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## High resolution $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records from an annually laminated Scottish stalagmite and relationship with last millennium climate

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## ABSTRACT

High-resolution (annual to decadal) stable isotope records of oxygen and carbon are analysed from an annually laminated stalagmite from NW Scotland. The sample, which was deposited for ~1000 yrs until 1996 AD, has previously provided annual resolution climate reconstructions of local rainfall and regional winter North Atlantic Oscillation (wNAO) from variations in annual growth rate. For our stalagmite, for which modern cave monitoring demonstrates that equilibrium deposition is highly likely for  $\delta^{18}\text{O}$  but not for  $\delta^{13}\text{C}$ , stalagmite  $\delta^{13}\text{C}$  originally derives from soil  $\text{CO}_2$  produced predominantly by microbial respiration, modified by degassing-related kinetic fractionation, and  $\delta^{18}\text{O}$  from the composition of infiltrating water during periods of infiltrating water. Both the presence of fluorescent laminae and modern drip-water monitoring demonstrate a drip hydrology that comprises both event and storage components. Over the instrumental period, no correlations between stalagmite or rainfall  $\delta^{18}\text{O}$  and precipitation amount or temperature are observed, but correlations are observed between rainfall  $\delta^{18}\text{O}$  and 500 mb height at regional IAEA monitoring stations. However, no correlations are observed between stalagmite  $\delta^{18}\text{O}$  and instrumental and reconstructed atmospheric circulation, preventing a simple palaeoclimate interpretation of the stalagmite  $\delta^{18}\text{O}$  proxy. Stalagmite  $\delta^{13}\text{C}$  has a stronger temporal autocorrelation than  $\delta^{18}\text{O}$ , indicative of soil mixing of respired  $\text{CO}_2$  and significant variability between drips and at different times; correlations with instrumental climate data are therefore not possible. The relative timing of changes in growth rate,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  are discussed, and interpretations compared with other regional climate records. We conclude that, over the last millennium at this mid-latitude cave site, neither  $\delta^{18}\text{O}$  nor  $\delta^{13}\text{C}$  cannot be interpreted as a simple paleoclimate proxy.

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## 1. Introduction

Stalagmite SU-96-7, from a cave in NW Scotland, contains annual fluorescent laminae for ~1000 yrs until 1996 AD, the year of its sampling. Variations in annual growth rate, determined from annual lamina thickness, have been shown to correlate with climate (Tan et al., 2006; Baker et al., 2008), specifically climate parameters that determine the water level in the overlying peat, which ultimately determines drip water  $\text{CO}_2$  concentration (Proctor et al., 2000, 2002). Instrumental temporal calibration demonstrates a correlation with annual rainfall amount and a weaker correlation with mean annual temperature, with the former signal dominating, allowing a 1000 yr record of annual rainfall which can also be interpreted as a proxy of

the winter North Atlantic Oscillation (wNAO) index (Proctor et al., 2000). Utilising other stalagmites from the cave, the record was extended back to another 2000 yrs (Proctor et al., 2002). Subsequently, Baker et al. (2002) analysed years of double laminae to construct a record of extreme winters for the last 1000 yrs, with second fluorescent laminae forming in years of significant snowmelt. Charman et al. (2001) undertook a paleoenvironmental analysis of the overlying peat deposits and compared this to stalagmite fluorescence proxies, and Smith et al. (2006) and Baker et al. (2008) used the temperature component found in the growth rate record as part of a Northern hemisphere temperature reconstruction from annually laminated stalagmites. Most recently, Trouet et al. (2009) combined the SU-96-7 growth rate record with a ~1000 yr reconstruction of aridity derived from Moroccan tree rings to derive a ~1000 yr record of low frequency NAO strength ( $\text{NAO}_{\text{ms}}$ ).

Following the work of Proctor et al. (2000, 2002), stalagmite SU-96-7 was archived pending the developments of sampling techniques

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required to sample carbonate stable isotopes at high resolution; annual accumulation of the stalagmite is in the range of 20–160  $\mu\text{m}$ . Recently this has been addressed by precision micromilling technology, permitting isotope sampling at 100  $\mu\text{m}$  resolution—therefore providing a high resolution (annual to decadal) record of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  for the last 1000 yrs. At the same time, we have undertaken a comprehensive monitoring of the modern cave environment, sampling a wide range of drip waters as well as the cave climate, including the isotope hydrology of the drip water feeding SU-96-7 (Fuller et al., 2008). This monitoring programme confirmed the very slow median drip rate of water feeding SU-96-7 (0.05 to 0.06  $\mu\text{l/s}$ ) as well as low variability of drip water  $\delta^{18}\text{O}$  ( $-7.07 \pm 0.36\text{‰}$ ) highlighting the dominance of storage flow for most of the year (although with a short duration event water component supplying peat-derived fluorescent organic matter and associated trace elements (Fairchild et al., 2001)). Fuller et al. (2008) calculated the values of  $\delta^{18}\text{O}$  of calcite and demonstrated that stalagmites are forming close to isotopic equilibrium and that kinetic effects are negligible.

