crushed with inclusion-free calcite spar, using a variety crushing procedures. Large isotopic fractionation (i.e. >200‰), has been observed with some methods, apparently due to partial loss of water vapour in the He stream. However, an optimal crushing procedure was achieved yielding δD values ranging from −53 to −61‰, with a mean value of −56±3.5‰, which agrees well with −54±0.8‰, the δD value of DTAP.

**Tests using a speleothem sample**

A 30 cm tall calcite stalagmite from Jacklah Jill Cave, Vancouver Island, which was not actively growing when collected in 2002 and has a basal age of 9.2 ka, was chosen for further testing of the new crushing line. The Holocene climate in this region is generally considered to be warm and characterized by cyclic cold events, but still relatively stable in comparison with glacial-interglacial transit periods. Therefore, the modern local meteoric water line should be assumed to be valid throughout the entire 10,000-year period. Four 3mm thick milky-white calcite slabs, weighing 1.1~2.4 g, were taken from one side of the speleothem close to its base. Each was crushed in 2 or 3 successive crushing cycles, and results are listed in Table 1.

Crushing of speleothems for < 5 min led to very fractionated (depleted) δD values although a large amount of water was liberated. Longer crushing time (>5~10 min) and/or repeated cycles of crushing of the same sample appeared to yield more consistent and identical δD values, which appear to

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Figure 1. The McMaster speleothem fluid inclusion extraction line.
agree with isotopic composition of local paleoprecipitation as suggested by paleotemperature calculation results. For reference, the measured modern cave temperature of the Con Cave, which is situated at a similar elevation in the same region, is 5.9 °C.

We obtained consistent δD values on water samples as small as 0.2 μl. This appears to be an improvement over previous methods and apparently requires shorter extraction times (30 min vs. 1 hr reported by Dennis et al., 2001).

**References**


**Table 1.** Speleothem fluid inclusion experiment results *

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Weight (g)</th>
<th>Crushing time (min)</th>
<th>Cal. H2O volume (μl)</th>
<th>δD(‰) (VSMOW)</th>
<th>δ18Oc (‰) (VPDB)</th>
<th>Cal. ToC</th>
<th>Cal. T°C</th>
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<td>Stal-1-1</td>
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<tr>
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<td>10</td>
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<td>-7.6</td>
<td>5.9</td>
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<td>-7.8</td>
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<td>-7.8</td>
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<tr>
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<td>-7.8</td>
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<td>-7.2</td>
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<td>-7.2</td>
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<td>-7.2</td>
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<tr>
<td>Stal-4-1</td>
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<tr>
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<td>rejected</td>
<td>-7.5</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>

* Using the annual meteoric water line of Victoria, British Columbia: δD=7.88δ18O+2.9 (Clark and Fritz, 1997)


Archives of Climate Change in Karst

CLIMATE RECONSTRUCTIONS
IS SOLAR FORCING A CONTROLLING FACTOR OF ENSO VARIABILITY?

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Whereas the physical links between solar irradiance and terrestrial climate are still poorly understood, an increasing number of proxy climate records provide circumstantial evidence suggesting solar inputs as a dominant controlling factor of global climate changes. Here we report the results of an investigation of stalagmites from a mid-ocean island in the South Pacific located at the epicenter of oceanic ENSO that contains a detailed and continuous millennial record of rainfall and ENSO variability. Spectral analysis of the proxy records suggests a strong linkage between solar cycles and ENSO variability during the first millennium AD.

Processed in the frequency domain to quantify the variance, the proxy stable isotope data yield high frequency cycles at 2.6 to 7 years matching modern interannual ENSO periodicity bands. Importantly, frequency peaks at 11, 22, 72 and 108 years exceeding the 90% confidence level and matching precisely known solar periodicities (Schwabe, Hale, Gleissberg and deVries cycles) are clearly discerned in the oxygen isotope spectral power. The low frequencies cycles exhibit phase alternations between prolong ENSO events manifested in severe droughts that are succeeded by “normal” ENSO events and abundant rainfall. The new mid-ocean stalagmite record offers compelling evidence bearing on the coupling between solar cycles and ENSO variability through time.

Global climate shifts during the 7th and 8th centuries AD (Cold Dark Age) and during the 12th and 13th centuries AD (Medieval Climate Anomaly) correspond to prolonged El Niño-like dry phases manifested by distinct 18O and 13C enrichments amounting to several per mil in the stalagmite records. These implicit dry phases are corroborated by contemporaneous reductions in ice accumulation on the Quelccaya Ice Cap on the high Peruvian Andes whose link to ENSO-driven precipitation has been amply demonstrated.

The low U concentration in the range of 44.2 to 97.5 ppb renders dating by 230Th/234U method impractical considering the youthfulness of the stalagmite and the amount of available material. Three alternative dating techniques were used to derive a robust chronology: (i) 226Ra/234U by TIMS; (ii) radiocarbon by AMS, and (iii) couplets counting. In conjunction the three dating methods indicate that the 160 mm stalagmite section spans a time interval from 490 to 1354 years AD. Whereas interannual and interdecadal-scale variability are the largest components of variance in the millennial-long oxygen and carbon isotope time series, century-long phase transitions are prominent in the records.
This paper presents preliminary results of the first speleothem-based palaeoclimatic investigation of the central Zagros region of Iran. This is part of a larger project which aims to construct speleothem-based palaeoclimatic records from caves which lie on a transect running from southern Iran, through the Zagros Mountains, to the Taurus Mountains in central Turkey (Figure 1).

Excellent work has already been conducted in Israel (e.g. Bar-Matthews et al., 1999, 2000; Frumkin et al., 1999) and Oman/Yemen (e.g. Burns et al., 1998; Fleitmann et al., 2003) highlighting the utility of speleothems in nearby arid/semi-arid regions. These records, however, do not shed much light on the palaeoclimatic history of our study area as they are dominated by the climatic evolution of the E. Mediterranean (in the case of Israel) and the SW Asian Monsoon (in the case of Oman/Yemen). Our transect aims to refine the findings of these studies by delimiting the spatial extent of their influence: in the S/SE reaches of our transect we hope to determine the northernmost extent of the ITCZ’s migration in the Late Quaternary and in the N/NW reaches we hope to detect the slow attenuation of Mediterranean domination and its replacement by more localised signals. In the intervening 2000 km, we hope to characterise these local signals and their interrelationships with those of the surrounding regions.

Stalagmite SHAP, the first analysed so far, comes from the central part of the study area, approximately 100 km west of Shiraz (Figure 1). The stalagmite covers the interval from approximately 108–84 ka, coinciding with MIS 5d/c–5a. Preliminary δ¹⁸O analyses show a 3.8‰ range and the first-order structure shows increasingly positive values (by ~1.7‰) at ~105 ka, followed by relative stability from ~105–94 ka (figure 2). After ~94 ka, there is a gradual change towards more negative values (in total ~2.5‰) ending at ~85 ka, followed by a relatively sudden rise (of 1.8‰) and cessation of growth at ~84 ka. Superimposed over this is a second-order structure comprising shorter (~1 ka) periods of both negative values (prominent at 97, 94, and 89 ka) and a positive peak (at 98 ka).

Modern precipitation over central Iran comprises an approximately equal mixture of Mediterranean- and Arabo-Persian Gulf-derived moisture. Comparison with the Israeli record from Jerusalem (Figure 2) shows markedly more positive values (by up to ~2.8‰) in the Iranian record relative to the Israeli one in the period from ~105–90 ka. Outside that time-range, however, the records tend towards similar values. The initial rise in the Iranian record (at ~105 ka) coincides with a sharp drop in the Jerusalem record (identified as MIS 5e) and persists through the presumed subsequent fluctuations of 5b and 5a. We hypothesise that these relatively positive values represent a change in source of precipitation: periods of eustatically lower sea-levels lead to a marked regression of the Arabo-Persian Gulf, which has an average depth of only 35m. As it accounts for up to 50% of local precipitation at present, its regression can be expected...
to lead to a significant drop in the δ¹⁸O of local rainfall as the remaining Mediterranean-derived precipitation would undergo significant rainout (due to continental and altitude effects) by the time it reaches the central Zagros. Conversely, Gulf-transgression during periods of eustatically higher sea-levels can be expected to result in an increased contribution of less evolved (and therefore more positive) moisture to local precipitation. This is corroborated by the resemblance between the Iranian record and that of global sea-level from the Huon Peninsula (Chappell and Shackleton, 1986) and from the Red-Sea (Siddall et al., 2003; Figure 3) which also appears to be insensitive to the presumed fluctuations of 5b and 5a. Further support for this idea comes from a comparison of the Iranian record with the benthic North Atlantic Marine record off the Iberian Peninsula (Shackleton et al., 2000; Figure 4), which shows an anti-phase relationship, suggesting that the Iranian record does not directly reflect changes in ocean-water composition. Moreover, the modern relationship of δ¹⁸O precip. vs. air-temperature in Iran (Figure 5) suggests that temperature effects on the isotopic composition of cave calcite are negligible, but a comparison of the δ¹⁸O of presently-forming calcite from the same cave (−2.09‰) with those of calcite formed in the Lateglacial (~16 ka; −6.00‰) shows a significant (~ 4‰) difference that cannot be accounted for by temperature-effects alone.

Testing of this hypothesis would involve a) measurement of the deuterium-excess of fluid inclusions in the calcite to establish the provenance of palaeo-precipitation with more certainty and b) the construction of further records from the region to increase sample size and rule out the possibility of anomalous records. This work is currently being carried out at the University of East Anglia, Norwich, in collaboration with Shiraz University.

Our results, so far, propose a new mechanism (Gulf absence/presence) whereby climate in the central Zagros can peri-
odically break with Mediterranean patterns and also present some tentative evidence that this mechanism has, indeed, operated in the past.

References


In this study we compare the carbon and oxygen isotopic records of speleothems from the Eastern Mediterranean (EM) with a pollen record from the SE Levantine Basin (MDV AL 9509 at 884 m water-depth) located at the distal part of the Nile Delta.

The palynological analysis compared with Soreq Cave speleothems isotopic record covering the last 90 kyr allows reconstructing the paleoclimate conditions of the EM region based on two independent land proxies. The paleoclimatic conditions based on the isotopic composition of Soreq Cave speleothems were discussed previously in several publications (e.g., Bar-Matthews et al., 2003) and the main conclusions were that during sapropel S3 event at the end of Marine Isotopic Stage (MIS) 5 and sapropel S1 event at the early Holocene conditions were very wet. Climate conditions during MIS4 and MIS2 were dry, with warming and wetter conditions at ~54 kyr. Important events such as the Younger Dryas (YD), the cooling event at 8.2 kyr and the Last Glacial Maximum (LGM) were clearly identified. Our interpretation of the paleoclimate was almost entirely based on the oxygen and carbon isotopic profiles, which can come to be questioned because of the many variables that determine the isotopic composition of speleothems.

In this study we have for the first time an independent palynological proxy for terrestrial paleoclimate from a nearby marine core. The results of the pollen assemblages clearly support our paleoclimate reconstruction based on the speleothems record. The pollen record spans the last 90 kyr from the end of MIS5 to the Holocene, with the time control used in this study being based on the $\delta^{18}O$ stratigraphy that was established using the planktonic foraminifera Globigerinoides ruber and correlated with the well-dated (U-Th) speleothem records of the Soreq Cave.

The pollen record can be divided into different pollen zones, mainly based on changes in the Arboreal Pollen/Non Arboreal Pollen (AP/NAP) ratio. After a relatively humid period during sapropel S3, the beginning of the last glacial (MIS4) shows some drying. During MIS3 the high AP levels and low values of Artemisia (sagebrush) and Chenopodiaceae (goosefoot) indicate more humid conditions, with some cooling [e.g. peaks in Cedrus (cedars) and Abies (firs)]. A sharp decrease in AP levels and a simultaneous rise in Artemisia and Chenopodiaceae ratios characterize the dry LGM around 19 kyr (MIS2). More humid conditions returned during the deglaciation. The Holocene is characterized by relatively high AP levels and a simultaneous rise in Artemisia and Chenopodiaceae ratios characterize the dry LGM around 19 kyr (MIS2). More humid conditions returned during the deglaciation. The Holocene is characterized by relatively high AP levels and a simultaneous rise in Artemisia and Chenopodiaceae ratios characterize the dry LGM around 19 kyr (MIS2). More humid conditions returned during the deglaciation. The Holocene is characterized by relatively high AP levels and a simultaneous rise in Artemisia and Chenopodiaceae ratios characterize the dry LGM around 19 kyr (MIS2). More humid conditions returned during the deglaciation.
Reference

A HIGH-RESOLUTION MULTI-PROXY STALAGMITE RECORD FROM MECHARA, SOUTH-EASTERN ETHIOPIA: PALEOHYDROLOGICAL IMPLICATIONS FOR SPELEOTHEM PALEOCCLIMATE RECONSTRUCTION

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Ach-1, a 25 cm long stalagmite sample from Mechara area of Southeastern Ethiopia (Figure 1) has provided a high-resolution multi-proxy record. This annually and visibly laminated stalagmite (Figure 2a) grew over a period of 443 ± 8 years starting at 5023 years BP (± 160 years), as determined by lamina-tuned U-Th dating. The speleothem shows three growth phases (Figure 2b): (1) an initial phase (0–18 cm) where the stalagmite has a candlestick shape, deposited by relatively slow rate drip water; (2) a middle growth phase (18–23 cm) where laminae grow on the flanks, suggesting faster drip rates; and (3) a final growth phase (23–25 cm) where calcite was deposited with a thinner shape due to a decrease in drip water supply towards the end of deposition.

Morphometry, annual growth rate (Figure 2c), fluorescence index (Figure 2d), and 234U/238U isotope ratio show marked difference between the three growth layers, while $\delta^{13}$C and $\delta^{18}$O isotopes (Figure 2e) do not show significant variation, except towards the top of the stalagmite where they have

Figure 1. Location of the Mechara area and the Achere-Aynage cave system. Inset shows the location of the Ethiopian Rift valley.
higher values. The multiproxy evidence suggests a switch in the hydrologic regime between growth phases with dominantly surface connected flow during the first phase to dominantly storage but with some fissure flow with faster drip rate during the second phase of growth, while the last phase of growth was associated with storage flow as all surface connections were lost (Figure 3).

The study indicates that multi-proxy approach is crucial as the different proxies respond to different climate signals differently, and can be widely applicable to distinguish the relative importance of the various proxies in recording cave ‘external’ (climate, hydrology) and cave ‘internal’ (e.g., evaporation processes). Our results demonstrate that multiproxy analysis is vital to correct interpretation of past climatic or environmental change and accurate prediction of future climate changes, implying a non-linear response to a linear climate change.

Figure 2. (a) Enhanced Ach-1 stalagmite image; (b) schematic view of the stalagmite where sample points for dating and isotope analysis are marked. Three growth layers and their boundaries along with some traces of visible lamina are also shown; (c) Lamina thickness-vs-lamina number; (d) Fluorescence Index (FI)-vs-lamina number; and (e) δ¹³C-vs- lamina number and δ¹⁸O-vs-lamina number graphs. The stalagmite (a and b) are aligned with respect to the variations in the proxies (c to e). Vertical dashed lines mark the boundaries of the three growth phases.

Figure 3. Cartoon showing the changes in flow routes of water during deposition of calcite to form Ach-1 stalagmite: (a) Surface connected paleohydrological regime with mixed storage and fissure flow sources, with stored water dominating; (b) a switch into higher flow regime to a new mix of storage (where mudstone and marl layers dominate the stratigraphy) and fissure flow sources, where although the storage component is increasingly dominant, a new fissure flow source is connected (at least seasonally) permitting faster drip rates and intermittent surface (soil) connections; (c) a final paleohydrological phase where storage flow comprises all the flow, and all surface connections are lost.
In this study we present a comparison between the δ¹⁸O and δ¹³C records of well-dated (U-Th) speleothems from Frasassi Cave, Italy and Soreq Cave, Israel. The time period covered by the speleothems from both caves is from ~95 kyr to ~10 kyr B.P., including the last part of MIS5, most of the last glacial, and the early Holocene.

The Frasassi Cave system (43°24'N, 13°02'E) is located in the Umbria Marche region of central Italy, on the Adriatic side of the Apennine Mountains, ~40 km from the east coast of Italy. The whole cave system ranges from 200 m.a.s.l. (at present day river level) up to about 500 m.a.s.l. The present day climate within the base of the gorges is temperate subcontinental, with an annual mean temperature of 13°C and an average annual precipitation of 900 mm. At higher elevations, an Apennine continental climate prevails with a mean annual temperature of 11°C and a precipitation amount of 1100 mm. The vegetation is composed of two distinct kinds: Mediterranean thermophile species dominate the warmer northern slope of the gorge, whereas trees with caducei are prevalent on the colder southern inclination.

Soreq Cave (31°45'N, 35°03'E) is situated within the steeply westward dipping flank of the Judean Hill anticline and is located approximately 40 km inland from the eastern Mediterranean (EM) Sea and 400 m above sea level in dolomitic host-rock. The soil cover above the cave is about 30 cm thick, with typical Mediterranean C3 type vegetation. The climate in the cave area is typical of EM semi-arid conditions, with mean winter temperatures of 14°C, and mean summer temperatures of 26°C. Most of the rainstorms are associated with Mediterranean fronts. Average annual precipitation above the Soreq Cave is 500 mm.

Comparison between the isotopic records of Frasassi speleothems with those of Soreq enables to understand how paleoglobal climatic events influenced the climate in the north-central and the eastern Mediterranean regions. A de-
Detailed comparison reveals that many isotopic events shown by the Soreq Cave speleothems are also evident in the Frasassi record. $\delta^{18}$O values of Frasassi speleothems are usually more depleted compared with Soreq by $\sim$2‰ to 4‰ (similar to present-day), reflecting the temperature and rainfall gradients between north-central Mediterranean and the EM region. $\delta^{13}$C values of Frasassi speleothems are usually enriched by more than 3‰ (similar to present), reflecting different vegetation, probably a higher proportion of C4 vegetation overlying the Frasassi Cave system compared to that of the Soreq Cave area.

During a unique time interval from $\sim$85 to 80 kyr, known as sapropel S3 in the EM, the $\delta^{18}$O profile of Soreq speleothems shows an opposite trend relative to that of the Frasassi speleothems. This is due to enhanced hydrological activity in the EM resulting in sapropel formation that is not evident in the north-central Mediterranean. A major pronounced isotopic event during the last glacial both in north-central and the eastern Mediterranean is observed between $\sim$54.5 and 52.5 kyr, reflecting a major wet and warm period in the entire region.
ANNUAL RESOLUTION CLIMATE RECONSTRUCTION IN ETHIOPIA
USING MULTIPLE STALAGMITE PARAMETERS: CAVE AND INSTRUMENTAL CLIMATE CALIBRATION

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Introduction

The African climate system, and its surrounding monsoons, are key elements of the global atmospheric circulation. Rainfall is, in many parts of Africa, dependent on prevailing patterns of sea surface temperature (SST), atmospheric winds, the El Niño Southern Oscillation (ENSO), and regional climate fluctuations in the Indian and Atlantic Oceans. Much remains to be understood about the interaction between the African climate system and its land surface, and the surrounding ocean-atmosphere climate variability and the global climate system. The Ethiopian highlands are a classic example of such an African rain-sensitive region, where future forecasts are hampered by inadequate understanding of historical patterns, their wider associations, and causes. Rainfall and temperature records are relatively short and of poor quality (see overview by Conway et al., 2004). The few long records demonstrate that after El Niño years, the spring rains are heavy and the main summer rains are reduced (Glantz, 1996). This agrees with a strong multi-year spectral peak in rainfall records for the region that correlates with Atlantic and Indian Ocean SSTs (Nicholson, 2000). However this correlation is too weak to enable drought forecasts and the calibration time period is too short. In addition, the spring rains also fail and lead to famine; their cause is more complicated with a dependence on a low level moisture influx towards Ethiopia and an upper trough with cooling in the mid-upper troposphere (Camberlin and Philippon, 2002). Spring rainfall failures are, to date, not predictable.

Long, high resolution climate records are required to investigate the nature of rainfall variability, the frequency of failure of either rain period, as well as investigate the presence of longer term periodicity in climate that cannot be detected through short instrumental series. Speleothem records are the best prospect for tackling this urgent problem in E Africa, as to date other potential proxies have failed to yield high resolution climate reconstructions. Speleothems are known to provide high resolution climate archives (e.g., Burns et al., 2002) and by now the study of calcareous speleothems as archives of climate change is a major area of paleoclimate research (e.g., reviews in McDermott et al., 2005; Fairchild et al., 2006). Here we use a multi-proxy analysis of duplicated speleothems from a single climate region: a multi-proxy approach would permit a better constraint on both the absolute climate signal and its associated uncertainty. For example, our previous investigations clearly indicate that a multi-proxy approach in stalagmite palaeoclimate reconstruction is crucial because the various proxies respond differently (rapidly, lagged, linearly, non-linearly) or with different degrees of smoothing to climate signals (Fairchild et al., 2006), depending on the processes affecting speleothem deposition. These are rapidly becoming more completely understood (McDermott et al., 2005; Fairchild et al., 2006). Because each speleothem is fed by a unique plumbing system, there is always the possibility of contingent variation related to factors unique to that drip (i.e. plumbing reorganization), and in principle each speleothem may have different sensitivities and thresholds to change. For this reason, there is a need to at least duplicate records wherever possible, and to establish records involving multiple parameters to establish internal consistency, and to account for unique hydrological factors for a given drip from changes affecting whole caves or different caves in a region. Comparison with modern instrumental records is particularly useful in establishing the nature of modern transfer functions which exist between speleothem and climatic parameters, and to establish the responses (e.g. rapid, lagged, linear, non-linear), or degree of smoothing.
Caves in the Mechara karst were first discovered by the Huddersfield Expedition in 1996 (Brown et al., 1998), for location see Figure 1. Most of the caves are easily accessible, have been surveyed in detail, require no technical caving skills to explore, and, most importantly, contain actively growing and dripping stalagmites suitable for monitoring and climate analysis. In addition, the caves contain active stalagmites and which grew at one of the fastest rates observed in the world (~0.2 to 0.5 mm yr⁻¹), as predicted to occur in such a warm and wet climate (Baker et al., 1998). In our recent expeditions (2003 to 2005) to the Mechara karst we have collected stalagmites to undertake a multi-proxy climate reconstruction for the last millennium. This has included the collection of drip and pool water samples for isotopic and geochemical analysis, the measurement of cave temperature and humidity, the analysis of regional climate data and the collection of actively growing soda straw and stalagmite samples. These results provide a modern baseline from which we can understand contemporary processes and contextualize past variability: these results are presented here.

### Results

Rukiesa Cave drip waters give an example of those typical of those of the region. They have an electrical conductivity of 678±177 µS, calcium ion concentration of 44.3±22.9 ppm, magnesium ion concentration of 33.2±23 ppm and strontium ion concentration of 101.5±49.7 ppb. Cave air temperature is 22.0±0.3°C, humidity 95.6±1.0% and CO₂ concentration ~1500 ppm. From these values, we can predict, for example, modern stalagmite growth rate (~0.2 to 0.3 mm yr⁻¹), and this agrees with observed modern growth rates. Modern drip water isotope data (Figure 2) falls on the meteoric water line, and demonstrate the dominance of degassing processes. Although clustering around the weighted annual mean value, they also show seasonal variations of up to 2 per mil in δ¹⁸O, with samples collected after spring rains isotopically heavier, reflecting the composition of the spring rainfall.

All actively depositing stalagmites that have been sampled from the region (n=11) contain continuous visible annual laminae, generated by the seasonality of rainfall. We know that these speleothems will provide very high resolution, multi-proxy climate records once calibrated, as has already been demonstrated by a detailed, multi-proxy, high-resolution study of one such mid-Holocene stalagmite (Ach-1) by us from the Achere cave in Mechara (Asrat et al., in press), as well as our analyses on modern stalagmites and cave waters. We have conducted preliminary analyses on (actively
growing when sampled) stalagmites for the last 140 year time period (collected in 2004, with confirmatory bomb $^{14}$C on the top surface, and shown in Figure 3). Analysis of stalagmite proxy variability over the period of instrumental climate records allows the calibration of proxies against climate, as well as an analysis of the different but logical responses of proxies to surface climate forcing. Analysis of local meteorological station data shows that records from Mechara, Bedessa and Gelemso (Figure 1) are largely homogenous but discontinuous, but together with the regional stations at Harrar (homogenous from 1902 AD) and Addis Ababa (homogenous since 1901; Conway et al., 2004), permit the tuning of the local climate data to that of Addis Ababa / Harrar to provide a continuous climate record for the last 100 years (essentially; Mechara spring rains are greater and summer rains less but longer lasting then at Addis Ababa).

Figures 3 and 4 show an example from two of the actively growing stalagmites. Asfa-3 and Merc-1 have similar stratigraphies, with periods of white porous calcite deposition (WPC; sensu Genty and Quinif, 1996) correlating between samples, particularly between 1905 and 1930 and around 1984 AD, periods of known drought. WPC formation is associated with deposition under drier/less humid conditions, and leads to a more rapid growth rate due to the change in calcite texture. The stalagmites have differing growth rate variability; Asfa-3 a coefficient of variation of 33% and Merc-1 of 13%, typical of stalagmites with different proportions of stored groundwater components. When calibrating the growth rate records against instrumental data, principal components analysis demonstrates the best correlation of growth rate with high May and June rainfall and low September and October rainfall. High May / June rainfall maintains soil CO$_2$ productivity and a high drip rate, and therefore growth rate, between rainy seasons, whereas a dry September / October decreases cave atmosphere relative humidity and increases growth rate through the formation of WPC whilst drip rates (from the preceding summer rains) are still high. Correlations between growth rate and this rainfall ratio is however weak; highest for Asfa-3 ($r=0.21$, very weak but statistically significant) for Asfa-3 whilst Merc-1 has no correlation, differences that match growth rate variability. For periods of dark compact calcite (DCC; sensu Genty and Quinif, 1996) deposition only, an improved correlation between growth rate and May/June rainfall is obtained. Thus for samples where laminae change from compact to porous forms, this non-linear (threshold) response limits a simple (linear) regression against instrumental climate. These results confirm the need for multiple proxies to obtain a quantifiable climate record, the results of which (for example, $^{13}$C, $^{18}$O, trace elements) will be presented. For example, oxygen and carbon isotopes can provide a record of one or all of rainfall source variations, temperature, or kinetic fractionation (McDermott et al., 2005). Our previous studies in the region (Asrat et al., in press) suggest that for samples comprising WPC, it is probable that carbon and oxygen isotope variations are dominated by changes in disequilibrium deposition, which can be correlated with moisture variations.
In contrast, or modern drip water (Figure 2) suggests that modern samples that are comprised primarily of DCC will have oxygen isotope variations that are in equilibrium, and which will reflect variations in rainfall seasonality and amount. Therefore samples for stable isotope measurements were drilled at regular intervals along the central growth axis of the speleothems: to avoid aliasing effects, these were at time integrated samples of 3-5 years (1-3 mm depending on growth rate) duration.

**Conclusion**

Water availability rather than temperature is the crucial issue in semi-arid areas, and climate-triggered hydrological change are the major factor driving speleothem proxies in such settings. Our improved understanding of the controls of annual lamina thickness, stable isotopes and trace elements indicates that when used together, they provide a powerful approach to deriving palaeohydrology. Over the past two years, we have been piloting a study of speleothem sites from Ethiopia and are now in a position to show that speleothems offer the most promising approach to characterizing the variability of rainfall in this densely populated region, which offers important scientific challenges in the understanding of the dynamics of rainfall variability.

**References**


INTEGRATED STUDY OF CAVE DRIP HYDROLOGY AND HYDROCHEMISTRY, AND THE ASSOCIATED PALEOCLIMATE RECORDS FROM NORTH AMERICA

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The secular variations of isotopic and trace element compositions of speleothem calcite provide valuable continental based indices of paleoclimate change, with a spatial distribution complimentary to that of polar ice cap and marine core records. Two interlinked research challenges presently at the forefront of paleoclimate reconstruction from speleothem records are: developing an advanced understanding of karst vadose zone hydrological processes which control the surface climate components captured in the speleothem calcite, and the derivation of absolute and calibrated records of climate change, notably temperature.

The focus of this paper is progress towards an integrated trans-North American study of the calcite-cave drip-climate system that was initiated in 2004 to address these interlinked research challenges. Study sites include six caves, including three on the Pacific coast of Vancouver Island and one each in the Bow Valley of the Rocky Mountains, the mid-west (southern Indiana) and the north-eastern U.S. (upstate New York). The research programme includes four concurrent lines of investigation:

1. Absolute temperature records from fluid inclusions

In principle, the absolute temperature of calcite formation may be calculated from the partitioning of oxygen isotopes between the speleothem calcite and the formation water using the calcite-water fractionation equation of O’Neil et al. (1969). It is therefore necessary to determine the $\delta^{18}O$ of the formation water, which may be determined from aliquots of this water obtained from fluid inclusions within the calcite matrix. Speleothem usually contain 0.05–1.0 wt. % of fluid inclusions (Schwarcz et al., 1976; Harmon et al., 1978; Schwarcz and Yonge, 1983; Yonge et al., 1985). The analyses of fluid inclusions from sample Holocene speleothems are currently in progress; methodological advances towards the efficient extraction of these fluid inclusions include a continuous He flow combined with crushing-heating system presented elsewhere in this volume (Zhang et al., 2006).

2. North American Holocene paleoclimate

The selected caves for this study form a west-east transect broadly across the middle of the continent close to the modern mean position of the meteorological Polar Front, with the Pacific sites also being close to the intersection of the north and south Pacific gyres (Figure 1). Nine actively growing speleothems have been collected, and age models, based on U/Th TIMS dating, are being developed to provide a framework for interpretation of the secular variations in $\delta^{18}O$ and $\delta^{13}C$ of the calcite along the growth axes. The new Holocene paleoclimate records for these sites, combined with existing records from associated studies (van Beynen et al, 2004; Yonge, 1982), will elucidate several questions of interest, including: The gradient in $\delta^{18}O$ of the precipitation across the western cordillera of North America (from Vancouver Island on the Pacific coast to Bow Valley, Alberta) thus providing insight to the evolution of shifting of storm tracks as they move eastward from the Pacific into the rain shadow of the Canadian Rockies. The three caves on the Pacific Coast of Vancouver Island are located over a range of altitude from sea level to 750 m asl. Here we hope to observe shifts in the boundary between the northern and southern Pacific gyres which would affect the isotopic evolution of precipitation generating recharge to the caves, as well as assess the constancy of the adiabatic lapse rate over coeval growth periods. Contemporaneous records from the mid-west (Indiana, recipient of chiefly precipitation from the Gulf of Mexico) and north-east (New York, Gulf + Atlantic precipitation sources) will be used as continent-wide points of comparison.

Figure 1. Location of cave study sites.
3. Hydrology and hydrochemistry of cave drip water

A prominent aspect of this project is the integrated study of the drip water hydrology and hydrochemistry associated with the speleothems from which the Holocene paleoclimate records are derived. Custom drip monitoring stations were deployed late in 2004 through to 2006 to provide high frequency 15-minute records of temperature, electrical conductivity as a proxy of total dissolved solids, and drip rate at three adjacent drips (<30 m distant) in each of the six caves, while monthly bulk water samples are captured for isotopic and chemical analysis (Figure 2). Where possible, the monitored drips correspond to sampled actively growing speleothems. A specific advantage of monitoring closely spaced drip points is the potential to quantify the common elements of the drip hydrology and hydrochemistry independent of confounding environmental factors such as infiltration through distinct geological units above the cave, differences in surface land cover and vegetation units, vadose zone thickness, and distance from the cave entrance. These environmental factors may give rise to complexities that are often suggested as explanations of significant inter-drip differences often observed between monitored drips where longitudinal monitoring of distinct drip types along caves have been undertaken (Tooth and Fairchild, 2003; Vokal et al., 1999).

While the drip points monitored in this study were selected for their similar apparent drip rates, active precipitation of calcite, and close proximity, the hydrological data show that temporal variations in hydrological parameters are sometimes concurrent between drip sources located 10’s of metres apart in the same cave, while at other times each drip may display independent hydrological characteristics. Notably, the range in electrical conductivity between the three drips in one cave on Vancouver Island approaches the total range of the trans-continental dataset. These observations indicate that apparently self-similar adjacent drip sources are fed by varying proportions of fast flow (young) or slow seepage flow (old) waters that may have buffered seasonal signals due to mixing in vadose zone. These findings are consistent with other recent reports of differences between coeval speleothem records from the same cave: two coeval and adjacent speleothems from South Dakota were found to have a 4‰ offset in \( \delta^{18}O \), whilst their secular variations still revealed the same important climate events (Serefiddin et al., 2004), and Roberts et al. (1999) report non-coherent trace element records using laser ablation from UK speleothems from GB Cave. It is clear that while important climate signals are reflected in speleothem calcite, we may first observe directly that not all cave drips are able to deposit stalagmites (Figure 3) and secondly through speleothem analysis that these small-spatial scale differences in the karst vadose zone hydrology may impart some distinct features to the paleoclimate signals reflected in individual speleothem records.

4. Modern calcite

Upon decommissioning of the drip monitoring sites in late 2005 and early 2006, pre-weighed, acid-cleaned, frosted glass plates have been positioned under each drip site on which calcite is expected to grow over the coming 12–24 months. This modern calcite will be micro milled and analyzed for \( \delta^{18}O \) and \( \delta^{13}C \), with the resulting data interpreted within the context of the broad chemical and isotopic characteristics of the drip site. The integration of cave drip hydro-chemical data with the study of the paleo and modern
calcite will enable a more profound understanding of the Holocene paleoclimate records from the sampled speleothems. The results also serve to establish the relationships between modern drip waters and the fluid inclusions trapped in speleothems, such that analysis of these inclusions may provide calibrated paleotemperature records in the future. Results from time series analysis of the cave drip hydrological data, and isotopic analysis of the drip water (δD and δ18O) will be presented.

References


PALAEOMAGNETIC AND PALAEONTOLOGICAL RESEARCH IN RAČIŠKA PEČINA CAVE, SW SLOVENIA

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Palaeomagnetic and palaeontological studies were undertaken in Račiška pečina Cave located in Matarsko podolje, SW Slovenia at 590 m a.s.l. Račiška pečina Cave consists of a southward dipping gallery, approximately 10 meters wide, 5–10 meters high and 304 meters in length. The cave was formed under paragenetic or epiphreatic conditions. The studied section was about 13 m long and the sampled profile had a composite thickness of 552 cm. The lower section (177 cm) is built of 3 sequences which are individual growth stages of a huge vaulted stalagmite. These sequences consist of massive but porous speleothems with interbeds of red clays and unconformities. The upper section consists of subhorizontally laminated, mostly porous flowstones, occasionally with gours, red clays, calcitised silts and some fauna. Collapsed roof blocks cover clays with faunal remains. These clays and fauna are covered with collapsed roof blocks. The uppermost part of the profile is built of huge stalagmites; however, these have not been studied.

Palaeomagnetic properties were detected by using standard analytical procedures: thermal demagnetisation was performed on 18 samples and alternating-field demagnetisation on another 111 samples. In order to obtain a high resolution dataset, the distances between samples were in the order of centimeters.

Fossil remains were found by washing samples taken from the clay layer in the middle of the profile. They consist of rodents and rests of fresh-water crabs. Rodent (vole) remains consisted of a poor assemblage of fragments of rooted teeth (molars). The character of the mammal assemblage, especially the root form and the teeth internal texture excludes them from those associated with the Quaternary age. The mammals were determined to be Borsodia (Lagurini) – B. cf. hungarica, Mimomys pitymyoides groups and Apodemus (Sylvaemus) cf. sylvaticus indicating Pliocene biozone MN17 (Villányian, cca 1.8 to 2.4 Ma).

The character of speleothems, especially those of high porosity, can indicate rapid growth in warm and humid climates and syn- and postdepositional corrosion. Clay intercalations indicate periods of flooding carrying allochthonous loads. The alternation of normal and reverse polarised magnetozones and the palaeontological content enable to fix well our data with the GPTS. The bottom of the Olduvai subchron (1.77 to 1.95 Ma) was detected within the clay containing faunal remains. A short normal chron just below the detected Olduvai bottom compares well with the Reunion subchron (2.14-2.15 Ma). The lower part of profile can be assigned to the dominantly normal polarised Gauss chron (from 2.581 Ma). According to the arrangement of the individual subchrons, the studied profile terminates at about 3.2 Ma. The geometry of subchrons in the profile is changed by numerous breaks in deposition.

The data indicates the duration of individual breaks is approximately up to 150-250 ka, which would also explain the 36° difference in declination values of samples from the upper and lower parts. These declination differences indicate paleorotations of the respective tectonic block. Collapsed roof blocks in the clay containing the fauna indicate some tectonic unrest at about 1.9 Ma.
ANTHROPOGENIC IMPACTS ON VEGETATION OVER THE PAST 350 YEARS IN PUZHEHEI, YUNNAN, CHINA, AS EVIDENT FROM THE CARBON ISOTOPIC RECORD OF STALAGMITES

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Introduction

The relationship between the vegetation cover above caves and carbon isotopic composition of stalagmites has been widely discussed, as for example by comparing carbon isotopes of modern stalagmites from Brown’s Folly Mine with well-documented re-vegetation above a mine. Baldini et al. (2005) empirically demonstrated that vegetation density can control $\delta^{13}C$ values, with lower values reflecting the increased input of isotopically light biogenic carbon to the total dissolved inorganic carbon. During the recent years, Wang et al. (unpublished) compared $\delta^{13}C$ values of drip waters and modern calcium depositions in caves with different vegetation cover in Guizhou, China, and found that $\delta^{13}C$ of calcium depositions in caves with dense forest above is distinctly lower compared with caves located below bare rock and thin vegetation cover. In order to distinguish between anthropogenic impact and natural change, we use $\delta^{13}C$ records of stalagmites to determine whether: 1) the $\delta^{13}C$ values of stalagmites record vegetation change in the karst region from Southwestern China, and 2) once we know the stalagmites record the change, can we tell when the anthropogenic impact did occur and how serious the effect was.

Three actively growing stalagmites were sampled during Oct. 2003 from Xianren Cave in Qiubei County, Yunnan Province, China (24°07'52" N, 104°07'54" E, entrance at 1371 m a.s.l.). The cave developed in an isolated karst cone in Puzhehei village. ICP-MS $^{230}$Th dates indicate that the three stalagmites (YNXR-2, YNXR-4, YNXR-5) grew during the past 303±3 yrs, 199±2 yrs and 351±8 yrs. They are about 133 mm, 115 mm and 200 mm long and the average deposition rates are 0.44 mm, 0.58 mm and 0.57 mm/year, respectively. Stable isotope samples were converted to CO$_2$ by reacting with pure phosphoric acid and kept for at least 8 h at 25 ºC and then measured by MAT-253. All values are reported in per mille (‰) relative to PDB.

Results

The centennial-scale trends of the variations in the $\delta^{13}C$ values for all three stalagmites are synchronous except for the last 50 years. Combining the three records, the entire profile appears to show three phases during the past 350 years. In Phase I, from the 1670s to the 1780s AD, $\delta^{13}C$ values of YPXR-2 and YPXR-5 slightly decrease from –10.5‰ to –11.3‰. During Phase II, from the 1780s AD to the 1960s AD, $\delta^{13}C$ of the three stalagmites gradually increase from about –11.3 to –9‰. During this phase it is notable that the three stalagmites display different increasing rates although the $\delta^{13}C$ trends are similar. During phase III, from the 1960s AD to present, $\delta^{13}C$ of stalagmites YPXR-2 and YPXR-4 decrease slightly, followed by an abrupt increase. $\delta^{13}C$ values of sample YPXR-5 show a reverse trend, increasing during the early stage of this phase and then showing a $\delta^{13}C$ decrease.

Discussion and conclusion

The climax forest in Puzhehei is a mixed deciduous broadleaf and evergreen broadleaf forest. The forest is still conserved above three isolated karst cones around the village. However, due to tree cutting, sparse shrubs cover the other cones. Although they worship trees, the regional people of Yi nationality, who migrated to Puzhehei from the north three hundred years ago, cut the trees for firewood on most hills, causing the present vegetation above Xianren Cave to be dominated by thin shrubs and bare rock. The following conclusions can be drawn from linking the history of the human activity in this area with the $\delta^{13}C$ trends of the stalagmites.
During phase I, the natural vegetation changes were negligible, and the $\delta^{13}C$ trend of stalagmites record the natural climate change as well as biologic and karst hydrological processes. From the 1780s AD, after continual deforestation, the vegetation became thinner. As a result, the $\delta^{13}C$ values of stalagmites increased gradually, ultimately peaking during the 1960s when the vegetation was ruined drastically and karst rocky desertification occurred. This period, between 1959 and 1961, is known as the “Great Leap Forward”. During phase III, the $\delta^{13}C$ values of the stalagmites slightly decreased in response to the gradual vegetation recovering.

Reference

SPATIAL AND TEMPORAL VARIATIONS OF RAINWATER AND DRIPWATER GEOCHEMISTRY IN MALAYSIAN CAVES

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Speleothem geochemical records can provide valuable constraints on the history of precipitation variability in many regions of the globe, yet quantitative calibrations of the relationship between precipitation and speleothem geochemistry are rare. A dripwater and rainwater collection program at Mulu National Park (4ºN, 115ºE) in Northern Borneo provides an opportunity to investigate how precipitation amount affects dripwater geochemistry from October 2003 to December 2005.

Here we compare bi-weekly timeseries of rainwater $\delta^{18}$O, dripwater $\delta^{18}$O, $\delta^{13}$C, Mg/Ca, Sr/Ca, and drip-rate to contemporaneous precipitation data collected at Mulu and adjacent stations. Rainwater $\delta^{18}$O data ranges from -3‰ to -10‰, and resolves a ~3-4‰ seasonal cycle that corresponds to the seasonal changes in precipitation, consistent with the so-called ‘amount effect’. Dripwater $\delta^{18}$O data fall in a tighter range (-4‰ to -8‰), yet contain variability that resembles the rainwater $\delta^{18}$O variability through time. Dripwater $\delta^{13}$C ranges from -4‰ to -8‰, with some evidence for weak seasonality, while dripwater Mg/Ca, Sr/Ca, and [Ca] display large (25-50%) variations. A complementary dataset constructed from dozens of dripwaters sampled across several kilometers of cave networks reveals relationships between different dripwater geochemistries that aid in the interpretation of the dripwater timeseries.
NEW DATA ON THE CHRONOLOGY OF THE TERMINATION II AND PALEOClimATE DURING MIS 5, BASED ON THE STUDY OF A STALAGMITE FROM CLOȘANI CAVE (SW ROMANIA)

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Several paleoclimatic and paleogeographic studies based on cave deposits from the karst of Romania have been carried out during the last 10 years but they are mostly focused on Holocene and Late Pleistocene speleothems (Lauritzen and Onac, 1999; Onac et al., 2002; Constantin, 2003, Tâmaș et al., 2005). Here, we present the first isotopic profile of a stalagmite from Romania that grew during Marine Isotope Stage (MIS) 6–3.

The stalagmite C6 was collected from Cloșani Cave (Southern Carpathians, Romania). This cave has been used since the 1960s as an underground laboratory by the “Emil Racoviță” Institute of Speleology and its mineralogy and climatology were studied in great detail (Diaconu, 1990; Racoviță et al., 1993). It is a dry cave located at about 80 m above the current Motru riverbed and, except for the entrance area, shows remarkable microclimate stability with a multi-annual mean temperature of ~11°C and a relative humidity of 99–100%.

