Speleothems as environmental recorders
A study of Holocene speleothems and their growth environments in Sweden

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Thesis Contents

This doctoral thesis consists of a summary and four appended papers which will be referred to in the text by their Roman numerals.

List of papers

I Sundqvist, H. S., Seibert, J. and Holmgren, K. Understanding conditions behind speleothem formation in Korallgrottan, northwestern Sweden. Submitted to *Journal of Hydrology*.

II Sundqvist, H. S., Holmgren, K. and Lauritzen, S.-E., 2007. Stable isotope variations in stalagmites from northwestern Sweden document changes in temperature and vegetation, during early Holocene. *The Holocene,* 17(1).

III Sundqvist, H. S., Holmgren, K., Moberg, A., Spötl, C. and Mangini, A. Stable oxygen isotopes in a stalagmite from Jämtland, NW Sweden, record large temperature variations over the last 4000 years. Submitted to *Geophysical Research Letters*.

IV Sundqvist, H. S., Baker, A. and Holmgren, K. 2005. Luminescence in fast growing stalagmites from Uppsala, Sweden. *Geografiska Annaler*, 87 A (4): 539-548.

The co-authorship of Papers I-IV
I have planned and designed the study, carried out the field work, performed most of the analyses and led all the paper writing. In paper I Jan Seibert did the HBV modelling. In paper II Stein Erik Lauritzen contributed with data from a Norwegian cave and the samples were dated at his laboratory. Christoph Spötl and Augusto Mangini contributed to paper III by being responsible for the stable isotope and dating laboratories used. Anders Moberg contributed to the scientific discussion and to the choice of statistical treatment of data in paper III. In paper IV, I and Andy Baker jointly performed the luminescence analysis. The thesis project was initiated by Karin Holmgren who made the first visits and did the first sampling in them. She has also participated several times in field and contributed to all papers through scientific discussions and improvements to the text.

Introduction

To understand human impact on climate today we need to reconstruct and understand how climate has varied back in time, well before the industrial revolution. Knowledge about natural climate variability is also essential in studies of how human societies have been affected by and have adapted to climate change in the past. Climate change can be studied in a number of natural archives. Speleothems, or cave drip stones are one of those archives which, like ice cores, tree rings, peat and lake sediments, can be used for reconstructing past climate change. Carbonate speleothems are secondary deposits of calcium carbonate, chemically precipitated in caves from carbonate seepage water. They are deposited either through degassing of carbon dioxide or through evaporation (Schwarcz 1986). Speleothems are well suited for uranium-series dating, producing ages directly in calendar years (Smart 1991, Ivanovich and Harmon 1992) and the mechanisms controlling speleothem growth are sensitive to external, often climatically driven, processes. Therefore, many variables that can be measured in speleothems, such as stable carbon and oxygen isotopes, laminations and trace element composition, may serve as climatic proxies (Lauritzen and Lundberg 1999a). Even though the advantages are acknowledged, problems still exist in using speleothems as palaeoclimatic archives (Smart and Richards 2003). Like other climate archives, speleothems are individuals. Each speleothem is unique with its own response to external processes; therefore ideally more than one sample from each cave should be used. However, this ambition can conflict with issues concerning cave conservation. Furthermore, karst processes are characterised by non-linear and threshold responses. To understand these, laboratory and field experiments are needed to determine the specific factors affecting speleothem deposition at different sites.

In Sweden, caves with speleothems are found in Lummelundagrottan, developed in Silurian limestone, on the island Gotland, and in caves developed in Precambrian limestone or marble in the Caledonian mountain range in northern Sweden (Engh 1981). The speleothems in Lummelundagrottan have been thoroughly described by Engh (1981). A study of growth layers in a stalagmite from Lummelundagrottan was performed by Carlsson (1998). While the speleothems in Lummelundagrottan have proved to be difficult to date, because of low uranium content in the Silurian limestone, the speleothems from the mountain caves contain enough uranium for precise uranium series dating, using available high resolution dating techniques.

Project objectives

The overall aim with this PhD thesis is been to contribute highly resolved regional palaeoenvironmental information for the Holocene time period through studies of speleothems and their growth environments at different locations in Sweden. The specific objectives were:

1. To determine if speleothems from three Swedish sites are suitable as palaeoclimatic archives.

2. To obtain an understanding of factors that control and affect the growth and properties of the speleothems at these specific sites.

3. To examine if stable isotopes, luminescence and trace elements in the speleothems can be used as proxy indicators of past environmental change.

4. To provide palaeoclimatic data for the Holocene time period and compare it with other proxy data from the region.

Speleothems as climatic archives

Speleothems often hold a remarkable archive of data, describing local and global climatic and environmental conditions for the period of time in which they grew (Henderson 2006). The first palaeoclimatic studies of speleothems were conducted almost forty years ago (Hendy and Wilson 1968, Thompson *et al.* 1974). The most important analytical development since the first studies is the improvements in the technique of dating speleothems. Unlike other continental archives speleothems are not commonly dated with the radiocarbon method owing to the variable proportion of "dead" carbon from the bedrock (Genty *et al.* 2001). Instead speleothems are almost ideal for U-series dating. Uranium (^{238}U, ^{235}U, ^{234}U) is bound in silicate and oxide minerals in rocks and is co-precipitated with the calcium carbonate forming the speleothem. It decays into daughter isotopes (^{230}Th, ^{232}Th), and as thorium is insoluble in water, is therefore absent at the time of deposition. The production of ^{230}Th from disintegration of ^{234}U thus serves as a measure of time (Smart 1991, Ivanovich *et al.* 1992). However, contamination of the daughter isotope ^{230}Th may occur as a result of co-precipitation of ^{232}Th attached to clay particles present in the cave drip water. However, it is possible to corrected for this. Another problem is that results from different dating labs are not strictly comparable because of the different spike calibration and correction methods (McDermott *et al.* 2006). The dating techniques are straightforward and have been described thoroughly elsewhere (Smart 1991, Ivanovich 1992). The advances in Thermal Ionisation Mass Spectrometry (TIMS) have increased precision and reduced the sample size, making it possible to achieve chronological precision as good as 0.3-0.6 % (Lauritzen and Lundberg 1999b). The recently introduced high-resolution magnetic-sector field ICP-MS (inductively coupled plasma mass spectrometry) techniques require even smaller sample sizes than the TIMS-technique (Halliday *et al.* 1998, Shen *et al.* 2002). In this thesis, the main speleothem variables studied are stable isotopes and luminescent laminations and therefore a short summary of the theory behind these proxies is given.

Stable isotopes

When there is slow degassing of CO_2, stable temperature and no evaporation, calcium carbonate can be precipitated in isotopic equilibrium with the parent drip water (Hendy 1971). This means that the partitioning of light and heavy isotopes between the aqueous and solid phase is only a function of cave air temperature (Lauritzen and Lundberg 1999b). The calcite-water fractionation is –0.24 ‰ $°C^{-1}$ (O´Neill *et al.* 1969). Characteristic features of equilibrium deposits are according to Hendy (1971):

1. Insignificant changes in stable oxygen isotopic composition of calcite along a single growth layer.

2. Any slight variation in stable oxygen isotopic composition does not correspond to similar changes in the stable carbon isotopic composition of calcite along the same growth layer.