In this paper we present the 100  $\mu\text{m}$  resolution  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  time series for SU-96-7. Firstly, we will compare the isotope data for the last ~100 yrs to instrumental climate and rainfall  $\delta^{18}\text{O}$  data, and investigate any modern climate relationships. We then use these relationships to attempt to derive proxy climate interpretations for

the last 1000 yrs. Finally, we compare the various proxy series from this stalagmite (NAO<sub>ms</sub> derived from growth rate, winter snowmelt from double laminae, moisture source from  $\delta^{18}\text{O}$ ) with other relevant proxy reconstructions, to improve our understanding of the relative timing of changes in temperature, wNAO strength and moisture source in NW Scotland.

## 2. Site description and methodology

Stalagmite SU-96-7 was deposited in the Uamh an Tartair (UAT) cave system (National Grid Reference NC276206, Lawson, 1988), situated 3 km east of Inchnadamph and 220 m above sea level (Fig. 1). UAT is an active river cave with multiple entrances, and SU-96-7 was sampled from the Grotto, a location relatively distant from the entrances but with the active stream flowing through the base of the same chamber. Previous monitoring of the cave climate has demonstrated that air temperature in the Grotto varies over an annual cycle from 4.8 to 9.5 °C (mean 7.2 °C) (Fuller et al., 2008). Discontinuous cave air  $p\text{CO}_2$  measurements ranged from  $-2.81$  to  $-3.38$  (Fuller, 2007): highest mean concentrations were observed in summer, although  $p\text{CO}_2$  variability was also observed over hourly and daily time periods, indicative of the Grotto being strongly ventilated, probably driven by water movement through the chamber. UAT is