The 25 cm length of C6 speleothem represents the tip of a longer stalagmite whose basal 90 cm was covered by overgrown large pool-spar crystals. The whole sample is of translucent columnar calcite. The upper part displays very fine lamination. Despite a low U-content (between 0.02 and 0.06 ppm), a series of eight U-series thermal ionization mass-spectrometry (TIMS) dates was successfully measured at Bergen University (Norway). The dates showed that the speleothem grew continuously between c. 183 ka and c. 39 ka with growth rates varying between 0.63 and less than 0.1 cm/kyr. A stable isotope profile was measured at 0.5 cm intervals (also at Bergen University) yielding the best resolution record for the highest growth period: this was between c. 183 ka and c. 103 ka, which corresponds to MIS 6 to 5c.

The δ¹⁸O record and the growth rates (Figure 1) represent the average paleoclimatic conditions during the transition to the Eemian in Romania (Figure 1). The basal part of the profile displays several oscillations that may be attributed to MIS 6 stadials at ~180 ka and ~166 ka respectively which were recognized in several other records (e.g. Winograd et al., 1992; Desmarchelier et al., 2000). A clearly-marked cooling period follows between ca. 166 and 156 ka, followed by an abrupt isotopic increase of ~3 permil during only ~7000 years which may be interpreted as the onset of the Termination II.

In contrast with the “classical” SPECMAP chronology (Schackleton and Opdyke, 1973; Martinson et al., 1987; Schakleton et al., 2002) which broadly places the beginning of the Eemian at some point in time between 140 ka and 130 ka, numerous speleothem records show an earlier warming. The Devils Hole profile shows an early warming at ~140 ka (Winograd et al., 1992), while studies of speleothems from North Norway have shown that the deglaciation must have occurred at high latitudes as early as 145 kyr ago (Lauritzen, 1995; Berstad et al., 1997). The C6 speleothem profile suggests an even earlier warming at ~45 °N that may be placed as early as 155 ka, well in advance of the SPECMAP chronology.

However, the C6 profile also shows a plateau and relatively slow growth during ~150 and ~135 ka which is followed by a short and rapid cooling recorded at c. 132 ka. This may suggests a “two-step” pattern of the deglaciation similar to the “Zeiffen-Kattegat” episode (Seidenkranz et al., 1996).

After this oscillation, growth rate increased markedly and the isotopic signal rises again to reach a maximum at c. 126–123 ka. This correlates with both the “classical” MIS 5e
maximum in the SPECMAP profiles and also with the isotopic signal of the LFG stalagmite from the Western Carpathians (Lauritzen and Onac, 1999).

For the next 20 kyr, the climatic oscillations corresponding to interstadials 5d and 5b appear surprisingly large as compared with the LFG record. LFG grew in the Western Carpathians while C6 grew in the Southern Carpathians: it is possible that the mountain chain may have acted, at different times, as a barrier between two different sources of atmospheric circulation, depending on the position of the wind systems.

Acknowledgements

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CRYSSTALLINE FABRICS AND STABLE ISOTOPE COMPOSITION OF SPELEOTHEMS FROM CAVE ENTRANCES: EXAMPLES FROM SW FRANCE

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Last Interglacial stalagmites precipitated in cave entrances have been studied in order to see the possible influence of such open environmental conditions on their petrography and stable isotope composition. One of them developed a particular fabric that turned out to be difficult to classify; in thin section, it generally appears as a porous structure constituted by parallel-fiber bundles. Actually, this fabric seems to be one of the end of a continuum, function of porosity. The other end is represented by a compact columnar fabric composed of joint thick fibers. This hypothesis is confirmed by SEM observations.

Moreover, fabric locally looks dendritic but this could be misleading. The reason why this scaffold-like structure appears on the thin sections is not clear: overlap of two crossing parallel-fiber bundles? sporadic lateral overgrowths? alteration and/or partial recrystallization?

These specific fabrics are compared with those of recent speleothems developed in artificial tunnels, also widely open to the external atmosphere. Some structure similarities appear. In particular, the presence of lense-shaped laminae seems recurrent. They have in common to substitute for a regular lamination; their walls are constituted by compact calcite and their center presents intercrossed crystallizations, growing from the walls, as inside a geode, and allowing a high intercrystalline porosity. However, we have observed typical regular columnar fabrics in speleothems from a similar open site, demonstrating that ventilated environments do not systematically generate these peculiar fabrics and raising the question of their origin.

$\delta^{18}O$ and $\delta^{13}C$ values of these fibrous fabrics from ventilated environments are compared with those obtained on speleothems with more classical fabrics, from open caves and deep endokarst. On the few examples we have, it appears that the $\delta^{13}C$ changes with the type of fabric. This $\delta^{13}C$ variation could be linked to several parameters: thickness of the roof passed through by percolations, vegetation density, percolation rate and degassing duration and intensity.

These results lead attention on the difficulties of fabric identification in speleothems because of their large variability and highlight the necessity to pursue such petrographic and environmental studies.
STABLE ISOTOPE ANALYSIS OF SPELEOTHEMS DEVELOPED IN ARCHAEOLOGICAL CONTEXT: CONTRIBUTION TO STRATIGRAPHIC AND PALEOENVIRONMENTAL STUDIES OF SITES. EXAMPLES OF TWO PLEISTOCENE SEQUENCES FROM SOUTH-WEST FRANCE

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Speleothems slotted into archaeological sequences are commonly used to chronologically constrain prehistoric occupations (by $^{14}$C or $^{230}$Th/$^{234}$U dating). However, they are rarely the subject of a thorough investigation about paleoenvironments. In some case yet, they can provide high resolution information about regional climate evolution, particularly through stable isotope analysis, and then permit to better know prehistoric populations environments.

We present two examples of prehistoric sequences from South-West France located in cave entrances: Bourgeois-Delaunay (Charente) and Coudoulous (Lot). Speleothems precipitated alternately with detrital sedimentation.

Sedimentary filling and associated remains of each site were the subject of a multidisciplinary approach (geology, palynology, anthracology, paleontology, technology, anthropology, chronostratigraphy). Palaeoenvironmental and chronologic information provided by these studies are synthetically presented and completed with those derived from speleothem analyses.
HIGH-RESOLUTION HOLOCENE SPELEOTHEM RECORDS FROM SOQOTRA ISLAND, YEMEN AS A TOOL FOR INDIAN OCEAN CLIMATE RECONSTRUCTION

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Introduction

Soqotra is an arid tropical island in the Indian Ocean, situated between the Horn of Africa and the Arabian Peninsula. Here, the inter-tropical convergence zone (ITCZ) passes twice each year, resulting in a bi-annual rainy season, known as the Indian Ocean Monsoon system. The nature of the variability and the mechanisms that drive this possible heat engine of our planet as quoted by Black (2002), is not clearly understood. Only recent studies on Holocene speleothems from Southern Oman by Neff et al. (2001) and Fleitmann et al. (2003, 2004) demonstrated that high resolution stable isotopes profiles record changes in rainfall intensity in the region. Soqotran speleothems can provide continental, high resolution proxy-tools in this exclusive marine environment. Climate data monitoring and profound cave research made it possible to select some locations suitable for this Holocene speleothem study.

Results

Two sampled speleothems from Hoq (S-STM1) and Cazecas Caves (S-STM5) have formed over the last 6 ka BP and the last 1 ka BP (TIMS U/Th dating) respectively. δ18O and between -7‰ and -3‰ for δ13C (vs. VPDB). A clear co-variation (R² = 0.69) between δ13C and δ18O-values occurs throughout the complete time series, exhibiting long term (millennial) and short term (decadal) variations. The two sampling locations, distant of 20 km, display similar isotopic changes in both speleothems over the last 1000 years, although both 50 µm records show some differences. The speleothems also clearly registered seasonal variations, coinciding with the alternation of dark compact and white porous layers, present in both stalagmites. These observations suggest that the speleothems reliably registered climatic changes as demonstrated by Genty et al. (2001).

To qualify the climatic significance of these records, meteoric waters, vadose waters, cave drip waters and recent deposited calcite are analysed for their stable isotopic composition in order to understand the controls on the isotopic composition of nowadays calcite in the cave. Also the relative importance of SW versus NE Monsoon rainfall intensity and variability needs more comprehension in order to make paleoclimate interpretation as discussed by Fairchild et al. (2005) and McDermott et al. (2004).

References


LATE HOLOCENE $\delta^{18}O$ VARIABILITY IN A HIGH-RESOLUTION RECORD FROM A SPELEOTHEM IN KAITE CAVE, NORTHERN SPAIN

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Introduction

The $\delta^{18}O$ values recorded in calcite speleothems during the Holocene vary significantly from a place to another, frequently from -2 to -10‰ VPDB. This calcite composition is dependent on the water $\delta^{18}O$ from which it precipitates, the cave temperature, and/or the kinetic fractionation effects in the system. Nevertheless, during the Holocene absolute $\delta^{18}O$ variability for each site is commonly quite similar, ranging within 1-3‰. Differences between maximum and minimum values along the record could be the consequence of long-term trends in the $\delta^{18}O$, with the short-term fluctuations causing minor dispersion. On the contrary, other records present the short-term fluctuations having larger amplitudes than those from long-term oscillations. This is the case we present here. The aim of this work is to study variability of the record as well as to suggest possible mechanisms of its fluctuations. As the variability of ranges depends on the frequency observed, major trends and its $\delta^{18}O$ amplitudes are also identified.

The study site is located in northern Spain, only 50 kilometers inland and separated from the ocean by the Cantabrian Range (Figure 1). The Kaite Cave is a small cavity belonging to the Ojo Guareña Karst Complex, the largest Spanish karst with >100 kilometers mapped (Martín Merino, 1986). Nevertheless, the cave is an isolated gallery of 300 meters long formed only 10 to 15 meters under the surface. The humidity of the cave is elevated during all seasons, and most of the drips show constant rate during the year. The regional climate is temperate and humid with dry summers, with a mean annual temperature 11.9 ºC and mean annual precipitation 1052 mm.

Sample and methods

LV5 is a 106 cm long stalagmite with a complicated growth history. In this study we analyze its last 31 cm; this section of the speleothem is named LV5 Top. The sample was collected fallen on the cave floor, and no subsequent precipitations were found over the original LV5 site. Nine $^{230}$Th dates were measured along the growth axis of LV5 Top using a Finnigan ELEMENT inductively coupled plasma mass spectrometer (ICP-MS) at the University of Minnesota (Shen et al., 2002). The uranium concentrations range from 85 to 210 ppb and the sample size used for analyzing was 150 to 500 mg. Three of the samples have $^{230}$Th/$^{232}$Th activity ratios lower than 20 (from 8 to 16), but low ratios correspond with young ages. The stalagmite grew continuously from ~ 4000 yr ago until 310 yr BP, and all the ages are in stratigraphic order. The growth rates varies from 65 to 120 µm/yr, and are very constant compared with other speleothems from the same cave (Domínguez-Villar et al., 2004). The stable isotope study of the speleothem comprises 250 isotope analysis drilled along the central growth axis. The samples for isotopes were obtained with a 0.5 mm diameter dental drill. The samples were analyzed with a Finnigan MAT-252 mass spectrometer fitted with a Kiel Carbonate Device III. Duplicates from LV5 Top were performed every 20 samples. Most replicates are within 0.1‰ except one duplicate at
There is lack of correlation between δ¹³C and δ¹⁸O in LV5 Top, with an r²=0.06. This suggests that the deposition probably did not occur under isotopic disequilibrium conditions (Hendy, 1971). No current precipitation was observed over the LV5 speleothem. However, drip waters monitored in Kaite Cave suggest that precipitates have an isotopic composition in the same range of these from LV5 Top. The δ¹⁸O record of LV5 Top is plotted in Figure 2. Concerning the drill diameter and speleothem growth rate, each isotope sample comprises a time of 5.6 ± 1.2 yr (1σ error) and the analysis interval is 14.5 yr in average.

**δ¹⁸O variability**

The record shows a clear long-term oscillation and additionally, a great variability of values is superimposed to this millennial fluctuation (Figure 2). The range of δ¹⁸O values is 1.96‰, with a maximum of -5.43‰ and a minimum of -7.39‰. The isotope data follow a normal distribution with an average of -6.29‰ and a standard deviation (σ) of 0.295 (Figure 3). The normal distribution indicates that despite the long-term fluctuations, δ¹⁸O values are equally distributed with respect to the average. Therefore, there are no progressive trends either heavier or lighter during the whole record. Although the isotopic range in LV5 Top is equivalent to some other Holocene records (e.g., McDermott et al., 1999; Dykoski et al., 2005), its long-term oscillation has relative small amplitude, while short-term fluctuations dominates the variability of our record. To understand the nature of this range, we study the possible sources of the variability. As values of δ¹⁸O depend on the isotopic composition of rainwater even prior to entering epikarst, this is the first parameter to analyze. We have used the network of the ISOHIS database, monitored by the IAEA (IAEA, 2004). In the Iberian Peninsula there are 24 stations monitoring the monthly δ¹⁸O of rainwater, with available data since 1961. Seven of those stations have at least 10 years of measurements. The mean range of annual δ¹⁸O variability in these stations is 2.49 ± 0.71‰. This is consistent with the variability found in many other European stations (Rozanski et al., 1993). Most of these variations were reached within short periods, from 3 to 15 years. The amount of sample required for calcite δ¹⁸O analysis in LV5 Top comprises a time interval of ~5 years. Our analysis are not totally homogenizing the short-term variability of rainfall (in the case of the >5 years oscillations). Therefore, fluctuations larger than 1‰ should be expected in LV5 Top related to δ¹⁸O short-term variability in the rainfall.

Variations in kinetic fractionation effects and temperature could also contribute to the range of δ¹⁸O in the speleothem. Although no kinetic fractionation is expected during the calcite precipitation in LV5 Top, some fractionation could exist between rain and drip waters. This could be possible because of evaporation processes on the surface, or in the epikarst, as well as precipitation of carbonates in the ceiling of karst cave. The IAEA stations in the Iberian Peninsula were used to estimate those contributions. To calculate the mean annual rainwater δ¹⁸O composition at Kaite Cave, we take account both the altitude and latitude effects while interpolating the annual data. The modeled rainwater value at Kaite Cave is -7.89‰ VSMOW. The calcite δ¹⁸O composition precipitated under equilibrium conditions from this modeled water will be -6.43‰ VPDB (based on the equation of Kim and O’Neil, 1997). This value is very close to the most recent samples from the stalagmite, and has only a 0.14 ‰ difference with the average δ¹⁸O value of the whole LV5
Top record. We estimate that kinetic fractionation prior to the dripping over the stalagmite should be of minor importance compared to other factors. The relation of rainwater $\delta^{18}O$ with temperature in northern Spain ranges from $+0.24$ to $+0.34^{\circledast}C$. Subtracting the fractionation during calcite precipitation, the relation with temperature in speleothems $\delta^{18}O$ at Kaite Cave is estimated at $\sim +0.1^{\circledast}C$. Mean annual temperature oscillates within 3 to 4$^{\circledast}C$ in meteorological stations around the cave, based on instrumental records since 1971. These values should be also smoothed taking account the $\sim 5$ years interval required by each sample analysis, resulting in temperature changes $<2^{\circ}C$. This implies a maximum short-term variation of $0.2^{\circ}C$. Temperature is a factor that do not cause great variations compared with $\delta^{18}O$ rainwater composition; however, its effects do not should be mistreated. Therefore, the main cause of $\delta^{18}O$ variability in LV5 Top record should be assigned to variations to rainfall composition, whereas temperature and kinetic fractionation have minor effects.

**Discussion**

The variability of LV5 Top record composes of different frequencies. Here, we use different filters to individualize these signals. This method is not to carry out a spectral analysis, but to identify the main frequencies of oscillations and its characteristics amplitudes. First of all, we calculated the equation of the long-term fluctuation in the record, which resulted in a 6th order polynomial equation. The bulk data was filtered with this equation to calculate the $\Delta^{18}O$. Additionally, the $\Delta^{18}O$ signal was smoothed with a high-frequency filter, using an 11-points moving average. The duration of this filter is long enough to smooth the short-term variations in rainfall $\delta^{18}O$ measured by the IAEA. The resulting signals were plotted in Figure 4. The decomposition of the $\delta^{18}O$ record into three different signals provides a graphic illustration about the different time-scales affecting the variability. Thus, Figure 4 depicts clearly separated millennial, centennial, and decadal fluctuations. The amplitude of the different signals is progressively larger as larger is the frequency of study. The millennial $\delta^{18}O$ variability ranges from 0.2 to 0.5$^{\circ}$. In the centennial signal, the amplitude of variations is $\sim 0.5^{\circ}$. Finally, the short-term variability has the larger amplitude, $\sim 2^{\circ}$.

The large amplitude recorded in the decadal signal is in concordance with the large variability caused by short-term variations in rainwater $\delta^{18}O$. Moreover, temperature fluctuations could partially affect this variability. The centennial signal depicts a larger duration of anomalies. Its fluctuations could be explained by prolonged anomalies of rainwater $\delta^{18}O$; however, centennial-scale temperature oscillations also could be of significant contribution. Finally, the millennial-scale fluctuations could be related with both rainwater $\delta^{18}O$ and temperature long-term anomalies.

Variations in the rainwater $\delta^{18}O$ could be associated with changes in $\delta^{18}O$ composition of the ocean, or with storm variables (i.e., changes in: rainfall amount, seasonality, source of vapor, or changes in storm track trajectories). Although storm related parameters are able to have larger fluctuations in $\delta^{18}O$, ocean $\delta^{18}O$ composition oscillations in North Atlantic have a similar variability of these found in centennial and millennial scale in LV5 Top (Duplessy et al., 1992; Marchal et al., 2002). As the ocean has a larger inertia to change its $\delta^{18}O$, this source of variation shouldn’t be mistreated, especially for long-term oscillations.

**Conclusion**

The LV5 Top $\delta^{18}O$ record covers the last 4000 years. The amplitude of $\delta^{18}O$ variation is $\sim 2^{\circ}$. Most of this variability could be explained by short-term changes of rainwater $\delta^{18}O$. However, centennial and millennial time-scales fluctuations from 0.5 to 0.2$^{\circ}$ could be explained in terms of fluctuations of storm variables, changes in temperature, or even variation in ocean water $\delta^{18}O$ composition.

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NEW AGE CONSTRAINTS FOR THE LAST INTERGLACIAL FROM ITALIAN SPELEOTHEMS

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Introduction

The Last Interglacial (MIS 5e in the marine record) was the last time that Earth’s climate approximated the present-day. It is an important period for exploring how interglacials begin and end, and, potentially, how the current Holocene period will terminate. Outstanding issues in studies of MIS 5e include the timing of its onset, the nature of the preceding glacial-interglacial transition (G-IG), and the duration and timing of cooling events around the time of its cessation. These issues remain unresolved partly due to the lack of precise and accurate age estimates of key events recorded in marine sediments, which are the major source of information on ice-volume changes during the MIS 6-5e transition and major cooling events close to the MIS 5e-5d transition (McManus et al., 1994; Shackleton et al., 2002). The recent extraction of pollen sequences from marine cores (e.g. Sanchez Goñi et al., 2005) has increased the potential land-sea correlations, and thus time lags between climate change and terrestrial response. Yet the full potential of these vital insights cannot be realised until more precise and accurate chronologies are assembled.

Speleothems are capable of yielding continuous and precisely dated records of climate change during G-IG and IG-G transitions. However, they respond to climate change in complex ways, so replicate records are highly desirable. Recently, we used evidence from two Italian stalagmites (Antro de Corchia, Tuscany) to argue that full Last Interglacial conditions in southern Europe were reached by about 129 ka (Drysdale et al., 2005). Detailed stable-isotope and growth-rate measurements from one stalagmite (CC5) were supplemented by lower-resolution measurements from a second stalagmite (CC1). Here we present new high-resolution stable isotope data based on re-sampling and re-dating of the MIS 6-5e transition sections of CC1 and CC5, plus new high-resolution stable isotope data from a previously unreported stalagmite (CC7), which also grew through the MIS 6-5e transition. We also present new data on the MIS 5e-5d transition from a fourth stalagmite (CC28), which in CC5 is poorly resolved.

Methods

The MIS 6-5e sections of CC5 and CC1 were re-sampled using a micro-milling lathe, which extracted calcite powders at 100 µm increments, producing 297 and 134 samples respectively. Reconnaissance U/Th dating of stalagmite CC7 revealed at least eight growth phases over the past 303 ka, including a brief phase centred on 125 ka, which is the focus of the present work. The older half of this MIS 5e section was prepared for milling as per CC1 and CC5 to produce 239 isotope samples. Stalagmite CC28 was prepared for milling at the same resolution, yielding 1085 isotope samples. Each stalagmite section was carefully chosen and prepared to ensure as best as possible that the milling bit was cutting flat, parallel layers along the main axis. However, irregular growth-layer geometry at the micro-scale can lead to minor sample mixing (Fairchild et al., 2006). Hence, we estimate that the true sampling resolution for any 100 µm slice is more likely to lie between 100 and 300 µm.

All powders were analysed for $\delta^{18}O$ and $\delta^{13}C$ using an AP2003 continuous-flow stable isotope ratio mass spectrometer at the Scottish Universities Environmental Research Centre (UK). Reproducibility was 0.10 and 0.12‰ for $\delta^{13}C$...
and δ\(^{18}\)O respectively. U-series dating was performed on a Nu Instruments Plasma MC-ICPMS using the method of Hellstrom (2003). Corchia speleothems contain relatively high U concentrations. When combined with the MC-ICPMS technique, this allows us to utilize the leftover powders from the stable isotope analyses for U-Th dating, generating ages of well-defined isotopic excursions with excellent sampling precision. In the odd case where insufficient powders were available, two or more consecutive powders were bulked. As the full U/Th dating program is incomplete, we have fitted preliminary age models to all three MIS 6-5e time series.

In lieu of future MC-ICPMS ages, we have compiled a preliminary age model for CC28 based on reconnaissance top and basal ages and by tuning the intervening period to the published CC5 record (Drysdale et al., 2005).

**Results**

At the time scales under consideration here, our studies of Corchia stalagmites consistently show that δ\(^{18}\)O and δ\(^{13}\)C both decrease significantly during the transition from cold glacial to warm interglacial conditions. However, the shift

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**Figure 1.** δ\(^{18}\)O and δ\(^{13}\)C time series for the period 118-96 ka from stalagmite CC28, Antro del Corchia, Italy. CC5 data are from Drysdale et al. (2005) for the same period and are shown as dotted lines. Also shown is the NGRIP ice-core δ\(^{18}\)O record, the % IRD and % N. pachyderma (s) data from North Atlantic core V29-291 (McManus et al., 1994) and the SST data from western Mediterranean core ODP-977 (Martrat et al., 2004). The events C24 and C23 are the marine equivalents of NGRIP stadials GS25 and GS24.
towards lower δ¹³C during interglacials occurs more progressively, possibly due to the time necessary for post-glacial soils to re-establish above the cave. Increases in both isotopes typically correlate with known colder intervals.

The results from CC1, CC5 and CC7 show (within analytical error) that full Last Interglacial conditions were reached at ~129 ka, confirming our original low-resolution data (Drysdale et al., 2005). In our earlier work, we reported that CC5 preserved a ‘step’ in the δ¹⁸O profile during the MIS 6-5e transition, and argued that this probably represents the ‘Termination II pause’ identified from the marine record, including the nearby SST data of Martrat et al. (2004). This is now also revealed in the high-resolution data of CC1, but in CC7 its presence is less obvious. We also see the event preserved as a brief positive excursion in δ¹³C in both CC5 and CC1, and as a step in the δ¹³C of CC7. We currently place the age of this pause at ~130 ka.

The δ¹³C and δ¹⁸O data for CC28 are shown in Figure 1. The most distinguishing features of this record are the two prominent positive isotope excursions, which reach maximum values at ~111 ka and ~105 ka. Based on climate-isotopic trends in other stalagmites from Corchia, these excursions strongly suggest deteriorating climatic conditions, particularly as both isotopes are moving more or less synchronously. McManus et al. (1994) were the first to perform a detailed investigation of abrupt cold events in North Atlantic marine cores during MIS 5d. Using influxes of ice-rafted debris and increased presence of the cold-water-dwelling foraminifer, N. pachyderma (s), they identified two events (C24 and C23) (Figure 1) which correlated with cold stadials in the GRIP ice-core record. There is uncertainty as to whether the older event in the GRIP record is preserved intact due to stratigraphic disturbance at about 111 ka. The more recent NGRIP record (NGRIP Members, 2005; Figure 1) confirms the original observations of McManus et al. (1994), albeit with age differences of several thousand years. The two corresponding NGRIP stadial events (GS25 and GS24) are virtually indistinguishable in age (111-108.5 ka and 106-104.5 ka) from the two isotopic excursions in CC28.

We stress again that our age model for CC28 is preliminary, and further data (due in the coming months) will improve the accuracy and precision of this model considerably. Nevertheless, the similarity between NGRIP and CC28 is sufficiently convincing to indicate that North Atlantic cold events C24 and C23 (and thus NGRIP stadials GS25 and GS24) are preserved in this stalagmite. Indeed, the more pronounced amplitude of the older event is consistent with the suggestion that C24 was colder, causing a shift in SSTs of almost 50% of that expected from a full glacial-interglacial transition (McManus et al., 2002).

### Discussion and conclusions

The potential importance of these new Corchia data is worth considering further. Recent pollen evidence from marine cores along the Iberian margin (Sanchez Gõni et al., 2005) places the base of the Eemian at the brief post-zeifen stadial, which occurs during the MIS 6-5e transition. This stadial, which is clearly preserved in both western Mediterranean (Martrat et al., 2004) and Iberian-margin marine cores (Shackleton et al., 2002) correlates with the pause in the Corchia record at ~130 ka. Our estimate is about 3 ka older than these marine-core ages. According to Sanchez Gõni et al. (2005), the age for the top of the Eemian along the Iberian margin is coincident with the start of cold event C24, for which we assign a preliminary starting age of ~112 ka. Therefore, we suggest that the length of the Eemian in southwestern Europe can be bracketed tentatively between 130 ka and 112 ka.

### References


EMPIRICAL ORTHOGONAL FUNCTION ANALYSIS OF MULTIVARIATE STALAGMITE TRACE ELEMENT DATA: DETECTING THE 1982 EL CHICHÓN VOLCANIC ERUPTION

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Introduction

Although U-Th-Pa dating techniques have revolutionized the use of speleothems for paleoclimatic research, this method is constrained in some regions by low uranium concentrations. High-resolution speleothem chronologies in such regions are limited by a dearth of reliable regional or global chronologic marker horizons such as the tephrochronology used so successfully by the ice core community, e.g. Zielinski et al. (1994). We have analyzed modern trace element concentrations in a Belize stalagmite using LA-ICPMS, and show that Empirical Orthogonal Function (EOF) analysis is a promising data analysis technique for identifying tephra marker horizons in speleothems. A major perturbation in dripwater geochemistry occurred in 1982, coincident with local ash fallout from Mexico’s El Chichón volcano. EOF analysis was also successful at distinguishing a number of other modes of biogeochemical variability, providing a means to investigate their environmental triggers. Additional stalagmite tephrochronology research is needed to further develop and test analytical and statistical tools for low-latitude explosive volcanism.

AVHRR satellite imagery of the tephra cloud generated by the 1982 eruption of El Chichón volcano in Chiapas, Mexico shows that ash was transported over the cave Actun Tunichil Muknal in central Belize on April 3rd-6th. The eruption was classified as V.E.I. 5 on the Volcano Explosivity Index (Newhall and Self, 1982). Rampino and Self (1984) showed that the volcano is a source of unusually large quantities of cooling sulfate aerosols. Adams and co-workers (2003) showed that large ash plumes from equatorial volcanoes, such as El Chichón, can double the chances of an El Niño event the following winter. The volcano’s history is also of interest to anthropologists because earlier eruptions are associated with the decline of Maya civilization.

Investigations of annual to sub-annual relationships between trace element proxies and their controlling variables have been reported by a number of groups including Fairchild et al. (2001; in press), McMillan et al. (2005), Treble et al. (2003). As it is frequently the case that multiple factors affect individual measurable variables and modern calibration is required to establish any causal relationships between a speleothem record and volcanic eruptions, we were fortunate to have collected well-dated modern stalagmite material (Frappier et al., in revision) from a region that received fallout from the 1982 El Chichón eruption. The goal of our investigation was thus to test the potential to measure stalagmite tephrochronology signals by analyzing the multivariate trace element “fingerprint” of the El Chichón eruption. To distinguish the signature of event types which have affected the area (e.g. hurricanes, heavy rainfall, tephra fallout), we analyzed a large suite of trace elements and analyzed common modes of variability.

Methods

Actively growing stalagmites were collected from Actun Tunichil Muknal in January, 2001 (Frappier et al., 2002). The stalagmite was dated using layer counting after testing for annual growth patterns using the onset of 137Cs activity (Frappier et al., in review). Hendy tests for isotopic equilibrium deposition were positive, and age modeling yielded a recent growth rate in excess of 1.15 mm/yr. High-resolution (~weekly - monthly) stable isotope analysis across the most recent 24 years revealed strong correlations between δ13C and El Niño events; in addition, we observed low δ18O value excursions related to recent hurricanes in the vicinity of the cave site (Frappier et al., in review).

A small, polished chunk of ATM7 was analyzed for trace element concentrations at Terry Plank’s LA-ICPMS laboratory at Boston University. The methodology of Treble et al. (2002) was followed closely, with multiple trace element concentrations collected in rapid sequence during slow scans. We analyzed 11 parallel transects at 50 micron spacing. Preclean scans were performed prior to each transect to remove surface impurities. Blanks and standard (NIST 612) were analyzed along with the sample materials. LA-ICPMS was performed using a 50 micron beam spot, scanning at 100 µm/sec, and 18 chemical species were measured: B, Na, Mg, Al, Si, P, Ti, Ti, Mn, Fe, Rb, Sr, Y, Zr, Ba, Ce, Th, and U.
This sampling rate resulted in approximately weekly temporal resolution, and the age model error is on the order of a few months. All eleven records were stacked to retain common variability. The resulting stacked 18-species series was smoothed using a running mean, and Empirical Orthogonal Function (EOF) analysis was performed using L.D. Meeker’s Matlab script toolbox (Meeker et al., 1995). EOF analysis creates orthogonal axes, or modes, that explain different and decreasing amounts of the total variance present in the data. These modes describe the linear combinations of observations which are most efficient in explaining the variance in the data (Meeker et al., 1995). Eigenvector loading was recorded, and EOF modes were compared to the local historical record.

**Results**

Where the variance explained by each EOF Mode is greater than 1, the results can be considered meaningful. The first six EOF Modes accounted for over 75% of the total variance in the trace element dataset (Figure 1). EOF1 repre-

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**Figure 1.** Chart of EOF results showing loadings (percent variance explained by each species) for each of the first six eigenvectors. The total variance explained by each mode of variance (EOF) is indicated. *N.b.* Figures in this abstract show results from processing only the first five of eleven LA-ICPMS transects.

**Figure 2.** Timeseries plot of variance in the first four EOFs. The arrow marks the geochemical event in 1982, evident in EOFs 1 and 2, and coincident with the El Chichón eruption. A different perturbation in 1979 (EOF 1 and 2) is coincident with extreme precipitation in that year, when local rainfall was greater than three standard deviations above the norm.
presents a general trace element flux, EOF2 appears to rep-resent silicate minerals, P and Fe are primarily loaded on EOF3, EOF4 shows an unusual Zr signature, and the sodium load-ing on EOF 5 most likely represents an evaporative signal. Variance was partitioned evenly across the different EOF modes for Sr and Si; thus EOF is not a useful tool for inves-tigating these elements in this dataset. Timeseries plots (Fig-ure 2) show how these six different modes, or multi-variate fingerprints, varied over the last few decades.

Around 1978-1979, the stalagmite shows an increase in chemical species associated with silicates (EOF2) that is co-incident with color changes in stalagmite stratigraphy, sta-lagmite stable isotope perturbations, and two major histori-cal rainfall events. A hurricane struck the Yucatan in 1978, and rainfall in 1979 was over three standard deviations above the climatological mean. I interpret the trace element repre-sentation of this wetness (increase in EOF2) to indicate in-creased soil flushing into the deeper cave conduits. A major trace element perturbation around 1982-1983 points to the influence of the El Chichon eruption (EOFs 1, 2, 4). The negative EOF2 excursion in 1982 is consistent with this inter-pretation, because it reveals a substantial increase in spe-cies found in the volcanic ash: Fe and Ti. At the same time, the combination of EOF1 and EOF 4 reveals that the in-crease in Sr, Mg, Al, Si, and B associated with this event is smaller than for Fe and Ti.

Stable isotope and stratigraphic data can be included in a more multivariate EOF analysis. Additional information about biogeochemical variability is revealed through time-series analy-sis of individual EOF modes, although at this resolution, this application is limited by the linear nature of the annual age model (Frappier et al. 2002, Frappier et al, in revision).

Conclusions

An exploratory LA-ICPMS study of multivariate trace ele-ment signatures preserved in a rapidly growing, modern tropical stalagmite shows the influence of a number of envi-ronmental factors, including the 1982 El Chichon eruption, pluvial conditions during 1979, and heavy rainfall events. EOF analysis, used extensively by the ice core community, appears promising as a tool to reveal the common responses of the cave-epikarst biogeochemical system to various forcing factors. EOF analysis of multiparameter speleothem records through decomposition of dataset variability is a powerful method for investigating the underlying mecha-nisms of biogeochemical change in these sensitive geologic recorders. This approach may prove fruitful in the ongoing effort to understand interactions between the atmosphere, hydrosphere, biosphere, and rock record preserved in caves. In regions where speleothem uranium concentrations are low, tephra layer recognition may provide additional marker ho-rizons useful for dating. Elsewhere, it may be possible to use more precisely-dated speleothem records of ashfall events to investigate the history of low-latitude explosive volcanism.

References


HIGH-RESOLUTION STABLE ISOTOPE CLIMATE RECORD FROM TWO ANNUALLY LAMINATED HOLOCENE STALAGMITES IN NW SCOTLAND

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Introduction

Uamh an Tartair (UAT) is a well calibrated cave system in NW Scotland (Figure 1). This site is located on the North Atlantic Seaboard in a climatically sensitive area where precipitation relates to the NAO and temperature to ocean circulation via the North Atlantic Drift, and for which late Holocene annual climate reconstructions have been published from luminescent laminated stalagmites (Proctor et al., 2002; Proctor et al., 2000). This paper presents the stable isotope data of two actively growing stalagmites from UAT cave, with some initial climatic interpretation of the last 1000 years in NW Scotland. Sample SU967 is a 3 cm 1087-year-old sample collected in 1996 (Figure 2). SU032 is a 6.6 cm sample collected in autumn 2004. The top 326 laminae, down to an un-dated hiatus have been counted (Figure 2).

Figure 1. Map of the UK and the field site region.
The stable isotope records were obtained using two methods: the relatively new laser-ablation technique and micromilling followed by conventional analysis, with the latter providing a test for the former.

**Methodology**

Despite mass spectrometers requiring smaller sized samples, a significant problem in sampling slow-growing stalagmites is the resolution at which calcium carbonate can be sampled. Traditionally this has been done using a dentist drill and a 0.5 mm drill bit. When sampling faster-growing stalagmites, this does not pose any significant problem, since high resolution (annual - sub-annual) can still be achieved. The problem occurs when trying to sample slower-growing specimens such as those from NW Scotland or similar cold or high-latitude regions. In these slow-growing samples, a subsample taken with a 0.5 mm drill bit will lead to large time-averaging effects and hence low-resolution records will result. This essentially has been the driving force behind attempts to increase the resolution with which calcite can be sampled. A stable isotope record of Scottish stalagmite sample SU967 was obtained using one such new method: laser-ablation gas-chromatography isotope ratio mass spectrometry (LA-GC-IRMS), at the Royal Holloway, University of London, UK (McDermott et al., 2001). This sample was then reanalysed together with stalagmite SU032 using a high-precision micromill system and conventional acid-digestion methods at the University of Innsbruck, Austria (Spötl and Vennemann, 2003). This provided a test for the newly developed laser-ablation technique.

**Results**

The stable isotope time-series generated by both techniques are shown in Figure 3. The laser ablation data displays large shifts in $\delta^{18}O$ of higher frequency and higher amplitude when compared to the $\delta^{18}O$ time-series generated by micromilling and conventional analysis. Isotopic excursions of $\sim$1.5‰ exist within the drift-corrected data (no smoothing). This
variation is not thought to be true $\delta^{18}O$ variation (and thus not climate-driven). It is more probable that this reflects insufficient data correction for the fractionation of $\delta^{18}O$ between the CO$_2$ and CaO phases during the laser-ablation process and calcite imperfections. For the majority of the $\delta^{18}O$ time-series the values from laser ablation and conventional analysis agree within error. There is also good agreement between the $\delta^{18}O$ (micromill-conventional analysis) of both samples. It would appear that inter-sample variability is greater than intra-sample variability.

The similarity between the laser ablation and the micromill-conventional analysis $\delta^{13}C$ time-series of sample SU967 is impressive and better than that in the $\delta^{18}O$ time-series. Both data sets show the same variation, although some offset in the timing of the variations is apparent: this is thought to be due to the different locations of the two tracks (the micromill track being located toward the flank of the stalagmite) and the implications this has when the age-distance relationship is applied to these time-series. There is some disagreement between the two micromilled time-series (run A and run B) in the later part of the record, with run B showing lighter values of $\delta^{13}C$ in the post-1900AD period. Sample SU032 shows the same trend in $\delta^{13}C$. However absolute values are lower than in the $\delta^{13}C$ time-series (LA-GC-IRMS and micromilled) of SU967. There is also a large difference in variation at the beginning of the SU032 record with values fluctuating greatly over a short period of time (not replicated within the SU967 record). The SU032 record is a higher-resolution record (~annual resolution); therefore, it is possible that this is a product of this augmented resolution. Alternatively, it could be the result of local soil processes.

All $\delta^{18}O$ time-series show a shift to heavier values during the time-period 1700-1800AD, a trend also seen in the $\delta^{13}C$ record of SU967 (and to a lesser extent in SU032); this could be an expression of the Little Ice Age in these stalagmites (drier and cooler conditions). This period is then followed by a brief return to lighter stable isotope values indicative of wetter/warmer conditions. This is shown in both the oxygen and carbon records (1800 – 1840AD). This is then followed by a renewed period of heavier isotope values (drier/cooler conditions). These stable isotope records suggest that the stalagmites in UAT cave system are responding to climatic forcings in NW Scotland.

**Conclusion**

Micromill-conventional analysis provides the most reliable method since there are no fractionation effects that need to be corrected for and it is not affected by calcite imperfections (e.g. calcite crystal boundaries etc). The micromill system and the smaller sample sizes required mean that a higher resolution can be achieved (an annual stable isotope record for SU032). Laser ablation cannot yet achieve such a high resolution. However, the micromilling technique is both time consuming (the micromill is not fully automated) and there is room for sample handling error. It is also a costly analysis technique. Despite needing more correction, the laser-ablation technique is cheaper and faster and can be programmed to run for significant periods of time without intervention.

**References**


HIGH-RESOLUTION RADIOCARBON, STABLE-ISOTOPE AND TRACE-ELEMENT VARIATIONS IN BAHAMIAN SPELEOTHEMS DURING THE LAST GLACIAL PERIOD

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Significant fluctuations in the atmospheric concentration of radiocarbon (Δ¹⁴C) have been observed at decadal to millennial timescales and attributed to changes in terrestrial or solar magnetic fields, and/or changes in the carbon cycle, particularly ocean circulation. Speleothems have a high potential to be used as accurately dated high-resolution archives of climate and geochemical information. Previously, we presented a continuous record of atmospheric radiocarbon from 45 to 11 ka B.P. based on TIMS U, Th and Pa measurements and AMS ¹⁴C ages of a stalagmite (GB-89-24-1) from Sagittarius Cave on Grand Bahama (Beck et al., 2001). This record revealed elevated Δ¹⁴C for the duration of growth and a general decline in Δ¹⁴C between 26 and 11 ka B.P., from ~ 700 to ~ 100 ‰ which was considered too large to be solely a result of reduced production via increased shielding by the Earth's magnetic field and was probably related to redistribution of ¹⁴C during a mode of ocean circulation much different to the present day. Here, we focus on efforts to reproduce earlier results using another stalagmite from the same location and to further investigate the climate system using a multiproxy approach.

We present a high-resolution stable-isotope, trace-element and radiocarbon record of the stalagmite GB89-25-3 from Sagittarius Cave, Grand Bahama. A robust chronology for the stalagmite has been obtained using MC-ICPMS U and Th isotope measurements with high spatial resolution using sample sizes of 50 – 150 mg. The distance-age model was obtained using a spline fit. The bottom section of GB89-25-3 grew between 44 and 28 ka ago; so far we have analysed the part from 44 ka to 34 ka B.P. for trace elemental composition and stable isotopes using high resolution LA ICPMS techniques. The top section grew between 15 and 11 ka B.P. and has been completely analysed for trace elements and stable isotopes. Radiocarbon was measured for both sections at high resolution using AMS.

We compare the new ¹⁴C data obtained for GB89-25-3 to GB89-24-1 and to other radiocarbon archives such as the Cariaco Basin (Hughen et al., 2004). Furthermore, the profiles of stable-isotope and trace-element variations are indicative of changing climate and/or recharge. We find that the δ¹³C record, together with Mg-, P- and U-concentrations, are likely to be a proxy for changes between wetter and drier conditions in the Bahamas and suggest a major dry event at around 41 ka. This is probably related to Heinrich event H4. We compare our data to archives from other locations such as Cariaco Basin (Peterson et al., 2000), the subtropical North Atlantic (Sachs and Lehmann, 1999) and Greenland ice-core data (NGRIP members, 2004). Our data indicate a difference of the timing of H4 of more than 1000 a. Spectral analysis of the δ¹⁸O record of GB89-25-3 shows one significant cycle of 1480 a, similar to the proposed 1470 a Dansgaard-Oeschger cycle found in Greenland ice cores. The δ¹⁸O record of GB89-25-3 can potentially be used to improve the NGRIP chronology using an approach similar to that of Spötl et al. (in press).

References


AGE, DURATION AND STRUCTURE OF THE 8.2 KA EVENT IN A SPELEOTHEM FROM PIPPIKIN POT, NORTHERN ENGLAND

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The catastrophic release of meltwater into the North Atlantic at 8.2 ka is believed to be responsible for a slow-down of ocean circulation and the resulting cooling event observed over Western Europe at this time. This event is important for our understanding of future climate change scenarios and for climate model validation.

A 59 cm long stalagmite was collected in October 2001 from Pippikin Pot in the Yorkshire Dales to study Holocene palaeoclimate variability. Twenty U-series ages were obtained along the entire length of the stalagmite and indicate that it grew from 9.8 ka to 5.7 ka with a linear growth rate, followed by a hiatus and a terminal age of 4.4 ka; 95 % confidence limits of the linear age model are approximately ±75 years during the 8.2 ka event. Stable isotope samples were then taken at 3-4 mm intervals over the full length of the speleothem. The oxygen isotope record is largely invariant with a mean $\delta^{18}O$ value of -4.75 ‰, similar to modern-day rainfall in this area. The only significant oxygen isotope event occurs at 8.2 ka, and is a negative excursion of 1 ‰ lasting approximately 150 years (see Figure 1). The age, duration and magnitude of the 8.2 ka excursion in Pippikin Pot is similar to that observed in the Greenland ice cores.