This can be tested by analysing several calcite samples along a single growth layer and is referred to as the Hendy test. Although it is a scientifically sound test in theory, it is in reality often impossible to apply, since the size of stalagmite growth layers normally are less than the size of the drill used (0.5-1 mm) for extracting the sample. It has also been suggested that while non–equilibrium conditions occur at the flank of the stalagmite, equilibrium conditions still may prevail in the centre of the stalagmite (Dulinski 1990). Thus a negative result of the Hendy test will not necessarily indicate that kinetic fractionation has occurred. Isotope ratios in carbonates are expressed in the δ notation in parts per mille (‰) relative to V-PDB (Vienna Pee Dee Belemnite), a calcite fossil from a limestone formation. Water samples are expressed in relation to V-SMOW (Vienna Standard Mean Ocean Water):

$\delta^{18}O$ V-PDB or SMOW = (Rsample/Rref – 1)*1000,
where R = $^{18}O/^{16}O$
Similarly, $\delta^{13}C$ V-PDB = (Rsample/Rref – 1)*1000,
where R = $^{13}C/^{12}C$

Oxygen isotopes

The stable oxygen isotope composition of speleothem calcite formed in isotopic equilibrium is related to the isotopic composition of the drip water and the cave temperature. Studies have shown that the $\delta^{18}O$ composition of cave drip water can be constant throughout the year, and be approximately equal to the composition of the mean annual value of the outside precipitation (Schwarcz *et al.* 1976, Younge *et al.* 1985) and that the deep cave temperature is close to the mean annual temperature outside the cave (Wigley and Brown 1976).

The $\delta^{18}O$ composition of precipitation is a consequence of several factors such as latitude, altitude, distance from sea, amount of precipitation and air temperature reflecting the mass-fraction of moisture precipitated from clouds. The mean annual $\delta^{18}O$ composition of precipitation decreases systematically across Europe with increasing distance from the North Atlantic Ocean (Rozanski *et al.* 1993). Under present-day conditions, the temperature dependence in rainfall is about 0.59 °± 0.09 ‰$°C^{-1}$ for European sites (Rozanski *et al.*1993). Since this exceeds the –0.24 ‰$°C^{-1}$ calcite-water fractionation, a net shift to heavier O isotopes with higher temperatures is expected (i.e. a positive correlation between $\delta^{18}O$ in the calcite and temperature)(Tab.1). Depending on the site however, the temperature dependence in precipitation could be greater than, equal to, or less than the temperature dependence of $\delta^{18}O$ in calcite deposited in speleothems (McDermott 2004, McDermott *et al.* 2006). Also, the variable mixing of winter and summer precipitation in the cave drip water could lead to a negative instead of a positive relationship between $\delta^{18}O$ in speleothems and temperature (e.g. Lauritzen and Lundberg 1999b, Sundqvist *et al.* 2007, Vollweiler *et al.* 2006). On long timescales, factors other than temperature may also cause temporal variations in $\delta^{18}Op$. These include; (i) changes in the $\delta^{18}O$ of the oceanic source region of precipitation, (ii) changes in the temperature difference between the ocean surface temperature in the vapour source area and the air temperature at the site of interest, (iii) shifts in moisture sources or storm tracks, (iv) changes in the proportion of precipitation that has been derived from non oceanic sources, and (v) the amount of precipitation (Gascoyne 1992).

Under favourable conditions, the $\delta^{18}O$ signal of calcite can be transformed into absolute temperature. This can be achieved by measuring the isotopic composition in fluid inclusions in the speleothem (Harmon *et al.* 1979, Gascoyne *et al.* 1981, Goede *et al.* 1986, Younge *et al.* 1981). Fluid inclusions, representing fossil seepage water, are formed in speleothems when small volumes of drip water become trapped within the precipitating calcite (Rowe *et al.* 1998-1999). Methods for extracting and analysing fluid inclusion are still under development.

Carbon isotopes

Less attention has been paid to the stable carbon isotope composition of speleothem calcite. The $\delta^{13}C$ can be influenced by a number of different factors such as photosynthetic pathways (C3/C4 pathways), biological activity, overlying bedrock, rainfall, and drip rate inside the cave (Baker *et al.* 1997, McDermott *et al.* 2006). when studying environments where only one or two of these processes dominate a more exact interpretation of the signal is possible. Plants utilizing the C4 photosynthetic pathway respire and decompose into carbon dioxide with higher $\delta^{13}C$ values than plants utilizing the C3 pathway. C3 plants are more abundant in cool and moist climates whereas C4 plant predominate in warm and arid environments (Dorale *et al.* 1992). In high latitudes the vegetation uses only the C3 photosynthetic pathways, and thus changes in $\delta^{13}C$ must be explained by other mechanisms than fluctuations of C3-C4 plants (Tab. 2). Changes in $\delta^{13}C$ can be a result of changes in biomass even in regions with only C3 vegetation (Baldini *et al.* 2005, Sundqvist *et al.* 2007). In these regions decreases in the production rate of CO_2 as well as a decreasing vegetation density, give rise to higher $\delta^{13}C$ values. Natural changes in vegetation are often caused by changes in temperature and/or changes in humidity which also can cause changes in $\delta^{13}C$ (Linge *et al.* 2001, Niggeman *et al.* 2003, Onac *et al.* 2002). Some temperate-zone speleothems show values for $\delta^{13}C$ that are greater than -6‰; these values are higher than would be predicted if they were in equilibrium with the expected C3 vegetation (Baker *et al.* 1997) and should therefore be interpreted with care. Such changes are likely to be caused by kinetic effects, like evaporation or rapid degassing of cave drip waters or calcite precipitation in the unsaturated zone above the cave.

Luminescent laminae

Variations in crystal fabric, organic content, or trace contaminant content along the growth axis of the speleothem can be detected as various forms of laminae. These laminae are either directly visible or can be produced by optical excitation of the sample. It has been shown that both visible and luminescent laminae may be annually formed; however any timescale, from seasonal or single events to centennial-millennial timescales and up, may be represented by a lamina signal (Baker *et al.* 1993, Shopov *et al.* 1994, Genty *et al*. 1997, Tan *et al.* 2006).