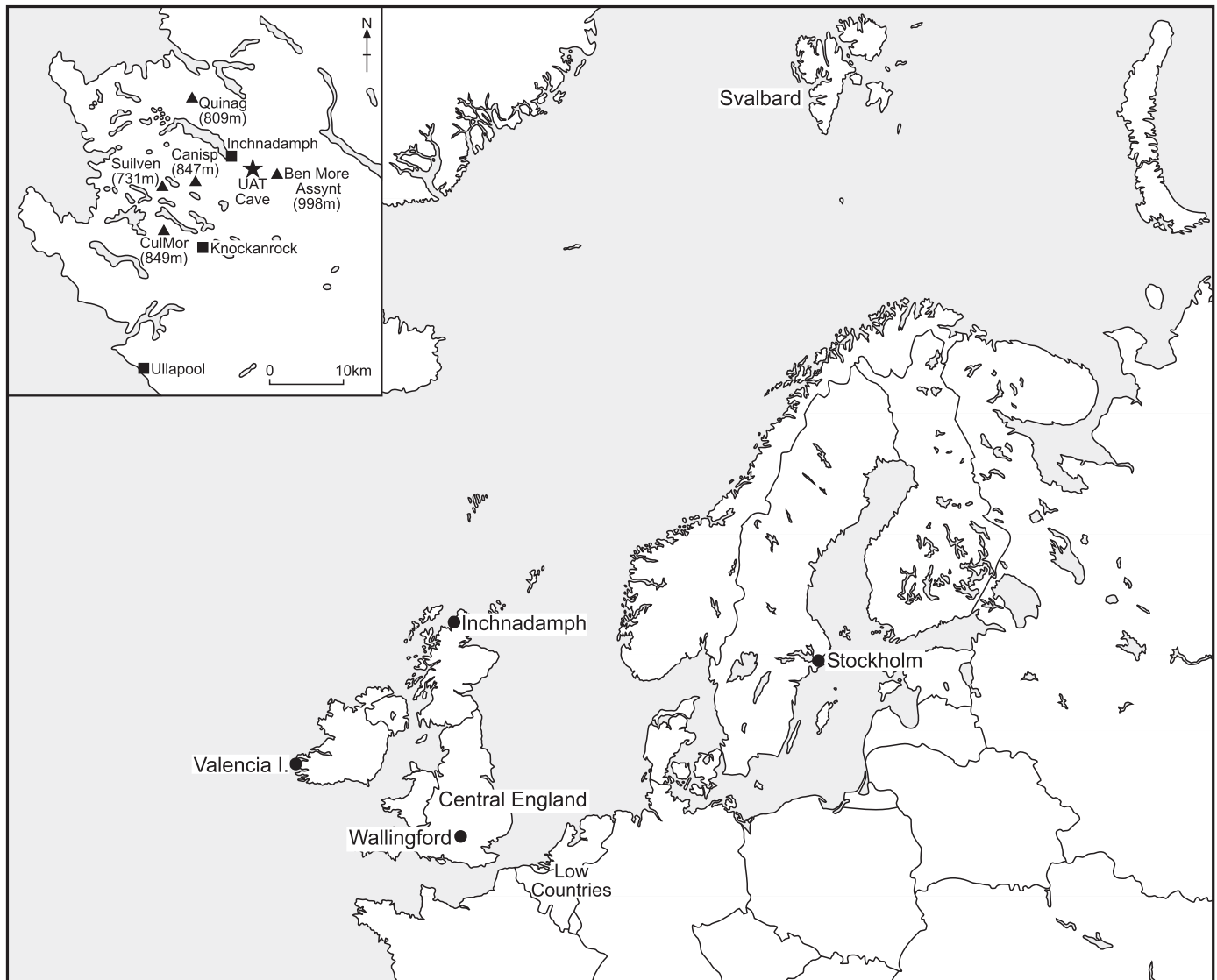


Fig. 1. Location of proxy climate sites mentioned in the text. Inset shows detail local to the study site, with the location of stalagmite SU-96-7 from Uamh an Tartair (UAT) marked.

situated within the Traligill Basin, a peat-dominated basin (near-basal radiocarbon peat age above the cave of  $2130 \pm 180$  cal yrs BP) (Charman et al., 2001) located within the montane environment of the Assynt region, located on the North Atlantic seaboard of NW Scotland (Fig. 1). Based on the 1971–2000 averages, the regional climate is oceanic with  $>1900$  mm rainfall, 250–270 rain days per yr, 4–6 snow days, and an average of 77% cloud cover annually (Proctor et al., 2000). Mean annual air temperature is  $7.1$  °C. The Assynt area shows a relationship between precipitation and the winter North Atlantic Oscillation (NAO) Index, and temperature and ocean circulation via the North Atlantic Drift Current (Colman, 1997; Hurrell, 1995).

Initial screening of the isotopic composition of stalagmite SU-96-7 was undertaken by in-situ analysis using an automated laser-ablation gas chromatography (LA-GCMS) system consisting of a  $\text{CO}_2$  laser bench (Synrad 25w  $\text{CO}_2$  laser operating at  $10.6$   $\mu\text{m}$ , spot size 100–150  $\mu\text{m}$ ) and a He flow sample chamber coupled to a Carlo-Erba NA1500 elemental analyser and a VG Instruments Optima mass spectrometer. Details of the operation and performance of the system are given in Spötl and Matthey (2006). Analyses were carried out along three traverses: T8 followed the growth axis, T4 was offset towards the flank and T7 followed a line close to the flank of the specimen (Fig. 2). Each traverse comprised a series of laser ablation sampling spots spaced at  $0.7$  mm as a forward and reverse profile along the line of the traverse; the return profile was offset by  $0.35$  mm such that the data for the entire traverse has a net resolution of  $0.35$  mm. Analytical runs consisted of alternating cycles of 20 spot analyses of Carrara marble, and traverses across the unknown sample, finishing with a

final block of 20 Carrara analyses (Spötl and Matthey, 2006). The average values for each block of Carrara data are used as a within-run drift monitor and drift corrected laser data are normalised to VPDB based on the difference in the grand mean of laser data for the whole sample and the mean of set of classical stable isotope analyses of drilled powders taken along the traverse. The corrections ( $-0.24\%$  for  $\delta^{13}\text{C}$  and  $-0.63\%$  for  $\delta^{18}\text{O}$ ) encompass solid–gas fractionations associated with laser decarbonation which are constant for a particular set of operating conditions (Spötl and Matthey, 2006). Reproducibility of laser analyses, measured on Carrara marble ‘standard’ blocks are better than  $\pm 0.2\%$  (1 sigma) for  $\delta^{13}\text{C}$  and  $\pm 0.3\%$  (1 sigma) for  $\delta^{18}\text{O}$ . Due to the laser pits obscuring adjacent annual fluorescent laminae, isotope data were not aligned to a time axis but instead used to derive an isotope surface for  $\delta^{18}\text{O}_c$  and  $\delta^{13}\text{C}_c$  which could be used as a multiple ‘Hendy-test’ (Hendy, 1971) to assess the presence of fractionation between growth axis and stalagmite flank.