A high-resolution study of stable isotope, trace element and radiocarbon variability from 8.4 ka to 8.0 ka is currently underway, to determine the detailed structure of the event. Excursions within the Pippikin Pot carbon isotope record correlate well with variations in the IntCal04 record of atmospheric $\Delta^{14}C$, enabling the chronology to be tuned within the existing U-series age constraints. Indications of solar forcing are also evident in the radiocarbon and trace element records. Ongoing monitoring of oxygen isotope variation of rainwater and cave drip water in the vicinity of Pippikin Pot is aiding our understanding of speleothem $\delta^{18}O$ in both the present day and in the early Holocene. Understanding this process is important for our work on data and climate model (HadCM3) comparisons of the oxygen isotope excursions in Greenland and Western Europe during the 8.2 ka event.

Figure 1. U-series age model and oxygen isotope excursion during the 8.2 ka event in Pippikin Pot, Northern England.
RECONSTRUCTION OF PALAEOCLIMATE OVER THE INSTRUMENTAL PERIOD USING SIX STALAGMITES OF DIFFERENT HYDROLOGICAL ‘SPECIES’ FROM TWO CAVES IN NE TURKEY

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Introduction

Stalagmites, deposited as part of the meteoric water cycle, are precipitated following degassing of carbonate labelled drip water as it enters the open space of the cave after percolating down through the karst aquifer (Soubiès et al., 2005; Holmgren et al., 2003), and are thus capable of retaining a modified chemical signal of environmental/climatic change over the period of deposition. Proxies such as stable isotopes ($^{18}$O, $^{13}$C), trace elements and variations in growth rate of annually laminated stalagmites may vary with the moisture/thermal regime of an area and thus prove useful climatic proxies.

Particularly climatically sensitive regions such as the Near and Middle East, where moisture deficits are the norm, are extremely vulnerable to any reductions in available surface and ground water (Cullen and deMenocal, 2000), thus an understanding of climatic changes over recent centuries has implications for future water resource management in climatically stressed and politically volatile regions of the world (Mann, 2002). Whilst Turkey has extremes in temperature, it benefits from all-year round rainfall in many areas (Turkeº, 1996), leading to a strong seasonality of climate in regions such as the NE, which is likely to produce annual laminations in stalagmites. Proxies such as those listed above of annually laminated stalagmites of this region will provide quantitative palaeoclimatic proxy records that could be validated against the instrumental record of the last 77 years.

For this reason, stalagmites were removed from two caves (Figure 1) during a recent visit to the Gümüšhane province of NE Turkey as part of Jex’s PhD project (and also forms part of the wider ENVÄNET project looking at environmental change in North East Turkey). Both caves are developed in Liassic-Lower Cretaceous limestone layers (Nazik et al., 1994). Akçakale cave, located 6 km SE of the town of Gümüšhane at an elevation of 1530 m, is much larger than Karaca and generally appears to be wetter, with an increased number of faster flowing drips and large waterfalls actively forming extensive flowstones.

Samples from both caves present an opportunity to identify the processes determining the stable isotopic and trace element composition of speleothems from different hydrological settings or ‘species’, and subsequently whether any patterns in stable isotope, trace element and annual growth rate variations in the stalagmites obtained of different ‘species’ relate in any way to the instrumental record for the region. As there is no prior research published on using stalagmites as palaeoclimate proxies in the region or indeed the country it is vital to understand how the isotopic and trace element signatures arrive in the stalagmite by such an approach.

For both caves, climate measurements and water samples (drip waters, pond waters) were obtained from throughout the cave over a 2 week period in 2005. Additionally, 6 stalagmites representing three different hydrological settings

![Figure 1. Location of cave sites (adapted image from www.multimap.com).]
(soda straw fed stalagmites, non soda straw stalactite fed stalagmites and drapery fed stalagmites) were collected.

**Species 1: Soda Straw fed stalagmites**

Upper Dikit and Lower Dikit (Figure 2a and b) were both collected from Karaca cave and each have continuous visible laminae, of width 1.26+/−0.5 mm and 1.56 +/-1.21 mm respectively. Assuming that the laminae are annual, growth rates within this range are predicted from modern dripwater electrical conductivity (a growth rate of ~1.1 mm/yr is predicted from an EC of 430 µS (equivalent to Ca²⁺ of ~80 ppm) and temperature of 10°C); suggesting that each sample has a deposition period of 71 and 56 years respectively.

**Species 2: Non-Soda-Straw fed Stalagmites**

Custard (Karaca cave) and Colin (Akçakale cave) (Figure 2c and d) each have continuous visible laminae, of width 0.54 +/-0.29 mm and 0.63+/−0.28 mm. Assuming that the laminae are annual, growth rates within this range are predicted from modern dripwater electrical conductivity (a growth rate of 0.5-0.9 mm/yr is predicted from an EC range of 270-440 µS (equivalent to Ca²⁺ of 50-85 ppm) and temperature of 10°C), suggesting that each sample has a deposition period of ~259 and ~162 years respectively.

**Species 3: Stalagmites growing within curtains/draperies**

2-Pac (Akçakale cave) and Lumpy (Karaca cave) (Figure 2e and f) each have continuous visible laminae, of width 0.58+/−0.65 mm and 0.38+/−0.38 mm respectively. Again, growth rates within this range are predicted from modern dripwater electrical conductivity (a growth rate of 0.5-0.9 mm/yr is predicted from an EC range of 310-390 µS (equivalent to Ca²⁺ of 50-75 ppm) and temperature of 10°C), suggesting that each sample has a deposition period of ~360 years.

**Results**

Initial lamina counting off images captured by a flat-bed scanner suggest some relationship between stalagmites of each of the hydrological species (Figures 3a – b), a marked difference in annual growth rate, despite the similar range of EC described earlier, is evident with the soda straw fed stalagmites (Figure 3a) having the fastest growth rates. These counts will be verified/improved upon using standard microscopy and hyperspectral imaging techniques. However these results are evidence for a species effect in these samples, and identify that the Ca content of the dripwater, rate of dripping and cave temperature suggested to be the dominant factors that control stalagmite growth across more north western sites in Europe (Baker et al., 1998), may not be the dominant growth rate factors in these sites. Here sta-
lagmite texture may be more important, with generally more porous stalagmites having the fastest growth rates.

ICP-MS results on stalagmites demonstrate greater levels of Sr (~500 ppm), Ba (~100 ppm) and S (60 – 180 ppm) in Akçakale cave than in Karaca cave (<100 ppm Sr, <25 ppm Ba and 2 – 55 ppm S). High-resolution ICP-AES of all stalagmites will provide trace element profiles, while trace element concentrations of bedrocks and cave waters samples will aid interpretations.

Current work includes 14C dating which will be used to confirm the annual nature of the laminae, U-Th dating to provide basal dates for the older samples; anion concentrations of cave waters, TOC and IC analyses of cave and surface waters as well as fluorescence analyses to identify the type and concentration of organic matter of the same cave and surface waters. These will help to understand the hydrological regime of the cave, which will subsequently allow any palaeoclimatic interpretations to be put into context. Results will be presented.

**Conclusions**

Evidence for a species effect is presented here, suggesting that in this region of NE Turkey, hydrology and calcite fabric may have greater influence over growth rate than climate (at least for the last 100 years). General differences in the trace element concentrations are seen between the two cave sites, possibly reflecting differences in surface soil and bedrock conditions.

**References**


Introduction

In recent years, numerous speleothem based proxy studies have significantly advanced our understanding of annual-to-decadal scale paleoclimate variability. While the majority of these studies have focused on the use of speleothem stable-isotope variations ($\delta^{18}$O and $\delta^{13}$C) to reconstruct paleorainfall, paleotemperature, and/or paleovegetation, several recent studies have investigated the paleoclimate proxy potential of annual trace-element variations preserved in speleothems (Huang et al., 2001; Roberts et al., 1998; Treble et al., 2003). Annual cycles in trace-element composition, a common feature of speleothems (Fairchild et al., 2001), may be useful as paleoenvironmental proxy records with seasonal resolution. Such seasonal records can provide powerful insight into the mechanisms driving climate and can have a large impact on paleoclimate research. Reconstructing past climate at seasonal resolution, however, has generally proven difficult as numerous climatic archives lack sufficient temporal resolution and chronological control. Speleothems, in general, are very well suited for high resolution paleoclimate reconstruction, as they experience no bioturbation; have relatively high growth rates compared to marine sediments; tend to be very well preserved; and can be precisely dated using U-series methods.

In order to use speleothem trace-element variations to reconstruct past changes in climate it is imperative that the proxies are well understood, well calibrated, and rigorously tested in any individual study area, because numerous environmental, climatic and geologic factors may affect the chemistry of speleothem calcite. Because the incorporation of different elements may have different environmental controls, it is desirable to use a multi-proxy approach to separate these mechanisms to obtain robust seasonal resolution speleothem records. In this study, we assess the potential for seasonal resolution paleoclimate reconstruction from annual geochemical cycles preserved in an annually banded stalagmite, HS-4, collected from Heshang Cave, Hubei Province, China (30.44°N, 110.42°E; Figure 1). HS-4 grew during the last 9.5 kyr and exhibits annual cycles in multiple geochemical proxies. We have performed an ultrahigh-resolution study of the stable-isotope ($\delta^{18}$O and $\delta^{13}$C) and trace-element (Mg/Ca, Sr/Ca, Ba/Ca, U/Ca) composition across 16 annual growth bands to investigate the nature of these geochemical cycles (Johnson et al., in press). Based on the comparison of the observed annual cycles with modern calcite, drip water, climatic data, and a simple model, we suggest that annual trace-element (Mg/Ca, Sr/Ca, Ba/Ca, and U/Ca) and stable-isotope ($\delta^{13}$C and $\delta^{18}$O) cycles...
record past hydrologic changes which directly reflect past variations in summer monsoon rainfall. To test these proxies, we will also present seasonally resolved speleothem time-series from the 20th century, which can be directly compared with meteorological records and other high-resolution monsoon records.

Results

We report the presence of clear annual cycles in trace-element (Mg/Ca, Sr/Ca, Ba/Ca, and U/Ca) and stable-isotope ($\delta^{18}$O and $\delta^{13}$C) composition in an annually banded stalagmite from Heshang Cave. Through a combination of micromilling and in situ analysis (LA-MC-ICPMS), we measured geochemical variations across 16 annual growth bands, to assess their potential as seasonal resolution paleomonsoon proxies (Figure 1). To facilitate comparison with modern climatic and environmental data we created composite annual cycles for each proxy by stacking 6 well-defined years. Speleothem $\delta^{18}$O variations (-10.8‰ to -8.5‰) are controlled by seasonal variations in temperature and drip-water $\delta^{18}$O which lead to maximum values during May, around the time of summer monsoon onset. This provides a chronological marker which can be used to constraining the timing of the other geochemical cycles. The composite cycles reveal a strong positive correlation between Mg/Ca, Sr/Ca, Ba/Ca, and $\delta^{13}$C values in the micromilled section ($R^2 = 0.65-0.98$), with minimum values occurring around May. Maximum U/Ca values occur at the same time.

We present simple models which show that these correlations, as well as the observed ranges of Mg/Ca (14.1 to 22.4 mmol/mol), Sr/Ca (0.2 to 0.4 mmol/mol), and $\delta^{13}$C (-12.5 to -10.7‰), may be fully explained by progressive CO$_2$ degassing and calcite precipitation from an initially saturated solution (Figure 2). Using realistic initial conditions for Heshang Cave ($T = 18^\circ$C, Mg/Ca$\_solution = 0.84$ mmol/mol, Sr/Ca$\_solution = 0.69$ mmol/mol, $\delta^{13}$CTDIC = -16.75‰), we find that the observed relationships can be produced by using $D_{\text{Mg}} = 0.016$ and $D_{\text{Sr}} = 0.30$, within the range of expected values. The model suggests that the fraction of Ca removed from the solution ranges from 0-30% to produce the observed seasonal cycles. This variation may be due to two related processes which occur during drier periods: (1) increased prior precipitation of calcite in the epikarst or on the cave ceiling, and/or (2) a greater degree of CO$_2$ degassing and calcite precipitation on stalagmite surfaces when drip-rates are lower. Both mechanisms would have the effect of enriching speleothem Mg/Ca, Sr/Ca, Ba/Ca, and $\delta^{13}$C values during drier periods. Past variations in Heshang carbonate chemistry may, therefore, be useful as seasonal resolution proxies for past rainfall.

![Figure 2](image-url)

**Figure 2.** The modelled evolution of (A) Mg/Ca ratios, and (B) $\delta^{13}$C and pH as CO$_2$ degassing and calcite precipitation progressively removes C and Ca from a saturated solution which initially contained 5 mmol Ca. In (A), the evolution of Mg/Ca ratios in the instantaneous precipitate, the average precipitate, and the solution is shown. This model used an initial Mg/Ca = 0.84. In (B), the evolution of solution pH, $\delta^{13}$C of solution HCO$_3^-$, and the $\delta^{13}$C of instantaneous (or actual) precipitate and the average (or cumulative) calcite is shown. This model run utilized an initial $\delta^{13}$C$_{TDIC} = -16.75$‰, $T=18^\circ$C, and a slow CO$_2$ degassing rate.
References


PALEOCLIMATE RECONSTRUCTIONS FOR THE SOUTHEASTERN U.S.A. FROM SPELEOTHEMS IN DESOTO CAVERNS, ALABAMA

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Introduction

The driving forces of global climate change are poorly understood in part due to the lack of high-resolution terrestrial climate records. The study of speleothems (e.g., stalagmites) often provides uninterrupted millennia-long records of past terrestrial climate conditions at annual resolution. It is well documented that the growth and isotopic composition of stalagmites are primarily controlled by climatic factors including air temperature, soil microbial activity, and rainfall (McDermott, 2004). Proper analysis of stalagmites often produces well-dated millennia-long climate records for regions where other proxy records of equal resolution are not available.

The southeast United States (Figure 1) is glaringly lacking in high-resolution paleoclimate records that span the Holocene (Wurster, 2001). Our major research objective is to reconstruct a high-resolution continuous climate record during the Holocene for the Southeast by means of speleothems from DeSoto Caverns in Childersburg, AL (Figure 1). The climate record proxy is based on stable carbon and oxygen isotope profiles along the central growth axis of multiple stalagmites collected in 2002 and 2005. DeSoto Caverns is a large phreatic cave capped with Ordovician age dolomite in north central Alabama at an elevation of ~ 170 m above sea level. Its central position in the Southeast is ideal for archiving a climate record representative of the region as a whole (as opposed to a coastal study site). The close proximity (~100 miles) of the study area to the University of Alabama campus allows a unique opportunity to frequently sample drip water from multiple locations in the cave. Data collected from the cave samples can be compared to, and calibrated, with isotopic variations of rainfall measured at the University of Alabama campus.

This research will also test if continental speleothems contain an archive of past hurricane impacts. Recent studies in Belize have shown that a record of tropical storms (e.g., hurricanes) can be preserved in cave speleothems (Frappier et al., 2005). Rainfall from tropical storms is isotopically distinct from “normal” rainfall, which has allowed high-resolution negative shifts in δ18O in the growth profile of speleothem material to be attributed to known storm events. This method can be applied to identify both recent and prehistorical storms, thus having the potential of providing the longest and highest-resolution record of tropical storm activity through time derived to date. Data already collected for this study indicate that storm-related precipitation falling in north central Alabama is more negative (Hurricane Dennis, δ18O = -10.8 (‰ VSMOW)) than normal rainfall (δ18O = -4.2 (‰ VSMOW), n = 17 weekly averages). This approach will be tested at DeSoto Caverns to determine if this method can be used in other locations to further our understanding of hurricane variability for the Gulf of Mexico.

Methods

Calibration of the isotopic proxies against instrumental climate records is a key step toward deciphering how the measured isotopic fluctuations truly respond to known climate variability. For this purpose, instrumental climate records dating to 1930 from the surrounding area (Childersburg, Birmingham, AL) will be compared to the isotopic data measured from the stalagmites representing this “instrumental” period. Additionally, the relation between the amount and source of δ18O must be established. Currently, there are no long-term monitoring stations in the Southeast (except on the coast) that monitor both precipitation amount and isotopic signature of the precipitation. This relationship is being
determined for Alabama by measuring precipitation amount by means of a manual rain gauge from which water is collected for weekly isotope analysis ($\delta^{18}$O and $\delta D$) during a two-year period.

Two methods of sampling for isotope analyses are used for this study. Once the stalagmite is halved, a dental drill system is used to tightly sample along the central growth axis. Staggering of drilling locations allows for ~0.2 mm sampling resolution. A computerized micro-drill system allows for resolutions of 0.04 mm and will be used to test if individual tropical storm events can be resolved. A micro-extraction line is used to convert the drilled powder into clean CO$_2$ gas (following McCrea’s, 1950 method) from which stable isotope ratios ($^{13}$C/$^{12}$C, $^{18}$O/$^{16}$O) can be measured using a Finnigan Delta Plus gas source isotope ratio mass spectrometer.

For the cave system under study it is essential to determine if the drip-water (sourced in precipitation) is in isotopic equilibrium with the precipitated carbonate material before $\delta^{13}$C and $\delta^{18}$O proxies can be deemed representative of past climate conditions. Three conditions are indicative of isotopic equilibrium between the drip-water and precipitated carbonate including: 1) $\delta^{13}$C and $\delta^{18}$O do not strongly correlate along the length of the central growth axis, 2) $\delta^{18}$O does not show high variance when measured along a single growth horizon, and 3) $\delta^{13}$C and $\delta^{18}$O do not strongly correlate along a single growth horizon (Hendy, 1971).

Variation of isotopes during the growth of a stalagmite is meaningless unless the timing of the growth can be accurately dated. To ensure our chronology is accurate, four methods of dating will be utilized: Uranium-series, radio-carbon, $^{210}$Pb, and band-couplet counting. Uranium-series dating methods used here are based on the accumulation of decay products of uranium, also known as the daughter-deficiency method (Ku, 2000), and will give a chronology in absolute ages. Radiocarbon ages will be corrected for local reservoir effects and then converted to calendar years using the Internet accessible CALIB 5.0 program (Stuiver et al., 1998a; Stuiver et al., 1998b; Stuiver and Braziunas, 1993). Reservoir corrections are calculated by determining the amount of mixing between the soil CO$_2$ and the “radioactively dead” cap-rock. Accurate dating of the past ~100 years of deposition will be obtained by $^{210}$Pb dating. Radiometric dating will help determine if the band-couplets found in the stalagmites are annual in nature (following Asmerom and Polyak, 2004). Band counting and thickness measurement is possible with the help of a state-of-the-art Nikon stereoscope with a digital imaging system.

**Results and preliminary conclusions**

Isotopic measurement of precipitation collected at the University of Alabama campus has been ongoing since May 16$^{th}$, 2005 (Figure 2). A rain gauge is checked each morning with collected water stored in clean nalgene bottles while making note of the amount of precipitation. Any precipitation falling during the same week (Monday – Sunday) is stored in the same bottle, and once analyzed will represent a weekly average for $\delta D$ and $\delta^{18}$O. Values for $\delta D$ of precipitation are determined to check for evidence of evaporation and to develop a local meteoric water line (R$^2 = 0.94$). The local meteoric water line (Equation 1) is in very good agreement with the global meteoric water line presented by Craig (Equation 2; 1961) as shown below.

\[
\delta D = 8.0 \delta^{18}O + 10.2 
\]  
\[
\delta D = 8 \delta^{18}O + 10 
\]

The $\delta D$ and $\delta^{18}$O determinations show high variability from week to week and were strongly influenced by frequent tropical systems that impacted the Gulf Coast in 2005. Water collected specifically from Hurricane Dennis and Katrina show more “negative” values ($\delta^{18}$O = -10.8 and -6.3 (% VSMOW respectively) relative to average weekly measurements. As expected, a moderate negative correlation (R$^2 = 0.50$) exists between the amount of precipitation and the $\delta^{18}$O for samples collected to date. This relationship will aid in the interpretation of the isotope profiles extracted from the cave speleothems.

Initial analysis of a small (5.5 cm) actively growing stalagmite sampled from DeSoto Caverns in 2002 reveals that the conditions within the cave permit speleothems to form in isotopic equilibrium with the carbonate saturated drip-waters. Correlation of $\delta^{13}$C and $\delta^{18}$O along the length of the central growth axis is not strong (R$^2 = 0.55$). Twenty-one determinations were obtained along a single growth horizon (“Hendy Test”) to test for kinetic fractionation effects. No correlation (R$^2 = 0.16$) is observed along this growth horizon, and 3) show high variance when measured along a single growth horizon (Hendy, 1971).

![Figure 2](image-url) Weekly precipitation amount starting May 16$^{th}$, 2005 relative to $\delta^{18}$O (% VSMOW). Note that the $\delta^{18}$O scale has been reversed to better illustrate the correlation with precipitation amount. Gaps in data represent lack of precipitation.

Greek symbols used in the text:

- $\delta D$ - D delta
- $\delta^{13}$C - Carbon-13 delta
- $\delta^{18}$O - Oxygen-18 delta
- $^{13}$C - Carbon-13
- $^{18}$O - Oxygen-18
band, which is a sign of isotopic equilibrium for its deposition. With the omission of two data points, δ¹⁸O values stay within the accepted variance (0.5 ‰) with increasing distance from the central growth axis. The two “outlier” points are interpreted as the result of imprecise sampling as accurately drilling a single growth band is difficult (even under magnification). Variability of the δ¹³C and δ¹⁸O profiles along the central growth axis of the 5.5-cm stalagmite, representing ~400 years of deposition, show a good correlation to potentially climate-induced petrographic changes of the aragonitic sample. Interpretation of these changes is ongoing as the relationship of precipitation to drip water is better constrained and as radiometric ages become available. A second 50-cm long stalagmite collected in 2005 is currently being analyzed and is expected to reveal 3,000+ years of continuous climate information for the Southeast.

In summary, first indications are promising that a climate signal is preserved in samples collected from DeSoto Caverns. Analysis of local precipitation show interesting influence from tropical storm systems; as well as the anticipated negative amount vs δ¹⁸O correlation. Sampling of both precipitation and drip water from the cave must be continued to accurately understand the climatic factors that influence the isotopic signature of deposited material in DeSoto Caverns. Future work on a 50-cm long stalagmite will provide the longest high-resolution climate record for the southeast United States with an emphasis on precipitation variability and the likely driving force of these changes.

References


THE STABLE ISOTOPE AND THE PALEOMAGNETIC RECORDS OF
CALCITE SPELEOTHEMS IN NORTHERN YUKON TERRITORY,
CANADA: THEIR RELATION WITH CLIMATIC CHANGES DURING
THE PRE-PLEISTOCENE

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In the northern Yukon Territory (Canada), at the latitude of
the Arctic Circle, there is a significant group of limestone
caves located in an area that was not glaciated during the
Quaternary. Permafrost has played an important role in re-
stricting calcite speleothem growth in the caves. U/Th dat-
ing and stable isotopic studies indicate that the speleothems
form two distinct groups, the first group is younger than
350 ka BP, and the second is older than the 350 ka BP limit
of conventional the U/Th alpha spectrometric dating method.
Two large samples from the second group yield sequences
of magnetic declinations and inclinations with reversed and
normals polarity, perhaps dating back to the Tertiary (Lauriol
et al., 1997).

The flowstones analyzed in this study yielded at least two
reversed and one normal polarity chron or subchrons and,
possibly, as many as three reversed chrons separated by two
normal ones. The stable isotopic analyses are compared to the
fluctuations of the paleomagnetic results to verify if a relation
between paleoclimate and paleomagnetism exists.

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Yukon and its relation to permafrost: Canadian Journal of
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CLIMATE AND ENVIRONMENTAL VARIABILITY IN A MID-LATITUDE SAVANNA: OBSERVATIONS FROM THE COLD AIR CAVE STALAGMITES, MAKAPANS VALLEY, SOUTH AFRICA

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The Cold Air Cave project consisted of monitoring the conditions in a relatively small but enclosed dolomitic cave system in the Makapans Valley, and analysis of at least 2 continuous speleothem records, one a 6.5 ka aragonitic (T7) and the other a 24 ka part-calcite/part-aragonite stalagmite (T8). In this paper we discuss the implications of the oxygen and carbon isotope data and the scale and frequency of variability.

The scale of variability in the $\delta^{18}O$ series was immediately observed to be high, and the relationship to temperature direct rather than inverse, in direct contrast to the sole existing southern African speleothem record at that time, the Cango Cave stalagmite. However, the isotopic records for the two stalagmites agree well where they overlap, imparting confidence that the climate records are robust, and the results of our monitoring exercise and comparison with regional records all point towards an interpretation of the $\delta^{18}O$ series as reflecting primarily $\delta^{18}O$ of precipitation. The $\delta^{13}C$ reflects the relative proportions of $C_3$ and $C_4$ vegetation in the catchment, but the shifts and trends in vegetation are only intermittently concordant with those in $\delta^{18}O$. The main trends for both the $\delta^{18}O$ and $\delta^{13}C$ records of T8 in the late Pleistocene are low frequency quasi-periodic shifts. The glacial to interglacial shift is marked by a sharp change in mineralogy from calcite to aragonite followed by a hiatus, and isotope differences are mostly explained by this shift. In the Holocene the $\delta^{18}O$ trend is from more positive to more negative values culminating at AD 1700. Trends for $\delta^{13}C$ differ, from lower values in the early Holocene to higher values at 2-2.5 ka. Continuous wavelet transform analyses on T8 show that greatest strength in $\delta^{18}O$ variability occurs in the 4 and 0.75-1 ka ranges, along with frequency and amplitude modulation. The higher frequency end of the spectrum is very noisy and there is little indication of the presence of a 18-20 year cycle expected by climatologists. Surprisingly, the ~4 ka oscillation is more consistent and prominent in the $\delta^{13}C$ series, as is a band centred within 0.5-1ka.

These observations may suggest that controls on vegetation and rainfall cycles in these middle latitude zones are influenced more strongly by sub-precessional scale variability than by large-scale glacial-interglacial shifts.
EXAMINING SPELEOTHEM $\delta^{18}$O AND $\delta^{13}$C RESPONSE TO PRECIPITATION AND TEMPERATURE CHANGES

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The past decade or so has seen an upsurge in the application of speleothem $\delta^{18}$O records to high-resolution paleoclimate studies especially in the monsoonal regions. However, few such records have been compared with instrumental records to examine the influence of climate changes on the $\delta^{18}$O. In order to investigate climate and environmental significance of speleothem $\delta^{18}$O and $\delta^{13}$C, we collected a 20-cm long soda straw from Furong Cave of southeastern Chongqing in China on October 24, 2005 to conduct such a study.

The chronology of the sodastraw has been determined by $^{210}$Pb profile which shows: (1) the highest total $^{210}$Pb activity is at the tip end of the soda-straw from where cave water was dripping during the collection; (2) a $^{210}$Pb peak exists at ~14 cm depth that may indicate the peak of nuclear tests around 1960; and (3) relatively constant $^{210}$Pb activities between 0 and 10 cm, reflecting supported $^{210}$Pb activities when the samples were older than 120 years (Figure 1). Based on these three features and assuming a linear growth rate, we

**Figure 1.** $^{210}$Pb activity of the soda straw provides the detailed chronology.

**Figure 2.** The $\delta^{18}$O and $\delta^{13}$C records of the soda straw from Furong Cave, Chongqing.
established the chronology of the sodastraw with age uncertainties of about 5%. The sodastraw has continuously deposited since 1830 AD with a growth rate of 0.111 cm/yr.

A total of 34 subsamples at 0.6 cm/sample from the soda-straw were analyzed for δ¹⁸O and δ¹³C (Figure 2). The δ¹⁸O ranges from -9.67 to -7.28 (‰, PDB), with a decreasing trend from 1830 to 1900 and an increasing trend after 1900 AD. The δ¹³C fluctuated around -4.6‰ before 1900 and around -2.8‰ after. This 1.8‰ increase of the δ¹³C may indicate development of karst desertification under human impact above the cave.

Using the δ¹⁸O record of the sample and instrumental records of Chongqing climate since 1891 (5-yr running average shown in Figures 3-6), we examine the influence of climatic conditions on the δ¹⁸O values. Although the climate of Chongqing is strongly influenced by both East Asian monsoon and Indian monsoon, it shows two features which may be different from regionally monsoonal climates: (1) higher precipitations correspond to cold air temperatures (Figures 3 and 5); and (2) a decreasing trend of temperature existed since 1930 (Figure 5). From the comparisons shown in Figures 3-6, we observe that (1) although higher rainfall gives lighter δ¹⁸O in many intervals exhibited by Figure 3, a long-term trend of the δ¹⁸O is negatively correlated with the temperature trend (Figure 5). For the detrended records, the comparisons reveal clearly negative correlations between the Δδ¹⁸O and ΔP (Figure 4), and positive correlations between the Δδ¹⁸O and ΔT (Figure 6) on decadal time scales. Our observations will provide important evidence for interpretation of speleothem records in the monsoonal region of China.
HIGH-RESOLUTION CLIMATE VARIABILITY OF NORTHEASTERN CHONGQING, CHINA DURING 60-70 KA REFLECTED BY A STALAGMITE $\delta^{18}O$ RECORD FROM XINYAN CAVE

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A 26-cm long stalagmite (XY2) from Xinyan Cave in northeastern Chongqing (China) has been dated by means of ICP-MS $^{230}$Th/U in the Isotope Lab of the University of Minnesota. Six $^{230}$Th/U dates and depositional characteristics show that:

(1) the 0-2.3 cm part of the stalagmite was deposited during the past 4,500 years;

(2) a depositional hiatus exists at 2.3 cm; and,

(3) the growth of the 2.3-26 cm part determined by four $^{230}$Th/U dates was between 59.4 and 69.4 ka with a linear growth rate of 0.023 mm/yr. We have analyzed 190 samples for $\delta^{18}O$ and $\delta^{13}C$, mostly in the 2.3-26 cm part (Figure 1). The $\delta^{18}O$ and $\delta^{13}C$ between 59.4 and 69.4 ka reveal decadal-to-centennial climatic conditions during the glacial interval of Marine Oxygen Isotope Stage 4 (MOIS 4), exhibiting much higher resolution than the published Hulu and Dongge records during the same interval (Figure 2). The modern climate in northeast Chongqing is under strong influence of the summer monsoon including our study area can be used as a proxy of summer monsoon strength, with lighter values pointing stronger summer monsoon and higher precipitation, and vice versa. The results and comparisons shown in Figures 1 and 2 as well as

![Figure 1. The $\delta^{13}C$ (above) and $\delta^{18}O$ (below) variations in the XY2 stalagmite with depth.](image)
the growth pattern of XY2 allow us to conduct the following observations, interpretations and discussions:

(1) Three decreases in the $\delta^{18}O$ of XY2 record around 59.5, 64, and 68.5 Ka, may be corresponding to theDansgaard-Oeschger events 17, 18 and 19, respectively, indicating relatively stronger summer monsoon occurring in China during the warm episodes in high latitudes.

(2) The Heinrich event 6 (H6) can be identified in the record witha heavy $\delta^{18}O$ peak around 60 ka, showing strong weakening of

(3) The XY2 $\delta^{18}O$ record shows very rapidly change toward to the interstadial condition of the D-O event, but slow change toward to the cold stadial condition (e.g., the $\delta^{18}O$ decreased more than 1‰ with 100 years at D-O event 18 and gradually increased toward to the cold period of H6, then sharply decreased again at D-O event 17). This phenomenon found in the Greenland ice core records is first time observed in the speleothem records taking the advantage of the fast growth of XY2 during this glacial interval.

(4) According to the SPECMAP $\delta^{18}O$ record, the glacial maximum of MOIS 4 was around 64.5 ka with the boundary of MOIS 3/4 around 60 ka. Unlike the marine record, the speleothem records of China showed in Figure 2 exhibit much high frequent variations without an apparent glacial maximum during MOIS 4. However, the time of MOIS 3/4 boundary seems to be around 60 ka when the Heinrich event 6 occurred, agreeing with the marine record.

(5) Although the above similarities of the major climatic events such as D-O events 17-19, Heinrich event 6 and MOIS 3/4 boundary can be found from the comparison of three records in Figure 2, there are some discrepancies exist among the records. For instance, from 64 Ka to 60 ka, the Hulu $\delta^{18}O$ record remained relatively constant, whereas the $\delta^{18}O$ record of XY2 continuously increased and the Dongge $\delta^{18}O$ record had a decreasing trend. The use of growth rate of stalagmites as a climatic proxy should be done with caution as XY2 mostly grew during the glacial interval, which means that stalagmites do not necessarily grow faster under warm and wet conditions everywhere. Furthermore, the $\delta^{18}O$ values during the late Holocene are heavier than during the MOIS 4 interval of XY2 record and thus raises a question: is it true that the summer monsoon was weaker during the late Holocene than during the glacial MOIS 4?

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Figure 2. The comparison of $d^{18}O$ with the records from XY2, Hulu cave, Dongge cave and the GRIP ice core. H6 represents the Heinrich event 6 and the Arabic numerals 16, 17, and 18 denote the Dansgaard-Oeschger events. XY2-1 to XY2-4 is the $^{230}Th$ age (with errors).
PALEOCLIMATIC CONDITIONS RECORDED IN CAVE SEDIMENTS AS STUDIED BY MICROMORPHOLOGY AND MAGNETIC ANISOTROPY: DOLGANSKAYA YAMA CAVE SYSTEM, CENTRAL SIBERIA, RUSSIA

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Introduction
The cave sediments exposed in the Dolganskaya Yama Cave system, Central Siberia, Russian Federation were studied in order to determine the source of the sedimentary material and the mode of its transportation into the cave system. Such information can be interpreted in terms of governing paleoclimatic conditions in this particular area of Central Siberia.

Location and sampling
The studied cave system is located in the Yablonovy Range, approximately 300 km east of Lake Baikal (54º 30’ N, 113º 50’ E). Eight main caves can be found in broad vicinity of the studied area: Dolganskaya Yama, Plombir, Delfin, Amandak-1, Amandak-2, Pervaya, Izyubrinaya, and Imskaya Caves. The cave systems were developed in Cambrian limestones surrounded by Paleozoic metapelites, and granodiorites.

The Dolganskaya Yama Cave system is located in the NE margin of the Malyi-Amalat Basin (Malo-Amalatskaya Vpadina). The elevation of the surrounding terrain is between 900 and 1200 meters above sea level (m.a.s.l.). Three sedimentary sections located in the Dolganskaya Yama Cave and adjacent Delfin Cave were selected for sedimentological and magnetic anisotropy studies. The field work was carried out during the joint Russian-Czech expedition in March 2005.

Delfin Cave
The entrance of the Delfin Cave lies at an elevation of 1180 m.a.s.l. The studied section is located 36 m below the entrance (Figure 1). The oldest sediments are composed of clays, silts and silty sands deposited in stagnant water. The material of these sediments, possibly originating in surrounding metapelites, was transported over a long distance, and was strongly weathered after deposition. The presence of rounded and weathered quartz grains and a large amount of stable minerals is evidence of these processes. The layers with greater amounts of stable minerals are more radioactive due to increased zircon content. These layers contain more opaque minerals and thus possess a relatively higher magnetic susceptibility. The structure of those parts of the Delfin Cave system explored to date does not allow for long-distance sediment transport. Consequently, it can be inferred that at some point the cave must have been connected with some larger system, most probably with Dolganskaya Yama Cave. After deposition, the sedimentary material was influenced by freezing, and the formation of segregation ice. The evidence of these processes is the presence of cryogenic cracks filled with Fe-oxides (Fitzpatrick, 1984). As described
by Pissart et al. (1999), the origin of such cryogenic cracks is not necessarily connected with alternating freezing and thawing. Cryogenic cracks can exist due to the presence of permafrost, which signifies an average annual surface temperature less than – 4 °C (Small, 1978). The temperature inside cave systems usually reflects the average temperature on the surface.

The sedimentary material in the central part of the section is composed of a mixture of silts and microblocks of old clays. All sedimentary bodies of this type are affected by turbation due to freezing. Microtextures of this material contain segregation ice structures only inside clayey microblocks. Cryoturbation in such of such an extent is possible only under the special condition where there are temperature changes of more than 4 °C. Such conditions could not exist in a cave environment, especially at 36 m underground with no exchange of air, yet cryoturbation structures were observed. This anomaly can be explained only by a significant change in climatic conditions. The layers of clay and silt material originally deposited in stagnant water were later disturbed by frost, as evidenced by presence of permafrost. Later, as a result of climate change, the amount of rainfall increased. Such periods were described, e.g. at the beginning of the Holocene (Gasse, 2000). Due to increased rainfall, the fill of chimneys melted and was transported together with rainwater into the cave system. The original cave fills were disturbed and mixed by gravity. The temperature difference between rainwater and cave sediments was more than 4 °C. Warmer water induced thawing of sediments and recently supported them by water. Because of their thermal conductivity, surrounding rocks and sediments changed the temperature of sediments into the previous cooler phase (Small, 1978). This scenario was likely repeated several times and stimulated surface conditions typical for cryoturbation.

The upper part of the section is composed of poorly sorted silts with blocks of limestones and metapelites. The sediments are very porous and no stratification can be observed, indicating a colluvial origin, i.e. sediments transported in cave chimneys by gravity and rainfall. Colluvial sedimentation is usually triggered by increases in rainfall due to climatic change. This rainfall, probably melt chimney filling, and sedimentary material was transported into the cave by gravity and rain water. The sediments contain none of the microfeatures characteristic of freezing such as segregation ice, frost heaving, frost creep or cryoturbation.

**Dolganskaya Yama Cave**

The Dolganskaya Yama Cave, the largest cave in the area, predominantly consists of a system of vertical shafts. Its abyss-like entrance lies at an elevation of 1167 m.a.s.l. Although the cave system is very poor in sediments the pre-
Figure 3. A simplified sketch of the interesting segment in Dolgan 2 section.

Sedimentary fills reflect sedimentary conditions different to those in the Delfin Cave. Two sedimentary sections located 100 m and 120 m below the cave entrance, denoted as Dolgan 1 and Dolgan 2 sections, were studied.

Sediments from the Dolgan 1 section (Figure 2) originated in stagnant water during an earlier stage of the cave’s development. They are situated in a concave basin, probably connected with the cave system in its lower part. The material in this section was post-depositionally influenced by freezing. Freezing microstructures, as described by Fitzpatrick (1984) and Pissart et al. (1999), were observed in several parts of this section. Before deposition, the material was altered by long transport and weathering. The lower part of the section is probably older because quartz grains found there possess features typical of a longer period of weathering. Magnetic susceptibility findings reflect increasing amounts of more stable heavy and opaque minerals and more weathered material.

Sediments sampled in the Dolgan 2 section (Figure 3) originated in stagnant water. Later, they were influenced by freezing and redeposited into their current position. The material was altered by long transport and by weathering before deposition. Despite this fact small blocks (3 mm³) of primary clay sediments with frost structures can be recognized. Postdepositional frost structures connecting the clay blocks with the younger matrix were not observed. Sediments in the Dolgan 2 section are probably younger than the sediments in the Dolgan 1 section. Although the sediments in the Dolgan 2 section were not deposited during a very cold period some thermonannuel structures can be observed. This type of structure originates during slope processes when the base is composed of a freezing layer and the upper moving parts are composed of a thawing layer. As a result of such movement flame structures usually evolve.

**Magnetic anisotropy**

Anisotropy of magnetic susceptibility (AMS) has been widely used as a powerful and fast indicator of rock fabric for various types of rocks. In sedimentary rocks the magnetic fabric reflects the gravitationally induced preferred orientation of magnetic minerals. Primary depositional magnetic fabric is oblate in shape with magnetic foliation (plane normal to minimum magnetic susceptibility direction) being sub-parallel to the bedding. A weak magnetic lineation (direction of maximum susceptibility) is parallel to current direction, or, in case of turbidity flows, perpendicular to it (Hamilton and Rees, 1970). The degree of anisotropy, reflecting the degree of preferred orientation of magnetic minerals, depends on the amount of compaction imposed on the rock. For uncompacted sediments the degree of anisotropy usually does not exceed 5% (Rees and Woodall, 1975).

The magnetic susceptibility (MS), which indicates concentration of magnetic minerals in sediment, can be generally used for the determination of source material and for the correlation of different sections in the cave system. The magnetic susceptibility (MS) values for the entire set of studied samples are in the range of $46-3056 \times 10^{-6}$ SI. Such a wide range may reflect differences in the source material for the various part of the cave system. Indeed, the MS values in Delfin and Dolgan 1 sections are relatively low ($<100 \times 10^{-6}$ SI or $<250 \times 10^{-6}$ SI, respectively) compared to those of Dolgan 2 section where MS ranges between $100-1000 \times 10^{-6}$ SI. The red clays encountered in the uppermost part of Dolgan
1 section (Figure 2, no’s 14, 15, 16, 17) possess MS one order of magnitude higher than the MS of underlying sediments.

The shape of magnetic fabric for most samples is oblate. The degree of magnetic anisotropy varies in the range of 0.5–12 %. In Delfin and Dolgan 1 sections the anisotropy degree is very low, not exceeding 1.5 or 3 %, respectively. In contrast, some samples in Dolgan 2 are relatively highly anisotropic (up to 12%). These samples possess the highest MS values suggesting that the degree of anisotropy depends on mineralogy of different sedimentary layers.

There is no pronounced preferred orientation of the principal fabric elements in the sampled sedimentary sections (Figures 1, 2, 3, insets). Even though the magnetic foliation is sub-parallel to the stratification for the majority of samples, there are samples possessing magnetic foliation oriented almost perpendicularly to the general orientation of stratification. Although the orientation of magnetic lineation is very variable, the maximum susceptibility directions are confined to the planes of stratification. Despite that fact, no preferred orientation of magnetic lineations within the bedding plane is observed, and no current direction can be estimated. Such a dispersed pattern of principal susceptibility directions is not typical for undisturbed sediments. It seems that the primary depositional magnetic fabric was later disturbed by microturbation, most probably connected with the cryogenic processes.

Conclusions

Sedimentary conditions in the Dolganskaya Yama and Delfin Caves have been significantly influenced by climatic changes. These changes are evidenced by the apparent existence of deep permafrost during some earlier climatic phase and by increased rainfall, probably sometime at the end of the Pleistocene or beginning of the Holocene.

Acknowledgements

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Speleothem δ¹⁸O records have been used for paleoclimate reconstructions. However, as speleothem δ¹⁸O is a function of cave temperature, surface rainfall and δ¹⁸O of precipitation, etc., the interpretation of the δ¹⁸O is rather complicated. The lack of comparison of the δ¹⁸O with climate parameters such as rainfall and temperature recorded by instrument and historic documents obscures the climatic interpretation of the δ¹⁸O records. Here we attempt to use the δ¹⁸O record from Dongge Cave to compare with instrumental and historic records in the nearby cities of China (Figure A) for investigating the climate significance of the δ¹⁸O. In previous studies including Wang et al. (2005), stalagmite δ¹⁸O records in China reflect mainly monsoon strength, showing lighter δ¹⁸O values indicating stronger summer monsoon with higher precipitation; and vice versa. Our questions about the speleothem δ¹⁸O records in the monsoonal regions of China include: (1) does one single δ¹⁸O record represent regional climate change? and (2) does speleothem δ¹⁸O record reflect precipitation variation? In order to search the answers of these questions, we first check their similarities and discrepancies in climates in terms of wetness changes recorded by instruments and historic documents at different locations in the same monsoonal region; then compare the δ¹⁸O record from Dongge Cave with the record of wetness changes in the nearby city.