Many speleothems exhibit luminescence (light emission) when exposed to ultraviolet light sources. Absorption of energy by atoms in the mineral leads to the rising of electrons from the ground energy state to an excited level. Later these electrons fall down to a lower level while emitting light (photons). Speleothem luminescence predominantly originates from organic acids trapped inside the speleothem calcite. These acids occur in the overlying soil and are due to the breakdown of plant material (Baker *et al.* 1993, Shopov *et al.* 1994). Organic acids are divided into two groups, fulvic and humic acids. Fulvic acids are produced by photosynthesis and are released through the plant roots. They are readily soluble and are expected to enter speleothem feed waters preferentially during the growing seasons. Humic acids are products of organic decomposition in the soil and the epikarst below, and dissolve more slowly. Studies of soil extracts suggest that fulvic acids have a more intense luminescence and shorter wavelengths than the humic acids (Senesi *et al.* 1991). Together, the two groups can be taken as indices of productivity in the overlying soil and plant cover, and therefore, as a proxy measure of palaeoclimate (Shopov *et al.* 1994). However, climate is only one among many factors, such as pH and metal-ion interactions, that may influence fluorescence intensity and the wavelength of dissolved organic matter in the soil and in natural waters (McGarry and Baker 2000).

Field areas

The field work was carried out at three sites in Sweden (Fig. 1): the caves Korallgrottan (Papers I, II, III) and Labyrintgrottan (Paper II) in the Caledonian mountain chain and a cellar vault in the city of Uppsala (Paper IV).

Figure 1. Map of Scandinavia with field areas indicated.

Figure 2. View of the area above Korallgrottan.

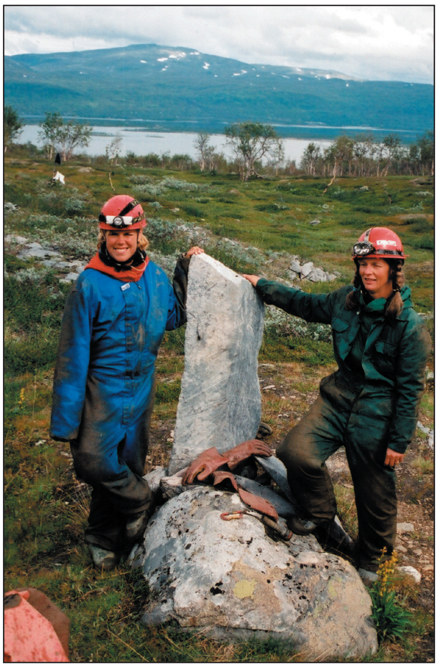

Figure 3. View of the area above Labyrintgrottan

Figure 4. View of the area above the cellar vaults in Uppsala.

Korallgrottan (64°53'N, 14°9'E, 540-600 m a.s.l) in northern Jämtland is the largest known cave in Sweden, with approximately 5.5 km of passages and has been described previosly by Isacsson (1994). Although most of the cave is closed to the public, guided tours with groups of 10-15 people, in a restricted area, are arranged between June and October. Korallgrottan has developed in a 200 to 300 m wide belt of Precambrian limestone. The bedrock surface above the cave is overlain by a 30-50 cm thick soil cover. The vegetation above the cave is rich in herbs, grass and mosses but also consists of sparse forest with old spruce and birch (Fig. 2). Nearby meteorological stations have an mean annual precipitation of 866 mm (Ankarvattnet 1961-90, 4 km south east) and an annual mean temperature of 1.4°C (Gäddede 1961-90, 50 km south) (Alexandersson and Eggersson Karlström 2001). From November to April most of the precipitation falls as snow and the snow cover generally lasts until May.

Labyrintgrottan (66°3´N, 14°41´E, 730 m a.s.l) is more than 2.4 km long and has developed in a limestone probably Ordovician in age that is partly crystalline and folded (Helldén 1973). The area is part of the most westerly of the extensive limestone branches that stretches from the central parts of Artfjället down to the northernmost slope of Lake Överuman. The entrance of the cave is located about 50 m above the present day tree limit. The bedrock is in places covered by a thin (few cm thick) soil cover with herbs and grasses (Fig. 3). A nearby meteorological station (Hemavan 1961-90, 30 km southeast) has an annual mean precipitation of 748 mm and an annual mean temperature of -0.5°C (Alexandersson and Eggersson Karlström 2001). From October to late April most of the precipitation falls as snow and the snow cover generally remains until June.

The city of Uppsala is situated in southeastern Sweden (59°54'N, 17°48'E) (Paper IV). Below the ground, next to Uppsala castle, two cellar vaults are situated (Fig. 4). The cellars were connected to a house that, together with parts of the castle, was destroyed in a fire in 1702. Both the cellar vaults and the house were probably constructed in the 1560s. These cellars, thought to have been completely demolished, where rediscovered by accident in 1976. Today the cellars are situated beneath a 4-9 m thick layer of soil and are in this way closed to the public. Access to the cellars is possible every fifth year when inspection of the ground subsidence is made. Stalagmites and stalactites of considerable size have developed inside the cellars. These speleothems must have formed after the fire in 1702 when the house was destroyed and water began to be able to penetrate through the ground. The speleothems are most likely a result of the dissolution of the calcareous mortar between the bricks in the roof. Uppsala (1961-90) has an annual mean precipitation of 545 mm and an annual average temperature of 5.6 °C (Alexandersson and Eggersson Karlström 2001).

Methods

All methods are described briefly in this chapter. For more detailed descriptions, see papers in appendices I-IV.

Fieldwork and monitoring

Stalagmites were sampled at the three sites. Stalagmites K1 (Paper II) and K11 (Paper III) were sampled in Korallgrottan during visits in 1998 and 2005 respectively, L4 (Paper II) was sampled in Labyrintgrottan during a visit in 1998 and U3 and U4 (Paper IV) were sampled in the cellar vault in Uppsala in 2000. An automatic sampling station, registering drip rate, conductivity of drip water, air pressure, air moisture, and temperature, was installed 200 m from the nearest entrance in Korallgrottan in June 2000. Air temperatures were also measured at four other locations inside the cave, using small temperature sensors. Stalactite drip water was collected during each visit for chemical analysis. The pH and electrical conductivity of the drip water were measured in situ when collecting the stalactite drip water. Visits to Korallgrottan were made once or more every year between 2000 and 2006. From April 2005 to April 2006 the cave was visited every second month. Water samples, both from different locations within the cave, and from the precipitation outside Korallgrottan, have also been collected. Information on the isotopic composition of local precipitation was obtained from observations at Bredkälen (1975-88) about 200 km south of Korallgrottan (Burgman *et al.* 1980, Calles and Westman 1989).

Laboratory analysis

All chemical analyses of stalactite drip water were performed at the Department of Geology and Geochemistry, Stockholm University (Paper I). The stalactite drip water was analysed for oxygen and hydrogen isotopes on a Finnigan Mat Delta Plus mass spectrometer, anions (F^-, Cl^-, NO_3^-, SO_4^{2-}) were analyzed on an Dionex IC DX 300 ion chromatograph and cations (Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Na^{2+}) on an Inductively coupled plasma Varian Vista AX. Saturation indices and pCO_2 where calculated using the Phreeqc Interactive programme.