To obtain a high-resolution climate record, calcite samples were obtained from stalagmite SU-96-7 using a micromill at the University of Innsbruck. Samples were milled at  $100$   $\mu\text{m}$  intervals and approximately  $150$   $\mu\text{m}$  depth, creating trenches  $2$  mm wide along the growth axis. To enable the milled samples to be aligned to the lamina chronology, every 10th sample was milled to a wider trench. Sample SU-96-7 was milled down the central growth axis from the top to within  $\sim 2$  mm of the base, where laminae became less regular in shape and prevented precise alignment of the milled powders to the annual laminae. The calcite powders were analysed by conventional acid digestion methods as outlined in Spötl and Vennemann (2003). C and O isotope values are reported on the VPDB scale. The  $1\sigma$  error for is  $\pm 0.06\%$  and  $\pm 0.07\%$  for  $\delta^{18}\text{O}_c$ . The annual fluorescent laminae in the milled section of the stalagmite were imaged using identical techniques as previously published (Proctor et al., 2000, 2002) and each  $100$   $\mu\text{m}$  isotope analysis aligned to a lamina year for the last  $\sim 1000$  yrs.

### 3. Results and discussion

#### 3.1. Stable isotope time series

Results of the LA-GCMS  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  analyses are presented in Fig. 2. The forward and reverse spot analyses are combined and have been smoothed with a 5-term moving average to reveal the topology of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  variations along the axis and towards the flank. The profiles would be expected to show systematic changes from axis to flank if disequilibrium kinetics had been operating throughout or for periods during stalagmite growth. Fig. 2 shows that for both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , allowing for errors in matching stratigraphy, the first order variations are reproduced in all three profiles, with only a short segment (e.g. from 6 to 9 mm for  $\delta^{13}\text{C}$ , and 17–20 mm for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , Fig. 2) showing a systematic increase from axis to flank indicative of the kinetic effects of degassing.

Comparison of stalagmite  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  micro-mill series, along with the published annual growth rate chronology for the last  $\sim 100$  yrs (which is based on a stack of a number of profiles) is shown in Fig. 3, and for the last  $\sim 1000$  yrs in Fig. 4. Also shown in Fig. 4 are the upper and lower range of 20th century values of each proxy. Inspection of the isotope series demonstrates that  $\delta^{13}\text{C}$  is very strongly temporally autocorrelated, more so than  $\delta^{18}\text{O}$ . Over the whole record, the first order autocorrelation of  $\delta^{13}\text{C}$  is 0.989 and  $\delta^{18}\text{O}$  is 0.976; over the period 1900–1995 AD the autocorrelation is 0.956 for  $\delta^{13}\text{C}$  and 0.802 for  $\delta^{18}\text{O}$ . For example, during the period  $\sim 1930$ –1960 AD (Fig. 3), when growth rate is highest, and the isotope sampling approaches annual resolution,  $\delta^{13}\text{C}$  shows almost no high-frequency variability. Given that both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  have both been identically transformed by mixing of waters in the peat and carbonate aquifer overlying the cave, and experienced identical cave