Our comparisons show that although strong similarities of instrumental rainfall records exist between Guangzhou and Guiyang, apparent discrepancies (around 1960 and after 1980) in the records indicate that the precipitation change in the monsoonal region is not uniform with certain distance (Figure 1a). These discrepancies decrease with the distance.
between two sites, e.g., between closer sites of Guangzhou and Hongkong (Figure 1b). Figure 1c exhibits good correlations between instrumental rainfall record of Hongkong and historic record of Drought-Wetness index in Guangzhou which was reconstructed from the officially written documents in the local government in the area back to 1470 AD, indicating the reliability of the historic record (1 denotes the wettest condition and 5 is for the driest condition). We further compare the historic records between Guilin and Guangzhou for the past 500 years to check their similarities and discrepancies in Drought-Wetness condition for longer periods, which shows that 60–70% of the records correlates well (Figure 2a). However, the correlations become less for lower resolution time scale (15-yr running average instead of 5-yr running average) (Figure 2b), which may imply different controlling factors of rainfall on various time scales at each sites though the two locations are only about 380 km apart. The controlling factors to cause such discrepancies remain unclear, but it is very important to find out these factors. In the last step, we compare the Dongge $\delta^{18}$O record with the historic drought-wetness record of Guilin for the past 500 years that has true chronology (Figure 3). Although the Dongge $\delta^{18}$O record has high-precision U-series dating chronology and calibrated with the well dated $^{14}$C record, it may still involve some age uncertainties compared with the historic record. Nevertheless, the comparison in Figure 3a still exhibits large discrepancies regardless of the age uncertainty. However, the detrended $\delta^{18}$O record seems to have better correlations to the historic DW record although poor correlations still exist before 1500AD and after 1900AD. These comparisons indicate that the $\delta^{18}$O record may not fully represent precipitation changes caused by monsoon variability, perhaps involving other influences such as temperature effect and moisture source change. Hence, these other influencing factors on speleothem $\delta^{18}$O must be evaluated by detailed studies on the mechanisms of isotopic fractionations in cave stalagmites. Furthermore, a few speleothem $\delta^{18}$O records in a single cave may not reflect regional precipitation change even under the similar climatic settings.

Figure 2. (a) Comparison of the 5-years running averages of DW index records between Guilin and Guangzhou. (b) Comparison of the 15-years running averages of DW index records between Guilin and Guangzhou.

Figure 3. (a) Comparison of the $\delta^{18}$O record, and (b) 3-point running averages of detrended $\delta^{18}$O record from Dongge Cave with the 5-years running averages of DW index record in Guilin. Although Guiyang is more close to Dongge Cave, the geographic setting of Dongge Cave is more similar to that of Guilin.
In the summer of 2005, the Deutsche Forschungsgemeinschaft (DFG) approved funding for the Forschergruppe (FG) 668 (DAPHNE). In this interdisciplinary research group several researchers and scientists from Heidelberg, Bochum, Innsbruck and Trento collaborate to study speleothems over a period of six years. The intention of DAPHNE is to understand the basic mechanisms which control speleothem growth and composition by the combined application of field and laboratory experiments. In particular, the impact of kinetic fractionation processes on the oxygen isotope signals recorded in speleothems will be quantified.

The knowledge of these basic mechanisms will allow for the first time to obtain high resolution information about the intensity of past precipitation and temperature from stalagmites. Hereby, speleothems will advance to a precisely dated continental archive providing quantitative climate information. By the application to Late Quaternary speleothems we will reconstruct the temporal and spatial variability of precipitation and temperature on a supra-regional scale. These data will represent an important basis for prognostic climate modeling.
SEASONAL CHANGES IN THE ISOTOPIC COMPOSITION OF CAVE AIR, WATER AND SPELEOTHEM CALCITE IN NEW ST MICHAELS CAVE, GIBRALTAR: UNWANTED NOISE OR A TOOL FOR DECODING SPELEOTHEM CLIMATE RECORDS?

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Introduction

The Gibraltar peninsula is in a unique maritime location at the western entrance to the Alboran Basin, where airflows are channeled E-W between the Sierra Nevada and Atlas Mountains. The strongly seasonal climate features hot, dry summers (average 24.3°C) and wet, cool winters (average 13.5°C). Caves containing speleothems are well developed in Gibraltar with St Michaels Cave known since Roman times. Many other natural caves have been developed for civic or military purposes but Lower St Michaels Cave was not discovered until 1942 when a new entrance tunnel at 340 m a.s.l. exposed a rift leading to a lower series of caves leading to a terminal lake. New St Michaels cave has a number of roof seeps and ephemeral drips with local development of active speleothem growth.

A small actively growing stalagmite (GIB04a) recently sampled was analyzed using the following methods: U-Th dating, C-O stable isotope analysis at decadal to sub-annual resolution, trace element geochemistry by ICP-AES and LA-ICPMS, and laminae counting. The 45mm tall speleothem is composed of a pale amber calcite with paired dark-light laminae averaging 750 microns in thickness, draping Pleistocene flowstone. Cyclical stable isotope variations across the paired laminae have been resolved by micromilling at 100 micron resolution (Mattey et al., 2005) with regular oscillations in δ13C about a relatively constant mean value of -11‰ VPDB. The lowest δ13C values are typically around -12‰ and rise by 1–2‰ before falling back to this base value. This pattern of variation is related to the fabric of the paired laminae with the dark compact calcite possessing the lowest δ13C values and the white dendritic fabric possessing the highest δ13C values. The δ18O profile is more complex but also shows oscillations that are correlated with δ13C, super-imposed on longer term variations of up to 2‰.

The correspondence of cyclical variations in stable isotopes with the paired laminae strongly suggests seasonal control on speleothem growth in New St Michaels Cave. Trace element analyses by LA-ICPMS have been performed along two short traverses to understand the relationships between the paired annual laminations (dark compact - light palisade or dendritic) fabrics. Results show that Sr, Mg and Ba show a sympathetic relationship with low Mg/Ca and Sr/Ca in dark calcite with rising values as white fabric develops. Significantly, P shows antipathetic behaviour with Mg and Sr with peak concentrations in dark calcite. These results provide strong evidence that dark calcite was precipitated during the winter with P flushed from soil by the first rains, then as the summer season developed and the cave dried, Mg and Sr rise as a result of increasing residence time in the aquifer, with the development of a light dendritic fabric.

In order to fully understand the origin of annual isotopic cycles and their significance in the interpretation of climate records a program of monitoring temperature, humidity, soil and cave air pCO2 and cave water chemistry has been carried out since June 2004. A series of sampling stations forming a transect from the show cave, though the entrance rift system, along the main chamber of New St Michaels Cave to the terminal lake have been monitored for temperature and humidity at approximately monthly intervals. Monthly environmental data have been augmented with continuous data logging since December 2004. Monthly air samples are collected by pumping into 3l Mylar bags for analysis of the abundance and δ13C of CO2 and CH4. Conductivity, alkalinity and pH of cave water collected from roof drips and the terminal lake are measured on site, and bulk samples taken for analysis of trace elements, DIC δ13C, δ18O and δD. Water drip flow rates have been monitored using high resolution acoustic drip counters. Additional background monitoring of temperature and the abundance and δ13C of CO2 and CH4 in soil above the drip site has been carried out.
and supplemented with meteorological data collected by the RAF Gibraltar Met Office 3 km from the cave site.

Summary of monitoring results

Temperature, 18.9±0.2°C, and humidity, >95%, do not show evidence of seasonal variation at the GilB04a site which is 130 m from the show cave area and separated by constricted passages before opening out into the large New St Michaels chamber. This contrasts with the show cave area that undergoes significant seasonal temperature and humidity variations. $pCO_2$ in the soil zone above the cave varies from 500 to over 2000 ppmv over the year and peaks in late spring then steadily falls as the summer drought develops, with a sharp peak in the late autumn immediately after the first winter rain. Cave air $pCO_2$ is also highest during the late winter (up to 3000 ppm) when the cave is wettest, and falls as the water and surface $CO_2$ supply declines, forcing increasing calcite supersaturation in cave seepage waters as the summer proceeds. Under winter conditions of high cave air $pCO_2$ and lower calcite supersaturation, calcite deposition takes place on the stalagmite under largely equilibrium conditions to form dark compact calcite. As drip rates and $pCO_2$ declines over the summer, calcite saturation rises, increasingly favouring early calcite precipitation as roof straws and elsewhere in the aquifer. Cave air $\delta^{13}C$ variations are related to mixing between background atmosphere and a cave end member with a relatively constant value around −22‰ degassed from cave drip water. Cave air CO$_2$–CH$_4$ relationships are particularly interesting and provide evidence of the extent of periodic deep ventilation of exterior atmosphere. Current data provide evidence of a period of deep ventilation during the spring although it remains to be seen whether this feature will be reproduced in 2006.

Drip monitoring has been carried out at 5 min resolution using acoustic drip loggers and shows a variety of hydrological regimes with an evolving picture as the 2005/6 winter wet season proceeds. At one site a 6 hour lagged response to rain events switched to a non-linear response pattern within 2 months of the onset of winter rain, when flow rates became variable and unrelated to rain input. Other drip sites have switched off intermittently as the winter season develops. Changes in flow regime are correlated with trace element chemistry and $\delta^{18}O$ analyses for drip water through the annual cycle are currently underway. Drip water cation composition, pH, alkalinity and DIC $\delta^{13}C$ all show subtle evidence of seasonal change consistent with increased calcite saturation during the summer. While soil $pCO_2$ concentrations show strong seasonal change, peaking in the early spring (before summer drought inhibits vegetative respiration) cave water DIC $\delta^{13}C$ variation is relatively small indicating that the seasonal change observed in the high resolution GIB04a record is driven by kinetic fractionation or prior calcite precipitation in the aquifer under lower water flow rates.

One of the implications of monitoring data is that variability (increasing) $\delta^{18}O$ of summer speleothem growth is a result of evaporation effects in the shallow unsaturated (epikarstic) zone, modified in wet years by more effective flushing of winter precipitation. Kinetic fractionation and/or evaporation within the cave during the summer months may also contribute to elevated $\delta^{18}O$ values. These are preliminary conclusions requiring further observational data over more yearly cycles (the winter of 2004/5 was exceptionally dry) but illustrate the importance of this work in understanding the isotope modification of rainwater through the unsaturated zone into the cave.

Discussion and conclusions

Seasonality is encoded in the stable isotopic composition of modern speleothem calcite in New St Michaels cave and arises from competing effects which are primarily the changing availability of respired $CO_2$ in the soil zone, and the influence of the hydrological flow regime on degassing rates which controls cave air $CO_2$ concentrations. Decreasing cave air $pCO_2$ over the summer forces calcite supersaturation and a rise in $\delta^{13}C$ values in drip water and is preserved in speleothem calcite. $\delta^{18}O$ values of drip water are relatively insensitive to kinetic processes in the cave environment but change in response to summer evapotranspiration processes in the soil zone and mixing in the aquifer. Winter speleothem growth is thus characterized by calcite with the lowest $\delta^{13}C$ values, coupled with low Mg/Ca, low Sr/Ca and high P/Ca from which the climatically significant winter $\delta^{18}O$ signal can be identified.

Seasonal variation in $\delta^{13}C$ and $\delta^{18}O$ in speleothems is a newly observed phenomenon, revealed in $\delta^{18}O$ by Treble et al. (2005), and in both $\delta^{13}C$ and $\delta^{18}O$ by Mattey et al. (2005) and Johnson et al. (2005) and may be a component of unresolved isotopic noise widely observed in moderate to high resolution speleothem isotopic records. Seasonality may generate biased climate interpretations if growth takes place preferentially in one or other season. However, fully resolved seasonal records provide new opportunities for detailed interpretation of isotope records both in terms of rainfall event frequency and secular change in mean annual temperature (Mattey et al., 2005).

References


RAINFALL SEASONALITY IN TROPICAL STALAGMITES DISCERNED FROM MAGNESIUM AND PHOSPHORUS PARTITIONING IN SUB-ANNUAL COUPLETS

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Introduction

Trace elements distribution in speleothems is an emerging and promising tool for climate reconstruction studies. Elemental variations in speleothems have been used to reconstruct groundwater residence time, rainfall, air temperature, and growth rates (Roberts et al., 1998; Fairchild et al., 2001; Finch et al., 2003; Treble et al., 2003). Among a plethora of trace element proxies used in speleothems, magnesium (Mg) and phosphate (as P) hold a prominent place because their chemical behavior in the karst hydrologic cycle is better understood than other elements (Fairchild et al., 2001). A recent study of stalagmites from five Western European caves by Fairchild et al. (2001) has suggested that Mg and P variability may be used as seasonality proxies. However, because Mg and P partition between drip water and stalagmite calcite are controlled by both temperature and rainfall variations, and the former shows high seasonality contrast in “cold” caves, it is still unclear what is the dominant ambient factor governing the distribution of both Mg and P in stalagmites.

The purpose of this study is to test whether sub-annual cycles in Mg and P are a feature of tropical speleothems from Niue Island (19° 00’S; 169° 50’W), a large uplifted former atoll in the South Pacific. The mid-ocean island of Niue offers unusually advantageous circumstances for performing the test on account of (Aharon et al., 2005; Rasbury and Aharon, 2006) (i) practically invariable cave air temperature of 26°C; (ii) humidity close to saturation point (89%); (iii) contrasting seasonal rainfall with abundant austral summer monsoon and relatively dry austral winter, and (iv) layered stalagmites consisting of couplets showing thick, light, calcite bands deposited during the austral summer alternating with thin, dark, calcite layers deposited during the austral winter.

Results

High-resolution X-ray mapping by electron microprobe (EMP) were conducted on a stalagmite (ASM1) sampled in 2002 in an active growing position from a flank-margin cave on Niue Island. The stalagmite shows absence of any growth interruption and contains conspicuous light and dark subannual couplets (see Figure 1 in Bersch et al., this volume). Its growth rate, based on AMS radiocarbon assays and couplets counting, is estimated to be 0.35 mm/yr (Rasbury and Aharon, 2006). Viewed this way, the 61 mm long stalagmite contains about 174 years of deposition record. Figure 1 shows X-ray maps of Mg and P distribution in an area of approx. 16 mm² at the bottom of the stalagmite. The maps indicate a consistent inverse relationship...
between Mg and P in accord with the findings of Treble et al. (2005) study of a stalagmite from a southern Australian cave. Comparison of optical couplets with the Mg map (Figure 2) indicates that relatively high Mg concentrations (~1.50 wt %) are generally associated with thin dark layers formed during the dry season. Conversely, optically light calcite layers formed during the wet season exhibit relatively low Mg concentrations (~0.51 wt %). Figure 2A also suggests that the top of optically dark, thin, Mg rich layers displays the maximum elemental concentration and likely represents the transition between dry and wet seasons. Thus, negatively correlated variations in Mg and P may act as reliable paleohydrology indicators in the case of the Niuean stalagmites. X-ray maps also provide useful information concerning the intricate growth pattern of the stalagmite that is absent in the optical images. For example, while the optical images exhibit a bladed transition between the sub-annual bands, the elemental distribution depicts a complex “crenulated” structure at the transition level (Figures 1 and 2). These observations are in agreement with the conclusion reached by Treble et al. (2005) using SEM images.

In addition to Mg and P, this study also examines the potential of using X-ray mapped sulfate (as S) variations as proxy for sub-annual cycles in speleothems from tropical climate settings. Preliminary results indicate that S correlates positively with P but negatively with Mg. Ongoing study focuses on determining the S source(s) in Niuean stalagmites, considering volcanic aerosol and seawater-derived sulfate as potential sources.

In summary, our results indicate that high-spatial resolution X-ray maps derived by EMPs are useful in determining the systematic incorporation of trace elements into speleothem calcite laminae. The technique is particularly successful in discerning the sub-annual growth cycles in stalagmites.

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100 YEARS OF VEGETATION AND LANDSCAPE CHANGES WITHIN WIND CAVE NATIONAL PARK, SOUTH DAKOTA, USA: A PHOTOGRAPHIC RECORD

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Introduction

Wind Cave National Park (WICA) in the Black Hills of South Dakota offers the opportunity to explore 114.5 km² of a once vast ecosystem, the mixed-grass prairie of the Great Plains (Figure 1). Many grasslands have been changed to accommodate increased tourism. Development has affected local watersheds, disrupted ecosystems, and altered cave hydrology. Many vegetation and landscape changes within the boundaries of WICA during the past 100 years are a consequence of environmental, climatic, and anthropogenic factors. Changes are also evident within Wind Cave, many of its small lakes have decreased number and size in recent years. In this paper, we compare photographs taken in the early 1900s to recent photography to determine the affects on local watersheds and ecosystems. Recent photographs reveal denser forests with an increase in Pinus ponderosa (Ponderosa Pine), expanding ranges and species types of invasive plants.

Species types are determined by environmental, climatic and anthropogenic factors. Predicting the effect humans have on the environment is often challenging because shifts in vegetation evolve slowly and are often difficult to recognize in short time spans. Climatic influences at WICA may include increased $p$CO$_2$ content, which has shown to decrease vegetation cover, leaving additional space for woody plants and trees (Srivastava, 2001). Increased global temperatures over the past 50 years are in part attributed to increasing greenhouse gasses. Human settlement of the area also influences vegetation; invasive plants follow human populations. Many invasive plants establish quickly and often outgrow native plants.

Geohydrologic setting

Wind Cave is a rectilinear maze with more than 188.8 km of surveyed passage. The cave underlies a surface area of 1.8km², and is formed within the Mississippian Pahasapa Limestone. A red shale in the lower Minnelusa Formation confines the Pahasapa Limestone, above which are 400-850 m of sandstone and sandy dolomite. The strata in the cave dip southeast at approximately 4 degrees (White and Deike, 1962). Passages in Wind Cave range from 1 to 10 m², but can be up to 100 m² or more (Bakalowicz et al., 1987).

Exploration in Wind Cave extends to the local water table, 160 m below the highest point of the cave (Ford et al., 1993). Historic measurements demonstrate that the water table has declined steadily 0.4 m every 1000 years since 400 ky B.P. (Ford et al., 1993). Calcite rafts, an indication of slowly declining or stagnant water table positions, are found in the cave 40 m above modern water levels; above this level no calcite crusts are present. Lakes within Wind Cave respond
to precipitation, suggesting a rapid travel time from the surface to the water table.

The isotopic composition of pervasive euhedral calcite in Wind Cave reveals global climate changes. In particular, during the most recent glacial maximum (ca. 20-25 ky B.P.), the water table was 10-20 m below modern levels (Clark and Mix, 2002; Ford et al., 1993). Lake levels have also fluctuated seasonally by approximately 1.5 m since their discovery in 1968.

**Changing vegetation patterns**

No quantitative records were kept in WICA during the early 1900s; therefore, the only means of comparison is through photographs. Although this does not give a precise means of comparison, extensive changes can be recognized and documented. Sixteen photographs taken in the early 1900s were located in WICA museum archives. Locations of thirteen photographs were established and re-shot during the spring and summer of 2004. The original photographs were compared to the recent photographs to determine changes in the vegetation patterns.

A quick look at each set of photographs reveals an increase in forested areas. A closer study will expose a change in the types of herbaceous plants present within the park (Figure 2). These changes are the effect of a variety of anthropogenic and natural causes. WICA quickly became a premier attraction in the early 1900s. As the number of visitors to WICA increased, the need for a larger visitor center, more parking, and a larger campground also increased. Each of these changes helped make the park more accessible to visitors but reduced the amount of natural vegetation in the area. Animal populations, local watersheds, and cave hydrology have each shown changes related to decreased vegetation and increased run-off.

Increased tourism heightened the introduction of non-native species. Currently, over 100 invasive species can be found throughout WICA boundaries as well as across the range of precipitation, suggesting a rapid travel time from the surface to the water table.

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**Figure 2.** Photographs for comparison of vegetative changes in WICA. Upper Photographs: Photographs were taken looking south, at the main road leading to the visitor center of Wind Cave National Park, approx UTM location: 622825 E, 4824675 N. Original photo circa 1915. The new photograph shows a widened road, enlarged parking lot, and an increase in number of Ponderosa Pines. The canyon in the left of the original photograph has been filled and is now covered by a dense forest. The canyon originally lied adjacent to Wind Cave. Lower Photographs: Photographs taken looking north, toward the visitor center and elevator building, approx UTM location: 623150 E, 482360 N. Original photo circa 1934. An increase in woody shrubs and invasive plants can be seen in the foreground including Yucca glauca (Small Soapweed), Crategus rotundifolia moench (Northern Hawthorn), and Juniperus communis L. (Common Juniper). An increase in Ponderosa pines can be seen surrounding the visitor center and in the hills in the background. The new photograph shows one hill which is not covered by a dense forest; a wildfire occurred here in 1988. Increased numbers of herbaceous plants were found here after the fire.
Western Great Plains. Today, 5-25% of all vascular plants in the United States are non-native (Vitousek, 1996). Invasive species often out-compete native plants, causing expensive problems for rangeland, crops, and commercial forests.

Throughout the past 0.75 million years, Earth has undergone repeated global cooling and warming cycles which are related to features of the Earth’s orbit (Alley, 2003; Zachos et al., 2001). These cycles have affected climatic variables such as the amount of radiation, precipitation, and the temperature determine rates of ecosystem processes from net primary production levels to soil development (Swetnam and Betancourt, 1998). Early Holocene grasslands contained numerous short and tall grass species. A rapid increase in area and species of mixed grassland occurred rapidly ca. 11000-9000 yr BP; however, the mid-Holocene unconformity (ca. 8000-4500 yr BP) suggests a lack of vegetation as a result of a drier climate (Fredlund and Tieszen, 1997). According to studies done by Guo et al. (2004) and Srivastava (2001) both species number and total biomass decrease during warming conditions. Grasslands once covered one third of the continent (Fredlund and Tieszen, 1997). However, grasslands represent only 24% of the vegetation in the world today; much of the area previously covered by grasslands has evolved into dense forests dominated by Pinus ponderosa (Ponderosa Pine trees) and small patches of grasslands which are overshadowed by non-native species.

A large increase in the number and size of Ponderosa Pine trees (Pinus ponderosa) can be seen in WICA. This has occurred in part because strict fire suppression has been practiced throughout the nation, particularly in the Western United States (Wienk et al., 2004; Guo et al., 2004). Wildfires occurred in 14-year intervals until 1879, when fire suppression began (Wienk et al., 2004). After this time no fire scars were found on trees in the Black Hills and Pinus ponderosa rapidly outgrew most other vegetation to become the only tree in many forests of the Black Hills (Hoffman and Alexander, 1987).

Wind Cave is naturally host to many small lakes which are present underground, existing within open cave passages. Recently, the number and size of these lakes has decreased, because of the reduction in available water present in the vadose zone. The amount of water has decreased presumably because of the increase in Pinus ponderosa, which are heavy, wasteful users of water (Thompson, 1971). An experiment by Thompson (1971) proved that clearing low quality pines can increase forage production up to 168,000 kg per km². Thinning dense pine stands would yield multiple benefits including profits associated with wood production, increased herbaceous plants and shrubs, and increased animal habitat (from an increase in vegetation).

Final remarks

The vast increase in Ponderosa Pines and invasive plants has significantly affected the local ecosystem and cave hydrology. Grasslands once present in WICA have decreased in size, some have completely disappeared. Because of shrinking grasslands, many animals have left the area, lakes present in Wind Cave have decreased in size and number, and less water is freely available in the vadose zone. Reintroducing fire cycles, removing low quality Ponderosa Pines, and reintroducing native plants would help to restore some of the lost qualities to WICA.

References


PRELIMINARY CLIMATIC INTERPRETATION OF SEDIMENTOLOGIC AND ROCKMAGNETIC DATA FROM THE CAVE PESTERA CU OASE (SOUTHERN CARPATHIANS, ROMANIA)

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Introduction

In this study we report the results obtained from a cave situated in the western part of the Southern Carpathians (Romania). The cave became famous following the discovery of the oldest modern human of the European continent (40500 cal. years BP, Trinkaus et al., 2003) and of a rich deposit of cave bear bones. The cave was used by bears for at least 4000 years around 43000 years BP (Quilés et al., in press).

A large shaft of the cave was filled almost completely with underground stream sediments in the beginning and uniform to laminated lake sediments in the final stages. Later on, the shaft was partially reopened and the sedimentary sequence exposed. We trenchened and sampled in detail 9m of this sequence for sedimentological and magnetic analyses. To identify climatic oscillations in our sequence, we compared magnetic and sedimentological data, examined the magnetic mineralogy in detail, and measured bulk sediment particle-size distributions. The very close correspondence between magnetic properties and paleoenvironmental indicators may result from one or more factors. Possible factors include detrital dilution of magnetic signals, diagenetic alteration of iron-oxide minerals, authigenesis of new magnetic minerals, and climatically-controlled catchment processes of weathering and sediment transport.

The upper age of the sediment is constrained by the age of a stalagmite taken from the surface of the clay deposit. Two exploratory 230Th dates were performed by alpha-spectrometry at the U-series laboratory, University of Bergen, Norway. The two ages are (16.4 ± 1.3) ka and (16.0 ± 1.7) ka. The next time control is provided by the presence of bear bones only in one of the coarse layers situated in the middle part of the section (between 5.2 – 7.2 m depth). This implies that at least the upper part of the section was deposited during marine isotope stages 2 and 3.

Sedimentological data

Trench logging provided information about sedimentary structures, rough grain-size distribution through the sediment column, colors and composition of the sediment (Figure 1). The upper 2 m are composed of dark red laminated clays and silts. Lamination is generally parallel but some wavy laminations also occur. The following 1.5m consists of massive red clays resting on 1 m breccia with 60% red clay matrix. Clast composition in the breccia unit is dominated by limestone and subordinate clay pebbles; upper limit is sharp while base limit was affected by differential compaction suggesting a mudflow unit. Half meter of massive red clays separates the upper breccia unit from a lower one. The second breccia unit (2 m thick) is densely packed, with less than 40% clayey matrix and composed only of limestone
and bone fragments. This could be a debris flow unit washed from the upper levels of the cave where bone deposits have been found. The next 1 m is a massive clay deposit containing scarce limestone clasts. The last 1 m is composed of stratified sands draped by thin silt units. Everything is resting on coarse grained terrace deposits with various allochthonous clasts.

In laboratory we analyzed calcimetry, organic matter, and grain-size distribution across sediments from the shaft. Calcimetry was determined by volumetric method measuring the CO$_2$ resulted from the reaction of dried samples with 4M HCl using the Eijkelkamp calcimeter. Loss on ignition after 6 hours at 550°C was used to quantify the organic matter. Almost all samples collected have been analyzed for calcimetry and organic matter.

Calcimetry values are quite different throughout the section with very low values (around 0.1%) in the upper 4m and high values (around 10%) downward (Figure 1). This difference is mainly given by the limestone pebbles content and not by climatic control on the fluid saturation. The persistence of low values over the entire fine grained deposit of the section could indicate the provenance of silty-clayey material from paleosoils or carbonate-free source material. This sediment could only be brought to the area around cave by winds or surface streams since it could not have formed solely from the weathering of the underlying limestone bedrock. However, such a continuous delivery of fine grained sediment to the cave needs a storage reservoir of the primary detritus, something like a slackwater pool. If the parental material contained some iron sulfides then their oxidation in a pool would have generate strong acid environment capable to dissolve any carbonate mineral and so delivering to the cave a carbonate-free fine grained material.

The organic matter has a reversed pattern in comparison to calcimetry: with high values in the upper 4m and low values downwards (Figure 1). It is a good correlation between the lamination structure which is only present in the upper 2 m of the analyzed sequence and the oscillating values of the organic matter. This aspect could reflect periodic input of organic matter from outside the cave together with coarser grains and mica which gives the lamination structure. When the sedimentary structure becomes massive the values are less oscillating. Generally, the organic matter content is rather high even when low relative values they reach 5%, while the highest values are around 15%. These high values are located just over the mudflow unit at about 3.5-3.7 m counted from top of section. Such anomalous high values for organic matter are hard to explain by pedogenesis solely. North of the cave, upstream along Ponor valley, Paleozoic organic rich sedimentary deposits crop out. They are composed of bituminous shales, siltites and sandstones with coal layers intercalated. It is highly possible that much of the organic matter from cave sediments is derived from Paleozoic rocks.

The entire sedimentary section is dominated by clays; even the breccia intervals have large amount of clay as matrix. Therefore, we performed grain-size analyses using hydrodynamic method in settling tubes dipped into a thermostatic bath. Samples have been passed through 2 mm mesh sieve, then cleaned for organic matter with peroxide and for authigenic carbonates with acetic acid, rinsed, dried and finally brought into suspension using a polyphosphate solution. Due to time-consuming procedure, both for sample preparation and for analyzes, the grain-size analyze was performed on selected samples.

One particular aspect of the grain-size distribution across the studied section is the arenite content: from top till 5.5 m there is practically no arenite fraction, after this level there is a jump towards coarse grained fraction. It seems that arenite and also silt content doesn’t contain any climatic control (Figure 1). More sensitive to climatic changes is the clay fraction, revealing some fluctuation in the upper part of the section. However in the studied section granulometry is not a climatic proxy itself only in correlation with other parameters like magnetic susceptibility. The fine grained sediment from the upper part of the sequence indicates that the shaft was almost completely filled with sediment deposited under quiet pool conditions derived from a filtered source, not from a direct stream.

**Rockmagnetic data**

Magnetic properties reflect the types, amounts, and magnetic grain sizes of magnetic minerals in geological materials. For the sediments sampled in this study, we measured several rockmagnetic parameters: magnetic susceptibility (MS), anhysteretic remanent magnetization (ARM), and isothermal remanent magnetization (IRM). Of the three magnetic parameters MS, IRM and ARM, susceptibility showed the least dependence on grain size (Peters and Dekkers, 2003). Susceptibility is therefore, perhaps, the best parameter for assessing magnetic concentration in environmental samples. For magnetite, both IRM and ARM decrease with increasing grain size so that large multi-domain grains contribute relatively little in comparison to smaller grains. IRM has no variation with grain size for high coercivities minerals (hematite and goethite). In comparison to IRM, ARM varies more strongly for very small grains (<1 µm) with ARM being particularly strong for magnetite grains with diameters on the order of 0.1 µm to 0.02 µm. Magnetic susceptibility (MS) and its frequency dependence were measured using a MS2B Bartington system. ARM and IRM were measured with JR5 spinner magnetometer. ARM was imparted using an alternating field with a peak intensity of 100 mT and a bias field of 0.05 mT. After measurement of ARM, IRM was first imparted in a 2T field (SIRM) and then in the opposite direction in a field of 0.3 T (IRM0.3T). The ratio, IRM0.3T/SIRM thus is a measure of the proportion of magnetite to all magnetic iron oxides. When values of this ratio,
called the S parameter, are high, the iron oxide population is dominated by magnetite (a maximum value of 1); decreasing values indicate increasing proportions of hematite.

Main rockmagnetic results are presented in Figure 2. According to the variation of the S parameter, magnetic mineralogy is dominated by high coercivity minerals. Analysis of IRM acquisition and demagnetization curves on selected samples shows that the high coercivity mineral is hematite. High concentration of hematite characterized the first 3 m from the top of the outcrop. The rest of the section shows several pulses of low coercivity minerals (magnetite and/or maghemite). These changes in magnetic mineralogy are well reflected in concentration dependent parameters (MS, ARM and IRM). Concentration dependent parameters show little variation on the first 2.3 m. The rest of the section is characterized by three peaks of these parameters. The MS variations are in close correspondence with ARM, S parameter and frequency dependence of MS variations. This indicates that MS oscillations are mainly controlled by an input of fine magnetite grains of pedogenetic origin.

The presence of hematite identified through rockmagnetic analyses is correlating well with the dark red color of the fine-grained sediment. Hematite’s source could be again the Paleozoic rocks cropping out north of the cave. These rocks don’t contain themselves hematite but they contain lot of iron sulfides, which were oxidized in still-water conditions. All the sedimentological parameters from the upper half of the studied section require the existence of a slackwater pool before the cave insurgence. This pool acted as a filtering system for the fine grained sediment, as an oxidizing environment for the iron sulfides and in the same time as an acidic pool which removed any carbonate mineral from the sediment.

Climatic interpretation of the results

From all studied parameters the best proxy for climatic oscillations seems to be the variation of rockmagnetic parameters produced by the enhanced input of pedogenetic magnetite. Following the interpretation of magnetic susceptibility variations in cave sediments of Ellwood et al. (2001), we have identified three warm periods when the magnetic signal is enhanced due to magnetically enriched soil washed, and entrapped inside the cave (Figure 2). These warm periods are associated with massive clay deposits. They are separated by two cold periods characterized by lower values for MS which correspond to the two breccia units. Fallen blocks are often connected to colder climate when taw-freeze cycles are more frequent (Courty, 1989) and can trigger mudflows and debris flows, therefore we tentatively associate the breccia units to cold periods.
The results correlate well with the response of Central European vegetation to rapid climate change during isotope stage 3 which shows several interstades with favorable climatic conditions separated by cold stadials (Ellwood et al., 2001; Müller et al., 2003). The upper part of the section dominated by high coercivity minerals and with little variation of magnetic susceptibility was deposited during the Late Glacial Maximum.

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ENVIRONMENTAL RECONSTRUCTION SINCE 2,500 YEARS AGO USING CAVE SEDIMENTS FROM BELIZE

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Introduction

The Northern Vaca Plateau in Belize (Figure 1) would likely have been among the first sites to be adversely affected during arid periods because it is located in a highly karstified upland region (Reeder et al., 1996). This well-drained, topographically diverse landscape is quite susceptible to climatic variability, which would be compounded by the effects of anthropogenic landscape alteration. In this paper, we present an analysis of environmental change on the Vaca Plateau, Belize through vegetation reconstruction using $\delta^{13}C$ of fulvic acids derived from cave sediments (Figure 2), which we propose are proxy records that incorporate both climate change and Mayan alteration of the environment. Previous studies show distinct regional differences in terms of the severity and timing of arid periods that would have affected human occupation and agricultural production throughout Central America (Hodell et al., 1995; Curtis et al., 1996; Haug et al., 2001; Shaw 2003; Hodell et al., 2005).

Methodology

In 2004, fifteen cave sediment samples were collected in stratigraphic order at ~5 cm intervals from a ~82 cm thick sediment bank along a narrow, isolated passageway halfway down the north branch of Reflection Cave. The samples were bagged, sealed, and brought back to the University of South Florida’s Soils and Physical Geography Lab for analysis. Here, each sediment sample was air-dried for 24 hours prior to analysis. To establish a chronological record of deposition for the sediment, nine radiocarbon dates were obtained from layers where sufficient organic carbon was present in the form of charcoal, seeds, wood, and organic matter. Dating was performed at the University of Arizona AMS Lab, and dates were calibrated to calendar ages using the CalPal computer program and reported to within the 95.4% confidence limits of the calibration (Weninger et al., 2005). The $\delta^{13}C$ signal of the fulvic acids in each sediment sample were analyzed by mass spectrometry. The FAs were extracted according the methods described by Hayes et al. (1997), which is the most common method to extract FAs from soils. The technique relies on the behavior of different organic acids under changing levels of pH. The various organic acids were extracted from the mineral component of the soil using distilled water to create a solution. By acidifying the solution the FAs remain suspended, while the other organic components precipitate. After numerous purification procedures, only the FAs are left in solution. Then the FAs fractions were isolated, excess water was removed, and the samples were frozen at ~75° C and finally freeze-dried. The mass spectrometry of the powdered FAs was performed at the USF’s College of

Figure 1. Map of the IX CHEL Archaeological Site study area on the Vaca Plateau, Belize (from Reeder, 2003).
Marine Science Paleolab using a Keil III carbonate-extraction system connected to a ThermoFinnigan DeltaPlus XL continuous flow isotope ratio mass spectrometer.

Results and discussion

Variations in the $\delta^{13}C$ values from the sediment fulvic acids (FAs) indicate periods of vegetation change caused by climatic and Mayan influences. The $\delta^{13}C$ values ranged from -27.11‰ to -21.52‰, a shift of ~5.59‰, which suggests significant changes in the vegetation above the cave, although the range indicates C3 plant dominance throughout the last 2,500 years with periods of C4 plants present on the landscape during Mayan agriculture. Mayan activity in the study area began around 2,600 cal yr B.P and lasted until approximately 1,500 cal yr B.P., after which agricultural practices waned in the area and gradual reforestation occurred. A similar reforestation occurred approximately 2,350 cal yr BP. These changes in forest density were in response to changes in available water resources, with increased aridity leading to the abandonment of agricultural fields and gradual forest recovery. The IX CHEL archaeological site, located in the study area, is a highland site that would have been among the first agricultural settlements to be affected during periods of aridity. During these periods, minimal water resources would have been available in this highly karstified, well-drained area, while supplemental groundwater extraction would have been difficult due to an extreme lowering of the water table.

References


A TWO CENTURIES LONG ANNUAL RECORD OF RAINFALL AND ENSO VARIABILITY ARCHIVED IN THE OXYGEN ISOTOPE PROFILES OF SOUTH PACIFIC STALAGMITES

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Continuous, high-resolution, century to millennium-long records of the El-Niño/Southern Oscillation (ENSO) phenomenon are desired in order to improve the understanding of its mode switches and persistence through time. Niue Island (19º 00’S, 169º 50’W), an uplifted carbonate atoll located on the edge of the Pacific Warm Water Pool (PWWP) and lying close to the heart of the South Pacific Convergence Zone (SPCZ), has the potential to provide such records via speleothems. Rainfall on the island is dominantly controlled by the phase of ENSO, where El-Niños affect the position of the SPCZ, the heart of South Pacific rainfall, and leave Niue under drought conditions. Century long instrumental records have been kept on the island and reveal that annual air temperature has not fluctuated by more than 1.5ºC degrees on average in more than 30 years but that annual rainfall has been highly variable over the last 95 years (839 mm to 3865 mm).

Four active, coeval, stalagmites were collected from a flank margin cave. These stalagmites have alternating couplets of light and dark calcite lamina shown to be annual in nature via AMS radiocarbon assays and growth rate analysis (average = 0.34 ± 0.04 mm/yr, n = 604). The range of the stalagmite δ¹⁸O values (-2.8‰ to -7.7‰ PDB) over the last two centuries supports our premise that rainfall amount is the dominant control on the oxygen isotopic values of the stalagmites, especially because annual air temperature variability has been negligible. Both Niue annual rainfall (NAR) and the stalagmite δ¹⁸O profiles show a marked increase in their variability since 1970 to the present that is coincidental with a known interdecadal switch in the mode of ENSO. Power spectral analysis of the δ¹⁸O profiles and NAR reveals significant (above the 90% confidence level) inter-annual periodicities typical of the ENSO phenomenon (3.5 to 7 years). An interdecadal component of 18 to 22 years in the δ¹⁸O profiles suggests a modulation of the ENSO via solar variability (see paper by Aharon et al., this volume).

Further evidence that the stalagmite δ¹⁸O profiles archive changes in the phase of ENSO is derived from a comparison between the stalagmite records and the contemporaneous Southern Oscillation Index (SOI). In general, low SOI phases correspond to ¹⁸O-enriched values while high SOI phases correlate with ¹⁸O-depleted values.

The two centuries-long records provide a basis for further study of the Niuean stalagmites that have the potential to provide much longer, continuous, atmospheric ENSO records than any in existence for the Pacific basin. These ENSO records combined with the SST records from Pacific corals can improve significantly the understanding of ocean-atmosphere interactions and help to unravel the underlying factors that modulate the observed interdecadal phase switches.
In this study we compare the carbon and oxygen isotopic records of speleothems from the Eastern Mediterranean (EM) with the high-resolution oxygen isotopic composition of the planktonic foraminifer *Globigerinoides ruber* (*G. ruber*) and with total organic carbon (TOC) and its isotopic composition \(\delta^{13}C_{\text{org}}\) in two marine cores, during the last 90 kyr. One core is from the NE Levantine Basin (MDVAL 9501 at 980 m water-depth) and the other from the SE Levantine Basin (MDVAL 9509 at 884 m water-depth) in the distal Nile Delta.

The Soreq Cave record together with *G. ruber* allows us to reconstruct the paleoclimate conditions of the EM region, while the TOC and its isotopic composition enable us to reconstruct the periods of increased Nile River discharge, i.e., increased monsoonal activity in the Ethiopia Highlands. The time control used in this study is based on the \(\delta^{18}O\) stratigraphy that was established using the *G. ruber* and correlated with the well-dated (U-Th) speleothem records of Soreq Cave.

The *G. ruber* \(\delta^{18}O\) record from both cores is generally very similar in pattern to the Soreq Cave speleothem record but with higher \(\delta^{18}O\) values in the NE Levantine Basin mainly due to colder temperatures. The similarity between the land and marine records indicates that both land and sea are under the influence of the same climate regime. However, detailed high-resolution examination shows that the difference between the *G. ruber* \(\delta^{18}O\) values and the \(\delta^{18}O\) values of Soreq speleothems \(\delta^{18}O\) (which depend on Rayleigh distillation between sea and land), is not constant due to climate changes.

The TOC values are always 2-3 times higher (0.6–0.9%wt) in the SE Levantine Basin when compared with the NE basin (0.2-0.3%wt), indicating a strong link between Nile River discharge and primary production in the distal parts of the Nile delta. During sapropel events of the early Holocene (S1) and last interglacial (S3), TOC content is significantly higher all over the Levantine Basin, coinciding with minimum \(\delta^{18}O\) values of speleothems and *G. ruber*.

The \(\delta^{13}C_{\text{org}}\) values are different in the SE and NE basins, although in both sites they reflect a marine source. In the north, the values range between -20‰ and -30‰, significantly lower compared with -15‰ to -22‰ in the south. In the Nilotic province, the highest values are during the MIS3, and decrease considerably during the S3 and S1 sapropel events with very little changes in the northern part of the basin. The differences in TOC and \(\delta^{13}C_{\text{org}}\) values between the north and south Levant reflect a strong N-S gradient in climatic and environmental conditions, indicating a significant and continuous contribution of the Nile River to the southern basin but with little effect on the climate on land. At the same time, the northeastern basin seems to reflect a climate regime influenced mainly by the Mediterranean - North Atlantic system similar to the land record.
ORIGIN OF THE CYCLES FROM 2000 YEARS TO 14 DAYS IN PALEOLUMINESCENCE INSOLATION PROXY RECORDS

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Introduction
Calcite speleothems usually display luminescence which is produced by calcium salts of humic and fulvic acids derived from soils above the cave. These acids are released by the decomposition of humic matter. Rates of decomposition depend exponentially upon soil surface temperatures that are determined primarily by solar infrared radiation (Shopov, 1997). So the microzonality of luminescence of speleothems may be used as an indirect Solar Insolation proxy index. From a speleothem from Cold Water Cave, (Iowa, USA) it was obtained a high correlation coefficient of 0.90 between the luminescence record and the Solar Luminosity Sunspot index measured since 1700 AD, and with the reconstructed sunspot numbers since 1000 AD with a precision within the experimental error of the measurements. Intensity of luminescence in the record was not dependent on actual precipitation (zero correlation). We obtained luminescent solar insolation proxy records with different resolution from this speleothem to study the origin of the short period insolation cycles.

Results
We used a new real-space periodogramme analysis algorithm to calculate and compare the real intensity of the cycles in speleothem luminescence time series (representing cycles of solar radiation at the Earth’s surface) in speleothems from Cold Water Cave, Iowa. Obtained power spectra demonstrate that speleothems recorded many cycles of the soil temperature in the region with duration coinciding with that of the solar cycles (like 11 and 22 years). The last solar cycles produce variations of the solar constant with amplitude of less than 0.4%. Cosmic rays influence on the atmospheric transparency provides a mechanism of strong nonlinear multiplication of the solar variations in the insolation at the Earth’s surface. Cosmic rays have strong modulation by the solar wind, which roles their concentration at the Earth’s atmosphere.