Samples for analyses of stable oxygen and carbon isotopes in speleothem calcite were sampled using two different techniques, manual drilling using a dentist drill (Paper II) (Fig. 5) and semi automated micromilling (Paper III) (Fig. 6). The main difference between the methods is that micromilling techniques are capable of continuously sampling sections of speleothems (e.g. Frappier *et al.* 2002) at spatial resolution ranging from few tens of microns to fractions of a millimetre, as compared to conventional drilling where samples are drilled at intervals of 0.5-1 mm. Results from a study comparing both techniques (Spötl & Mattey 2006) show that the drilling data tend to miss extreme values picked up by the micromilling data.

In Paper II drilling was conducted using a standard dentist drill (0.5 mm in diameter). Vertical holes down to about 2 mm in depth were manually drilled at 1 mm increments. The samples were analysed with Isotope Ratio Mass Spectrometry (IRMS) at the Department of Geology and Geochemistry, Stockholm University. The IRMS instrument used is a Finnigan Mat 252, equipped with an online Kiel device. In Paper III micromilling was performed at 0.1 mm steps. A trench about 2 mm wide and 0.2 mm deep was micromilled concordant to the lamination; these are proportions suggested by Fairchild *et al.* (2006). Both the micromilling and the mass spectrometry analysis were performed at the Department of Geology and Paleontology, the University of Innsbruck. Isotope ratios are reported in the δ-notation relative to the V-PDB standard in parts ‰ with a precision better than ± 0.1 ‰.

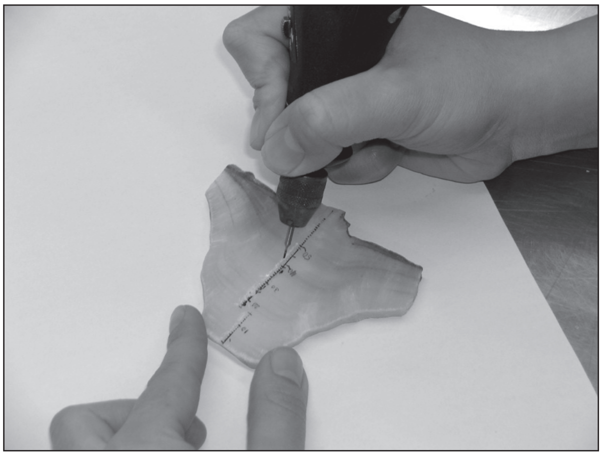

Figure 5. Conventional drilling

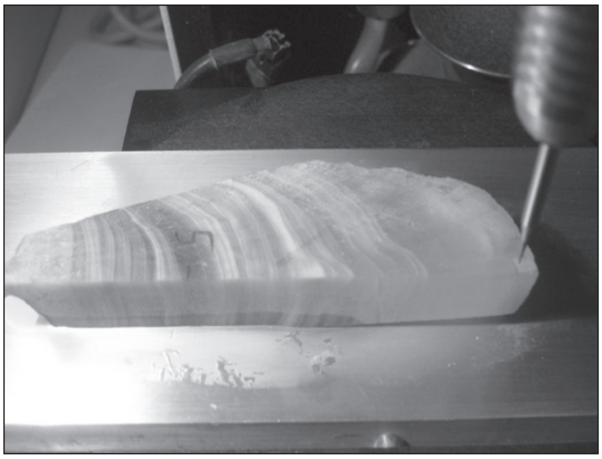

Figure 6. Micromilling

Luminescence analyses were performed on stalagmites from Uppsala (Paper IV). A complete representation of the luminescence properties down the central axis of the stalagmites were collected, using a Perkin-Elmer LS-50B luminescence spectrophotometer with a Perkin-Elmer fibre-optic extension and moving stage, in order to construct excitation-emission matrixes. Continuous luminescence intensity records were obtained by scanning the stalagmites at fixed excitation and emission wavelengths. To avoid problems with laser light scattering, which can cause the emitted signal to reflect calcite porosity, at least three scans were performed down and parallel to the central axis of the sample.

The speleothems studied in this thesis were dated at the U-series dating laboratories at the University of Bergen, Norway, on a Finnigan MAT 262 mass spectrometer (Paper II) and at the University of Heidelberg, Germany on a Finnigan MAT 262 RPQ mass spectrometer (Paper III).

The speleothem from Uppsala was dated with AMS radiocarbon dating at the Ångström Laboratory at Uppsala University and calibrated with INTCAL 98 (Stuiver et al. 1998).

Results

The following is a short summary of the four papers included in this thesis.

Paper I

Sundqvist, H. S., Seibert, J. and Holmgren, K. Understanding conditions behind speleothem formation in Korallgrottan, northwestern Sweden. Submitted to *Journal of Hydrology.*

The aim of this study was to investigate and characterise the environmental factors that control active speleothem growth in Korallgrottan, northwestern Sweden in order to assess whether fossil speleothems from the this site are suitable as palaeoclimatic archives. The cave microclimate and the $\delta^{18}O$ signal in speleothems, cave drip water and precipitation were monitored periodically between December 2000 and April 2006. The results show that the drip rate in Korallgrottan varies substantially following the seasons at fast dripping sites. Drip rates are highest during autumn and lowest during winter and very dry summers. At slow dripping sites however, drip rate and chemical composition are almost constant throughout the year. The drip water reaches the highest saturation level during the summer and autumn when biological activity is most intense and the partial pressure of carbon dioxide, which control limestone dissolution, is highest. A shortening of this period, such as during warm and dry summers, together with an early start of the winter, can cause a hiatus in the speleothem deposition at this site. The geochemical composition of drip water is fairly stable throughout the year, especially at the slow-dripping sits. This is explained by the presence of storage and mixing of water in the bedrock above the cave gallery. The cave temperature at the monitoring site is close to the atmospheric annual mean temperature outside the cave, while closer to the entrance temperatures show clear seasonal variations. Assuming that recent conditions can be applied back in time, the results from this study suggest that fossil speleothems selected from slow-dripping sites deep inside the cave are suitable for palaeoclimatic reconstruction of variations at annual or slightly longer time-scales.

Paper II

Sundqvist, H. S., Holmgren, K. and Lauritzen, S.-E., 2007. Stable isotope variations in stalagmites from northwestern Sweden document climate and environmental changes during early Holocene, *The Holocene*, 17(1).

This paper presents two early Holocene (9.6-5.9 ka BP) high-resolution stable isotope records of stalagmites from northwestern Sweden. The two stalagmites were collected from two caves, Labyrintgrottan and Korallgrottan, situated above and below today's tree-limit, respectively. The stable oxygen isotope records of the stalagmites confirm previous observations of the temperature evolution during the early Holocene with a gradual warming from c. 9.6 ka BP, interrupted by cooler conditions at 8.5-8.0 ka BP. The results indicate that, albeit the close proximity to the North Atlantic, the cooler conditions were driven by two-to-three abrupt cold events rather than by one so-called 8.2 event only. The period between 10 to 8 ka BP seems to have been an instable period which was affected by the melting ice sheets. Except for the cold events the stalagmite oxygen records show that between 7.8 to 5.9 ka BP temperatures in northwestern Sweden were warmer than today, with the interval between 7.8 to 5.9 ka BP most likely being the warmest.

It is proposed that the high-amplitude changes in the stable carbon isotope record of Labyrintgrottan are proposed to reflect changes in local vegetation, whereby at the time of stalagmite growth, between 9.5-7.5 ka BP the area above Labyrintgrottan was covered by much denser vegetation than today; it is not unlikely that between 9 and 8 ka the area was below the local tree-limit. Since temperatures are the dominant factor governing vegetation in northern Scandinavia the stable carbon isotope record from Labyrintgrottan support this interpretation that the conditions in Early Holocene were warmer than today, resulting in a denser vegetation cover, which could produce enough CO_2 to support speleothem growth in this high-latitude, high-altitude region.

Paper III

Sundqvist, H. S., Holmgren, K., Moberg, A., Spötl, C. and Mangini, A. Stable oxygen isotopes in a stalagmite from Jämtland, NW Sweden, record large temperature variations over the last 4000 years. Submitted to *Geophysical Research Letters.*

Paper III discusses the result from high-resolution stable isotope analyses of a stalagmite from Korallgrottan that has been growing over the last 4000 years. The stable oxygen isotope signal is proposed to record changes in the relative contribution of winter versus summer precipitation into the cave as a result of changes in seasonal temperatures. Cold temperatures would lead to relatively stronger influence of summer precipitation on the stable oxygen composition of the stalagmite resulting in enriched values, while warmer temperatures imply relatively more winter precipitation which would result in depleted $\delta^{18}O$ values in the speleothem. The temperature decrease, inferred from the $\delta^{18}O$ record, is interrupted by a number of distinct warm and cold spells of a few hundred years in length. The stalagmite $\delta^{18}O$ record agrees with the concept of a warm period, the so-called Medieval Warm Period (MWP), centred around AD 1000 and a cold period, the so-called Little Ice Age (LIA), somewhere between AD 1000 and today. However, based on the stalagmite results, it seems as if the minimum temperatures during LIA arrived 100-150 years earlier in northern Jämtland than in the northern hemisphere in general. Closer-spaced precise age determinations of this stalagmite may yield new and detailed information on the evolution of climate in northern Sweden.

Paper IV

Sundqvist, H. S., Baker, A. and Holmgren, K. 2005. Luminecence in fast growing stalagmites from Uppsala, Sweden. *Geografiska Annaler*, 87 A (4): 539-548.

In this paper the results of a study of luminescent properties in fast growing stalagmites from a cellar vault in Uppsala, southeastern Sweden, are discussed. The hypothesis was that the stalagmites have been growing continuously during the past 300 years and that the variations in luminescence and growth rate could be calibrated against available meteorological data. The results, however, indicate that the stalagmites have been growing during much shorter periods of time. These periods have been difficult to determine exactly, using available dating methods. The stalagmites consist of calcium carbonate but are precipitated by a different process than natural calcium carbonate speleothems found in limestone caves. They are deposited from hyperalkaline waters (pH>10) by the reaction $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ which is termed “concrete carbonation”. Speleothems deposited by concrete carbonation usually have accelerated growth rates, growing 1-20 mm a year. The stalagmites in the Uppsala cellar vaults display laminae that are suggested to be annual. The stalagmites will thus represent a period of 10-15 years with growth rates of 3-8 mm per year, which is similar to other fast-growing speleothems. Because the highest amounts of precipitation in Uppsala are received during the summer and autumn it is likely that the luminescent lamina are formed sometime during the autumn when precipitation is high and temperatures relatively low. AMS radiocarbon dating revealed ages that were older than the cellars themselves indicating that at least in part, the carbon has been deposited by another process than concrete carbonation. Owing to the uncertainty of the age of these speleothems it was not possible to compare the results with available meteorological data. In addition, the short amount of time covered by stalagmite growth further limits the possibility of undertaking such analyses.

Discussion

This thesis is the first detailed study of speleothems from Swedish caves for paleoenvironmental reconstruction. The monitoring study emphasizes the suitability of speleothems from Korallgrottan as environmental recorders. In addition, the similarities between contemporary samples from Labyrintgrottan and Korallgrottan demonstrate that also speleothems from Labyrintgrottan are good proxies for the regional environment and climate. Taken together, the stable isotope records (K1 and K11) from Korallgrottan together cover much of the early and late Holocene, although there is a gap of about 2000 years in the middle between 4000 and 6000 years BP (Fig. 7). When comparing the both records it appears that the late Holocene could have been more variable than the early Holocene. However, this could however be explained by the fact that the different sampling techniques were the conventional drilling tend to miss extreme values beacause of the lower sampling resolution and discontinues sampling (Spötl and Mattey 2006). The mean values of both of the $\delta^{18}O$ records vary around 9.1 ‰. It has however been reported that speleothems from the same cave can have $\delta^{18}O$ records varying around different mean values still displaying the same pattern of variability (Linge *et al.* 2001, Vollweiler *et al.* 2006). Since the records of K1 and K11 do not overlap it is hard to say if this is the case for K1 and K11. Thus it is not possible to judge whether the early Holocene was warmer or colder than the late Holocene.

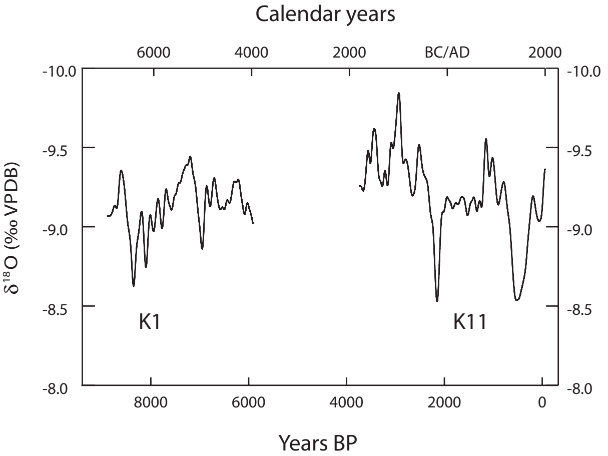

Figure 7. Both $\delta^{18}O$ records from Korallgrottan (K1-K11) low pass filtered (gaussian) corresponding roughly to a 100-year running mean.

Thus the results in this thesis contribute thus new information about the suitability of using small stalagmites from caves in the Caledonian mountains for high resolution reconstruction of relative changes in regional temperature, humidity and vegetation. The new techniques recently developed for stalagmite analyses provide new possibilities for sampling at high resolution. This implies that continued analyses of stalagmites from the caves studied for this thesis can contribute information on the evolution of the Holocene climate in northern Scandinavia at a time resolution that is of yet largely unavailable, except for in tree ring records (Briffa *et al.* 1992, Grudd *et al.* 2002, Gunnarson *et al.* 2003). The interpretation of $\delta^{18}O$ composition in stalagmites is however still not straight-forward. Since past variation in the $\delta^{18}O$ content of drip water is unknown at the sites studied it is not possible to retrieve absolute temperature variations. It is also not possible to objectively determine exactly the proportions of local site-specific influences versus regional changes. The solutions to these problems rely much on a knowledge of regional-local climate and atmospheric circulation conditions as well as on on comparison with other data. In paper II and III the stalagmite results were interpreted and discussed in relation to a number of different climate series. The following section discusses comparison with additional data that were not included in the appended papers.