In addition to the annual cycle produced by the Earth’s rotation we found a number sub-annual cycles in an extremely high-resolution luminescent record from Cold Water Cave, Iowa. Observed cycles with duration of 32, 30, 28.5, 27 and 14 days can be produced by the period of rotation of the Sun, which produces similar variations in the solar wind modulating cosmic rays flux. This period produces periodical appearance of the active zones on the Sun, which are major emitters of solar wind so produce strong variations of its density. The duration of the cycles of 30 and 27 days is close to the tidal cycles of 29.5, 27.55 and 27.32 days. We discuss both hypothesis of the origin of these cycles in the paleoluminescence record.

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STABLE ISOTOPE COMPOSITIONS OF SPELEOTHEMS FROM HUNGARY: CLIMATE CONDITIONS AND LOCAL VARIATIONS

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In the past decade an increasing number of cave-related paleoclimatological studies have been published to use mostly stalagmites as excellent continental climate records. Well studied speleothem occurrences from Central Europe are scarce and vary rare in Hungary. However, in the last years new projects have been started to cover and compare this region. Climate conditions in the studied area are in a special position between the Atlantic-Mediterranean-sub-Arctic influences.

In the present work we report isotopic profiles for some Hungarian, mostly contemporaneously deposited Holocene stalagmites. The U-Th analysis revealed that the samples studied were deposited mostly during or before early Holocene. All Hungarian samples collected in this work are younger than the cold and dry Younger Drias period - that has left traces all over the world - except one (Leany cave, North-Central Hungary) which started growing 12,500 years ago. This stalagmite shows no abrupt oxygen isotope shift at the oldest part spanning the major climate change during the termination of the Younger Drias and reveals only slight cyclical variation along the growth axis.

Another stalagmite sample collected from the same cave closer to the surface exhibits higher variability in carbon and oxygen isotope compositions. Besides isotopic pattern similarities at the contemporaneously grown sections (dated with MC-ICP-MS) the measured carbon isotope values are significantly higher in the case of the stalagmite formed at a higher level. This feature may be related to different infiltration pathways of the seepage water within the karst aquifer, or to considerable $^{13}C/^{12}C$ fractionation due to the escape of dissolved $CO_2$ along migration pathway.

Trace element (e.g. Mg, Sr, Ba, U) contents and stable C and O isotope compositions were determined across two active, syngenetic soda straw stalagmites from the Beke Cave (NE. Hungary) representing the last seven years to investigate the nature of these geochemical cycles and their potential for better understanding of past changes. The cold seasons are represented by low $\delta^{18}O$ values. The positive covariation of P concentration and $\delta^{13}C$ values of the soda straw suggest the presence of reduced activity in the soil zone during wintertime. Environment seasonality clearly shown by the Sr and Ba concentrations: higher values represent cold periods, suggesting that restricted infiltration caused higher salinity.

The observed variations call attention to the calibration of recent speleothems with well known local meteorological records which is essential in trace element related paleoclimatological studies.
RECONSTRUCTING HEMISPHERIC-SCALE CLIMATES FROM MULTIPLE STALAGMITE RECORDS

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Introduction

The magnitude of recent warming, and the variability of climate on centennial-millennial time-scales are compromised by questions concerning the ability of tree rings to capture low frequency climate fluctuations. The discrepancies between multi-proxy northern hemispheric temperature reconstructions have been blamed on the various methods of processing tree ring data to retain low-frequency variability, which can subsequently lead to significant differences in the magnitude of centennial to millennial-scale temperature fluctuations. The robustness of the low-frequency signal within current multi-proxy reconstructions is therefore questionable; emphasising the need for the development of annually resolved series from additional proxy sources, which are capable of providing information complementary to that of tree rings and ice cores. Speleothems can go some way to resolving the low frequency issues associated with tree-age related biases and segment length limitations as they grow under constant conditions on a centennial to multi-millennial time scale (e.g., Wang et al., 2005).

The annual lamination in speleothems is either defined by seasonal couplets differing in porosity or mineralogy or by seasonal infiltration events represented by luminescent laminae or by visible laminae observable in thin section, and/or geochemical (trace element) variations which can reflect aspects of both types of laminae. More recently, oxygen isotope variability has been found to correlate with visible laminae thickness in monsoonal climates (Fleitmann et al., 2004). The annual lamina thickness reflects a combination of driving factors affecting growth rate (dripwater Ca content, dripwater film thickness, cave $p$CO$_2$, Dreybrodt, 1988). Of these, variations in drip-water supersaturation due to variability in Ca content or drip water $p$CO$_2$ (as a function of degassing in the epikarst or in the cave) are the most likely to vary on a multi-year timescale. These factors controlling supersaturation primarily reflect changes in CO$_2$ production and storage in the soil and epikarst above the cave, which in turn are likely to be functions of temperature and rainfall. Hence lamina thickness series can capture a smoothed low frequency signal due to the inertial hydrological properties (mixing and storage) of the feeding system for the stalagmites (Proctor et al., 2000).

The ability of speleothems to preserve low frequency climate variability has been recognised by their inclusion in the multi-proxy reconstructions of Pauling et al. (2003) and Moberg et al. (2005). Traditionally, however, paleoclimate reconstructions from speleothems have used a single speleothem growth rate record in isolation. This is commonplace in speleothem studies, where conservation issues limit the amount of available samples, thereby restricting the degree of sample replication possible. The strength of the captured climate signal within speleothems has therefore been difficult to establish due to the lack of replicability; and the extent to which the signal contained is representative of low frequency climate fluctuations requires verification, independent of reconstructions which contain information from additional proxy sources. Here, information from three independent speleothem annual layer thickness chronologies is combined to produce an extra-tropical, mean annual, Northern Hemisphere temperature reconstruction for the past 500 years, derived solely from speleothem data. Since this is a pioneering development, the aim is not to derive a definitive reconstruction, but rather to examine the degree to which speleothems from spatially diverse environments contain a common low frequency signal that can be interpreted as a climatic response, and whether this signal is comparable to the phase and amplitude of the low frequency variability within dendroclimatological reconstructions.

Data and methods

The temperature reconstruction is derived using the annual stalagmite growth rate for three recently published stalagmite time series from northwest Scotland (Proctor et al., 2000), alpine Italy (Frisia et al., 2003) and eastern China (Tan et al., 2003). All three series show a significant relationship to hemispheric scale temperatures, but vary in the seasonal weighting of the relationship. The Chinese
The speleothem is representative of mean annual conditions, whereas the Scottish and Italian records have a stronger coupling with winter conditions. Here they are independently found to be significantly related to the Northern hemispheric mean annual temperature.

The time series were transformed using eigenvector techniques, to extract the common mode of variability contained within the three records. The principal empirical orthogonal function displays remarkably high, positive loadings with all three series and explains 55% of the total variance. The effect of this transformation is an improved signal to noise ratio, and increased confidence that although the datasets are spatially sparse, the established links with Northern Hemispheric climate suggest this to be the common mode of variability contained within the three records.

The reconstructed temperature series was derived using a simple ‘local calibration’ approach, which is based upon a linear regression method. The transformed dataset was calibrated to the instrumental temperature record (Jones et al., 1999; land areas north of 20°N) over the period 1870-1960 and validated using the remaining overlapping instrumental record, before extending back in time to encompass the last 500 years (see Figure 1).

Results and discussion

Although currently restricted by its length and the sparseness of available samples, the presented stalagmite temperature reconstruction provides strong evidence that speleothem growth rate is closely related to large-scale patterns of climate variability. Comparisons with a number of published northern hemisphere temperature reconstructions prove to be highly favourable (Table 1). A correlation of 0.9 exists between the speleothem reconstruction and the (non-calibrated; 1960 onwards) instrumental record of mean annual temperature, and significant correlations ($r > 0.43$; $p < 0.01$, after correction for autocorrelation) were found with all the reconstructions when smoothed with a 20-year low-pass filter over the past 5 centuries (see Table 1). Quantitative estimates of the uncertainty associated with the utilisation of a regression-based reconstruction, including the loss of temperature variance that such an approach can incur, were calculated using the method of Briffa et al. (2002). These are notionally 2 standard error estimates, but are subject to correction due to the autocorrelative structure of the merged stalagmite series. The dating errors associated with inaccuracies in annual laminae counts (~2%; Proctor et al., 2000) are considered negligible relative to the degree of smoothing.

The speleothem temperature reconstruction closely resembles that of Briffa et al. (2001), but the greater variability and more negative temperature anomalies evident in the early part of the reconstruction are comparable with those present in the Esper et al. (2002) reconstruction. The overall magnitude of warming in the speleothem reconstruction is 0.65 K, compared with around 0.4 K displayed by the reconstruction of Briffa et al. (2001). The 20th century, as with all the other reconstructions, is significantly warmer than the previous four centuries. The temperature is shown to increase by 0.35 K over the last century, compared with the 0.29 K increase that occurred between 1700 and 1780, and the 0.27 K amplitude change in temperature that occurred during the late 16th to early 17th centuries. With such a short dataset it is difficult to assess whether the amplitude of the temperature increase during the 20th century is truly anomalous relative to what occurred in the preceding centuries, but the recent warming does not appear as exceptional as that suggested by the borehole reconstruction of Huang et al. (2000), where the 19th and 20th centuries are responsible for 80% of the net temperature increase over the last 500 years. The discrepancy between borehole and speleothem records may be due to the European weighting of the speleothem reconstruction, as the borehole reconstructions show greater warming in North America and Asia compared to Europe (Huang et al., 2000). A recent temperature reconstruction for the past 2000 years, from an alpine speleothem oxygen isotope record suggests that there were periods in that region of Europe when temperatures were comparable (or even warmer) than today (Mangini et al., 2005).

The difference in amplitude of temperature variations within proxy reconstructions has been of recent concern (e.g., Esper et al., 2004), with a number of factors in methodological procedures highlighted as being responsible for anomalies in the magnitude of temperature change within paleoclimate records. The speleothem reconstruction displayed here has not been specifically manipulated to retain low frequency temperature variations or to preserve higher amplitude behaviour, but it does show a greater amplitude change over
the past 500 years than that displayed by reconstructions which have been derived using ‘traditional’ regression methods. Thus, the larger temperature range present within the speleothem reconstruction over the last 500 years provides further support for the capture of a more slowly evolving climate signal within the speleothem records.

**Conclusion**

Annually laminated stalagmites that have accumulated over the last 500 years from three Northern Hemisphere sites display a dependency of lamina width (i.e. growth rate) on Northern Hemispheric temperature, suggesting that stalagmites offer key annual resolution paleoclimatic information. This paper has used a relatively simplistic methodology to reconstruct large-scale temperature anomalies from annually laminated speleothems. There exist some data limitations within the three stalagmite series as it stands, particularly with respect to the dating of the earlier part of the reconstruction and the small size of dataset. The addition of further annually laminated stalagmites from the region will help overcome these issues. Here we emphasise the potential value of annual laminated speleothems and aim to encourage the collection of robustly dated, annual lamina width speleothem datasets which will ameliorate our understanding of past, low-frequency climate variability.

**References**


RECONSTRUCTION OF LATE HOLOCENE PRECIPITATION FOR WEST-CENTRAL FLORIDA AS DERIVED FROM ISOTOPES IN SPELEOTHEMS

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Stalagmites collected from two caves in Florida provided the first Holocene paleoclimate record for the Peninsula using speleothems. Two speleothems were collected from BRC Cave, and two from Briar Cave, both located in west-central Florida, USA (Figure 1). The Florida climate is subtropical with average temperatures in the study area of around 22 °C, and an average annual precipitation of 1300 mm. BRC Cave and Briar Cave are among the longest subaerial caves in Florida, each comprised of more than 1 km of surveyed passages. Both caves formed within the Ocala Limestone of the late Eocene age, each have only one entrance, and are well decorated with speleothems.

The purpose behind our study is to assess whether speleothems in Florida provide a reliable and complete record of Holocene trends in climate in a region that may be impacted by several, perhaps distant, atmospheric influences. In addition, we wanted to demonstrate that our speleothem records compare well to other regional paleoclimate indicators such as lake sediments, marine and tree-ring records.

Changes in precipitation over the last 4,200 years, which encompass two abrupt contrasting climate intervals, the Medieval Warm Period (MWP), from 1000 to 1300 AD, and the Little Ice Age (LIA), from 1400 to 1850 AD, can be attributed to changes in atmospheric circulation patterns.

Figure 1. Location of study sites, and results of U/Th and stable isotopic analysis from Briar Cave speleothem. 1) Location of Briar Cave. 2) Location of BRC Cave. Photo of stalagmite BRIARS04-02 (black ovals represent the location of U-series dates). The oxygen and carbon isotope record from BRIARS04-02 extends 4,200 years BP, and changes in the speleothems isotopes show enrichment during the dry conditions of the Little Ice Age and depletion during the wetter conditions of the Medieval Warm Period.
Both stable isotope analysis and TIMS Uranium-series disequilibrium analyses were performed on all speleothems. Results showed that in subtropical Florida, an increase in the amount of precipitation was recorded by depleted speleothem $\delta^{18}O$ isotopes and an increase in forest density produced depleted $\delta^{13}C$ values. These variations in the speleothems $\delta^{18}O$ composition reveal abrupt changes in precipitation amount, fluctuations that appear both regional and hemispheric in nature.

In order to determine whether our interpretation of Florida’s Holocene climate, as derived from speleothems, agrees with previous paleoclimatic studies, the speleothems $\delta^{18}O$ records were compared to other paleoclimatic records. The speleothem BRIARS04-02 was selected for this purpose because of its continuous record over the last 4,200 years (Figure 1) and its representativeness of the other speleothem records. Strong similarities between the speleothem $\delta^{18}O$, $\delta^{D}$ record from Lake Tulane, Florida (Cross et al., 2004), and the South East USA tree-ring record (surrogate for spring precipitation - Stahle and Cleaveland, 1992), suggests a regional atmospheric influence on Florida’s precipitation. A comparison between the speleothem record and the changes in sea surface temperature as recorded by NINO3 (Cane, 2005) and a record of titanium concentration in the Cariaco Basin of the Caribbean Sea (Haug et al., 2001), suggests global atmospheric influence.

The three major causes of changes in precipitation are proposed to be changes in phases of the Atlantic Multi-decadal Oscillation (AMO - Enfield et al., 2001), the changes in intensity of El Niño (Cane, 2005), and changes in the relative positions of the Intertropical Convergence Zone (ITCZ - Haug et al., 2001) as it influences the North Atlantic High. Comparison between the speleothem $\delta^{18}O$ and surrogates of these influences, show all three have some effect. AMO and El Niño have short-term (decadal) influence and the ITCZ-NAH has a long term (centennial) influence. The contributions of these climatic effects have implications for teleconnections involving Florida’s climate; the AMO correlation shows higher latitude influence, while El Niño and the ITCZ show tropical influence on sub-tropical Florida.

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In the paleoenvironmental research community working on speleothems there is currently a tendency towards sampling large, meter-long stalagmites in an attempt to obtain high-resolution records spanning thousands to tens of thousands of years of (semi)continuous calcite deposition. Not only does this approach result in logistic challenges, but it also runs into conflict with cave conservation rules.

We will present a case study of a very small flowstone sample which — despite its mere thickness of 38 mm — preserves a growth history that is very relevant for the Quaternary climate history of the eastern part of the Alps during Marine Isotope Stages 5c to 5a. These calcitic flowstones are present in fractures in the Inn Valley near Innsbruck, and record periods of carbonate precipitation in the unsaturated zone between ca. 101 kyr and 70 kyr, constrained by U-series disequilibrium dates. The oxygen isotope composition, obtained by high-resolution micromilling, shows a pattern of negative excursions that are largely mirrored by times of higher stable carbon isotope values. The occurrence of these speleothems, their carbon isotopic composition and the lack of infiltrated siliciclastic material demonstrate that the central Inn valley — which harbored one of the most extensive valley glaciers during the Last Glacial Maximum — was ice-free during Marine Isotope Stages 5c to 5a, providing the first well-dated constraints on the extent of ice in the Eastern Alps during the early part of the last glacial cycle. Climatically warm periods, separated by distinct drops in the oxygen isotopic composition of the speleothem calcite, can be correlated within the uncertainty of the individual U-series dates to interstadials 23, 21, 20 and 19 identified in Greenland ice cores. The youngest calcite layer formed 70 kyr ago places a maximum age limit on the likely expansion of alpine glaciers during the Marine Isotope Stage 5/4 transition, consistent with other speleothem records.
APPLICATIONS OF STALAGMITE LAMINAE TO PALEOCLIMATE RECONSTRUCTIONS: COMPARISON WITH DENDROCHRONOLOGY/CLIMATOLOGY

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Introduction

The rapidly expanding peer-reviewed published literature of paleoclimatic reconstructions derived from stalagmite growth layer thickness has shown that a number of stalagmites certainly contain climate-responsive annual growth layers that then provide long continuous chronologies from which annual climatic information can be extracted. However, the work on stalagmite layers has not yet been widely utilised, and this may be partly due to uncertainty as to where to find long annually laminated records, or lack of established methodology. Laminated stalagmites should be held to the same rigorous standards in chronology building and climatic inference as annually resolved tree rings. This argument demands a serious consideration of the methodology used in high-resolution stalagmite/climate reconstruction work. Here we attempt to outline the methodology from which climatic reconstructions from stalagmite laminae have been or are being established in our research groups.

Stalagmite lamina-chronology

Three main kinds of stalagmite growth laminae from widespread global locations have been reported, these laminae types are not mutually exclusive and individual stalagmites can exhibit all three types of laminae within their growth, although this is uncommon. Firstly, luminescent laminae have been reported. This luminescence, normally observed using conventional mercury light source UV reflected light microscopy (or exceptionally by transmitted laser excitation or confocal microscopy), is caused by the intrinsic fluorescence of natural organic matter, which causes the majority of UV excited fluorescence in cave calcites. Luminescent laminae require regular fluxes of this luminescent material from the overlying soil onto the stalagmite. Secondly, laminae can be observed in calcite stalagmites using conventional transmission and reflection light microscopy. Visible laminae require a regular (often seasonal) alternation of the arrangement in space of crystals with a well-defined morphology (texture or fabric; Frisia et al., 2000). One description of laminae in hand specimen is an alternation from ‘dark compact calcite (DCC)’ to ‘white porous calcite (WPC)’ as defined by Genty and Quinif (1996) and can be formed by either regular alternations in dripwater chemistry or cave atmosphere. The precise controls on the formation of WPC and DCC are poorly understood. Finally, alternations of aragonite and calcite growth layers have been reported. Again, the processes generating this lamina type are poorly understood: many factors have been implicated in the formation of aragonitic stalagmites (including temperature, drip rate and dissolved magnesium concentrations) and by inference calcite-aragonitic laminated stalagmites require such a threshold to be crossed with regular alternations. We have archived examples of these three types of stalagmite laminae from all over the world in our International Stalagmite Laminae Bank (http://www.gees.bham.ac.uk/collections/stalagmitetdbank/search.asp).

The observation of regular laminae in stalagmites does not presume that they are annual in nature. Four methods of determining if the layers are annual have been reported.
1) To compare the number of layer counts between well dated layers. This might be by comparing radioisotope dates and the interval of time dated, through the difference between uranium-thorium age determinations (e.g. Baker et al., 1993), or radiocarbon age determinations (making the assumption of a constant ‘dead’ or geological carbon contribution, e.g. Broecker et al., 1960).

2) The increasing number of observations of regular and rhythmic laminae in stalagmites in geographically widespread regions of the globe that have a strong surface climate seasonality suggests that annual laminae could be hypothesized to be the typical mode of deposition in such regions. In regions where there is a strong seasonal contrast of surface climate, either in rainfall amount (monsoon or low latitude climates affected by the ITCZ), a seasonal soil moisture excess (mid latitude climates), or snowmelt (high latitudes), this climate signal may be transferred via either organic or inorganic natural tracers in the groundwater to the stalagmite. If stalagmites are sampled from relatively shallow (typically less than 30 m) depth, this would permit enough smoothing of this surface signal by mixing with stored groundwater to remove sub annual ‘event’ signals, yet preserve the regular annual geochemical trace of surface climate in the cave drip water. Therefore, another test of the annual nature of laminae is the observation of drip waters in caves where laminated stalagmites are found, which can not only determine if the layer is annual but also demonstrate how and when the layer forms.

3) A third test of the annual nature of laminae is to compare the observed lamina width with that theoretically predicted through the work of Wolfgang Dreybrodt (Baker et al., 1998).

4) A fourth test is to carry out in-situ calcite growth experiments to recognize the annual formation of laminae observed in stalagmites, for example by placing a tile upon the surface of a sampled stalagmite for several years and counting the number of laminae.

The development of a stalagmite lamina-chronology can only proceed if, in each case, the laminae can be confirmed to be annual. Additionally:

1) The (annual) layer division has to be clearly visible (this is often achieved by adjusting image contrast and/or brightness using image analysis computer software

2) Supra annual or sub annual layers must be distinguished, if they exist, before establishing a chronology. The most direct way is to distinguish the nature (structure, shape, intensity) of the annual layers.

3) Missing annual layers should not be commonplace. The most obvious sign of missing layers is the presence of a “hiatus”, which can be observed in polished or thin section though the identification of an erosion (dissolution) layer or through the deposition of detritus. However, a lamina might not form over the whole of a stalagmite surface if the water film does not cover all top surface of the stalagmite while calcite precipitates. Therefore it is important to count as close to the centre of the stalagmite as possible, to duplicate the count and to check all of the section for such features.

An accurate layer chronology is therefore more likely to be derived from stalagmites without any hiatuses, and therefore more likely to be from a suitable depth such that the stalagmite is buffered from short duration hydrological extremes, as well as from a climate zone warm and wet enough to sustain deposition. Ideally the stalagmite should be active when it is collected, as this will provide a precise start date as opposed to a floating chronology constrained by uranium-thorium analyses. Placing a glass thin section on the stalagmite to be sampled for one month or more is the best way of determining whether the precipitating of calcite is occurring. Finally, the accuracy of any resultant lamina count must be reported. Comparisons between duplicated lamina counts both within and between samples can also provide an estimate of counting error, as can comparison of counts between operators.

Stalagmite lamina-climatolgy

If the change in the layer thickness can reflect surface climate variations, then the methodology of quantitatively reconstructing climate from stalagmite growth layers can be defined as a “stalagmite lamina-climatolgy”. Each record has a different sensitivity to surface climate due to the many factors that determine stalagmite growth rate, each of which have different sensitivity to surface climate forcing processes. Indeed the lamina thickness climatology (LTC) may be sensitive to seasonal or annual surface precipitation or temperature, similar to tree ring sensitivity, although the latter usually show only a spring or summer response maximum whereas stalagmites may respond to any season, depending on the forcing mechanism. Individual stalagmites may have a different sensitivity to surface climate, depending on the relative amounts of storage and fissure flow components. It is important to recognize that although stalagmites within a cave may show similar LTCs, a lack of correlation between stalagmites suggests different sensitivities to climate, due to different filtering of the climate signal by the karst system. Therefore, calibration of the LTC with instrumental or historical monthly-observed data (rather than annually averaged data) is very useful to understand the precise climate sensitivity of any one stalagmite.

The assumption that the annual layer thickness represents the amount of annual deposition for a stalagmite when using the layer thickness as a climatic proxy is best if the stalagmite has a typical ‘candlestick’ shape. We therefore sug-
suggest the use of columnar stalagmites for climate reconstruction as much as possible. Even with this ideal specimen shape, often the annual layer thickness at the early growth stage are a product of deposit geometry (for example, the angle of slope upon which the stalagmite is growing, or movement or slumping of the growing stalagmite into soft sediment), rather than drip water quantity or quality. Due to the complexity of many basal growth stratigraphies, thickness climatologies should not be constructed except in some exceptional cases where the basal growth trend is predictable and can be removed by a fitting function (e.g. polynomial) so that the basal laminae can be used to reconstruct climate (Tan et al., 2002, 2003). Additionally, over the whole period of stalagmite growth, lamina thickness may demonstrate a long term trend of either increasing or decreasing growth rate. Such trends might be due to local or regional surface climate trends, or related to long term changes in stored groundwater characteristics that can make up a significant proportion of the drip water. Care has to be taken to understand the process(es) generating these long term trends, before one can be confident in removing (or keeping) the low frequency component within the dataset.

In more irregularly shaped samples, we frequently observe a within lamina variability of thickness that is greater than the between lamina variability. Although this is not a problem for determining a lamina chronology, it limits the use of these stalagmites in lamina-climatology. The data derived from any one measuring track may not represent the mean amount of annual deposition and measurement should proceed along several routes and their average can be used. Errors on the thickness measurement of each layer should also be supplied.

The LTC need not have a linear correlation with surface climate. Tan et al. (2006) show that a non-normal stalagmite laminae width distribution is typical, with greater inter annual laminae width (and therefore climate sensitivity) at lower growth rates for most samples. If universally observed in stalagmite lamina width climatologies, then this suggests that data treatment should be considered only after careful exploration and understanding of the lamina width data.

Comparison with dendrochronology/climatology

LTC should also be comparable with contemporaneous tree ring width (density) chronologies (RWC) from the same region if their growth is controlled by the same climate-related factors (Betancourt et al., 2002). There exists a wealth of literature concerned with the intricate relationship between tree rings and annual climate, across varying temporal, high frequency to low frequency and spatial, localized to hemispheric scales. In addition, the number of samples which comprise a single chronology, and the vast network of tree ring chronologies, enable averaging of intra- or inter-site data, which minimizes the local effects and biases of individual trees, as opposed to speleothem proxies where generally climatic information is derived from a single sample. This suggests that it may be more appropriate to seek commonalities between reconstructions from tree rings and those from a suite of speleothem LTCs at a larger spatial scale (eg. Northern Hemisphere; Smith et al., in press).

It should be noted that there are important differences, as well as similarities, in the way in which stalagmites and trees preserve a surface climate signal. Most notable is the possibility of obtaining long (102-103 year) continuous stalagmite lamina records, that by the nature of the smoothing introduced during groundwater mixing, are capable of preserving low frequency climate information at annual resolution, as opposed to tree ring records for which there are many more samples that are better at preserving high frequency climate variability but which are limited in their ability to retain climate variations on a multi-centennial time scale (Esper et al., 2004; Moberg et al., 2005). Comparisons between stalagmite reconstructions and tree ring reconstructions may reveal whether methods of retaining low frequency behaviour in dendroclimatological series are successful, and may assist in the refinement of estimates of the temperature amplitude during pre-industrial times.

Conclusions

Stalagmite laminae must be used more frequently and effectively in paleoclimate reconstruction, both as a chronology for other proxies or as a directly useable ring lamina width climate proxy. A basic issue for stalagmite lamina-climatology now is to precisely understand the relationship between growth rate and surface climate and environmental conditions, so that further laminated sequences can be discovered and so that we can develop further climate-responsive LTCs. Process based (modern cave monitoring) and multi parameter (both different proxies within stalagmites as well as between different climate proxies) studies are essential in this regard. A second issue is the need to develop ‘rules’ or reporting conventions for future papers using annual speleothem lamina for climate reconstructions. These should include: (a) reporting the number of transects counted for each given time period and the standard deviation of those measurements, (b) reporting the reproducibility of the replicated annual layer identification and measurement between different researchers, (c) report calibration statistics with local climate parameters, (d) fully reporting U/Th statistics used for verifying hypothesized annual laminations, (e) providing a full description of cave and subsurface hydrology, (f) reporting and interpreting the processes explaining any correlation (or lack of it) between lamina widths of overlapping speleothems, (g) fully describing and providing the rational for any normalization / detrending procedures. Similar reporting rules in dendrochronology serves that community well, allows the quality of any chronology to be evaluated by others, and would provide the same opportunity for stalagmite palaeoclimatology.
References


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Millennial scale climatic events, between 90 and 30 ka, have already been found in the isotopic records of two distinct stalagmites from the Villars Cave. The $\delta^{13}$C records quite well these events with typical ~3–5‰ variations between cold and warm phases while the $\delta^{18}$O displayed a slightly more smoothed record. Recently, a 114 cm long core made in a flowstone just nearby and U-Th (TIMS) dated shows a nearly continuous growth from ~180 ka to the Holocene. Isotopic results from a first coarse sampling (every cm) along the core permitted to see clearly the stage 5e and the last deglaciation. This is particularly visible in the $\delta^{18}$O signal. Here we present the isotopic results of a high resolution sampling (between 0.5 and 3 mm) made on this core on the period that cross cover the growth period of the other two stalagmites. We will discuss, first, the differences observed between the isotopic record of the core and those of the already studied stalagmites, and second, the difference observed between the $\delta^{13}$C and the $\delta^{18}$O records.
A 14-cm long stalagmite (DJ) collected from Jingdong Cave in northeastern Beijing, China, has been investigated for the responses of stable isotopes and trace elemental ratios to climate and environmental changes. Currently, we have 360 $\delta^{18}$O and $\delta^{13}$C measurements in the upper 9 cm section and 4662 data points (30 $\mu$m interval) of laser ablation HR-ICPMS analyses on each elemental ratio including Mg/Ca, Sr/Ca, Ba/Ca, Al/Ca, P/Ca, U/Ca and Pb/Ca through the whole stalagmite.

Although the chronology of the stalagmite is still under construction by using U/230Th ICP-MS dating and lamination counting methods, we estimate that the stalagmite is younger than 4000 years old based on 210Pb dating results and stable isotope features.

We currently focus on our discussion on correlations among $\delta^{18}$O, $\delta^{13}$C and the elemental ratios and their climatic meanings. As the cave is located in the monsoonal region where >75% of annual precipitation comes from summer monsoonal rains, the $\delta^{18}$O record can be used as an indicator of monsoon variability with lighter values reflecting stronger monsoon, and vice versa. The $\delta^{13}$C record on time scales longer than decades mainly reflects vegetation changes above the cave, with lighter values indicating more vegetative cover and/or higher C3/C4 plant ratios under wet climates. In DJ stalagmite, $\delta^{18}$O and $\delta^{13}$C have similar trends and exhibit strong centennial fluctuations (Figure 1).
record may provide information on variability of cave temperature. Figure 2 shows a generally negative correlation between Mg/Sr and $\delta^{18}$O, reflecting stronger monsoon conditions corresponding to warmer conditions.

Positive correlations exist between Ba/Ca and Sr/Ca (Figure 3), and between P/Ca and $\delta^{13}$C (Figure 4), showing similar geochemical behaviors of these proxies. These elemental ratios may give insight not only into temperature variations but possibly also into changes in dust input, rock weathering, and nutrient conditions of surface sediments. Combining the stable isotope records with the elemental ratio records, we may observe a weakening of the summer monsoon after ~2.5 ka (ca. 80 mm depth), a warm/wet Medieval Warm Period (MWP), and a relatively cold/dry Little Ice Age (LIA) in northeastern Beijing.

**Figure 2.** Comparison between Mg/Sr and $\delta^{18}$O profiles in Stalagmite DJ. The Mg/Sr variation trend is controlled by both temperature and Mg/Ca of cave water. It shows a generally negative correlation between Mg/Sr and $\delta^{18}$O, reflecting stronger monsoon corresponding to warmer conditions.

**Figure 3.** A strongly positive correlation between Ba/Ca and Sr/Ca laser ablation data profiles exists in Stalagmite DJ. This correlation indicates that Sr and Ba have the same source which may give us some insights about changes in dust input, rock weathering and nutrient conditions of surface sediments.

**Figure 4.** Comparison of P/Ca and $\delta^{13}$C shows a similar variation trend except where the $\delta^{13}$C experienced strong changes. The similar patterns of the profiles may reflect similar geochemical force or behavior (e.g., soil, vegetation, and organic materials) on the two parameters.
PALAEOClimatic events and cycles determined from late pleistocene to holocene speleothem $^{18}$O and $^{13}$C records from New Zealand

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Two composite records of $\delta^{18}$O and $\delta^{13}$C are produced from 9 stalagmites from northwest South Island (NWSI) and from 6 stalagmites from western North Island (WNI). The NWSI record extends to 25.40 ka and the WNI record to 14.31 ka BP. Each series has a variable data density, but average resolutions of 41 and 37 years respectively. The NWSI chronology is underpinned by 51 TIMS uranium series ages and the WNI chronology by 24 TIMS ages. Both records are adjusted for the ice volume effect. Speleothem calcite $\delta^{18}$O values show a positive relationship to temperature, with precipitation having a minor negative influence. $\delta^{13}$C responds negatively to water surplus, increases in biological activity, and atmospheric CO$_2$ concentration.

The NWSI $\delta^{18}$O record shows late-glacial climatic amelioration commencing ~18 ka and culminating at 14.8 ka. Following this a negative excursion took place centred on 12.69 ka which, if defined between the mid-points of falling and rising limbs, occurred from 13.21-11.69 ka. This overlapped the ACR and spanned the YD. The WNI series also shows the reversal, but less strongly.

The Holocene $\delta^{18}$O record commences with a culmination (climatic optimum) in WNI from 11.3-10.6 ka and in NWSI from 11.7-10.7 ka. WNI has an oscillating negative trend until 3 ka, whereas NWSI shows variability about a roughly horizontal trend. In the late Holocene both have positive $\delta^{18}$O excursions; at 1-0.5 ka (WNI) and 0.7 -0.6 ka (NWSI). In NWSI $\delta^{13}$C values were high from 23.2-17.9 ka and then abruptly decreased to 17.2 ka at the end of the Last Glaciation. A slower decline continued to 10.97 ka (10.9 ka at WNI). Both series show a gradually rising trend throughout the Holocene.

Seven climatic events can be identified: (1) LGM; (2) late-glacial warming ~18.2-14.77 ka; (3) late-glacial optimum 14.77-13.55 ka; (4) late-glacial reversal 13.53-11.55 ka; (5) early Holocene optimum 11.55-10.64 ka; (6) mid-Holocene variability; and (7) late Holocene warm interval 0.9-0.5 ka. Statistically significant cyclicity at decadal-to-century and millennial scales is a characteristic of all records. In the NWSI $\delta^{18}$O record for 25.4 ka and 15 ka, three periodicities are prominent: 3470-3420, 155, and 100-95 years. In the shorter WNI record, the periods are 3860, 220 and 80 years, the latter appearing as 65 years in the last 6 ka. Spectral analysis of the noisier $\delta^{13}$C series confirms these periodicities, although the peaks are less clearly resolved.
EAST ASIAN MONSOONAL RECORDS IN THE SODA STRAW OF THE LIMESTONE CAVE IN KOREA

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Limestone caves are extensively developed in Gangwon-do and Chungcheongbukdo (Korea) and more than 1000 caves are estimated to be present. A variety of numerous speleothems are actively growing in these caves today. A potential to use soda straws as regional paleoclimate proxy was investigated. Monsoonal climatic variations can be detected from the soda straw in Seopdong Cave, which grew for five years (July, 1999 ~ July, 2004). This soda straw is ca. 20 cm long, and this implies that the growth rate is 4 cm/yr. Excess $^{210}$Pb variation coincides well with the amount of precipitation during its growth, and the values are high during rainy summers and low during dry winters. This indicates that radioactive-decayed $^{210}$Pb incorporated into rainwater reached the cave very rapidly due to the short transit time of rainwater into the cave.

Oxygen and carbon isotopic compositions of the soda straw are -8.6 ~ -7.7 and -7.8 ~ -5.8 per mil (PDB), respectively. Carbon isotope contents are relatively more depleted from 2000 to 2001, and this was probably due to the smaller amount of precipitation during this interval. It is believed that the smaller amount is reflected by more depleted $\delta^{13}$C values, because degassing rate of CO$_2$ decreases with decreasing supply rate of cave water from overlying limestone. On the contrary, the periods of higher precipitation (1999, 2002~2004) show more enriched $\delta^{13}$C values. The overall trend suggests that $\delta^{13}$C of soda straw should be controlled by the degassing rate of CO$_2$. Higher degassing rate can be confirmed by higher partial pressure of CO$_2$ (1500 ppm) of cave atmosphere during summer, and lower pressure (430 ppm) during winter. Three different trends of elemental variations can be observed in the soda straw: 1) La, Zr and Y shows strong linear correlation with overall rainfall trend, 2) Ba, Sr, U and Mn show inverse correlation, and 3) P only shows the quantitative changes of annual rainfall. Especially, the second group indicates the distinctive peaks only during the periods of low annual precipitation.

High-resolution geochemical signals recorded in the soda straw of Korean limestone cave may promise a great potential for the reconstruction of climate and environmental changes during the last hundred or thousand years or so.
Increasing amounts of sulphur emitted into the atmosphere from anthropogenic combustion of fossil fuels, has played a dramatic role in altering the biogeochemistry of sulphur cycling at local and regional scales. Consequently, atmospheric sulphate aerosols are now regarded as a key mechanism in forcing both climatic change and acidification of late twentieth century sensitive catchments. Ice cores are currently used as the premier archive of past atmospheric concentrations and climatic change, although such records reflect a relatively clean atmospheric boundary layer and provide little information on mid-latitude processes. A paucity of records from mid latitude, low altitude locations, is currently limiting our understanding of the role of sulphate aerosols in modifying regional climate (Smith et al., 2001).

Speleothems represent multi-proxy archives of palaeoclimate, recording changes in mean annual temperature, rainfall variability, atmospheric circulation and vegetation through variations in trace element ratios, stable isotopes, changes in growth rates and organic precursors (McDermott, 2004). Trace amounts of S as sulphate discovered in speleothems suggest that in carefully chosen locations, stalagmites may also act as archives of sulphur deposition, thereby recording key aspects of atmospheric variability in sulphate content in mid-latitude locations (Frisia et al., 2005). However, sulphur atmospheric inputs gained from sea salt, volcanic and pollutant sources may be buffered by processes of storage, release and transformation within the overlying karst ecosystem. Given the extensive variety of sulphur containing compounds and its widespread occurrence within the lithosphere, hydrosphere and atmosphere, natural environmental isotopes of sulphate $^{34}$S/$^{32}$S are being used to help differentiate between the impact of other sources, sinks and transformations of sulphur within the ecosystem prior to incorporation within speleothem calcite.

Two field sites (Ernesto Cave, Italy and Rukiesa Cave, Ethiopia) are currently being studied to determine the transfer functions between sulphur contained within atmospheric deposition and that contained within the speleothem calcite. At Ernesto cave, Italy, micro X-ray fluorescence (XRF) and X-ray absorption spectroscopy analyses have shown a substantial rise in sulphate-S concentrations since 1880 (Frisia et al., 2005), which was interpreted as being related to anthropogenic emissions, although the impact of ecosystem buffering could not be determined. At Rukiesa cave, Ethiopia, very high stalagmite growth rates, modern deposition and high sulphate concentrations in drip waters make this an ideal site for high resolution analysis. Both sites show annual laminations and are well constrained with $^{14}$C analyses which are being used as part of the multi-proxy approach to establishing transfer dynamics. Sulphur concentration and isotopic analyses of cave drip water, speleothem calcite, bedrock, soil and other components of the overlying ecosystem are currently being monitored, enabling the extent of ecosystem buffering and isotope fractionation to be established in both these localities. From determining these transfer functions it is hoped isotope ratios of carbonate-associated-sulphur within speleothems can be successfully used as a direct indicator of environmental change and ecosystem storage over the past ~150 years.

References


A high-resolution record of paleoclimatic change over the past 2300 years has been reconstructed using the absolute-dated $\delta^{18}O$ and $\delta^{13}C$ time series of a stalagmite from Dongge cave, Libo, China. This record contains eight cycles interpreted as cold-warm or dry-wet fluctuations.

(1) The cooling period from 2300 to 1800 yr BP (year before 1950). This was, in general, a relatively dry and cold time period. The temperature decreased gradually together with the waning of the Asian summer monsoon and the waxing of the Asian winter monsoon.

(2) The warming period from 1800 to 1080 yr BP. The Asian winter monsoon slowly weakened and the summer monsoon slightly strengthened, suggesting a semi-humid and moderately warm environment.

(3) Another cooling period from 1080 to 680 yr BP. The temperature in this period decreased and the winter monsoon strengthened again. However, the rainfall in the winter seems to increase, indicating a cold, but moderately humid climate.

(4) The centennial warm event from 680 to 550 yr BP. During this short period, the air temperature increased significantly and the Asian summer monsoon intensified quickly, indicating a warm and humid climatic event.

(5) The centennial cold event from 550 to 400 yr BP. This event is characterized by an abrupt drop in both temperature and intensity of the Asian summer monsoon. It was the coldest period in the past 1000 years.

(6) A short warming trend from 400 to 364 yr BP. Both the Asian summer monsoon intensity and temperature increased in this interval.

(7) A short cooling trend from 364 to 324 yr BP. Both the Asian summer monsoon and temperature decreased in this interval.

(8) The strong fluctuation period from 324 yr BP to present. The Asian monsoon varied frequently.

Based on the stable isotope records of this stalagmite from Dongge Cave, some important centennial-scale climatic events and decadal fluctuations in the monsoon precipitation and temperature have been documented over the past 2300 years. These climatic fluctuations seem to be analogous to the Greenland ice core records, providing a linkage of climate change between the low-latitude monsoon and high-latitude temperature.
VARIOUS EFFECTS OF PALEOCLIMATE AND PALEOVEGETATION ON STALAGMITE PROPERTIES

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The time series of carbon and oxygen isotopes from two stalagmites in Guizhou, China (D4 in Dongge Cave and Q4 in Qixing Cave) demonstrate different vegetation responses to climate changes. Our study indicates that vegetation would adjust itself to climate changes, or try to resist some climate shifts.

The results show an important relationship between climate, vegetation and stalagmite growth rate, and carbon and oxygen isotope records. Poorly-developed vegetation (D4: 12~15.5 ka B.P.; Q4:12~14 ka B.P.) responded quickly to climate shifts such as Younger Dryas and H1 events, through shifts in carbon and oxygen isotopes; growth rate was also low. But when there was more vegetation (D4: 9~4 ka B.P.; Q4:14~16 ka B.P.) with strongly negative δ13C, carbon and oxygen isotopes had no obvious relationships, but the stalagmite growth rate revealed a good relationship with carbon isotope records. When there were intermediate levels or transitional vegetation (D4: 10~12 ka B.P.; Q4: 34~42 ka B.P.), it appeared to adjust itself slightly when there were large climate shifts, or remained stable except in major events, and stalagmite growth rate had much with joint influence from vegetation and climate.
Ten stalagmites and one flowstone from the Villars Cave yielded a composite stable isotope record of the last 130 kyr. Several of them are contemporaneous with each other which permitted to see the in situ variability of the $\delta^{18}O$ and $\delta^{13}C$ signals. Hendy’s tests do not show kinetic fractionation, but this might not be true for cold, dry and slow growth rate periods. We also discuss the slight difference observed between the stacked stalagmites and the flowstone records, possibly due to their different mode of deposition. The global pattern of this stack record shows clearly the last deglaciation, the glacial interstadial events (DO/H) and the Last Interglacial. The Holocene appears much more variable. In all Villars speleothems, warm climate is associated with low $\delta^{13}C$ and low $\delta^{18}O$ values, while, during cold periods, both isotopic ratios increase. The later is associated with growth rate decrease or even stops, like for the 67-62 kyr (~ MIS 4, H6), the 32-16 kyr periods (~ MIS 2), and possibly during the YD. Villars Cave $\delta^{18}O$ stack record displays great similarities with the Soreq Cave record (Israel), the most striking common feature being the huge $\delta^{18}O$ negative peak (from $-3\%$ to $-8\%$) observed between 129.8 and 119.5 kyr (~ MIS 5e). In both sites, it appears that the $\delta^{18}O$ negative incursion was much more pronounced during the Last Interglacial than during the Holocene, and that this difference is more marked at Villars. These differences will be discussed, as well as the timing of the MIS 3 millennial climatic scale events.
STALAGMITE RECONSTRUCTIONS OF TROPICAL PACIFIC CLIMATE FROM BORNEO DURING THE LAST DEGLACIATION

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Oxygen isotopic and Mg/Ca records of stalagmites from caves on Borneo (4°N, 115°E) are used to reconstruct precipitation in the West Pacific Warm Pool during the last deglaciation. The stalagmites are U/Th-dated using a Multi-Collector Inductively Coupled Mass Spectrometer (MC-ICP-MS). Preliminary stalagmite $\delta^{18}$O timeseries reveal clear YD/BA transitions, although the amplitude of these events are smaller than corresponding events in Chinese speleothem $\delta^{18}$O records. A prominent excursion towards heavier $\delta^{18}$O at ~16kybp strongly resembles a similar event in Chinese speleothems, and may indicate the impact of Heinrich event 1 on precipitation in the Warm Pool. A decrease of ~2.5‰ in speleothem $\delta^{18}$O from glacial to the early Holocene indicates relatively dry conditions during glacial times in the West Pacific Warm Pool.
CAVE LEVELS, MARINE TERRACES, PALEOSHORELINES, AND THE WATER TABLE IN PENINSULAR FLORIDA

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Problem statement

Levels of passages are a common feature of many cave systems around the world. Likewise, coastal and marine terraces are common in coastal plain settings. This paper extends the discussion of cave levels from traditional research sites in the interior lowlands of the United States to the Atlantic Coastal Plains, namely peninsular Florida. Are there levels in Florida caves, and is there a link between the elevation of cave levels, marine terraces, paleoshorelines, and thus the water table, above and below present sea level in peninsular Florida?