Comparison with other $\delta^{18}O$ speleothem records from northern and central Europe

The $\delta^{18}O$ signal of the analysed stalagmites (Papers II and III) is inferred to be of regional character and primarily reflect changes in temperature. Similarities between the stalagmite records and other climate proxy records support this hypothesis. As a test of the regional representability of stalagmite $\delta^{18}O$ records as recorders of temperature changes, the $\delta^{18}O$ record of stalagmite K11 from Korallgrottan (Paper III) is compared here to previously published records of stalagmite $\delta^{18}O$ records from northern and central Europe (Fig. 8, Tab. 3). The records in the comparison were chosen beacause of due to their relative geographical closeness to each other and their influence by North Atlantic climate. Two of the records, SG93 from northwestern Norway (Lauritzen and Lundberg 1999b, Linge *et al.* 2001) and COMNISPA from Austria (Vollweiler *et al.* 2006), both have been interpreted as showing a negative correlation between speleothem $\delta^{18}O$ and past temperatures, mainly because the speleothems are believed to receive a higher proportion of light winter precipitation during warm winters. COMNISPA is a combination of three stalagmite $\delta^{18}O$ records from Spannagel cave in Austria that together cover the last 9000 years. In this comparison which covers the last 4000 years COMNISPA is composed of the record of stalagmite SPA 12, which spans between 70 and 2560 years ago and the average curve of stalagmites SPA 12 and SPA 128 from between 2560 and 4000 years ago. In the third stalagmite record, stalagmite CC3 from southwestern Ireland (McDermott *et al.* 1999, 2001), the $\delta^{18}O$ record is believed to have a positive correlation with temperature. The strongest argument for this hypothesis is the positive correlation between $\delta^{18}O$ and growth rate. The comparison reveals both similarities and differences between the records. Differences in the records that are easily explained are, for example, the variation in amplitudes between the records (Tab. 3), with the Irish record having the highest amplitude of 2.0 ‰ compared to the Norwegian record, which has the lowest amplitude of 0.8 ‰. This difference can partly be explained by differences in bedrock thickness, with the Norwegian cave having a bedrock thickness of about 100 m which results in more mixing of waters of different ages, as compared to the others having thicknesses in the order of 10-20 m. In like with the precipitation patterns in Europe today (Rozanski *et al.* 1993) the mean value of the oxygen isotopes decrease with distance from the Atlantic ocean and with latitude/altitude. This explains why the Swedish record displays the lowest isotope values while the Irish displays the highest. Even if the mean values and amplitude differences between the records can be explained it is obvious that many differences still exists. Similarities in the records of the last millennium include the Little Ice Age drop in temperature apparent at AD1300-1800 in K11, at AD1400-1800 in COMNISPA (SPA 12) and the two two-stage drop at 1400-1800 in CC3. In SG93 it is expressed as a general decline from AD 1200 until recent times. A Medieval Warming is apparent at AD 800-1200 in CC3, AD 1100-1300 in

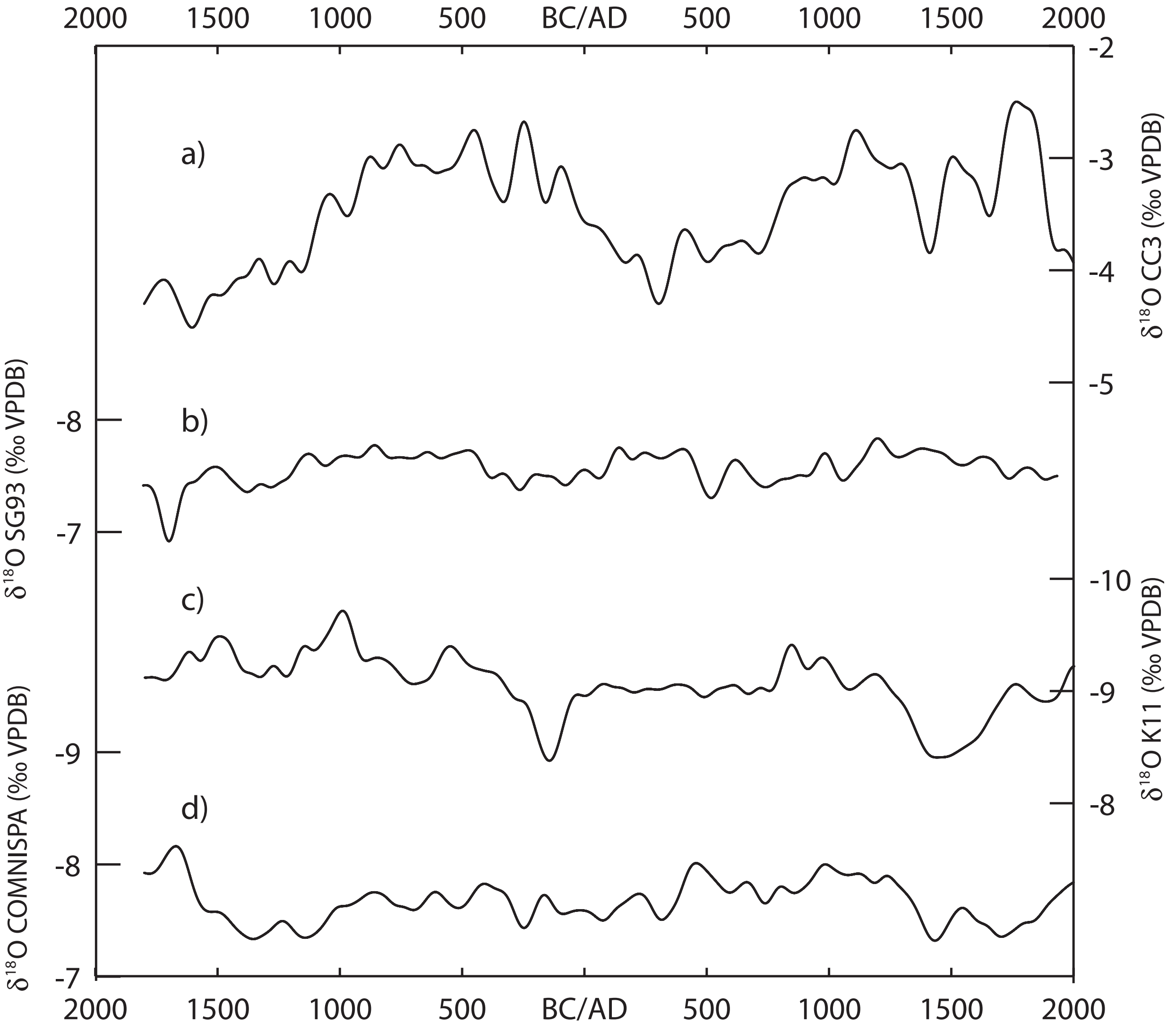

Figure 8. A comparison between four different $\delta^{18}O$ stalagmite records from Western Europe. a) CC3, Crag Cave, Ireland (McDermott et al. 1999, 2001), b) SG93, Søylegrotta, Norway (Lauritzen and Lundberg 1999b, Linge et al. 2001), c) K11, Korallgrottan, Sweden, this thesis, d) COMNISPA, Spannagel cave, Austria (Vollweiler et al. 2006). Note that the $\delta^{18}O$ scales are reversed for SG93, K11 and COMNISPA. The records have been low pass filtered (gaussian) corresponding roughly to a 100-year running mean.