Historical development

The study of cave levels spans at least a century. In the United States, Davis (1930) cited levels of caves as evidence of his two-cycle theory for the origin of caves. Swinnerton (1932) proposed that the cave levels develop near the water table. Mammoth Cave, Kentucky, USA, was perhaps his best-known example. Cave levels at Mammoth Cave align with terraces of the Green River, which has experienced staged down-cutting and sediment aggradation during the past 3.5 Ma (Granger et al., 2001). The Mammoth Cave levels, therefore, are tied to the advance and retreat of continental ice sheets.

Continental ice sheets also influenced the position of sea level. Long-term records from the past 65 Ma demonstrate periods of higher and lower sea level superimposed upon a long-term decrease in sea-level elevation (Haq et al., 1987). Of particular relevance to this study, terraces in the Atlantic Coastal Plain of the southeastern United States have long been identified with Quaternary highstands of sea level (Muhs et al., 2003). The ages of these terraces are not well constrained, and it is probable that they do not represent a complete record of highstands. Although Cooke’s (1945) notion that higher terraces are older still seems reasonable, it is difficult to make interregional correlation of individual terraces with specific sea-level elevations (e.g. Walker and Coleman, 1987). In Peninsular Florida, study of marine terraces is limited mainly to Cooke’s (1945) original identification; the Silver Bluff (+2.4 m), Pamlico (+7.6 m), Talbot (+12.8 m), Penholoway (+21.3 m), and Wicomico (+30.5 m) are the five lowest, and hence youngest, of Cooke’s seven terraces.

Mapping of subaerial caves in west-central Florida by the first author and colleagues (Florea, In revision) shows that these caves differ from the classical, well-studied example of Mammoth Cave and have more in common with caves in the young limestones of the Bahamas and the Yucatan Peninsula of Mexico (Florea and Vacher, 2006). The mapping also shows that the caves of west-central Florida occur in vertically restricted and laterally continuous horizons. This discovery prompted us to hypothesize that the cave levels are controlled either by the geological framework of the aquifer or by variations in the position of the water table tied to sea-level highstands.

The second possibility – caves formed at the water-table, the positions of which are linked to sea level stands – is not new to Florida hydrogeologists. Twenty years ago, Wilson (1988) reported 63 central Florida wells that intersect cavities, with the cavities clustering into an upper cavernous zone at ~100m below the modern water table. Wilson noted that “the upper cavernous zone coincides quite well with low sea-level stands that occurred during the Pleistocene Epoch… when sea level repeatedly dropped below 400ft (~120 m)” (Wilson, 1988, p. 7). Twenty years earlier, Stringfield and LeGrand (1966, p. 39) had stated in reference to Florida, “Lateral zones of solution cavities at different depths were formed… when the water table stood at higher and lower levels in response to changes in sea levels in Pleistocene time” (Stringfield and LeGrand, 1966, p. 39). However, they also said (Stringfield and LeGrand, 1966, p. 23): “Only general information is available about the vertical distribution of cavities in the limestones of the southeastern states”. How does this notion of water-table control coupled to changes in sea level stand up to elevation data now?

Data

Our data come from several sources including caves, well records, topographic databases in west-central Florida, bathymetric data from the west Florida shelf, and the well-cavity data from Wilson (1988) (Figure 1). Collectively, the data cover a large portion of the Florida Peninsula.
Cave survey

To date, the first author and colleagues have surveyed seven subaerial caves in the uplands of west-central Florida. These surveys comprise 497 individual survey stations that include distance between stations, azimuth corrected for magnetic declination, inclination, and passage width and height. After processing, these data provide 497 cave elevations relative to modern sea level.

Existing cave maps

Data from 63 cave maps in the Florida Cave Survey archives provide 574 spot elevations. Twenty-three of the caves are subaerial, and 40 are underwater. We found that the peaks in histograms of the cave-survey and spot-elevation data from subaerial caves coincide and lie at a constant elevation relative to sea level regardless of location. We also found that the passages in underwater caves lie at consistent depths below the modern water table, which is not at a constant elevation above sea level. Therefore, we recast the spot-elevation data of the underwater caves, changing them from depth below sea level to depth below the modern water table and found that the elevation data form peaks in the histogram.

Well cavities

Following Wilson (1988), we include cavities in well logs from the Florida Geological Survey and the Southwest Florida Water Management District from 26 drilled wells and cores in west-central Florida. We include several other terms that are an indication of a cavity such as “bit drop”, “recovery of sand”, and “loss of circulation.” As for the spot-elevation cave data, we cast these data in terms of depth below现代水位.

Elevation histograms

We produced histograms of land and sea-floor elevations from various sources (Figures 1 and 2). Data for Citrus and Hernando Counties originate from publicly available, 1.5m-contour interval DLG (digital line graph) data converted into a raster data set of more than 8.4x10⁶ data points. We used similar, 1.5 m-contour interval DLG bathymetric data for a 40 km-wide band off the shore of the Florida Panhandle to produce a raster data set of approximately 1.4 x10⁶ data points. For Pinellas County, we created a histogram from a county-wide ALSM (airborne laser swath mapping) data set of more than 91x10⁶ data points (Seale, 2005).
**Discussion**

The data confirm our initial observation that caves in Florida are tiered. The cave levels in Florida are widespread and at similar elevations over large geographical areas. They do not follow the large-scale structure of the Floridan Aquifer.

**Water table and cave levels**

The elevations of the water table and sea level are related, but they are not equal. Sea level is an equipotential surface; the water table is not. As a result, the sea-level datum and the water table are not parallel; they intersect at the shoreline. The shoreline is a horizontal contour; absent tectonics, we expect the marine terraces in Florida to be at consistent elevations because they are the direct result of erosion and deposition along shorelines; The water table is a complex 3-dimensional surface; we expect that the elevation of caves in Florida relative to sea level will vary regionally across the peninsula if they are the product of dissolution near the water table.

We observe (Figure 2) that, just as levels of passages in Mammoth Cave correlate to sediment terraces on the Green River, cave levels in Florida correlate in elevation to marine terraces above and below modern sea level. However, this correlation is not immediate. One needs to make a correction to the spot-elevation and well-cavity data. Subaerial caves correlate at the same elevation (relative to sea level) over wide areas, and underwater cave levels organize according to depth below the modern water table. The difference is understood by considering the location of a cave with respect to the shore at the time of cave development.

Because of the slight slope of the west Florida shelf, small changes in sea level result in large shifts in the position of the shoreline. For example, when sea level was at -120 m during the last glacial maximum, the shoreline was approximately 220 km further west in the Gulf of Mexico (Figure 2); the subaerial peninsula was twice as large. The karst features in present-day west-central Florida were in the center of the then peninsula. In contrast, when the Penholoway and Wicomico terraces formed, sea level was at +21 m and +30.5 m respectively; much of present west-central Florida was flooded (Figure 1).

Assuming that the Florida caves formed at the water table, cave levels in Florida then separate into two genetic types -
those that were inland at the time of formation, and those that were near the coast at the time of formation. Caves that formed near the shoreline formed near the sea level of the time. Caves that formed inland formed above sea level. Conveniently for our data correction, the division between these two types appears to be cave levels above and below the modern water table.

Marine terraces and cave levels

Marine terraces above and below modern sea level are Quaternary, although their individual ages are not constrained. How well do they match up with the cave levels indicated by the histograms? Are the data consistent with a correlation of terraces and cave levels?

Not every named terrace is evident in the cave data. For instance, Cooke’s Wicomico (+30.5 m) terrace is well represented in the elevation (land) histograms, but not in the cave-survey or well-cavity data (Figure 2). A possible reason is that a sea-level elevation of +30.5 m would submerge almost all of west-central Florida. In contrast, the Penholoway (+21 m) terrace is strongly represented in the data; more than 30% of the cave-survey data occur at this elevation (Figure 2). The Talbot (+12.8 m) terrace is well represented in the elevation histograms with a peak at +14 m; the cave-survey data do not reveal a peak at this elevation, but individual cave maps do show cave development at this horizon.

The Pamlico (+7.6 m) terrace is observed in the Pinellas County histogram, and the Silver Bluff (+2.4 m) terrace is strongly represented in the elevation histograms above modern sea level (Figure 2). In the cave-survey and well-cavity data, a prominent peak occurs between the elevations of these two terraces (Figure 2); however, the resolution in our data set makes it impossible to associate the peaks to either of the two terraces. In west-central Florida, the difficulty arises because the vertical span of the cave levels is in part controlled by the seasonal fluctuation of the water table, which is more than 3 m.

Offshore paleoshorelines and cave levels

In shallow water, a terrace between –10 m and –15 m is suggested by the offshore bathymetric data (Figure 2), and this range agrees with paleoshoreline features identified by Rodríguez et al. (2000) at –15 m. This elevation agrees with strong peaks in the spot-elevation data and both sets of well-cavity data. The bathymetric data also suggest a terrace at -30 m, which corresponds to broad peaks in the spot-elevation and well-cavity data.

In deep water, the presence of an intact barrier island complex (Jarrett et al., 2004) strongly suggests a paleoshoreline at about -70 m which agrees with peaks in the spot-elevation and well-cavity data (Figure 2). Small peaks in the spot-elevation and well-cavity data and a strong peak in the well-cavity data of Wilson (1988) suggest a cave level between –100 m and –120 m. These data agree with a -120 m sea-level lowstand during the last glacial-maximum. Survey data from deep, underwater caves are meager because of extreme technical challenges. Underwater data are biased toward the shallower and easier-to-explore underwater caves.

Concluding statement

The cave-elevation data are striking. Not only are caves in Florida tiered, but subaerial caves occur at consistent elevations above sea level over broad areas, and underwater caves occur at particular depths below the modern water table. Subaerial cave levels that align with nearby terraces above modern sea level affirm the hypothesis of a water-table origin for Florida caves linked to sea level stands. The underwater caves that align with distant paleoshoreline features, however, present a quandary. Did the presently underwater caves form when the distant shoreline and the water table were at nearly the same elevation? Was the gradient of the water table nearly flat between the caves and the distant shorelines during sea-level lowstands? Further investigation into the levels of caves in Florida will certainly involve these and many other questions.

References


SEA-LEVEL POSITION AT ~80 KA BASED ON PHREATIC OVERGROWTHS ON SPELEOTHEMS FROM MALLORCA

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Quaternary sea-level history provides a globally averaged record of continental ice volume variations throughout time and therefore a link between orbital forcing and Earth’s climate (Lambeck et al., 2002). An important role in reaching an understanding of the mechanisms involved in controlling climate change is to define the so-called “global sea-level curve”. For this purpose, sea-level data from a range of locations worldwide are increasingly being compared. To date, the primary evidence of a close link between climate, sea-level changes, and ice-sheet growth and decay comes from deep-sea sediments and precisely dated coral terraces (Shackleton, 2000; Gallup et al., 2002; Alley et al., 2005; Thompson et al., 2005). Unfortunately, the relative estimates of the sea level appear to show discrepancies that were attributed to errors in elevation due to reef erosion or uplift, assumptions about the water depth above the reef, and questions concerning transport of the analyzed sample. Therefore an independent source of data is required in order to precisely document the elevations and timing of sea level.

Mallorca is the largest island of the Balearic Archipelago, in the western Mediterranean Sea (Figure 1, inset). The coastal caves of Mallorca are highly decorated by a variety of speleothems (e.g., stalactites and stalagmites) that formed in Early Quaternary when the caves were air-filled chambers. Throughout the Middle and Upper Pleistocene, the caves were repeatedly flooded because of fall and rise of the Mediterranean Sea level (events that are related to variations in global ice volume). The water level of each flooding event left a clear mark (Ginés et al., 1981; Vesica et al., 2000) as a distinct encrustation of calcite or aragonite over existing speleothems and along cave walls (Figure 1). In Dimoni and Cala Varques caves, carbonates are precipitated at and just below the air-water interface, thus providing an excellent modern analogue that helps us interpret former depositional environment and sea-level variations. This type of carbonate precipitation is rare in other coastal caves worldwide, and thus provides a unusual chance to study the exact elevation of Mediterranean Sea level at a given time. Whereas not all encrustations can isotopically be dated, well-chosen ones (coarse crystalline calcite with little internal corrosion) are ideal materials for precise and accurate U/Th dating method.

Here we present direct and precise determination of the timing of sea level during marine isotope substage (MIS) 5a using U/Th TIMS technique. For this we collected five speleothems from five different caves scattered along the south and southeastern coast of Mallorca (Figure 1). The elevation of samples ranges between 1.05 and 2.25 m (± 5
cm) above present sea-level. Two subsamples were dated out of each overgrowth, except for CCVB, which is a 7-mm thick calcite coating deposited on the cave wall. The main subsample used for dating was extracted from the widest part of the overgrowth, thought to represent the mean sea-level position. In addition, one other subsample was drilled out within 3 to 5 cm above or below the main level and was interpreted as appertaining to the tidal range at the time the overgrowth was precipitated. Speleothem mineralogy was analyzed using a calibrated X-ray diffractometer. Four subsamples were calcite, three were high-Mg calcite, and two were aragonitic.

We find that between ~81.6 and ~79.7 ka the sea level during MIS 5a in Mallorca was ~1.5 m above the present, closely following the 65°N summer insolation peak, showing therefore the pattern is consistent with the Milankovitch insolation-forcing model. Differences in height of coeval phreatic overgrowths are related to small tectonic tilting affecting eastern Mallorca, which have been already evidenced in previous investigations (Fornós et al., 2002).

References


Figure 1. (A) Geologic map of Mallorca and its location in western Mediterranean Sea (inset); (B-C) Present-day carbonate encrustations; (D) Internal morphology of an encrusted stalactite; Paleo-levels of encrusted speleothems related to higher (E) and lower (F) sea-level stands.


SEA LEVEL CHANGE DURING MIS 5a RECORDED IN SUBMERGED SPELEOTHEMS FROM THE EASTERN ADRIATIC SEA (CROATIA)

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Introduction

In order to reconstruct relative sea-level changes on the Eastern Adriatic coast, 16 speleothems were collected from submerged caves and pits along the Croatian coast. Their growth provides an unambiguous indicator of former low sea levels and can be used to constrain past sea level elevation and timing. Two of them, taken from the U Vode Pit on the Krk Island, apparently recorded Late Pleistocene transgression known as marine isotope stage (MIS) 5a that occurred at ~ 80 ka. Similar research, for example, has been undertaken on submerged speleothems from the Tyrrhenian Sea (Bard et al., 2002), Bahamas (Richards et al.; 1994, Lundberg and Ford, 1994), Balearic Islands (Fornós et al., 2002) and Eastern Adriatic Sea (Vrhovec et al., 2001; Surić et al., 2005).

The Adriatic Sea is a semi-enclosed epicontinental basin situated between the Apennines and Dinaric mountain ranges, characterized by a relatively shallow northern part (0 to -120 m) with low gradient (0.02°). Such morphology makes it very sensitive to the eustatic changes, so after the Last Glacial Maximum (LGM), postglacial sea-level rise generated eight-fold widening of the shelf area (Correggiari et al., 1996; Cattaneo et al., 2003). Much of submarine Eastern Adriatic and Croatia is karstic, developed mostly in Cretaceous and Palaeogene limestones. During the global sea-level low stand associated with the LGM (~121 ± 5 m, Fairbanks, 1989), much of the coastal submarine karst (caves, pits with speleothem deposits) would have been above sea level. More than one hundred submarine caves and pits have been discovered and most of them have been explored, but comparing with adjacent coast and islands, their density is probably several times higher. Currently, the deepest speleothems found within them are those from the submarine of Ist Island from the depth of 60 m (Vrhovec et al., 2001).

Krk Island is the second largest Croatian island and situated in the northern part of the Adriatic Sea (Figure 1). Two stalagmites from the depths of 14.5 m (K-14) and 18.8 m (K-18) were collected from the U Vode Pit situated in the southern part of the island. Pit is formed in the Upper Cretaceous limestone and it is not completely submarine feature. The

Figure 1. Cross-section of U Vode Pit showing the locations of the sampled speleothems.
entrance of the pit is on the coast, at the elevation of 5.5 m, and the bottom is at -24 m. Relatively thin bordering bedrock allows free circulation between the pit and open sea, as well as settling of marine organisms (serpulids) within the pit. Only the upper 0.5 m is filled with brackish water.

Methods and results

Stalagmites K-14 (26 cm long) and K-18 (15 cm) were taken from their growth position and elevation recorded with digital depth gauge. Each sample was cut along the growth axis and polished to enable insight into the growth layers. Subsamples (230-415 mg) for MC-ICPMS U-Th measurements were drilled from the polished surface to constrain the timing and duration of what appeared to be hiatuses in deposition – recognised by changes in crystallography, morphology and colour of speleothem calcite and a thin red sediment layer (arrows in Figures 2 and 3). After several days of being exposed on the air, a white substance also appeared on the discontinuities that contain the red layer. The nature of this material was analysed using X-ray diffraction measurements directly on speleothems.

U-Th: The age range of sub-samples is ~94 to 54 ka (Figures 2 and 3). Uranium concentrations are low (30 - 70 ng g⁻¹) and errors are typically 1-6% (2σ), depending on the extent of detrital contamination. Combining the data for both samples, three phases of growth are observed >90 to 80 ka, a short period at ~80 ka, and ~65 to ~54 ka. We consider the initiation of the extended hiatus in K-18 (and perhaps also that in K-14) to be related to the sea level high event correlated with marine isotope stage 5a. In addition to changes in the morphology, crystallography and colour of calcite between the growth phases, initial ²³⁴U/²³⁸U also shows abrupt shifts indicating substantial differences between the hydrological regime for each phase of growth.

XRD: Qualitative X-ray diffraction measurements were done by PANalytical X’pert Pro theta-theta diffractometer equipped with multilayer parabolic monochromator using CuKα radiation. Measurements were performed directly on speleothems. On both speleothems, in the region marked by red line, halite and gypsum peaks were recorded in addition to calcite. No evidence for gypsum was observed for in situ
analysis of the speleothem growth just above and below the hiatuses, where only small peaks for aragonite and halite were found in addition to calcite.

**Discussion and conclusion**

According to the results obtained by radiometric measurements and X-ray diffraction, we can assume that deposition of speleothems K-14 and K-18 had been more or less continuous in subaerial conditions from 94 to 80 ka and 65 to 54 ka (and perhaps another short period of growth at ~ 80 ka). Sea level must have been lower than -14 to -18 m at these times.

Minerals recorded within hiatuses (calcite, gypsum, halite) are common cave minerals, but this assemblage also coincides with the suite of minerals that precipitate due to the evaporation of seawater (Ca-carbonates, gypsum, anhydrite, halite, K-Mg chlorides, arranged from less to the most soluble) (Seibold and Berger, 1996). Halite could, presumably, crystallize from the sea water that penetrated through the porous parts of speleothems due to its high concentration in the sea water, but it is unlikely that gypsum precipitated from the same water. It is more likely that it has been precipitated in situ at a time of exposure to marine conditions in a sea regression period. In accordance with obtained U-Th ages, this sea-level oscillation can be attributed to MIS 5a interstadial that was marked with two distinct sea-level highstand at ~84 and ~77 ka (Potter and Lambeck, 2003). Growth in the speleothem K-18 ceased from 79 to 65 ka, while the shallower speleothem, at ~14 m, experienced shorter period of submerging ~80 ka, so we can presume that the highest MIS 5a relative sea level in this region was slightly above ~14 m.

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**References**


Archives of Climate Change in Karst

FOSSIL REMAINS IN KARST AND PALEOCLIMATE
In spite of the fact that numerous paleontologically important cave sites that may be dated into the time period MIS 5 to MIS 9 are known in Central Europe (e.g., Döppes and Rabeder, 1997; Koenigswald and Heinrich, 1996, 1999), we found only 12 sites in the literature for which numerical dates have been published. A total of 31 layers have been dated in these sites. Most of them yielded dates corresponding to MIS 5, a few represent MIS 6 and 7 and only one can be correlated with MIS 8 (Rosendahl et al., 2006). Older numerically dated sites have not yet been characterized. More than half of the faunal strata have been dated because they are part of archeologically important sites. Numerical dates of purely paleontological sites are rare even though the archive cave and its rich bone beds offer enough potential for a systematic study. There are several reasons why this has not been done yet:

First of all, cave sites are not easily accessible (compared to open air sites); second, the mechanisms of deposition are complicated and can only be understood by investigating the genesis of the respective cave and its sediments in general. Cave studies therefore require additional knowledge in general speleology before the specific site can be interpreted correctly. The most important point why so few dates exist is related to the dating itself. Beyond the reach of the 14C method, bones, as mentioned above, can only be dated by the 230Th/U or ESR methods. The 230Th/U method is the one most commonly used. From today’s view, ESR dates of bones are highly problematic and should not be used (e.g. the dates of the Einhornhöhle). Only ESR dates of tooth enamel seem to be correct (e.g., Krapina).

TL dating used for speleothems exclusively (e.g., Grotte Scladina), is methodologically also of doubtful quality and TL dates should today be regarded with caution and their usage should be discontinued. Even the 230Th/U dating of bones is methodologically problematic due to the fact that bones very often prove to be open systems (for a discussion see Bischoff et al., 1995). The unusual standard deviations of the dates of unit J of Vindija (Wild et al., 2001) may be caused by exactly this open system problem. Therefore it is essential that prior to the dating, both the excavator and the dating geochemist discuss the chronostratigraphy, paleoecology and paleoclimatology of a site in detail. Even though, there are isotopists who view all 230Th/U bone dates critically and suggest they be discarded all together (e.g., Geyh, 2005).

The 230Th/U dating technique of speleothems has improved substantially, resulting in more reliable results since the 1990s. These have been used for the reconstruction of Middle to Upper Pleistocene climate and environment (e.g., Winograd et al., 1992; Kempe et al., 2002; Genty et al., 2003; Holzkämper et al., 2005). However, the dating of bones is still lagging behind and only a few laboratories (e.g., Vienna and Warsaw) are currently applying it. It would therefore be profitable if the technique of dating bones with 230Th/U could also be improved in the future. Interesting suggestions in this direction have been made by Hercman and Gorka (2000), Pike et al. (2002) and Eggins et al. (2005). Hoffmann and Mangini (2003) describe also an interesting method to date teeth and perhaps bones from open systems. Even though speleothem dating with the TIMS 230Th/U method is also not entirely free of methodological problems, TIMS speleothem dates are the best dates available today to establish cave based chronologies. Flowstone layers above or below the faunal strata can thus be dated, bracketing the ages of the bones (e.g. Schwabenreith-Höhle). The sites without speleothem-supported age models should therefore be revisited and additional samples should be dated to give the currently available bone dates further credibility. For climatic and ecological investigations of speleological faunas we should...
therefore target those cave sites which can be dated via speleothems. Additionally bones could be dated with TIMS $^{230}$Th/U and teeth with ESR in order to advance dating techniques in general.

Since the open system problem induces a substantial inaccuracy regarding dates of bones and teeth, a critical assessment of specific faunal assemblages with respect to their exact stratigraphical position remains difficult. In addition, numerical dates have certain standard deviation caused by methodological problems. This deviation can be quite substantial with the consequence that only two of the faunal assemblages suitable for ecological discussion can be attributed to either a Glacial or Interglacial. These two faunas are Layer 12-13 of the Bisnik Jaskinia (attributed to MIS 5e) and the fauna recovered from the pit of the Repolust Cave (attributed to MIS 7).

In case of Bisnik Jaskinia only the *Rangifer tarandus* component is in contrast to its Eemian age, but the faunal remains of the Repolust Cave combine both Glacial and Interglacial species, i.e. *Rangifer tarandus* and *Megaloceros giganteus* occurs together with *Capreolus capreolus* and *Sus scrofa*. Thus the presence of cold climate species is in contrast to the numerical Interglacial date. The accuracy of the numerical dates of all other sites and layers do not permit to attribute the faunas into a specific Glacial or Interglacial. Thus the faunas cannot be evaluated regarding their ecological and climatic character. Contradicting occurrences of Glacial and Interglacial faunal elements cannot be resolved as long as the numerical dates allow for both possibilities.

In conclusion, the now available numerical dates of palaeontological sites in Central Europe do not allow – with the exception of Bisnik Jaskinia and the Repolust Cave – a critical discussion of their faunal assemblages as to their ecological-climatic distribution. But even those two sites are not without contradicting faunal elements and it remains doubtful if they represent either Glacial or Interglacial faunas.

In spite of all these problems, palaeontological cave sites represent a rich archive that can deliver important contributions to the reconstruction of the Middle and Upper Pleistocene paleoclimate of Central Europe, provided many additional dates can be obtained to verify results obtained from other terrestrial archives.

References


PALEOCLIMATIC SIGNIFICANCE OF THE MAMMAL ASSOCIATIONS FROM UPPER PLEISTOCENE KARST DEPOSITS OF DOBROGEA, ROMANIA

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During the Upper Pleistocene, the Dobrogea region (eastern Romania) was characterized by a cold climate with strong continental influence alternating with temperate periods (interstadials). In this time interval in Dobrogea arrived some species adapted to cold areas, like the wooly mammoth (*Mammuthus primigenius* Blumenbach) (Table 1), wooly rhino (*Coelodonta antiquitatis* Blumenbach), reindeer (*Rangifer tarandus* Linnaeus), artic fox (*Alopex lagopus* Linnaeus), narrow-headed vole (*Microtus gregalis* Pallas), tundra vole (*Microtus oeconomus* Pallas) and steppe and extreme steppe elements like bovides (bison and *Saiga tatarica* Linnaeus antelope), equids (*Equus cf. transilvanicus*, *Equus spelaeus* spp., *Equus* sp., *Hydruntinus hydruntinus*), rodents (jumping voles, genus *Allactga*, steppe lemmings, genus *Lagurus* and *Eolagurus*) and steppe fox (*Vulpes corsac* Linnaeus).

Dobrogea represents the westernmost point were the yellow steppe leming (*Eolagurus luteus* Eversmann) was found. This species is adapted to dry steppe and deserts from Central Asia. Today the yellow steppe lemmings live in dry regions from western Mongolia, north-western China and Zaisan depression (Kazakhstan). The migrations of artic species of genus *Lemmus* and *Dicrostonyx* to the south ended in northern Romania.

The glacial and steppe mammal associations have regression period, retreating to the northern latitude of the European continent in interglacial phases but wanting the actual climate. The decrease of the frozen surfaces in the north allowed the steppe vegetation and forest to grow. In this period in Dobrogea came different species like the giant deer (*Megaloceros giganteus*, Blumenbach) and the red deer (*Cervus elaphus*, Linnaeus).

During the warm period of the first part of the isotopic stage 3 (local stages Adam I and Adam II equivalent to Hengelo-Les Cottes stages from Western Europe) (Samson, 1976), some herbivores like the wild ox (*Bos primigenius*, Bojanus) came in Dobrogea. In the second warm period of the isotopic stage 3 (Vistorna I local stages) (Samson and Radulescu, 1959; Samson, 1971), we found woodland-adapted species like the marten (*Martes* sp.) and the leopard (*Panthera pardus* Linnaeus), which were uncovered from “La Adam” Cave (Dumitrescu et al., 1963).

The short warm period from the last glacial cycle (isotopic stage 2) put in evidence species like the wild boar (*Sus scrofa*, Linneus) associated with *Megaloceros* and *Hydruntinus*.

| Fam. Mustelidae: | *Mustela lutreola* Linnaeus<br>*Putorius eversmanni* Brisson<br>*Mustela nivalis* Linnaeus<br>*Martes* sp. |
| Fam. Felidae: | *Panthera pardus* Linnaeus<br>*Panthera cf. spelaea* Goldfuss |
| Fam. Hyaenidae: | *Crocuta spelaea* (Goldfuss) |
| Fam. Ursidae: | *Ursus arctos* Linnaeus<br>*Ursus spelaeus* Rosenmuller |
| Ord. Artiodactyla | Fam. Suidae: | *Sus scrofa* Linneus |
| Fam. Cervidae | *Megaloceros giganteus* Blumenbach<br>*Cervus elaphus* Linnaeus<br>*Rangifer tarandus* Linnaeus |
| Fam. Bovidae | *Saiga tatarica* Linnaeus<br>*Bos primigenius* Bojanus<br>*Bison priscus* Bojanus<br>*Ovis cf. orientalis* Gmelin |
| Ord. Perissodactyla | Fam. Rhinocerotidae: | *Coelodonta antiquitatis* Blumenbach |
| Fam. Equidae: | *Equus cf. transilvanicus* Teodoreanu<br>*Equus spelaeus* sp.<br>*Equus* sp. (massive form) |
Table 1 (continued)

Equus scythicus Radulescu & Samson
Hydruntinus hydruntinus (Regaliá)

Ord. Proboscidea
Fam. Elephantidae:
Mammuthus primigenius Blumenbach

Table 2. Macromammal species from the last glacial cycle (Wurm, Vistula), Dobrogea.

Ord. Insectivora
Fam. Erinaceidae: Erinaceus europaeus Linnaeus
Fam. Talpidae: Talpa europaea Linnaeus
Fam. Soricidae: Sorex minutus Linnaeus
Neomys fodiens Pennant
Crocidura leucodon Hermann
Crocidura suaveolens Pallas

Ord. Lagomorpha
Fam. Leporidae: Lepus timidus Linnaeus
Lepus europaeus Pallas
Fam. Ochotonidae: Ochotona pusilla Pallas

Ord. Rodentia
Fam. Castoridae: Castor fiber Linnaeus
Fam. Sciuridae: Citellus citelloides Kormos
Fam. Gliridae: Dryomys nitedula (Pallas)
Fam. Dipodidae: Allactaga jaculus (Pallas)
Sicista subtilis (Pallas)
Scirtopoda telum Lichtenstein
Fam. Cricetidae: Cricetus cricetus Linnaeus
Cricetus migratorius ssp. 1 - 2
Cricetulus migratorius Pallas

Allocricetulus eversmanni (Brandt)
Mesocricetus newtoni ssp 1 - 2
Mesocricetus newtoni Nehring
Fam. Muridae: Mus musculus Linnaeus
Apodemus sylvaticus Linnaeus
Apodemus flavicolis Melchior
Fam. Microtidae:
Clethrionomys glareolus Schreber
Lagurus lagurus dobrogicus Rădulescu & Samson
Lagurus lagurus thracicus Rădulescu & Samson
Eolagus luteus rumanus Rădulescu & Samson
Eolagus luteus tomidanus Rădulescu & Samson
Eolagus luteus axshaenicus Rădulescu & Samson
Arvicola terrestris Linnaeus
Stenocranius gregalis ssp. (tundra form)
Stenocranius gregalis anglicus (Hinton) (steppe form)
Microtus epiroticus ssp. 1 - 2
Microtus agrestis Linnaeus
Chionomys nivalis (Martins)
Microtus oeconomus Pallas
Pitymys subterraneus de Sélys-Longchamps
Chionomys nivalis (Martins)

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THE PALEOENVIRONMENTAL SIGNIFICANCE OF SOME LATE PLEISTOCENE (MIDDLE VALDAI) DIPTERA PUPARIA (CALLYPHORIDAE) FROM THE EMINE BAIR KHOSAR TRAP-CAVE (CHATYRDAG, CRIMEA)

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Introduction
Climate signals from terrestrial records are extracted with a wide range of techniques, some of them based on biological evidence. In this respect, the coleopteran records and chironomid evidence seem to offer great potential (Walker, 2001). Other dipteres (including flies) also became important for paleoenvironmental and climatic reconstructions. Their remains were found in various Quaternary sediments (especially peat bogs, permafrost, organic silt/sand, etc.), but also, recently, from cave deposits. Fossil or subfossil fly puparia are commonly recorded mainly from archaeological sites (Egyptian mummies, Mexican tomb shafts and various settlement organic sediments) but also from Pleistocene deposits in Western Europe, associated to large mammal bones (Germoupre and Leclercq, 1994). Late Pleistocene fly puparia were described from steppe wisent horn core cavities and woolly rhino skulls in Late Eemian—Weichselian fluviatile deposits in Belgium (Gautier and Schumann, 1973). In North America, fly puparia are also found in Pleistocene open-air sites (Matthews and Telka, 1997) and caves (Bain et al., 1997). The preservation and/or mineralization of such organic remains in caves are linked to particular micro-environments.

Paleontological investigations carried out in caves from the Crimean high mountains (Crimea peninsula, Ukraine), especially on the Chatyrdag karst plateau (985–1527 m a.s.l.), revealed some interesting trap-caves containing passive vertebrate mass accumulations (Vremir and Ridush, 2002; Ridush and Vremir, 2004). The most interesting site is the Emine Bair Khosar (EBK) cave, which functioned as a natural trap at least for the last 50,000 years. Eleven paleontological sites were investigated inside this cave, providing over 7,000 identified specimens belonging to more than 40 vertebrate species (mammalian, avian and herpetological materials) as well as human remains. Beside the huge amount of vertebrate fossils (Vremir and Ridush, 2005), the invertebrates are represented by terrestrial snails marked by entrapped species (Helicidae) as well as troglophylic species (mainly Enidae) and insects. For this study, insect remains represented by Diptera (fly) puparia were collected from certain levels of EBK-Bc and EBK-Be2 sites. The preservation state of the organic remains (including fairly well preserved dung and stomachal content remains associated to a complete mammoth skeleton) suggest special tapho-faciesal conditions.

Task orientation
The necrobiotic processes include the cause and mechanism of death of an organism as well as the decomposition until the last stage of decay. In vertebrate carcass decomposition, five stages are separated until complete skeletonization, each characterized by particular biochemical and physical transformations (Blanco, 1992). The insects are the first opportunistic organisms which start to recycle the decomposing tissues. The succession of insects from the initial colonization of the carcass until skeletonization is predictable and important for forensic enthomologists to determine the moment of death. Insects feeding directly from carrion are known to arrive within minutes of death, followed by necrophagous/predatory organisms of a wide taxonomic variety. Among the first arriving insects very important are certain flies, especially the Callyphoridae and Sarcophagidae (blow and flesh flies). The development stages of fly larvae are well documented (Kamal, 1958) and forensic enthomologists have shown the effect of various environmental conditions on the rate of maggot development, one of the most important being the air temperature. Because the physical environment directly affects the development cycle of larvae, the comparative base of forensic enthomology linked with additional paleontological, palynological and sedimentological data can be used to determine the paleoclimatic and paleoenvironmental conditions during the carcass accumulation in the EBK trap cave.

From a meroclimatic point of view, the paleontological sites providing autochtonous fossil fly puparia are located at the limit of the entrance and interior facies of the cave, under the influence of seasonal temperature variations. The insect
colonization activity could indicate minimal temperature values, according to the tolerance regime of particular taxa. This is the first attempt to determine the meroclimatic conditions in some caves of the Crimean high mountains during the early-middle Valdai cold stage.

Site description

EBK, the largest cave in the area, is a good example of multiphase karst system with a total length of 1460 m and a depth of -125 m. Morphological data and its presumed development stages were discussed by Dubliansky et al. (1987) and Vremir and Ridush (2005). The collapse pit entrance (7-8 m diameter, 13.3 m deep) is located on the northern edge of the Chatyrdag plateau (990 m a.s.l.) and was opened by erosional processes. The present day meroclimatic regime inside EBK cave (according to the Onyx Tour database), varies trough the whole year, summer (July) mean temperatures measured at Museum chamber and Middle Bair passage (close to the fossiliferous sites) are 5.5–6.2 ºC.

EBK-Bc site represents an ascendant passage and a small room located at the depth of –41 to –37 m and somewhat below the main debris-cone. Hundreds of pupal remains were recovered by screenwashing from units EBK-Bc2b and EBK-Bc3. The mineralised (calcium phosphate) pupal cases were more or less dismembered. Even if the majority of pupal remains are rather fragmented, there is no doubt on their autochtony. EBK-Be2 site is located 25 m from the end of the main passage, 15 m under EBK-Bc at the depth of –53 m. The 25 complete puparia found in emerged stage were collected from around a disarticulated saiga antelope skeleton. Generally, the preservation is linked to very high organic matter content of the sediment in the entrance facies of this peculiar cave type, providing a rather good preservational microenvironment.

Species identification

The puparium of flies (Figure 1) is composed of the outer skin of the 3rd instar stage larvae, retaining many characteristics important for species identification. Larvae of most Callyphorid species are scavengers of carrion and dung and most likely constitute the majority of the maggots found in such material, however very few Pleistocene fossil species have been identified. From both sites, the pupal cases were found in emerged stage (empty). Most pupal remains from the Bc site are fragmented and difficult to reconstruct, but the general morphology, structure, size and colour are characteristic to Calypterate (Smith, 1931). The pupae from Be2 site are better preserved mainly because of the depositional setting and collecting technique. The puparia belong most likely to the Callyphoridae (obviously a cold and shade tolerant species). Size differences could be influenced by environmental factors (especially low temperature), carcass size and decomposition stage. The EBK pupae (5–7 mm in Be2 site, less than 6 mm in Bc site) are significantly smaller than those of P. terranovae and the majority of Sarcophagidae. Until we obtain a more precise taxonomic identification, we must note that certain differences exist between the development stages of various species, but in low temperature conditions (especially under 10 ºC), the larva- and/or oviposition rate and development trend decrease significantly and show statistically quite similar values in all common species (Ames and Turner, 2003).

Entomo-etological analogies and comparison

In order to define and evaluate the climatic and/or environmental signals potentially extracted from the fly-puparia materials, the most important analogies are listed following forensic-entomological studies (see also Figure 2).

Figure 1. Puparia of blow-flies (Callyphoridae) from EBK cave (Chatyrdag, Crimea): a – puparia in emerged stage in lateral view; b – same in caudal view, showing the pair of cylindrical processes.
**Nocturnal behavior**

Blowflies are inactive at night, oviposition being expected only during the day. A substantially reduced oviposition rate at night or in a cave entrance facies (30%) may be obtained only due to the attraction of new food sources. A decomposing carcass will attract certain species (especially Callyphoridae) however the low temperature will substantially influence the structure, oviposition and larvae development rate of the invading species. In EBK-Be2 and possibly in EBK-Bc, monospecific colonization is registered. The distribution and number of puparia-dispersal index (which not necessarily indicate the number of initially developing maggots), is quite low in EBK Be2 and rather high in EBK Bc, comparing to the size of colonized carcasses. The high dispersal index could indicate a temperature regime warm enough (over 5–6°C) to permit the successful development of a large number of pupae.

**Sheltering**

The larvae number decreases proportionally to the decomposition stage. Callyphores are more suitable than Sarcophages to colonise and oviposit in shade and sheltered settings as well as caves, even in low temperature regimes.

**Oviposition**

The females of blow and flesh flies deposit eggs or larvae mainly in and around the natural orifices of the carcass. Adult Callyphores oviposit, and some species are known to lay their eggs only outdoor (cave environment excluded). The initial species structure and colonisation of carrion depends by the environmental conditions and carcass size (Davies, 1999). A larger size carcass in open land is rapidly colonized by different species producing full sized individuals (the size of carcass could eliminate the competition). In a cave, even in large size carcasses, the limiting environment will directly influence the oviposition procedure, the maggot-cluster size and their development trend, so that undersized larvae could occur.

**Development**

The larvae (1st instar) feed rapidly and shed their skins (2nd instar). Feeding and growing rate accelerate and the outer skin develops completely (3rd instar larvae) before migrating from the food source to pupate. After roughly two weeks (in normal temperature conditions) an immature adult fly emerges from the rigid pupal case. The development rate of the larvae varies significantly due to temperature variations (Kamal, 1958; Anderson, 2000). The developmental sensitivity and increased mortality of pupating larvae to low temperature is explained by the pupae increased metabolic demands due to extensive tissue remodeling (Myaskowiak and Doums, 2002).

**Migration**

Fully developed larvae (3rd instar) normally migrate away from the carcass in order to find a suitable site to the prepupal and pupal stages. The distance varies depending on the substrate (burrowing) and/or presence of shelters, puparia frequently being reported from below or around the carcass. In EBK the empty pupal cases were found closely around and under the carcasses. In the Bc site it is difficult to determine a precise distribution, however they were commonly found around and under large herbivore skeletons in several units. This could indicate that carcass accumulation and their colonisation was a common and foregoing process and certainly not an isolated event.

**Temperature as influencing factor**

Low temperature has been reported to stop insect development under 4°C and even if oviposition takes place, the larvae cannot fully grow. Diapause and quiescence are the main physiological responses to low temperature condition (Myaskowiak and Doums, 2002). Diapause is a period during which growth and development of the insect is suspended, while quiescence is a drop in insect metabolism in response to a drop in temperature and only stops development for a short time, having effect on biometry as well. Only the rigid pupal case (puparium) could be fossilized, thus the larve must have reached the 3rd instar stage prior to temperature decrease.
Other palaeoenvironmental indicators

Pollen unit 2 is characterised by an open landscape (with *Artemisia*) followed by a more forested environment dominated by *Pinus* (unit 3). Malaco fauna consists of terrestrial snails, represented by xerophytic species with temperate affinities. *Helix albescens* is regarded as entrapped specimens, however some Enidae are shade-demanding but characteristic of a dry-ground open habitat, retreating in caves during winter and forming huge colonies. Their winter survival requires temperatures over 4°C. Herpetofauna is represented by lizards and forming huge colonies. Their winter survival requires temperatures over 4°C. Herpetofauna is represented by lizards and snakes, some of them warmth-demanding. The presence of Colubridae within unit 3 could indicate the proximity of a wooded environment. Avifauna - most specimens belong to the juvenile mountain chough (*Pyrrhocorax graculus*) and rock dove (*Columba livia*), quite frequent in European alpine karst, representing rests of pray associated to the peregrine falcon (*Falco peregrinus*) identified within unit 2. The sky lark (*Alauda arvensis*) is also typical for open landscapes, but the the fieldfare (*Turdus pilaris*) and eagle owl (*Bubo bubo*) in unit 3 are linked more to wooded areas, even if the owl prefers hunting in open landscapes. Theriofauna - the herbivores are represented mainly by steppe species (*Bison priscus*; *Saiga tatarica/borealis*; *Equus hemionus*; E. cf. *latipes*) within unit 2, including also arctic elements (*Mammuthus primigenius*, *Coelodonta antiquitatis*). Unit 3 is dominated by cervids, indicating wooded areas. The carnivores are represented mainly by the steppe fox (*Vulpes corsac*) and wolf (*Canis lupus*) and the steppe polecat (*Mustela eversmanni*), indicating an open landscape. The abundance of saiga antelope and steppe fox all year long year indicate mild winters and very low snow accumulation. The arctic elements (especially mammoth and wooly rhino of unit 2) are probably linked to winter migration events.

Discussion and conclusions

From a chrono-stratigraphic perspective based on the faunal assemblages and 14C AMS ages, the bone accumulation belongs to the early-middle Valdai cold stage (~ 40 Kyr. BP). The whole EBK-Bc section indicates a warming episode, from cold steppe (Bc2 a) to warmer dry steppe (Bc2 b–Bc3 a), preceded by a cold phase (Bc1 part). The upper unit (Bc3) indicates transition to a more forested (*Pinus* - dominated) and wet environment in the vicinity (Vremir and Ridush, 2005). This is most probably a warming episode within the OIS3 correlable with the lower Vitachev soil complex (Ukraine) and upper Moershoofd (The Netherlands), respectively Krasnaya Gorka (NW Russia) warm phases.

Brief (100–1000 years) and sharp climate oscillations mark OIS3 (57-24 Kyr BP) in the Greenland GISP2 and GRIP ice cores. The NW European pollen records display a number of warm intervals, such as Moershoofd (49–41 Kyr BP), Hengelo (39–36 Kyr BP) and Denekamp (32–28 Kyr BP). Similar oscillations, that might correspond to events in the North of the Alps, have been identified in Southern Europe (Van Andel and Tzedakis, 1996). As the fine structure of OIS3 still needs chronological improvements, the precise correlation with East European climatic oscillations is still problematic. Pedostratigraphical and palinological studies in Dniper valley in central Ukraine indicate a series of climatic and environmental variations during this interval (Rousseau et al., 2001). The succession of loess and soil complexes suggests rapid vegetational changes during the early and middle Valdai, especially in the interval of Pryluky and Vitachev soil complexes (70–27 kyr BP). According to Gerasimenko (2004), the Vitachev phase (50-27 Kyr BP: 14C and ESR dating) in Ukraine was characterised by the spreading of brown forest soils. Several soil horizons divided by loess are recognised, belonging to vt1 and vt2 stages. During the substages vt1b1 (approx. 44–50 Kyr BP, correlated to Moershoofd) and vt1b2 (approx. 39–44 Kyr BC, correlated to Hasselo), the Crimean foothills were characterised by forest-steppe. A cooling event (vt1b1/b2, correlated to Hasselo) is marked by loess formation, interbedded between the vt1b1 and vt1b2 soil horizons; the decrease of deciduous species and extension of steppe characterized the Crimean plain.

According to Van Andel and Tzedakis (1996), a brief interstadial event, about as warm as today, which seems to have followed a previous phase somewhat drier and colder than present, has occurred in NW Europe approximately 43 to 41 Kyr BP. The warmth ended suddenly, with a switch to an extreme cold phase (probably correlable to H4 Heinrich event). The sparse datings on the Vitachev soil complex, as well as the lack of comprehensive pollen diagrams and the few radiocarbon ages from the EBK section, cannot precisely indicate if the whole Bc sequence includes the equivalents of upper Moershoofd and Hengelo warm phases (49–36 kyr BP), or is restricted to a single warming event. The palynologic and paleofaunistic data show a gradual warming (from unit Bc 2a to Bc 3) which may be contemporaneous with a Mousterian butchery-site from Western Crimean lowlands (39.8 +/- 5 kyr BP; Patou-Mathis and Chabai, 2003). The paleoecological context, pollen and faunal assemblage indicate a mild period (a transition from steppe to forest-steppe), similar to that registered in EBK cave.

Taking account of the present day geomorphologic features of the area (steppe plains and dry grassy or forested hills in the N, high mountains reaching 1540 m a.s.l., and plateaus with abrupt, forested or rocky slopes to the Black Sea coast in the S), a huge variety of environments and biotopes are represented. The temperature variations over the mountains from North (plains) to South (sea coast) are remarkable, with winter gradients of +/- 10°C. The main reason of such differences is represented by the proximity of the Black Sea and the warm Anatolian current (from the E), and by the chain of the Yayla mountains, protecting the Southern coast from

...
Northern cold winds. Even if we consider the no-analog palaeoenvironments of the Late Pleistocene, and especially the status of the Black Sea basin, the Crimea certainly had a complex environmental and local-climatic structure and particular biomes. The sea (or a brackish lake) probably functioned as a natural thermostat, keeping temperatures higher in Southern Crimea than to the North in the Ukrainian plain. Crimea functioned as a refuge even for relict mediterranean species. This particular geomorphologic situation could explain why this mid-Valdaian warming event could eventually be more pronounced here (even in higher altitude) than in other regions of Central and East Europe.

Acknowledgements

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References


Theoretical and Applied Karstology

(off-topic contributions)
NATURAL AND ANTHROPOGENIC HAZARDS IN THE SREBARNA KARST WETLAND (BULGARIA)

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Introduction

The “Srebarna” tectonic wetland is situated in the W part of the Ajdemir Lowland, NE part of the Danubian Plain. The altitude of the lowland is 10-40 m in the strip along the Danube River, while the rest of it falls within the hypsometric zone of up to 100-120 m. The “Srebarna” tectonic wetland is situated in the W part of the confluence of the Kulnezhka and Srebarnenska Rivers. The wetland is not only a geological-tectonic phenomenon, but also a biosphere reserve under the protection of UNESCO. The development of the relict slope surfaces in the investigated region was a long and continuous process. It was connected with the rearrangement of the Fore-Carpathian and Euxine-Caspian Basins during the Neogene, the Black Sea Basin – during the Quaternary, and the morphostructural building and development of the Diagonal Swell. The tectonic development of this part of the country depended on the regional geodynamic circumstances at the boundary between the North Bulgarian Arc and the Lower Danubian Plain and on the local development of the single blocks. The tectonic differentiation of the blocks formed the board, plateau and depression, river terraces, main direction of the Danube River and rearrangements of its tributaries, flood terrace width, asymmetric and canyon-like valleys, etc. A paleoseismic dislocation has been established in the “Srebarna” region. This earthquake event took place in the Pleistocene-Holocene (Angelova, 1995, 1996, 1999). It was accompanied by considerable disturbances of the relief and geological environment. It provoked the disappearing of the Kulnezhka and Srebarnenska River mouth, river terrace deformations and limestone block collapse. The “Srebarna” wetland was formed with boggy sedimentation in front of this block. No catastrophic earthquake events have been established within the Ajdemir Lowland during the subsequent stages. The differentiated tectonic development was reflected in the quantitative parameters of the contemporary occurring morpho-genetic processes: erosion (soil, linear and surface one), accumulative, gravitation, karst and other processes.

Results

The consequences of the contemporary tectonic processes and related destructive geological-geomorphologic processes and phenomena, would have their reflection on the whole social life in the region. This problem has not been systematically considered until now. The information gathered during the present study provides the possibility to assess the hazardous processes and phenomena displayed in the region of Srebarna, as a result of the slow and rapid tectonic movements. These assessments have been presented using the classification of Broutchev et al. (1994) (Table 1, next page).

The purpose of the present paper is to study the slopes as a genetic surface with different inclination and to analyze the tectonic control of their spatial and temporal initiation and development. It is focused on the evaluation of the hazards geological, geomorphologic, tectonic and anthropogenic factors within a territory of strategic position in the geodynamic evolution of Europe. For the study purposes, different types of specialized and assessment maps are prepared.

After a short period of time (1980-1993) it was established that the average level of the river Danube was decreasing and that this could not solve the problem concerning the refreshing of the waters of the reserve. A canal had to be dug to replace the old natural drainage canal and canal-locks had to be built to prevent the waters of the reserve it now it is much more often that waters from the Danube enter Srebarna.

In 1974, in order to meet the growing tourist interest to the Srebarna reserve, the district council of the town of Silistra opened a small natural history museum in the village of Srebarna. In the same year, the Ecological Station of the Bulgarian Academy of Sciences was also restored.
Table 1. Assessment of hazards processes in the Srebarna karst wetland area.

<table>
<thead>
<tr>
<th>Type of destructive processes</th>
<th>Degree of hazard and possible consequences</th>
<th>Affected areas</th>
<th>Forms in plan</th>
<th>Duration</th>
<th>Velocity</th>
<th>Degree of prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Earthquakes with primary and secondary seismic effects</td>
<td>Disaster</td>
<td>Regional</td>
<td>Surface, point</td>
<td>Short-term</td>
<td>Sudden, rapid</td>
<td>Low</td>
</tr>
<tr>
<td>Tectonic movements along faults</td>
<td>Catastrophe</td>
<td>Zonal</td>
<td>Linear</td>
<td>Constant</td>
<td>Slow</td>
<td>High</td>
</tr>
<tr>
<td>Barring of river valleys</td>
<td>Disaster</td>
<td>Local</td>
<td>Linear</td>
<td>Constant, short-term</td>
<td>Sudden</td>
<td>Low</td>
</tr>
<tr>
<td>Mud-rock torrents</td>
<td>Disaster</td>
<td>Local</td>
<td>Linear</td>
<td>Short-term</td>
<td>Sudden</td>
<td>Low</td>
</tr>
<tr>
<td>Floods</td>
<td>Disaster</td>
<td>Regional and local</td>
<td>Linear</td>
<td>Short-term</td>
<td>Sudden</td>
<td>Low</td>
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<tr>
<td>Destruction of the dike, engineering equipment for water supply in Srebarna</td>
<td>Disaster</td>
<td>Local</td>
<td>Linear</td>
<td>Short-term</td>
<td>Sudden</td>
<td>Low</td>
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<tr>
<td>Erosion:</td>
<td>Disaster</td>
<td>Regional</td>
<td>Linear</td>
<td>Constant</td>
<td>Slow</td>
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<tr>
<td>- Linear</td>
<td>Accident</td>
<td>Regional</td>
<td>Surface</td>
<td>Constant</td>
<td>Slow</td>
<td>High</td>
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<tr>
<td>- Surface</td>
<td>Catastrophe and failure</td>
<td>Local</td>
<td>Linear, surface, point</td>
<td>Long-term</td>
<td>Rapid, sudden</td>
<td>Low</td>
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<tr>
<td>Gravitation (landslides, rockfalls)</td>
<td>Failure</td>
<td>Local</td>
<td>Surface</td>
<td>Constant</td>
<td>Slow</td>
<td>High</td>
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<tr>
<td>Slope creep</td>
<td>Failure</td>
<td>Local</td>
<td>Surface</td>
<td>Constant</td>
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<td>High</td>
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<td>Sediment deposition</td>
<td>Failure</td>
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<td>Point</td>
<td>Short-term</td>
<td>Average</td>
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<td>Groundwater table fluctuations</td>
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<td>Bog formation</td>
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<td>Suffosion</td>
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References


PRELIMINARY STUDY OF SOIL TILLAGE ERROSION IN A KARST MOUNTAINOUS AREA OF CHINA

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The karst area in China is about 3,340,000 km² and mostly located in the southwest region. Over the past several decades, karstic desertification has become a serious environmental and ecological problem in the karst region of China due to deforestation and farming activities. Besides the impact of changes in natural conditions (e.g., climate changes) on soil erosion, human influence such as tillage by hoe, plough or machine has accelerated soil erosion in the karst mountain region. As an important part of soil erosion, soil tillage erosion which is defined as the movement of soil redistribution in a certain area remains poorly understanding. In order to understand the controlling factors of soil tillage erosion, we have conducted an experiment to monitor the impact of farming activity by hoeing plough in the mountain hill of Zhongliang Mountain in Chongqing, using a simple but traditionally tracing method (Figure 1). Using gray gravels (3-7 mm in size) as tracers mixed in the tillage soil, we have selected five experimental sites (1 m by 0.2 m in size) with different slopes in the studying area to monitor the erosion rate of the tillage soil (Table 1). Our study results show that the movement of the studied soil ranges from 0.21 to 0.3 m with the maximum of ~1 m and the flux of soil movement is in a range of 4.26-10.78 kg/m per tillage. Based on the observation, we estimated the rate of soil tillage erosion in the area is on the order of 14.20~35.93 ton/hm² per tillage event. The experiment results also reveal that the erosion rate is proportional to the slope of the studying sites. In karst region, the land surface is generally fragile with steep slopes and abundant limestone rocks. Soil erosion in such an area is an irreversible process, so that proper use of the landscape in the area becomes an important issue to keep the earth surface healthy. We plan to use radioisotopes such as $^{137}$Cs, $^7$Be and/or $^{210}$Pb as tracers to accurately determine the soil erosion rates in the karst region of China.

Table 1. The results of our tracing experiment on soil tillage erosion. Five studied experimental sites with different slopes have been conducted. The total recovery of the tracers is each experiment is greater than 97%, indicating the accuracy of the results. Calculation equations: $T_m = \int_0^L (1 - C_x/C_0) M_s dx$ and $R = 10 T_m/L_d$, where $T_m$ is the amount of shifted soil per unit distance; $C_0$ and $C_x$ are weight of tracer at initial position and distance X; $M_s$ is solid dry weight per unit area; L is the maximum distance of measurement; R is the erosion rate; and $L_d$ is the length of the slope.

<table>
<thead>
<tr>
<th>Slope of studied sites (%)</th>
<th>Tracer recovery (%)</th>
<th>Shifted distance of soil (X) (m)</th>
<th>Soil dry density (kg/m³)</th>
<th>Tillage depth (m)</th>
<th>$T_m$ (kg/m)</th>
<th>R (t/hm²)</th>
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<tr>
<td>Before tillage</td>
<td>After tillage</td>
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<tr>
<td>3.5</td>
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<td>24.9</td>
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<td>1174</td>
<td>0.17</td>
<td>6.93</td>
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<tr>
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</tbody>
</table>
**Figure 1.** (a) Photograph of a typical karst mountain region, generally with steep slopes, abundant boulders and fragile surface. Soil erosion in such an area is irreversible; (b) Photograph showing the study site and the simple tracing method.

**URSUS SPELAEUS RELOADED**

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*Ursus spelaeus* was described in more than 50 caves in Romania, mainly in the Southern and Western Carpathians, including among others Peștera Ureșilor de la Chișcău, Onceașa Cave, Rece Cave, Peștera cu Oase etc. Some of these caves host remains of hundreds of exemplars, while in others only traces of life can be found.

In this paper we report the main results of 40 years of research regarding the presence of *Ursus spelaeus* (Cave Bear) in Romanian caves. We firstly present general aspects regarding the cave bear (*i.e.*, distribution, inventory of traces of life, taxonomy); while in the second part we present the interaction between humans and bears. Here we briefly discuss the possible presence of cave bear worship, the problem of the hunting of the bear by prehistoric man; in the end some remarks being made upon the disappearance of the cave bear, at the end of the last ice age, due (or not) to human impact.

Also, given the presence of *Ursus spelaeus* mainly in high mountain areas across Europe, we speculate on the term “Alpine bear” as an alternate term for “cave bear”.
EUTROPHICATION PROCESS IN THE PLITVICE LAKES, CROATIA, AS A CONSEQUENCE OF ANTHROPOGENIC POLLUTION AND/OR NATURAL PROCESSES

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Introduction

The Plitvice Lakes are series of lakes, tufa barriers and waterfalls located in the karst region of northwestern Dinarides in Central Croatia (Figure 1). According to Polšak (1979) the impermeable Upper Triassic and Lower Jurassic dolomites and marly limestones prevent vertical water circulation. The permeable regions are characterized by karst dolinas, swallow holes, caves and poljes. Tufa are deposited on either limestone or dolomite bedrock.

In the Plitvice Lakes calcium carbonate precipitates from the water in form of tufa forming tufa barriers and in form of fine-grained lake sediments. Conditions for tufa precipitation at the Plitvice Lakes including water chemistry, isotopic measurements of water and tufa/lake sediments and diagenesis of tufa were studied previously (Srdoč et al., 1985; Horvatinčić et al., 1989; Chafetz et al., 1994; Horvatinčić et al., 2003). All these studies showed that process of tufa precipitation is very sensitive to any kind of environmental pollution including water, soil and air.

In the last decades enhancement of eutrophication process in this area, particularly in some lakes, has been observed. This process is usually the consequence of inflow of nutrients into the lakes. The reason for the intake could be anthropo-
genic pollution, but the natural origin of nutrients in the water is not excluded, e.g. input of percolating water from the humus surrounding the lakes (the land area is covered mainly with leaf forest).

Lake sediments as the results of calcium carbonate precipitation from the dissolved inorganic carbon (DIC) record any kind of pollution in the water from the recent time, but also from the past. For this study we used surface lake sediments, the uppermost 40-45 cm, except location 4 up to 20 cm, from four different karstic lakes at five sampling points (Figure 1). The main characteristics of the sampling points are presented in Table 1: name of the lakes, lake area, water depth at the sediment sampling and sedimentation rate based on $^{137}$Cs and $^{210}$Pb measurements (Obelić et al., 2005). Sediment cores were taken from the uppermost Lake Prošće to the lowermost Lake Kaluderovac and the sites included lakes with strong eutrophication (locations 2, 3, 5) and with less pronounced eutrophication process. Samples for analyses were cut from the frozen sediment cores into 1–2 cm thick layers and dried at 120 °C. The following analyses have been performed: mineralogical and organic elemental analyses, analyses of radiocarbon isotope $^{14}$C and stable isotope $^{13}$C, and trace element analyses.

### Results

The results of $^{14}$C activity and $\delta^{13}$C values vs sediment depth for all five locations are presented in Figure 2. $\delta^{13}$C for the most sediment samples are between −9 and −7‰ and these values correspond well to the previous measurements of $\delta^{13}$C values of tufa and lake sediments from the Plitvice Lakes area (Horvatinčić et al., 2003). The exception is location 3 with $\delta^{13}$C values between −5.5 and 5.0‰, and also $^{14}$C activity of this sediment is much lower (30–35 pMC) that at other locations. This site is close to the mouth of Rječica brook to the Kozjak Lake and transport of some mineral components, but also organic material from the stream of Rječica to the Kozjak Lake is possible. For all other locations the calcite in sediment is mainly formed by authigenic precipitation from DIC in lake water. The $^{14}$C activity of sediments shows steady increase from the uppermost Lake Prošće (mean value 68.8 pMC), through Lake Gradinsko (site 2, mean value 76.5 pMC), to the lowermost Lake Kaluderovac (site 5, mean value 81.2 pMC). It is again in good correlation with the previous results of increasing of $^{14}$C activity of DIC in water in downstream flow of Plitvice Lakes (Srdoč et al., 1985), that is due to the isotope exchange process between atmospheric CO2 and DIC in water. The distribution of $^{14}$C activity in sediment shows slight increase of $^{14}$C in the first 5–10 cm. The peak activity between 5–10 cm is the consequence of bomb-produced $^{14}$C activity in the atmosphere in the sixties of last century. The 1963 peak values of $^{137}$Cs in Plitvice sediments are at 7 cm for site 2 and at 9 cm for site 1 (Obelić et al., 2005) that is in good agreement with the $^{14}$C peak activity. According to the $^{14}$C and $^{137}$Cs activity distribution in the sediments we can determine approximately the sedimentation rate of lake sediments. Roughly approximated, the upper first 10 cm of most sediments correspond to the last 50 to 100 years.

The results of mineral composition, organic composition (C-H-N analyses) as well as trace element analyses including B, Ba, Cd, Cr, Cu, Mn, Ni, Sr, Pb and Zn are presented in Figure 3. The concentrations of measured values are presented according to the sediment depth.

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**Table 1.** Data about lake areas, water depth of sediment sampling and sedimentation rates calculated according to $^{137}$Cs and $^{210}$Pb.

<table>
<thead>
<tr>
<th>Lake</th>
<th>Prošće</th>
<th>Gradinsko</th>
<th>Kozjak K2</th>
<th>Kozjak K1</th>
<th>Kaluderovac</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake area (km²)</td>
<td>0.68</td>
<td>0.08</td>
<td>0.82</td>
<td>0.82</td>
<td>0.02</td>
</tr>
<tr>
<td>Water depth (m) of sediment sampling</td>
<td>19</td>
<td>5</td>
<td>2</td>
<td>21</td>
<td>3</td>
</tr>
<tr>
<td>Sedimentation rate (kg/m²yr)</td>
<td>$^{137}$Cs</td>
<td>0.54 - 0.92</td>
<td>1.4</td>
<td>0.76</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>$^{210}$Pb</td>
<td>1.2 - 1.3</td>
<td>3.4 - 4.4</td>
<td>0.8 - 0.95</td>
<td>2.6 - 2.72</td>
</tr>
</tbody>
</table>

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**Figure 2.** $\delta^{13}$C values and $^{14}$C activity vs. sediment depth for all five locations (K2 and K2-1 are the same locations but the sediment cores were taken in different time). $^{14}$C activity is expressed in percent of modern carbon (pMC).
The mineral composition of sediments shows that the major component at all locations is calcite (80–99%), showing slight increase with depth, except at location 3. This is also proved by δ¹³C values of carbonates from different locations that were discussed above (Figure 2). In mineral composition the dolomite, quartz and some minor components...
as aragonite, feldspars and phyllosilicates were also detected (Figure 3).

Analyses of organic components in sediment show different content for different locations. Steady decreasing of organic component from the uppermost Lake Prošće (7.5–10.9%) to the lowermost Lake Kaluderovac (1.9–3.4%) is observed. Exception is again Lake Kozjak, site 3, with much higher content of organic part (11.4–36.6%) and the explanation for this was given above.

The distribution for the most of trace elements (B, Ba, Cr, Cu, Ni, Cd) along sediment depth (Figure 3) is quite uniform for all sediments. The concentration of some elements slightly increases at the top 10 cm of sediment, that according to $^{14}$C, $^{137}$Cs and $^{210}$Pb dating corresponds to last 50-100 years. This is the case for phosphorus in all sediments, lead in sediment at sites 1 and 4, zinc in sediment at sites 1, 2, 3 and 4, and strontium at sites 2 and 5. Concentration of most trace elements including phosphorus is the highest at the location 3 in Lake Kozjak. This is the consequence of the high degree of the eutrophication process in this area. The content of trace elements as well as organic matter decreases in downstream direction, from Lake Prošće to the Lake Kaluderovac. This fact indicates that the most of trace elements in sediments could be of natural origin due to the transport from the main springs into the Lake Prošće and their steady deposition along downstream lakes. There is no significant difference among the trace element concentrations in the upper part of all sediments, corresponding to last 50 years when higher anthropogenic influence can be expected, and the lower part of the sediments, corresponding to the period 100-200 years before present. Higher concentrations of phosphorus and some other elements in the lake sediment can be a consequence of input of natural organic matter to the lake water by natural process, e.g., humus deposition in the lake sediments from the environment.

Acknowledgements

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Apulia, located in the foreland of the Apennine thrust belt, has long been considered a stable area of the Italian peninsula. The exception is the Gargano region, where active tectonics is well known. In recent times, however, the first evidence of active tectonics, which is also producing a moderate seismicity, is coming from various disciplines: geophysics (Del Gaudio et al., 2001, 2004), structural (Fracassi et al., 2004) and geomorphological analysis (Iurilli et al., 2005; Mastronuzzi et al., 2003), historical seismology, archaeology.

As already known, karst is also controlled by tectonics, which can appear recorded in its forms. For this reason, together with its conservative environment, endokarst and related sediment analysis represent a useful tool for the study of active tectonics (Forti and Postpischl, 1984). On this basis, surveys in several caves have been carried out and have shown interesting evidence such as: axial displacement within the growth of stalagmites, broken columns, relative shifts between stalactites and corresponding stalagmites, and blocks breakdown.

The results of this first test point to a hypothesis of active tectonics both along the western and the southern border of Murge karst plateau (Altamura fault scarp, and Soglia Messapica fault step). Here some currently studied caves permitted numerous interesting data to be collected. For example, close to the Soglia Messapica step, Nove Casedde cave preserves karstic deposits showing alternating deposition and breaking phases, some younger than 240 ka (radiometric age). Therefore, taking into account the lack of sufficient data concerning neo-tectonics in Southern Apulia, detailed studies of caves and speleothems as recorders of tectonic events have been planned, according to the following:

1 – exploration of caves along the most evident tectonic alignments of the Apulian karst;

2 – study of cave-filling sequences and of neotectonic displacements they may have recorded;

3 – instrumental monitoring of the most interesting structures (Šebela et al., 2005).

At the present, dimensional measurement devices have been installed on two selected tectonic structures in that cave, for a long-term monitoring of possible future tectonic displacements.

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AN APPROACH TO THE KARST GROUNDWATER RESOURCES ASSESSMENT

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Introduction

The management of groundwater flow systems in karst regions appears, at present, to be the most important proceeding for solving water deficiency problems during recession periods. Faced with a lack of data for characterising the karst aquifers, analyses of spring hydrographs, in first stages of investigation, may provide indirect information about the structure of karst hydrogeological systems. Water supply potentials were evaluated on the basis of groundwater budgets and applied in case studies from Eastern Serbian karst. The results obtained through these analyses presents a first estimation of karst groundwater potentiality and contribution to feasibility studies and condition of sustainable groundwater management.

Initial characterization of karst aquifer

Karst aquifers are characterized by high heterogeneity, discontinuity and spatial variability of hydrogeological parameters. Facing such particularities, it is necessary to point to the “duality” of karst (Király, 1995), in particular the duality of the groundwater flow (White, 1969, Atkinson, 1997). Presence of this duality causes a widely known phenomenon, named “inversion of hydraulic gradient” (Drogue, 1980). Therefore, it is very important to establish the relationship between those two-type interconnected flows, as they provide valuable information about the storage capacity. Determination of this parameter not an easy task, thus analyses of spring hydrographs could provide valuable indirect information on the structure of karst hydrogeological system (Larocque et al., 1998, Bonacci, 1993, Krešić, 1997). The method of implementing time series analyses was developed by Mangin (1984).

The systematic approach is mainly referring to input-output relationship. As an initial step for characterisation of a karst aquifer, the results of autocorrelation, spectral density and cross-correlation were taken into consideration (Figures 1, 2).

Altogether, the analysis presented shows large storage capacities for all springs, with exception to the Grza spring. Water is stored in these karst hydrogeological systems during the recharge period and is later released during the dry season. Dynamic resources are the consequence of a significant role of matrix porosity and small fissured system along with presence of storage in the epikarst zone, provide slow and subsequent water release.

Regarding the potential for groundwater tapping based on “loan” of deeper stored water, the optimal sources is Krupac and St. Petka. The reasons for this are well developed karst channels, small fissured system and matrix porosity which provide, respectively, the amount of water to be loaned from storage during the recession period, and relatively fast water compensation during the recharge period. On the contrary, Grza spring is not suitable for application of such measures. As for the Nemanja spring, there is a possibility for applying of such measures, but defining the optimal exploitation capacity must be done with great attention due to the probability for overexploitation. This was proven during further hydrogeological exploration using by mapping, geophysical methods, borehole drilling etc.

In addition to the analysis previously presented, hydrograph separation, to assess base flow, was also undertaken. Considering the fact that base flow represents drainage of previously accumulated water, the remainder must be newly-infiltrated water (Krešić, 1997). This graphical procedure does not estimate a “real” values of base flow, thus showing only the ratio between two separated components of hydrograph. According to Base Flow Index (BFI) which is the ratio between base flow and total flow, information concerning storage capacity could be easily obtained.

Karst groundwater budget and assessment of exploitation capacity

As a first step towards rational management and use of karstic water resources, it is necessary to estimate the total (overall) water potential, based on groundwater budget. The lack of available data is often conditioned by the determination of effective infiltration using the stochastic-conceptual model (Zhang et al., 1996; Jemcov et al., 1998). System is simulated as a Lumped-Parameter Model. Considering the functioning of karst hydrogeological system is mostly non-linear, usage of a multiple non-linear regression (MNC) is recommended.

In karstic environment aim at assessing the effective infiltration rate (R) is closely related to the evaluation of potential
and real evapotranspiration. Because of their simplicity, the
Thornthwaite method for estimating potential evaporation
were used (Thorntwaite 1948). The infiltration values (R)
are obtained by calculating the rates between rainfall and
evapotranspiration values by means of daily budget method.
The computed values were calibrated in order to obtain a
better fit between recorded and simulated values (Jemcov et.
al. 1998). From this calculation the average annual infiltra-
tion values are ranging from 60% to 30%.

Based on the inflow and outflow relationship, the values for
changes in storage (DVi) were obtained by varying the con-
tinuous cumulative values to the initial storage. The most
sensitive part of this analysis is the estimation of initial stor-
age, which should be calibrated through model, and knowl-
edge of this parameter is strictly connected to the level of
hydrogeological exploration.

Using the estimated water resources stored in the karst aquis-
fer as a baseline point, further analyses were conducted to
assess variations in storage under artificial conditions (ex-
ploration potential and limits). Considering the fact that the
concept of water tapping was based on a ‘loan’ from karstic
reservoir storage, various exploitation scenarios were applied
and tested. The optimal capacity does not mean avoiding
overexploitation of karstic sources, thus the rational exploi-
tation demands respect certain limitations, such as the eco-
logical limitations (guaranteed minimal and sustain flows
downstream of tapped source).

**Conclusion**

The applied concepts provide valuable information’s about
storage changes in karst reservoirs and a consequent assess-
ment of exploitation capacities. This could lead towards
commensment of both, feasibility studies and research pro-
grammes, i.e. promotion of a principle of sustainable man-
agement of karst aquifers.

After presented initial stage of research, further steps od
model development will include analyses of additional vari-
ables as snowmelt, soil moisture regime, interception, etc.
The final outcome of model improvement will be applied
and ended up on spatially distributed model.

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Few citizens of the world would have trouble understanding the terms springs, ground water, geology, or hydrology. Newer water terms that are less familiar include: bottled water, sparkling water or mineral water, all of which now come in vessels of different shapes, sizes, colors and labels. Note that a glass of cold, refreshing tap water will cost about 1 cent, whereas the same glass of sparkling cold bottled water will cost 100 or more times that price, and even more than a gallon of gasoline. The term karst is not as well known, and it is the most pertinent objective of this meeting to bring about a better knowledge and understanding of karst and climate.

“The past is a key to the future.” A wise statement; however, as an editor of the international journal of Environmental Geology, I am repeatedly reminded that some of my fellow younger and perhaps a few older scientists, particularly those in the consulting area, are not well aware of the stepping stones they have inherited from the past. This is evidenced by this use of phrases in submitted papers for publication, such as, “development of a new concept, method, or solution” that had been published many years before. A suggestion: “do your homework” and adequately carry out reference research while preparing your project proposals. Acknowledge primary contributors on your subject. Sometimes a list of carefully selected references is more important to a fellow scientist than the paper itself.

Historically, the use of karst spring waters dates back to the earliest civilizations. Cuneiform tablets provided the first written records of hydrological research that describes an expedition in 852 BC by the Assyrian King Salmanassar III to the headwaters of the Tigris. The source of the Tigris is a karst spring. Inscriptions near the entrance to the cave from which the spring discharges states that it is the source of water to the Tigris and immortalize Salmanassar III. It is the first known reference to the formation of stalagmites. Other examples from the Bible include the principal sources of water for the ancient city of Palmyra in Syria where a spring called Efca discharges water that is warm (33°C), sulphurous and radioactive. It was believed by some to have curative powers. In Biblical times, karst-caves or systems provided water in Sinai and at Shobek, Kirhareshet, Lachish, Jerusalem, Hazor, and Gezer.

In China, a book, “Annotation on Water Scripture” by Li Daoyuan, published during the second century A.D. describes hot springs, and the water from Lisbon Spring, in China, is recorded in 1134 BC as being used for medical purposes by many monarchies.

In Europe, one of the most famous springs is Bath in England. It is the site of an early spa during Roman times, where soldiers enthusiastically visited these hot springs for rest and relaxation. This source became contaminated and represents one of the earliest recorded problems with pollution of spring waters. Hot springs were famous throughout the Roman Empire; and many remain today as health resorts.

In 2004, Dorothy Crouch, in her books, Water Management in Ancient Greek Cities (1993) and Geology and Settlement Greco-Roman Pattern presents two of the most comprehensive texts on interrelationships between water supplies and development of civilization in karst. The books illustrate that many of our basic hydrogeologic concepts of karst were developed by early philosophers of ancient Greece and were used in the sighting, planning, and construction of Syracuse, Corinth, Delphi, Miletus, Ephesus, plus five other sites that were studied and compared representing 1400 years of urbanization by the Greeks and Romans. In Persia, Egypt and other places in the Middle East, groundwater was developed from qanants, and the early development of artesian wells occurred in the desert areas of Egypt.
The applicability of resistivity methods in ground water investigations is well recognized since a long time. As water-saturated rock formations have a lower electrical resistivity than dry ones, conducting an electrical resistivity survey of a certain ground section - by means of conventional geoelectric methods (Kelly and Mares, 1993) – should result in identifying low resistivity anomalies, that provide hints about favorable locations for ground water tapping. However, because of the extreme in-homogeneity of karst areas, resistivity investigations in such environments are subject to certain specificities.

Resistivity investigations specificities in karst terrains

In terms of fluid permeability, carbonate rocks bodies are known to exhibit extreme in-homogeneities. Such permeability contrasts are not immediately discernible in low topography terrains, where hydraulic gradients are inevitably bounded to small values. In this kind of environment, a gently undulating water table strongly obscures permeability disparities, which are accommodated by corresponding contrasts in groundwater velocities. There results a continuously saturated groundwater body, which moreover, fails to display significant contrasts in terms of its electrical resistivity. The only way by which resistivity methods can efficiently investigate the structure of such a natural setting is by taking advantage of contrasting water salinities: a fresh water / salt water contact (for instance at the border of a sea or of a salt lake), or the artificial injection of an electrolyte in a freshwater swallet, well, etc.

Alternatively, in rough topography terrains, hydraulic gradients may dramatically steepen within the low permeability blocks. Additionally, seepage faces may appear at the boundaries which separate such blocks from high permeability, unsaturated flow paths (open fractures, caves). As a result, the water-saturated domain may appear as highly discontinuous, and thus resistivity contrasts should be readily discernible. At the same time, the results interpretation in such cases is not straightforward: large electrically conductive domains can represent the water-saturated rock bodies, whose fluid-permeability may be however poor; alternatively, fast flow conduits, which in many cases may be unsaturated, occur as slender objects that are not detectable as clear anomalous features. Provided that a punctual access to such a flow path exists (a swallet, an outlet, a shaft, etc.) optimum results can however be obtained by means of the so-

Figure 1. Water table map and hydrogeological section in Dâmbul Nîțchii area, interpreted from resistivity data. Legend: 1. water table contour (in meters); 2. draining fracture; 3. flooded area.
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**Case studies**

A) In a rough topography terrain - Padurea Craiului Mountains, mining for bauxite has required detailed resistivity mapping of water-saturated limestone bodies (Mitrofan, 1984). In this case, the vertical electrical soundings have been performed by means of less conventional, pole-dipole (Lögn) arrays that are less sensitive to spurious anomalies induced by the rugged topography. A sloping mine gallery that had accidentally reached a water-saturated domain (revealed by uniform, although not quite severe seepage all around the gallery ceiling, walls and floor) has provided a calibration point for the position of the top of the water-saturated low resistivity layer. Further resistivity mapping of that layer revealed a water table aquifer displaying a rather common pattern, except for the rather steep piezometric gradients (Figure 1).

B) A fast flow conduit pathway had to be traced in a rugged topography karst terrain, at Baile Herculane: during rainy periods, the commercial exploitation of Hercules thermal spring was obstructed by inflows of cold meteoric water that were presumably conveyed along karst conduits. In
order to mitigate such adverse effects, schemes have been devised for tapping the cold-water carrying karst conduits and diverting the concerned water outside the thermal spring flow network.

In this case, the “mise à la masse” method was considered to be the optimum investigation tool (Mitrofan et al., 1995). An electrode for injecting electrical current has been placed into the spring, the other one being positioned at theoretically infinity (actually at a very large distance). Two sets of records have been conducted: in one case no treatment was applied to the water that sank in a swallet known to be connected to the spring (Figure 2); in the other case, 50 kg of NaCl were added to the sinking water. In both cases, resistivity records have outlined an “anomalous” lineament that runs for more than 400 m in the prolongation of the underground stream course already explored in Hercules spring cave (Figure 3). For both measurements sets (i.e. with, and without injection of electrolyte into the swallet) the anomaly location was virtually the same, yet the signal definitely “sharpened up” when NaCl had been injected. The lineament thus identified probably follows the path of the main karst conduit that leads to the spring. In a nearby area, at Pisetori, just the resistivity minimum anomaly was able to outline the narrow flow path toward a karst outlet (Figure 4).

C) In Bihor Mountains, in Padis cave area, there has been investigated the theoretically ideal case of a shallow, broad and dry cave (Mafteiu, 1991). By means of vertical electrical soundings, an unambiguous resistivity maximum anomaly has been delineated, both when conventional Schlumberger, and when pole-dipole (Lögn) arrays have been used (Figure 5). Yet, as theoretically postulated, the anomaly vanished when the ratio between the cave depth and the cave radius became too large.

**Conclusions**

Besides being fast, low-cost and environmentally non-destructive, resistivity methods have also been proven to be highly efficient in karst studies. Mapping highly irregular water tables and delineating concealed flow paths have been the main applications of resistivity methods in karst studies in Romania. There has been also confirmed the possibility that broad, shallow and dry caves can be detected as resistivity maximum anomalies.
Figure 5. Geophysical measurements at the cave of Padis. Legend: a. resistivity cross section based on data provided by VES performed with Schlumberger arrays; b. geological cross section; c. resistivity cross section based on data provided by VES performed with Lög arrays. 1. resistivity high; 2. karst cavity; 3. resistivity contours; 4. measurement site.

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HYDROGEOLOGICAL CHARACTERISTIC OF SOME DEEP SIPHONAL SPRINGS IN THE CARPATO-BALKANIC MOUNTAIN ARCH (EASTERN SERBIA)

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Introduction

Very complex hydrogeological characteristics of karst, particularly directions and zones of groundwater distribution, are not yet explained enough. Numerous attempts, undertaken so far in the course of researching the complex regime of karstic aquifer, often did not have satisfying results. Even after detailed and complex research of geological, hydrogeological and geomorphologic characteristics, some rules of karst hydrogeology and groundwater circulation in karst have remained unclear. Explanation of hydrogeological relations, aerial arrangement, correlation and circulation of groundwater in that kind of environment is very hard, and sometimes includes a lot of assumptions but not enough established facts.

Data collected during speleodiving research contribute considerably to the analysis of karst evolution process in the region of Carpato-Balkanic arch, which is very important in evaluating the depth of karstification and determining the main direction of the groundwater flow. In the past 30 years, in Serbia speleo-divers have investigated a huge number of caves and springs with hydrogeological function and among them some springs deeper than 80 m.

The karstic springs are the most interesting phenomenon from hydrogeological point of view, and their investigations needs particular attention. Most of significant karstic springs are located on the rims of erosion basins which are in Serbia river valleys, sea coasts and contact areas between karst aquifers and hydrogeological barriers. General characteristic of springs regime is the direct correlation between precipitation and spring discharge. Moreover, hydrogeological regime of these springs also depends on size of the catchment area, karstic aquifer retardation capacity, total porosity, as well as lithological and structural characteristics.

Hydrogeological settings of deep karstic springs

The deep siphon karstic springs, generally means karstic springs with large discharge and significant discharge fluctuation. Often it is not assume that waters flowing through these systems are just an overflow of large underground storages, and that significance of these karstic aquifers is in tapping technology for water pumping from deeper aquifer levels.

Unfortunately, only a relatively small number of morphological patterns of this type have been thoroughly investigated. These kinds of patterns are mostly found in the siphon “vauclusian” springs, which are very difficult in terms of exploration. Channel depth can vary from tens to hundreds of meters, for example:

- Fountaine de Vaucluse, France: Surveyed by J. Hasenmayer, 1983 down to –205 m, and by Modexa (automatic diving instruments) down to –315 m, Emergence de la Chaudanne, Switzerland: Surveyed by C. Brandt, 1988 down to -140 m, Fontaine des Chartreux, France: Surveyed by C. Touloumdjian, 1989 down to –137m, Wakulla Springs, USA: Surveyed down to –111 m etc.

Karstic siphons are channels, with two or more openings, filled with water. By their hydrogeological function, they can be continual or temporary, often directly linked to groundwater levels and fluctuation. By their characteristics: hydrogeological role, depth, overall dimensions of channels and relation to the groundwater level, they can be divided to: a) siphon springs, b) siphon channels, c) siphon passages, d) siphon barrier, f) suspension siphons, g) siphon pockets (Figure 1).

Siphon springs (the most significant hydrogeological pattern) are karstic channels with role of main drainage channels and are larger in aperture then other siphon forms. Bottom of siphon channel -deepest point of the main base flow channel -is usually covered with gravel and sand deposits. In general, according inclination the siphonal channels can be divided at two types:

- the first type are springs with sub-vertical and vertical main drainage channels in discharge zone - channels inclined 45° - 90°, with depths greater then 70 m. These are the springs in which the bottom of siphon is very close to the discharge zone, in horizontal distance.
- the second type are springs with lower angle of main drain-
Age channel (less than 45°) but with final depth greater than -70 m or -100 m, in which the deepest point of siphon channel is far from the discharge zone. In these cases, bottoms of siphon channels are located hundreds of meters from the spring outlet, often with distances that can be measured in kilometers.

Research results of the most significant karstic springs

In Serbia, the largest number of investigated deep siphon karstic springs belong to the Carpathian-Balkan mountain range, where more than 35 cave springs have been investigated, so far, by speleological and speleodiving methods. Main characteristics of the five most significant springs are shown in Table 1.

After investigation of these hydrogeological active caves, conclusions have been made that there are very promising deep karstic channels, with regard to possibilities of their use for water supply.

Case studies

During preparation for tapping of Krupac Spring near the Niš city, speleodiving investigations of the deep siphon channels provided the key contribution. Speleodivers have investigated and mapped the main channel of karst spring at distance of 170 m and depth of -86 m (in relation to the spring overflow level). Based on this investigation, location of the temporary tapping structure was determined, i.e. the testing wells were drilled directly into the karstic channel. By installation of two pumps of 2 x 200 l/s capacity at 30 meters of depth was made possible to organize pumping tests in the period of several years (periods of minimum discharge), and to provide the data about available quantity of water (Figure 2).

Table 1. Some characteristic karstic spring investigated or partially investigated in Eastern Serbia.