SG93, AD 900-1100 in K11 and COMNISPA (SPA12). Both the record from Ireland and the one from Sweden have slightly increasing $\delta^{18}O$ values during the last 4000 years, which is interpreted to reflect a gradual temperature decrease at the Swedish site and as a temperature increase at the Irish site. A possible explanation for this could be that the increase observed in both stalagmite records is caused by changes in the atmospheric circulation pattern or in the isotopic composition of the source water.

It is evident that interpretation of temperatures made from $\delta^{18}O$ variations in speleothems is complicated and as can be seen by the differences existing between the four records it is also clear that temperature is not the only factor influencing the oxygen isotope signal of these stalagmites. The amount of rainfall, or other local factors, also could have controlled the oxygen isotope composition also. Further tests and comparisons with other proxy records can tell which of these records are the best proxys of past temperature changes.

Comparison between stable isotope data of K11 and a tree-ring chronology from Jämtland

One of the conclusions from Paper III is that the $\delta^{18}O$ record of stalagmite K11 captures regional temperature variations. The $\delta^{13}C$ record has some features similar to the $\delta^{18}O$ record, which indicates that $\delta^{13}C$ is partly

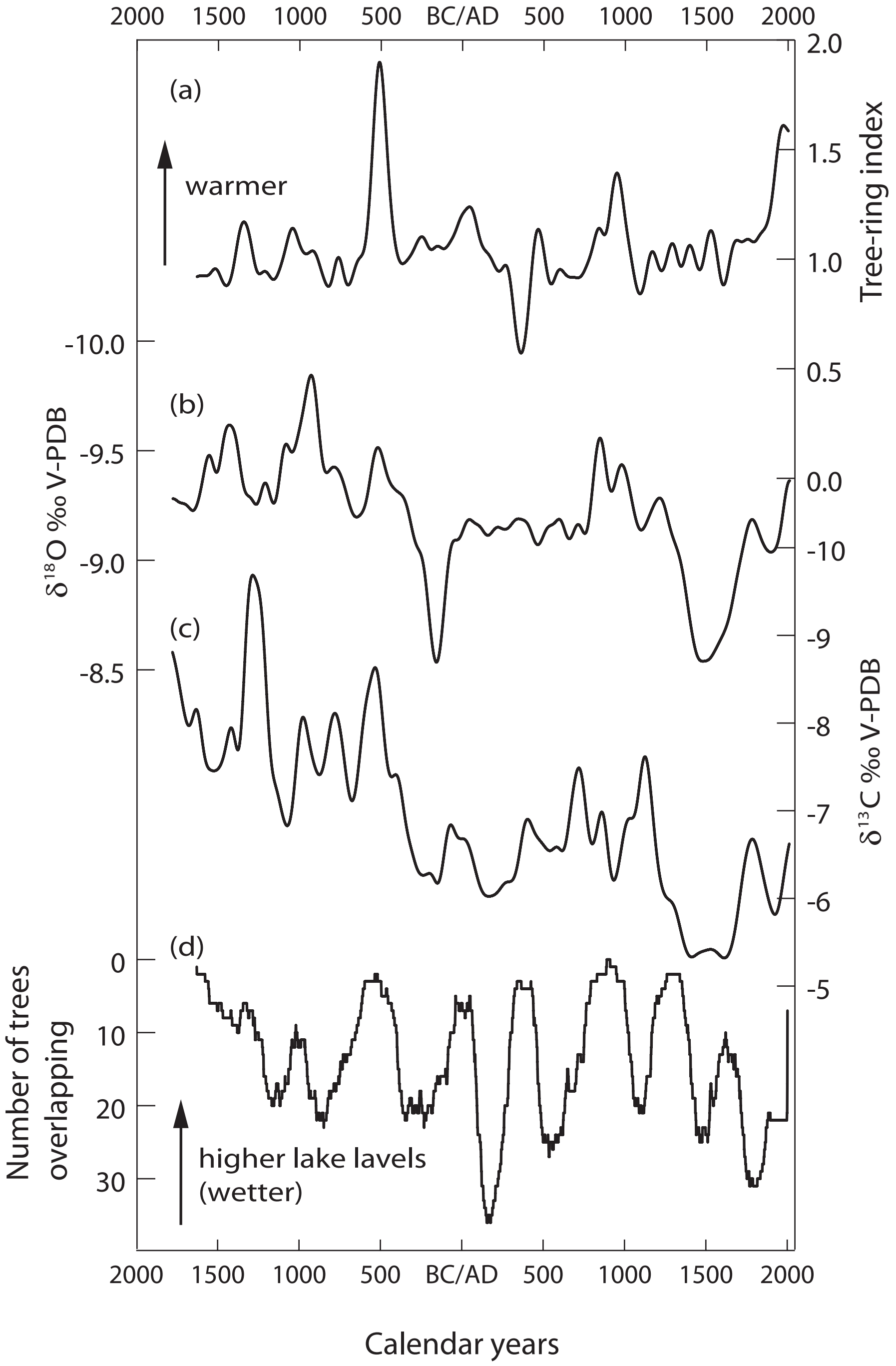

Figure 9. A comparison between the Håckren tree-ring chronology (SW Jämtland) (Gunnarson et al. 2003) and stable isotope data from K11, Korallgrottan (NW Jämtland). (a) tree-ring index from Håckren (b) stable oxygen isotopes of K11 (c) stable carbon isotopes of K11 (d) sample depth changes through time of the Håckren chronology. Data in (a)-(c) are low pass filtered (gaussian) corresponding roughly to a 100-year running mean.