<table>
<thead>
<tr>
<th>Spring name</th>
<th>Location</th>
<th>Length</th>
<th>Depth</th>
<th>No. siphons</th>
<th>Continues</th>
</tr>
</thead>
<tbody>
<tr>
<td>S. Mlava</td>
<td>Zagubica</td>
<td>120m</td>
<td>73m</td>
<td>1</td>
<td>continues</td>
</tr>
<tr>
<td>S. Krupaja</td>
<td>Beljanica</td>
<td>150m</td>
<td>72m</td>
<td>2</td>
<td>continues</td>
</tr>
<tr>
<td>S. Krupac</td>
<td>Niš</td>
<td>170m</td>
<td>86m</td>
<td>1</td>
<td>continues</td>
</tr>
<tr>
<td>Jelovicko s.</td>
<td>Pirot</td>
<td>65m</td>
<td>30m</td>
<td>1</td>
<td>continues</td>
</tr>
<tr>
<td>Kravljansko s.</td>
<td>Niš</td>
<td>30m</td>
<td>15m</td>
<td>1</td>
<td>continues</td>
</tr>
<tr>
<td>Topiko s.</td>
<td>Niš</td>
<td>50m</td>
<td>22m</td>
<td>1</td>
<td>continues</td>
</tr>
</tbody>
</table>
Krupaja Spring is situated at the northwest rim of mountain Beljanica, in the zone of red Permian sandstone, laying on the top of Urgonian limestone layer, at about 340 m above the sea level. The water discharges with well connected system of submerged channels. Channels are divided into shallow - up to 20 m of depth, which at 70 m distance come out into dry siphon hall - and deeper, which go down vertically, to the maximum investigated depth of -72 m (Figure 3a). Entrance is located at the fault zone trended in NE-SW direction. Spring is not tapped, and part of its water is used for nearby fish farm and mill. Discharging capacity of this spring varies from 380 to 2800 l/s.

Mlava Spring is situated at the north rim of Beljanica Mountain, at 314 m above the sea level. The spring is typically ascending, with deep karstic channels. At the discharge outlet there is a lake, -30 m deep. From this lake the channel continues almost vertical. At depth of -73 m the channel shape increase in the funnel shape and then continue even deeper (Figure 3b). Mlava Spring is situated on the contact line between Urgonian limestone and base part of Tertiary formation. Position of this spring is directed by fault with E-W direction, along which was found evidence of sinking of the northern block. Discharge of this spring varies from 300 to 15,000 l/s.

**Conclusion**

The above presented examples are only part of the experiences that point out the importance of investigating deep karstic channels in the karst areas of Eastern Serbia. Great possibilities of speleodiving in investigations of large karstic aquifers are obvious. Contribution of speleodiving in solving the water supply problems and specific problems during construction of hydrotechnical structures in karst is already confirmed. Together with other geological, hydrogeological and geophysical methods, speleodiving appears as very powerful tool in karst investigations.
GEOLOGY AND DYNAMICS OF UNDERGROUND WATERS IN JIUL DE VEST – CERNA VALLEY/BAILE HERCULANE (ROMANIA)

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Introduction

In the Southwestern part of Romania, near the Danube River and the border with Serbia, thermal springs are associated with a geothermal anomaly in the Baile Herculane area. The thermal springs, located in a narrow graben, is the site of a resort for the last 2000 years. There are three hypotheses regarding the origin of thermal waters: 1. Juvenile water, involving thermal and mineralizing solutions rising through fissures from magmatic sources; 2. Surface water through an underground pathway is recharging the water reservoir and due the geothermal gradient the spring temperatures increase; 3. A combination of both.

In late 1970’s the Romanian government constructed a hydro-electric system on three rivers: Cerna, Motru, and Tismana. Dams were built on Cerna and Motru rivers, including their main tributaries. The waters from Cerna Lake were channeled through tunnels to Motru Lake and then to Tismana, the location of the power station.

The volume of water in the recharge area for the reservoir of thermal water has been substantially diminished. A study was requested by the Romanian government to determine the effect of water withdrawal from the Cerna River on the thermal water reservoir, and to evaluate potential hydrogeologic connections between the Cerna River, its tributaries, and the thermal water reservoir. The karst study for the project was contracted to the “Emil Racovita” Institute of Speleology, Bucharest, Romania (Ioan Povara, Cristian Lascu) by the Geological and Geophysical Prospecting Company, Romania (Georgel Simion, Gheorghe Ponta, and Neculai Terteleac).

At the beginning of the 20th century, 14 caves were known in the Baile Herculane area. In 1961, the “Emil Racovita” Institute of Speleology initiated an extensive study in the Cerna Valley, during which 62 new caves were identified. The speleological and hydrogeological studies were continued by Povara who surveyed the thermal caves in the area and performed several dye studies.

Beginning in 1978, Focul Viu Bucuresti Grotto, Cristal Timisora Grotto, and several others local grottos, began an extensive search for caves in the Jiul de West–Cerna Valley. By 1982 over 980 new caves were surveyed in the area (a cave is a vertical or horizontal cavity, at least 5 m long). The longest one surveyed was about 1,500 m long.

The results of these studies, including the dynamics of underground waters in the Jiul de West-Cerna Valley/Baile Herculane area, with emphasis on the geology, hydrogeology, and recharge areas of the main springs are presented in this paper. 34 tracer studies conducted between 1970 and 1982 support the hypothesis that perennial and intermittent streams recharge the thermal water reservoir from Baile Herculane.

Geology

The Jiul de West and Cernisoara rivers are located in the western part of the Southern Carpathian Mountain Range and form the natural boundary between the Retezat and Godeanu Mountains to the north and west respectively, and the Vlcan Mountains to the south. The Cerna Valley represents the geographical boundary between the Cerna Mountains to the west and the Mehedinti Mountains to the east.

The geology of Jiul de West - Cernisoara the area is comprised of Danubian Autochthonous’s units and of metamorphic formations of the Getic Nappe. In the north the metamorphic rocks and granites are overlain by Jurassic deposits consisting of Liasic sandstones and Middle Jurassic-Aptian limestones and dolomites (the Cerna – Jiu sedimentary zone). These deposits are exposed in a synclinal structure. A fault transects the southern slopes which is the contact between limestones and crystalline rocks. The Jiul de West River sinks along a parallel fault, and recharges the Cerna Spring through underground pathways. Cerna Spring has a base flow of 800 liters per second (average 1,400 l/s) and is the second largest spring in Romania.
In the Cerna Valley, the geology of the area is composed of Danubian Autochthonous units (the Cerna and Presacina sedimentary zones) and of metamorphic formations of the Getic Nappe. The karst is developed on the carbonate rocks belonging to the Cerna and Presacina sedimentary zones.

**Dynamics of underground waters**

The dynamics of underground waters are presented from North to South:

- **Jiul de West-Cernisoara**
  - Cerna Valley-Baile Herculane
  - Cerna Syncline
  - Cerna Graben
  - Virful lui Stan – Domogled Anticline (Mehedinti Mountains)

**Jiul de West-Cernisoara**

The Retezatul Mic Mountains are located between the Buta and Jiul de West rivers and are an alpine karstic plateau (2,000 m above sea level) of Jurassic limestones. On this plateau an extensive network of dry valleys was developed and shaped by glaciers, which deeply eroded the carbonate (limestones) and noncarbonate rocks.

The Jiul de West-Cernisoara karst area in the Retezatul Mic Mountains is about 41 km², where 10 active sinking streams have been identified. In 1982 the Geological and Geophysical Prospecting Company with the Institute of Nuclear Physics (IFIN) Bucuresti completed a tracer study in the Scorota sinking stream on the plateau. The stream is situated at the contact between impermeable crystalline rocks and the Jurassic limestone at an altitude of 1,390 m and 13,350 m from Cerna Spring, which is at an elevation of 700 m above sea level.

On August 9, 1982, 100 grams (g) of Indium-EDTA was used in the Scorota sinking stream which has a flow of 25 l/s. The travel time of the tracer to Cerna Spring, 13.3 km away and 700 m lower in elevation, was 28 days. Based on this study, Cerna Spring’s recharge area included the entire karst area of Retezatul Mic Mountains.

**Cerna Valley – Baile Herculane**

South of Cerna Spring, Cernisoara River becomes Cerna River, which flow along the Cerna Graben. Structural features such as the Cerna Syncline, the Cerna Graben, and the Virful lui Stan – Domogled Anticline (Mehedinti Mountains), converge in the Baile Herculane area, creating a complex hydrogeological system.

**Cerna Syncline**

Pascu (pers. comm.) carried out tracing experiments with radioactive isotopes in two sinking streams located on the Cascada Valley (1.5 km from the spring) and Slatina Valley (3.5 km from the spring). The tracer was intercepted in the Hercules I thermal spring after 20 hours and 42 hours respectively, confirming that the sinking streams of the Cerna Syncline are recharging the thermal water reservoir.

Povara (1976, 1977) conducted a dye study in the same sinking streams, obtaining similar results, with a longer transit time (2-7 days). The dye was also detected in the Apollo II thermal spring, about 200 m downstream from the Hercules I spring. Povara also completed two other dye-studies using fluoresceine: the first one in the Grotta Cu Aburi, and the second directly on intensely fissured limestones located 100 m from the cave. The dye injected in Grotta Cu Aburi cave was detected in the Hercules I spring, after 85 hours. The second dye, injected in the intensely fissured limestone, was not intercepted.

To define the extent of the recharge area of the thermal water reservoir, Simion, Gaspar and Povara conducted a multi-tracer experiment in 1978 with radioactive tracers (Iodine-131 and Au-91) and dyes (fluoresceine and ammonium dichromate) in the Iuta Valley (Q=20 l/s), 20 km north of Baile Herculane. The sinking stream of the Iuta Valley is situated 300 m upstream of the confluence with the Cerna River. Dyes were intercepted 50 minutes later in the Piatra-Puscata karstic spring, situated 200 m upstream of the Iuta’s junction with the Cerna River.

In 1979, Simion, Ponta, Terteleac, and Gaspar conducted a tracer study with Iodine-131 in Poiana Tesna, 13 km north from Baile Herculane. This sinking stream is located at the contact of nonkarstified rocks with the Jurassic limestones. Twenty days later, the tracer was intercepted in the Hercules I, Apollo II, and 7 Izvoare Calde Dreapta thermal springs, confirming the extension of the recharge area at least 13 km upstream of the Cerna River, from Baile Herculane.

The appearance of the tracer in the 7 Izvoare Calde Dreapta thermal springs, 2 km upstream on the Cerna River from the Hercules I spring, indicates the existence of an underground divergence of flow along transverse faults that create a hydrodynamical connection of the Cerna syncline aquifer with the Cerna Graben aquifer.

Also in 1979, the same investigators repeated the experiments of Pascu (pers. comm.) and Povara (1976) in the Cascada Valley sinking stream using Iodine-131. The tracer was found in all the thermal springs in Baile Herculane, except Neptun spring.

Based on the results of these experiments, the Cerna syncline hydrostructure is recharged by perennial sinking streams along the axis of the Cerna syncline (NNE-SSW). These waters are heated and mineralized at depth.
**Cerna Graben**

The NNE-SSW oriented Cerna Graben is 64 km long. Thermal and karstic springs distributed along transversal fractures in the graben indicate the presence of a groundwater reservoir.

The dynamics of underground waters of this structure were tested using Tritium injected in the Cerna River, 25 km upstream of Baile Herculane, at Bobot Gorges. The tracer was intercepted in the 7 Izvoare Reci springs, along with the Ghizela, Diana and Neptun wells, and confirmed that the Cerna River recharges the thermal water reservoir in the Cerna Graben.

In 1977 and 1978, Povara conducted a dye-study with fluoresceine in the Cerna River, 1 km downstream of the Bobot Gorges and confirmed that the Cerna River recharges the Cerna Graben aquifer because the dye was identified in the 7 Izvoare Reci spring ($Q = 300$ l/s), and the Ghizela and Scorillo wells.

Several transverse faults which form an uplifted granite unit intersects thee Cerna Graben in the 7 Izvoare Reci springs area. Along these faults, the underground water path being discharges through artesian springs. The granite unit is divided the Cerna Graben into two aquifers, a Northern and a Southern one. The Northern aquifer is primarily recharged by the Cerna River and by and large discharges through the 7 Izvoare Reci Springs. The Southern aquifer is recharged by streams in nearby geologic structures, such as the Cerna syncline and the western flank of the Mehedinti Plateau.

During rainy periods, the flow of the streams recharging the thermal water reservoir increases. The flow of the thermal springs also increases, but the temperature of the springs decline. To keep the temperature of the springs as high as possible, a tunnel was dug near the Hercules I spring to intercept the cold water of the streams that recharge the thermal water reservoir.

**Virful lui Stan – Domogled Anticline (Mehedinti Mountains)**

Between the Ivan Valley (6 km South of Cerna Spring) and the Arasaca Valley (25 km North of Baile Herculane) is a NE-SW oriented limestone ridge 20 km long and 200 to 300 m wide. This ridge is intensely karstified with numerous caves and sinking streams. Several dye studies performed by I. Povara defined the karst hydrogeology of the area. One of the dye-traces identified an underground-water pathway which flows against the direction of the Cerna River.

The limestone plateau in the Mehedinti Mountains is situated on the East side of the Cerna River, between the Arasaca and the Pecinisca Valleys and is a large anticline structure (Virful lui Stan–Domogled). Along the axis of the anticline, granites and metamorphic rocks of the Danubian’s Domain outcrop in several points, creating a watershed divide along the main ridge and dividing the plateau into a West and East aquifer.

In northern part of the Mehedinti limestone plateau next to Virful lui Stan, the Poiana Beletina (Beletina meadow) stream sinks. Poiana Beletina is located along the main ridge of Mehedinti Plateau. The sinking stream may recharge springs on both sides of the mountains; East (Izverna, Izvorul Alb), West (7 Izvoare Reci), or South-Southwest along the anticline axis toward Toplet and Birza.

**Conclusions**

Tracer studies completed between 1970 and 1982 prove that the thermal water reservoir in the Cerna Graben is fed by recharge from several sources including sinking streams of the Cerna River, Cerna Graben and the Mehedinti Mountains (Western flank of Virful lui Stan – Domogled anticline). These waters combine at depth with juvenile waters that are heated and mineralized and rise through fissures from magmatic sources and discharge from several thermal springs and wells in Baile Herculane area. To continue to recharge the thermal water reservoir, the Cerna River must maintain a minimum flow. In 1988 an additional dam was built on the Cerna River, 5 km North of Baile Herculane. The purpose of the dam was to generate power, water supply, and recharge of the thermal water reservoir.

**References**


SIMULATION OF SPRING DISCHARGE BY USE OF A MULTIVARIATE ARMA MODEL. APPLICATION TO THE MOTRU SEC – BAIA DE ARAMÁ KARST SYSTEM, MEHEDINȚI MOUNTAINS, ROMANIA

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Time Series analysis is concerned with data which are not independent but serially correlated, and where the relations between consecutive observations are of interest. One of main applications is to forecasting, and the Box-Jenkins approach is attracting more and more attention. There are now very few disciplines in the Sciences, Business and Technology, which are not investigating its possibilities, and this work is an example of its use in karst hydrogeology domain.

The Motru Sec-Baia de Arama karst system is a complex system with recharge both diffuse by precipitations and organized from Motru Sec river swallet. The outlet is a line of sources in the Baia de Arama zone. Labelings have proved both the Danubian Autochtone carbonatic deposits and karst system continuity under the Getic Nappe.

The ARMA bivariate model was used to simulate temporal variations of discharge from one of the most important springs of the system in connection with the flow of the Motru Sec river which recharge the system by its sinking. Simulated discharge was visually calibrated against measured discharge; the similarity between the two supports the validity of this approach. The model can be also used to study the effects of climate change on groundwater resources and their quality.
KARST DENUDATION CYCLES IN BULGARIAN KARST

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We studied annual variations of the karst denudation in 5 Bulgarian karst regions. For two of them we obtained monthly variations of the karst denudation in the last 34 years. The last 2 time series allow us to study the cycles of the karst denudation.

Usually estimates of the karst denudation rate are based on average values of the carbonate concentration in karst waters. But the procedures used to average these values (duration of the record of the measurements and their timing) are not unified, so it is not clear how correct is to compare different estimates of the karst denudation rate made by different authors. In order to estimate the range of the variations of the karst denudation and their cycles we studied all available continuous records from Bulgaria.

We found that the carbonate karst denudation exhibit tremendous variations from month to month. In Iskrec karst region, Bulgaria it varies over 81 times in the last 34 years from 53.9 to 4380.7 tons/month. In this region karst denudation exhibits strong annual variation with strongest cycles of 12 and 6 months. It exhibits also several longer cycles with duration of about 4 years (46.5 months), 64-73 months and 128-170 months.

Carbonate karst denudation in Devnya karst region exhibits different pattern of variations from 3334 to 6076 tons/month in the last 32 years. In this region karst denudation do not exhibit strong annual variation, but have a great number of other cycles strongest of which is of 4.5 months. It exhibits also several longer cycles with duration of 5.4, 7.3, 12.5, 16.9, 23, 51 and 85-102 months.

References

A CHARACTERIZATION OF THE EPIKARST FEATURES OF THE OZELLO KARST PLAIN

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The Ozello Karst Plain, located in coastal west-central Florida, USA, is characterized by a variety of epikarst features that provide evidence for coastal evolution. The plain, approximately 15 km wide and 25 km long with less than 2 m of relief, is bedrock cored with very little sediment present. The bedrock plain is cut by numerous estuarine tributaries, which have created many small islands a short distance from the mainland. Although the seaward side of the landform is exposed to low-energy waves, tidal activity is the dominant coastal process. The bedrock islands and peninsulas contain several karstic features that are observable where the natural coastal marsh and mangrove vegetation is not present. The surface of the bedrock is mantled by a resistant crust 1-2 cm thick. The surface karst features can be divided into two zones: 1) central peninsula and island zones, and 2) coastal zones. Within the central portions of the peninsulas or islands, bowl-shaped depressions 10-30 cm wide and up to 20 cm deep can be found, alongside smaller (1-10 cm), irregular cuspatdepressions. Both of these types of depressions are mantled with the crustal material. In addition, vertical depressions 5-20 cm deep are present. These depressions formed from phytokarst processes, and cut through the crustal zone to expose uncoated bedrock at depth. The coastal zone is characterized by three different conditions: 1) crust-covered bedrock coastline, 2) heavily weathered spongework coastline, and 3) freshly exposed porous bedrock. It is evident that rainfall collection and root activity enhances erosion of the land surface and are the dominant processes responsible for the karst weathering of the bedrock.
MEASURING AND MONITORING THE IMPACTS OF LARGE DAM ON KARST ENVIRONMENT

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Introduction

Construction and operation of a large dam implies many changes within bio and geo diversities. The consequences are direct and indirect, affecting physical environment at first, but there is also significant socio-economical impact. In case of building dam in karst environment many additional specific circumstances and problems require to be solved. Today, mitigate the impact of a dam represents the crucial step towards the positive decision and practical project implementation. This is a significant change concerning previous worldwide experiences. Awareness of environment protection as essential for sustainable development is continue to strengthening in accordance with general ecological, and consequently political trends during last decade.

How to predict these impacts, how to forecast and implement the mitigation measures and eventually how to observe the effects and maintain the operating system as a whole? Many of these specific issues have recently analysed and discussed in case of Bekhme dam, one of the world largest projects.

The Bekhme dam site is located in the northern part of Iraq (Iraqi Kurdistan). The aim of the multipurpose dam on Great Zab River is to control the flow, generate desperately missing electricity for Iraq, and provide water for the irrigation. After almost twenty years of discussion, evaluation and design, the works on Bekhme dam had started in 1988. Unfortunately during the Gulf War I and events in 1990-91, the most of basic installation and equipment (around 15% of required works completed) was destroyed. Following recent political development in Iraq the idea to continue and finalize the project was renewed. One of the necessary steps was preparation of the Environmental impact assessment study (EIAS), the work done by ISTC, Stucky and IK Consulting experts (Maran et al., 2005a). Further decision and project completion is depending mostly of evaluation of numerous positive and negative implications, in addition to insurance of large investment fund required for such big dam.

Physio-geography and geology

Cold and snowy winters and long, dry and warm summers characterize the north Iraq climate. Mountains and hilly areas as well as the foothill zones in the middle and northern part have higher precipitation rate, snowfall and lower air temperature. In the plains, typical semi-arid climatic conditions are prevailing.

Iraq territory lies in the border between two main geostructural units – Arabian part of African platform and Asian branches of Alpine geosyncline. Three major tectonic zones are developed in north Iraq (from N to S): 1. Thrust zone; 2. High folded zone, and 3. Low folded zone. The first two belong to Bekhme catchment.

The uppermost part of north Iraq is characterised by high mountains, which are elevated more than 2,000 m a.s.l. Mountainous ranges are intersected by deep incised valleys with steep sides due to reinforced youngest, neotectonic uplifting of the mountains. Three major types of terrain are characterized the north Iraq: mountainous ranges, foothill pediments and agricultural plains, as results of most active geomorphological processes such as karstic, fluvial and slope (delluvial, proluvial and colluvial; Stevanovic and Markovic, 2004).

During long geological history of the territory of north Iraq, especially in Mesozoic and Tertiary period, a lot of soluble rocks like limestone, dolomite and evaporites were deposited. This enabled development of strong karstification and forming surface as well as underground karstic morphology. The main sedimentary cycle of carbonate rocks deposition started during the Upper Jurassic-Lower Cretaceous and ended in Maastrichtian. During Upper Eocene a new cycle of sedimentation of carbonate rocks has repeated forming of thick deposits of Pila Spi or Sinjar limestone. Alpine folding and uplifting of mountains built of carbonate rocks was reinforced by numerous fissures, joints and fault surfaces, and deepening of basis of karstification (Stevanovic and Iurkiewicz,
2004a, b). Although quite different from the Alpine type of karst, this region is also characterised by holokarst development, i.e. karst landscape of fully developed surface and subsurface features. Surface karstic small forms, dimensions from cm to dm, occur practically in whole limestone’s area but compared with other karstic Euro-Asian mountainous ranges, formed during Alpine orogenic cycle (Alpides, Dinarides, Helenides, Taurides) typical larger surface forms, as sinkholes or dolines, are less developed.

Four main aquifer systems exist in north Iraq, each of great significance for groundwater exploitation (Stevanovic & Iurkiewicz, 2004). Formation with similarities in age, lithology, permeability and other hydrogeological characteristics were classified within the same aquifer system and named in accordance with the most widespread and well known formations: 1) “Bekhme’ karst aquifer; 2) fissured-karstic “Pila Spi”; 3) “Bakhtiari” intergranular aquifer and 4) complex aquifers (combination of the two or three aquifers mentioned above). The karst aquifer “Bekhme” includes mostly the Cretaceous formations (Qamchuga, Dokan, Kometan, Bekhme, Aqra, Sarmord, etc.) as well as formations, which belong to Paleocene age. The aquifer system is widespread in the catchment of Bekhme reservoir and its stratotype development is exactly in the gorge downstream of damsite.

### Bekhme dam site

The crucial importance for water management and water use in Iraq is in its northern part (Iraqi Kurdistan); it is the main domicile of water resources. In north Iraq two dams were constructed at Small Zab and Sirwan rivers during 1960’s. Planned Bekhme dam is located on the Great Zab River, the major perennial tributary of Tigris River (Figure 1). Great Zab originates in Turkey but most of its catchment is inside Iraq (62%). Two bigger tributaries of Great Zab before

planned Bekhme dam site are Sherwan Mazn and Rawanduz. The first originates also in Turkey while the second one derives from Iran. The large portion of Rawanduz catchment belongs to Balakiyan, Sidakar and Khalifan rivers as well as to the Bekhal aquifer basin (Figure 2). Above the Bekhme damsite catchment area is estimated on 16,600 km².

According to designed capacity, Bekhme dam is supposed to be among tenth largest dams worldwide. Bekhme dam is designed as multi-purpose rock-fill dam, 230 m in height, with 17 billion m³ reservoir, which is expected to provide irrigation water for 565,000 ha of land as well as energy production (1,500 MW) and flood control. Further, it is estimated that approximately 10 billion m³ will be Bekhme storage capacity which can be counted on as water resource helping to prevail and mitigate possible consecutive drought years in the region (Figure 1). To protect the project from hostile actions, the penstocks, powerhouse and switchyard are all designed underground along with the intake structure that will also be underwater. In addition to the spillway tunnels, four lines of bottom outlet, each with a diameter of 5.2 m, will be installed in order to promptly lower the reservoir water level in case of emergency.

### Identification and measuring of dam impacts

Construction of dam significantly changes particular river basin and its surrounding environment. The scale and extent of impacts can vary depending on dam characteristics as follow: 1. location; 2. dam size; 3. impounded area, and 4. human concentration in the river basin. Possible negative and positive effects of dam have to be considered at environmental and socio-economic levels.
**Positive effects**

Dam significantly anticipates in the economic development of whole region and river basin. Increases in food production from irrigated agriculture can lead to expand the purchasing power of farming households in irrigated areas, which also contribute to greater food security and improve nutrition at the household level. New energy services provided by dam have benefited urban populations and others connected to power distribution systems. In regions with low levels of energy services such as north Iraq, even small energy inputs bring significant welfare improvements. Employment gains are also engendered by construction work, hydropower production and other services provided by reservoir. Likewise, the creation of commercial and sport-fishing industries as well as reservoir-based recreation and tourism, may lead to job creation and can also provide substantial employment.

**Environmental consequences**

Dam-building is perhaps unique among such projects that they can have widespread and far-ranging environmental impacts due simply to the blocking of a river. They comprise effects upon ecosystems and their associated parts – biodiversity, wildlife, vegetation and forest cover classified as:

Impacts which entail the physical, chemical, and geomorphological consequences of river blocking and changing the natural distribution of stream-flow;

Impacts that involve changes in primary biological productivity of ecosystems including effects on riparian plant-life as well as on downstream habitat;

Impacts which involve modification of fauna and effect the reduction of biodiversity due to blocking movement of organisms.

Within the Great Zab/Bekhme catchment area, three main vegetation types are present: 1) conifer and oak species; 2) scrub and park-like forest with juniper and deciduous oaks, and 3) vegetation which occupies valleys, streams and rivers surroundings. These vegetation types are significant for wildlife as valuable genetic source. Further, north Iraq is well known as important area of bird diversity due to its position inside one of the world’s major avian migratory routes. It is also home to a number of globally threatened wildlife species. The result of modify the terrestrial, aquatic and riparian ecosystems by dam have different consequences for people who live in vicinity as well as downstream of dam site.

In addition, impounding carbonate rocks and karst aquifer can cause an increased rate of leakage from reservoir, thus preventive injection is planned as well as search for the new sources of water supply (some important springs will stay beneath water). Evaluated consequences also include deterioration of water quality in reservoir (eutrophication, stratification) and microclimatic changes (“green house” effect and assumed evaporation of high rate that can reach 2200 mm/year).

**Socio-economic consequences**

Bekhme impounding area is widespread on 220 km² along the Great Zab and its tributary valleys. About 42 villages that count 12,500 residents will be directly affected along with fertile land, natural pastures, as well as related infrastructures, road and cultural and natural monuments.

Effect on population is the crucial and most sensitive issue of dam built because it results primarily in the physical displacement of people. Relocation of people refers to both, “physical displacement” and “livelihood” displacement. Accordingly, the main dam benefit has to be adequate resettlement program, which will take in account all aspects of physical relocation (loss of properties, common resources, livelihood deficient and joblessness). Particularly, adaptation of those familiar with semi-nomadic “shepard” style of life in karstic environment and convert to “flat plain” or “lake shore” style cannot be an easy task.

As part of ancient Mesopotamia, the territory of north Iraq contains numerous archaeological and cultural monuments included in UNESCO list of World heritage. Among these, the Shanadar cave is the famous one. The cave was built into massive Lower Cretaceous limestones and represents one of largest speleological form in this region (Stevanovic et al, 2004). Aside, the Shanadar cave is well known as prehistoric site by Neanderthals remnants that are dated back to about 60,000 years ago. Although Shanadar would not be directly affected by dam construction, it would make overland access more difficult. Owing to possible effects upon the cave, practical advice for conservation is to spread up archaeological survey in order to enable relocation of potential discoveries (artifacts, remains).

**Monitoring the impacts of large dam**

In order to minimize impacts of dam on human and natural environment at local and regional levels, the Environmental Management Plan (EMP) and Monitoring Program (MP) is prepared (Maran et al., 2005b). Proposed a long-term monitoring program is based upon regular field data collection which is related to: a) observation of different stages of dam construction; b) observation of impounding phase; c) monitoring of water flows; d) monitoring of changes of climate conditions; e) monitoring of changes of water quality; f) effects of reservoir construction on population; g) observation of implementation of people resettlement program and its socio-economic implications; h) observation of changes in fauna and
flora diversity and density, etc. For many of these observations performance indicators are still going to be developed based on additional detail survey. Further planned survey and studies among others includes: RAP (resettlement action plan), social-economic plan, engineering geology and hydrogeology, hydrology and water quality as well as environmental research (ecosystems, climate, biodiversity, geodiversity, archaeologically and cultural heritage, etc).

**Conclusion**

There are many arguments for and against a new reservoir. These include economic chances versus economic losses, opportunities for developers, recreational opportunities and aesthetic considerations as well. However, it was concluded in case of large Bekhme dam that positive impacts are prevailing negative ones, while late could mostly be mitigate by adequate, but of course expensive measures.

**References**


Introduction

The freezing of mineralized water is accompanied by the concentration of solutes in the residual liquid phase eventually leading to mineral precipitation. Carbonate formed in relation to the freezing of karst waters occurs frequently in caves that contain ice under present-day conditions. In addition, carbonates can occur in caves that contained ice under past glacial conditions. These mineral precipitates, known as cryogenic cave carbonate (CCC), are frequently overlooked or in case of the caves that contain no present ice, not recognized. Most of the review papers on ice caves seldom mention the presence of CCC even though its occurrence in natural ice caves is an integral part of this environment. Formation of cryogenic gypsum is common as well, especially in caves with high sulfate content of drip waters (Andrejchuk and Galuskin, 2001; Andrejchuk et al., 2004). In this paper the formation of CCC is reviewed. Except in the typical modes of occurrence, the most useful tool to recognize CCC in caves is through analysis of its C and O stable isotope composition.

Carbon and oxygen stable isotopes

The common calcite speleothems that form in non-iced caves of the temperate zone usually precipitated in isotopic equilibrium with karst waters and usually plot in a relatively limited area in the $\delta^{13}C$ vs. $\delta^{18}O$ range. Shifts to higher $\delta^{13}C$ and $\delta^{18}O$ values are typically observed in environments where CO$_2$ escapes rapidly from the solution, kinetic isotope fractionations occurs, or with water evaporation (Hendy 1971). In contrast, cave carbonate deposition, in relation to water freezing, produces broader ranges of $\delta^{13}C$ and $\delta^{18}O$ data. Some published isotopic sample sets occupy the $\delta^{13}C$ vs. $\delta^{18}O$ plot sectors, where other natural carbonate types are seldom observed. Figure 1 shows C and O isotope data from carbonates collected in several caves, which are recently iced and from caves interpreted as being iced under glacial conditions. The existing sample sets are supplemented by new analyses of cryogenic carbonate powders and specific cave pearls from the Scârăsoara ice cave in the Bihor Mts. of Romania. (see Racoviță and Onac, 2000, for general information about the cave, and Žák et al., 2006, for analytical details.) Also shown are cryogenic calcite data from surface naled (aufeis, icing) environments in northern Yukon, Canada.

Figure 1 illustrates two types of trends of CCC C and O isotope composition. The first trend shows an inverse slope with decreasing $\delta^{18}O$ accompanied by a moderate increase in $\delta^{13}C$. The second trend is characterized by a high variability of $\delta^{13}C$ where a significant increase in $\delta^{13}C$ is accompanied by either none or a moderate increase in $\delta^{18}O$. These two types of isotope trends correspond to two modes of CCC occurrence, each related to different environments of deposition and different mechanisms of stable isotope fractionation. The critical factors controlling the direction of the trend in the $\delta^{13}C$ vs. $\delta^{18}O$ space are the open or closed nature of the system with respect to the escape of CO$_2$, the freezing and precipitation rate, and the absence/presence of simultaneous water evaporation.

CCC formed by slow water freezing in confined settings

The trends with inverse slope and with very low CCC $\delta^{18}O$ data, down to -24.1 % (PDB), have been measured from accumulations of coarse crystalline carbonate grains in three caves in the Czech Republic, Poland, and Slovakia (Žák et al., 2004). Richter and Niggemann (2005) described similar types of CCC with similar trends in the $\delta^{13}C$ vs. $\delta^{18}O$ range from four caves from Rheinischen Schiefergebirges, Germany (Figure 1). In all these cases, the carbonates occur as morphologically variable grains, sized from <1 mm to >10 mm, with the presence of forms resembling hemispheres (roughly half of a sphere), complex hemispheres and intergrowths, skeletal crystals, etc. The grains form loose
accumulations on the cave floor, with individual grains neither connected between them, nor to the ground. None of the caves containing this CCC type are recently iced. Available U-series data indicate CCC formation during the glacial periods when the caves were located in a periglacial zone south of the limit of the continental ice sheet. These forms are interpreted as being precipitated during conditions of slow water freezing under isotope equilibrium, in a system partly closed with respect to CO₂ escape. The shift to lower δ¹⁸O values results from Rayleigh-type fractionation between the ice (incorporating preferentially heavier oxygen isotope) and the residual solution. The formation of cryogenic calcite in a similar environment having partly closed conditions under isotope equilibrium was described from aufeis (Lauriol et al., 1991; Clark and Lauriol, 1997; see data in Figure 1). Aufeis (icing, naled) forms in Arctic terrestrial environments from groundwater-fed springs and rivers during freezing. During aufeis formation, ice tends to form dams between still liquid water and cold air (cryostatic pressure during slow freezing can build up under the ice, leading, eventually to the fracturing of the ice). In aufeis formed below the ice cover, cryogenic calcite can form in environments separated from the atmosphere.

**CCC formed by rapid water freezing**

The second CCC type occurs in high-ventilated caves which are recently iced and where rapid ice formation can be directly observed. CCC occurs here as fine-grained cryogenic carbonate powder (with grain size typically less than 1 mm, frequently only 1 to 5 µm, forming larger clusters), which precipitates during freezing of karst waters penetrating periodically into the cave. During the ice melting, cryogenic powder forms accumulations either on the ice surface or below the ablation walls of the ice blocks.

In the typical iced caves of the temperate zone (Scărișoara, Romania; Dobšinská Ladová and Silická Ládnica Caves, Slovakia, etc.) most of ice (and CCC) is formed during the spring surface snowmelt when the waters that penetrate into the caves interior which was cooled to sub-zero temperatures during the preceding winter. The drip-waters typically freeze quickly into thin layers, enabling quick escape of CO₂ from the solution under open system behavior. Typically, large shifts to high δ¹³C values and large ranges of carbon isotope data of the formed carbonate are observed. The isotope system can be further complicated by the fact that partial ice melting and water refreezing are common processes. Deposition of the carbonate in these ice caves results from the simultaneous processes of rapid CO₂ escape from the solution, ice formation, and locally, partial water evaporation. The usual processes of secondary cave carbonate formation (known from non-iced caves) can therefore combine with the effects of cryogenic carbonate formation in varying proportions. While in non-iced caves a significant proportion of the dissolved carbonate load is usually not precipitated and flows away from the cave, in the cryogenic environment, the proportion of precipitated carbonate is high. Extremely high δ¹³C values of CCC commonly observed in iced caves (either produced by kinetic fraction-
ation or by Rayleigh fractionation with extremely low proportion of the residual solution) are seldom observed in non-iced environments. In this type of CCC formation, large increases in δ¹³C are typically accompanied by either no increase or moderate increases in δ¹⁸O. There are two possible explanations; either there was little equilibrium between the water-ice oxygen isotope fractionation or the effect of this fractionation was out-weighed by kinetic bicarbonate decomposition or water evaporation. With the exception of these two clearly defined types, some other occurrences of speleothems with extraordinarily high δ¹³C values have been described. Geyh et al. (1982) recognized high δ¹³C values (up to +10.1 ‰ PDB) in several stalagmites in high-mountain caves in the Alps, generally in caves located above 1000 m a.s.l.. However, the possibility of carbonate deposition during water freezing was not mentioned in this paper.

**Freezing experiments**

There are both field and experimental evidence on the freezing of seawater leading to formation of highly-concentrated brine pockets in the ice and eventually to carbonate precipitation (Papadimitriou et al., 2004). Freezing experiments using low ionic strength carbonate-bearing solutions are less frequent and only several experiments were accompanied by measurement of C and O isotopic composition of produced phases.

Clark and Lauriol (1992) examined isotope fractionations during rapid laboratory freezing of calcium bicarbonate waters in a system in which (with respect to large volume of reaction vessel and small quantity of solution) the CO₂ escapes from the solution rapidly. They concluded that the high rate of reaction effectively precludes isotopic equilibration during bicarbonate dehydration. This results in a larger kinetic fractionation of ¹³C between the precipitated calcite and isotopically light escaping CO₂ than is the equilibrium fractionation.

Fairchild et al. (1996) found morphologically diverse calcareous precipitates (mostly calcite with traces of vaterite and/or aragonite) during moderate-rate ice growth (3 and 8 mm hr⁻¹) when experimentally freezing low ionic strength carbonate-bearing solutions. The freezing was conducted in a closed system with respect to CO₂ escape. Residual water δ¹⁸O became lighter because of the progressive formation of ice, some 3‰ heavier than co-existing water, with the lowest value of final water being shifted more than –5‰. The stable isotopic compositions of precipitates were extremely variable. Morphology and stable isotope composition of precipitates was interpreted to reflect micro-environments (i.e., formation of precipitate next to ice or gas bubbles) during rapid formation of precipitates accompanied by the formation of CO₂-rich gas bubbles. The data trend of the carbonate stable isotope showed lower δ¹⁸O and δ¹³C values from the equilibrium values, i.e. in trend direction, which is not observed in natural cryogenic carbonates. Based on the same set of experiments, Killawee et al. (1998) described segregation of solutes and gases in detail. Socki, et al. (2001) experimentally tested fractionation of ¹³C during rapid freezing of calcium bicarbonate solutions (with free CO₂ escape). They found progressive enrichment of both residual bicarbonate and (especially) of the precipitated calcite. Largest ¹³C enrichments in calcite were related to calcite formed by repeated freezing, melting, and re-freezing of the same solution.

**Mineralogy of cryogenic carbonate precipitates**

Low precipitation temperature and increased concentration of dissolved solids in the residual solutions during water freezing are factors which can result in precipitation of metastable carbonate phases instead of calcite. Traces of vaterite (the unstable hexagonal CaCO₃) were found in some of the freezing experiments of Fairchild et al. (1996) and Killawee et al. (1998). Depending on the solution chemistry, metastable hydrated carbonate phase ikaite (calcium carbonate hexahydrate) and/or monohydrocalcite (see, e.g., Dahl and Buchardt, 2006) can potentially occur in these environments. The presence of ikaite was mentioned in freezing experiments conducted by Socki et al. (2001). The mineralogy of CCC requires further study, with samples collected, transported, and analyzed at low temperatures.

**New data from the Scărișoara ice cave**

The stable isotope analyses of fine-grained carbonate powder from the main ice mass of the underground glacier in Scărișoara Ice Cave yielded high and variable δ¹³C values (up to +12‰ vs. PDB, see Figure 1) and high δ¹⁸O values. The high δ¹⁸O values are typical for cryogenic carbonate formed during rapid water freezing that is accompanied by swift kinetic CO₂ degassing. The second sample type studied was the famous Scărișoara cave pearl nests (Viehmann, 1960, 1963, and later; the first recognition of the importance of water freezing for precipitation of carbonate in caves). Cave pearls occur in the periglacial zone, at the limit of massive ice flow, in the cave section called Great Reserve. They are porous, less than 1 mm (micro-pearls) to 25 mm in size. Smaller pearls are usually more regular, spherical in shape, whereas larger pearls are frequently more irregular. U-series dating indicate that the pearls are not older than 2 thousand years (Žák et al., 2006). The data on cave pearls occupy a different field in the δ¹³C vs. δ¹⁸O diagram (Figure 1) than the cryogenic carbonate powder. Nevertheless, they follow a similar trend direction. Therefore, the pearls cannot be formed by simple mechanical accumulation of fine-grained cryogenic carbonate re-deposited from the main underground glacier. A different process of cave pearl formation is required. The most plausible explanation
is that the carbonate, forming the pearl, precipitated during water freezing in a system open with respect to water, i.e., in a system of partial water freezing, when a portion of non-frozen solution flows away. This is in agreement with their position in the periglacial zone, in front of the underground ice mass.

Acknowledgments

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References


Soil acidity is a function of climatic setting, lithology, geography, vegetation condition and human activity in an area. Generally speaking, the soil acidity in a karst region appears weakly alkaline due to calcification. The degree of soil calcification and soil pH have been increasing in many karst regions of southwest China as the karst-desertification has strongly increased over the past decades. Can the calcified soil be improved by changing environmental conditions and land use? What are the factors to influence the soil acidity in the karst region? These are very important questions to be answered for management of the soil and land use in the karst region. Based on the natural conditions and the land use patterns, we have chosen 12 soil profiles from the top to bottom of Jinfo Mountain, a typical karst region in south Chongqing, for studying the soil acidity and its influencing factors.

For every soil profile with thickness ranging from 0.4 to 1.3 m and elevation ranging from 600 and 2000 m a.s.l., we have measured pH values of the soils in 2-4 layers and averaged the pH values for each profile. Our results show that the soil acidity in this karst area exhibits pH ranges of 4.25-6.95 that is lower than the pH of calcified soil in other karst regions. On top of the mountain where the vegetation is abundant, soil is well developed and cation leaching is strong, soil calcification is weak. This is supported by low mean values of exchangeable Ca\(^{2+}\) (1.35 mg/g) and pH (5.06), but high exchangeable soil acidity (4.37 mmol/100g) in 5 soil profiles of high elevation sites. In contrast, seven soil profiles at the lower elevation sites down to the foothill reveal higher values of exchangeable Ca\(^{2+}\) (2.83 mg/g), pH (6.42), but lower soil exchangeable acidity (0.27 mmol/100g). The latter case is probably attributed to deforestation and intensively land use by human activity. As the area of uncovered rock increases, the renewing speed of exchangeable Ca\(^{2+}\) is strengthened, this causes stronger soil calcification. In addition, the soil acidity in the karst mountain region is influenced by the thickness of soil which is controlled by the slope of the mountain relief. In general, thicker soil layers (~100 cm) exist in the areas with gentle slope, in where exchangeable acidity is high (5.76 mmol/100g, mean value from 3 profiles) and pH is low (4.79). Thin soil layers (<50cm) associated with steep slopes is strongly affected by dissolution of limestone rocks, resulting in high pH (5.56) and low exchangeable acidity (1.60 mmol/100g).

Our research study shows that limestone soil acidity is affected not only by lithology but also by bio-climate conditions and local geographic setting. Under conditions of long humid climate and flourishing vegetation, calcified soil has less influence of lithology, and gradually evolves into an acid soil which corresponds to local climates. Therefore, it is necessary for us to keep good vegetation and environment conditions as well as proper land use to prevent karst desertification.
Groundwater vulnerability and its contamination potential analysis and mapping is a hotspot and frontiers of international hydrogeology study. It also is a prerequisite to the work of preventing groundwater contamination problem. Groundwater vulnerability assessment can be applied mainly to groundwater protection, management and land use plan.

The concept, meanings, development and perspectives of groundwater vulnerability study fully analyze the physical geography, karst geology and hydrogeology condition of the study area: Qianjiang County, Chongqing City – a typical area in southwest China karst. The development mechanism and the vulnerability characteristics of epikarst zone in southwest China are analyzed according to the stress-response relation in ground water vulnerability. The EPIKSVLG method is selected to assess the groundwater vulnerability of the epikarst zone. This method is based on a conceptual model of epikarst hydrogeological systems which considers six epikarst system attributes and two human activity attributes: Epikarst development, Protective cover, Infiltration conditions, Karst network development, Soil self-purification, Vegetation, Land utilization and Groundwater exploitation. Moreover, each of these eight attributes is subdivided into classes. In this way, indexes of quantitative assessment of ground water vulnerability in epikarst zone are established.
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