is affected by temperature as well. It is proposed that the $\delta^{13}C$ signal reflects changes in the vegetation density, which in turn is governed by a combination of temperature and humidity changes. The high-amplitude changes in the stable carbon isotope record of Labyrintgrottan were also proposed to reflect changes in the local vegetation (Paper II). In order to test this hypothesis further, I here compare the stable isotope records of K11 with the Håckren tree-ring chronology from SW Jämtland (Gunnarson *et al*. 2003) (Fig. 9). This data set was chosen for three reasons 1) it is geographically close to Korallgrottan (200 km south), 2) it is a perfectly dated calendar year record and 3) the tree-ring index (tree-ring width) capture variations in July temperature and the number of trees (sample depth) is proposed to capture fluctuating lake levels and thereby changes in humidity (Gunnarson *et al*. 2003). If the trees reflect temperature and humidity and the stable isotopes reflect temperature and vegetation then low oxygen isotope values could be expected to correlate with high tree-ring index (discussed in Paper III) and low values of the carbon isotopes to correlate with high tree-ring index combined with high lake levels (few overlapping trees). High $\delta^{13}C$ values should then correspond to cold and/or very wet/dry periods. This is an initial comparison and many sources of error exist, such as the limited number of datings on stalagmite K11 and the fact that the stable isotope data comes from one stalagmite only. The ring-index curve and the $\delta^{18}O$ curve, both of which are believed to reflect temperature changes, have many similar features. The ring-width curve shows periods with enhanced growth which coincide with low $\delta^{18}O$ values at 1400-1300 BC, 1000 BC, 500 BC, AD 900-1000 AD and AD 2000. The records do not match at 300-100 BC and at AD 400-500. In general low $\delta^{13}C$ values correspond to high summer temperatures and high lake level stands with one exception at 1300-1100 BC. High $\delta^{13}C$ values correspond to low temperatures and low lake levels at 300-100 BC, AD 100-200 and AD 1400-1600; high $\delta^{13}C$ values correlate with high temperatures and high lake levels at 1600-1400 BC and AD 900-1100. After a first attempt to compare these two records it seems that that carbon isotopes reflect vegetation density or soil zone conditions might hold true for this site; however, a more accurate age model and at least one more stalagmite from this cave would be needed to validate these results. In addition, tree-ring indices contemporary with low sample depth, like at 500 BC, AD 500 and AD 900 should be treated with caution since internal factors (e.g. microclimate, diseases) unique to a single tree may have a large impact when chronologies consist of only a few samples (Gunnarson *et al.* 2003).

Conclusions

With careful analysis and interpretation, it seems possible to use stable isotopes in fossil speleothems from Labyrintgrottan and Korallgrottan to provide high resolution information on regional climate variations in northwestern Sweden. Oxygen isotopes can yield information on relative changes in past temperature, whereas and carbon isotopes can provide information about relative changes in vegetation density. Still uncertainties regarding age precision and isotope interpretation exist, but much of these are likely to be overcome by more precise dating and further analysis both regarding general process studies and detailed isotope studies. In summary, the most important conclusions from this study are:

- The monitoring study in Korallgrottan underscores the importance of examining the local climatology, drip hydrology and geochemistry of drip water before selecting stalagmites for palaeoclimate analysis.

- The drip rate from fast-dripping stalactites usually shows larger seasonal and year-to-year variations and reflects the situation of the snow regime while slow- dripping ones have more stable drip rates. The slow- dripping stalactites also have a more stable, probably annual, geochemical signal in the drip water.

- Stalagmites fed by stalactites with slow and stable drip rates from deep inside the cave are the most suitable as palaeoclimate archives.

- The close similarities between the $\delta^{18}O$ records of stalagmites from Labyrintgrottan and Korallgrottan emphasize the potential of the speleothems from both caves for providing high resolution regional palaeoclimate information.

- The $\delta^{18}O$ signal in the stalagmites is interpreted as varying as a result of the variable mixing of summer and winter precipitation owing to changes in regional temperatures. The $\delta^{13}C$ signal is interpreted as reflecting changes in soil CO_2 production, which in turn may reflect changes in vegetation density.

- The stalagmite $\delta^{18}O$ records from northern Scandinavia indicate that between 9500 and 6000 years ago temperatures in northwestern Sweden were warmer than today, except for a number of cold events. During this period the interval between 7800 and 6000 years ago seems to have been the warmest.

- The area above Labyrintgrottan was most likely covered by much denser vegetation than today at the time of stalagmite growth (9500-7500 years ago) and was - unlike today – probably situated below the local tree-limit between 9000 and 8000 years ago.

- The stable isotope record together with changes in growth rate of a stalagmite covering the last 4000 years indicate a slight but general reduction of temperature and precipitation during the growth period. The temperature decrease is interrupted by a number of distinct warm and cold spells of a few hundred years in length. The record agrees with the concept of a warmer period, the so-called Medieval Warm Period (MWP), centred around AD 1000 and a colder period, the so-called Little Ice Age (LIA), somewhere between AD 1000 and today.

- Fast growing speleothems, like the ones from Uppsala, can provide an opportunity of studying luminescence properties in speleothems in greater detail than otherwise possible. The results indicate that the variations in luminescence intensity are annual and that the annual laminae of the luminescent record represent a flush of organic material. With good age control they can yield information about history and climate.

Future perspectives

Carbon isotopes

To further examine the hypothesis that carbon isotopes represent a vegetation density signal one could compare carbon isotopes with pollen data from a lake in the vicinity of the cave. This type of study would be of particular interest in the Labyrintgrottan area. Pollen data obtained from the lake sediments could provide information about changes in tree-limit positions that could possibly be coupled to the changes in $\delta^{13}C$ in the Labyrintgrottan stalagmite. The lake should then be situated at the same elevation or slightly higher than the cave. In addition, comparisons between carbon isotopes and trace elements ratios such as Mg/Ca and Sr/Ca which together could yield information about dry periods would be interesting.

Dating

Additional palaeoenvironmental information from Korallgrottan and Labyrintgrottan could be attained by dating more material. A better age model of K11 together with an age model of stalagmite K13, sampled about 1 m away from K11, which has got a bottom date of about 3000 years and is already sampled for stable isotopes for comparison and evolution of the results in Paper III.

Dating the base level of collected and not yet dated speleothems from Labyrintgrottan might reveal information about the time of deglaciation of the area.

A flowstone of Eemian age (125 ka) has been found in Korallgrottan. The sample has been dated by alfa spectrometry but a new age model together with stable isotope analysis might yield valuable information about the Eemian environment. It would also be interesting to test whether the negative correlation between the oxygen isotopes and temperature holds this far back in time or if other processes are more dominant.

Uppsala

The next opening of the cellar vaults in Uppsala is planned to take place in 2007. During the last visit in 2000 plastic slides were placed out on the floor. Hopefully calcite has precipitated on top of these. Then luminescence properties can be studied with great age control and directly compared to meteorological data.

Monitoring and modelling

To examine the contribution of winter precipitation versus summer precipitation of the cave drip water, the annual $\delta^{18}O$ in the precipitation should be monitored and compared it with the annual $\delta^{18}O$ in the drip water of a number of stalagmites (especially K11). This is a study that requires several years of sampling and a faster approach would be to calculate the contribution of winter precipitation compared with summer precipitation using the HBV model.

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