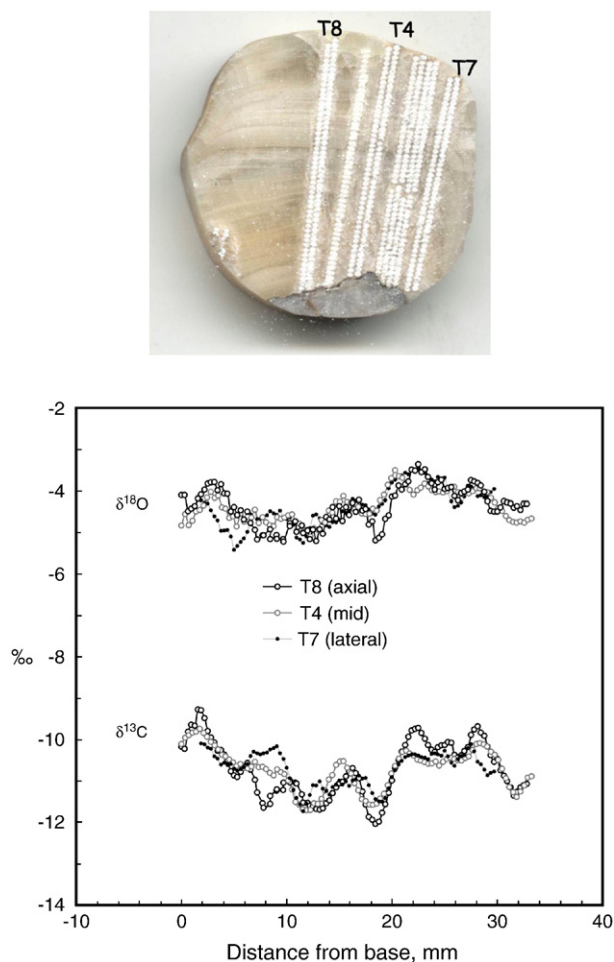
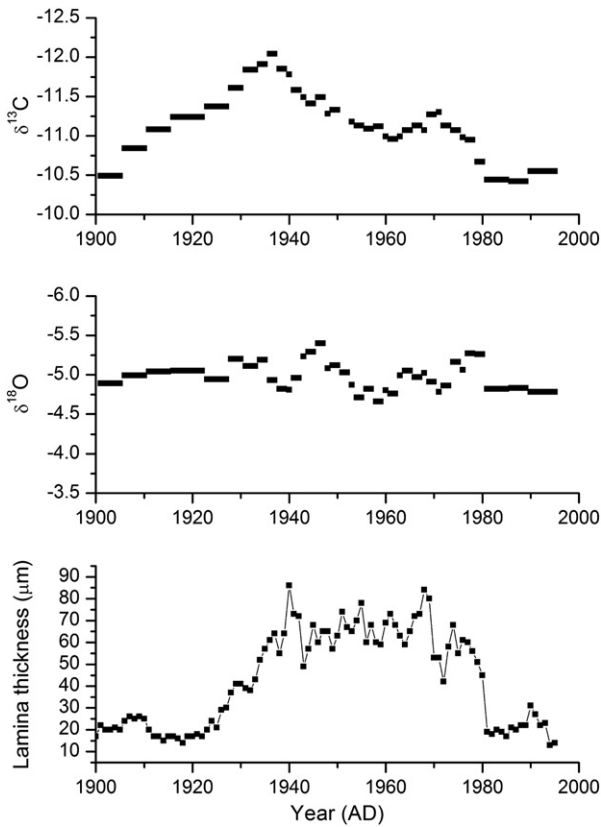
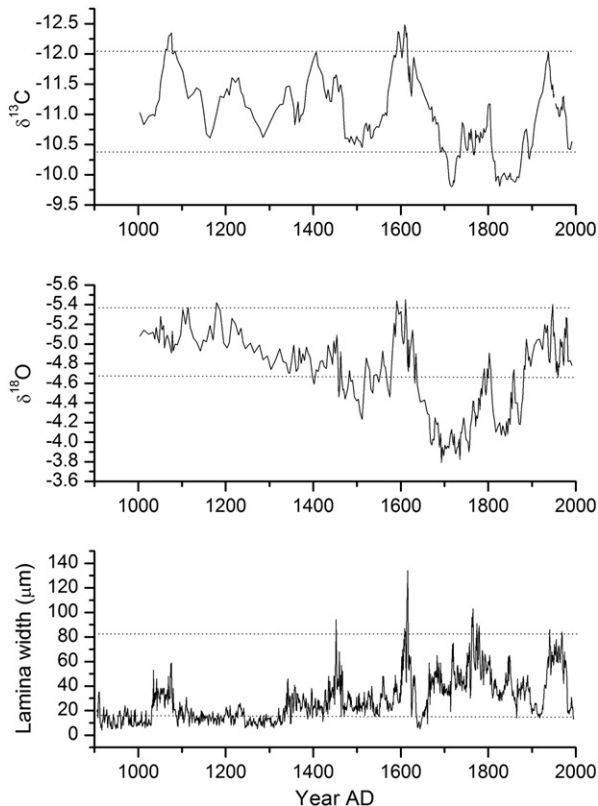


Fig. 2. (top) SU-96-7, showing locations of laser traverses. (base)  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  profiles for traverses T4, T7 and T8.



**Fig. 3.**  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$  and lamina width records for the period 1900–1996 AD. Isotope series are shown as horizontal bars indicating the period of time averaging of individual 100  $\mu\text{m}$  width samples. Note inverted y-axes for the isotope series.



**Fig. 4.**  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$  and lamina width records for the period 1000–1996 AD. Note inverted y-axes for the isotope series. The range of values for the period 1900–1996 AD is shown by dotted lines.

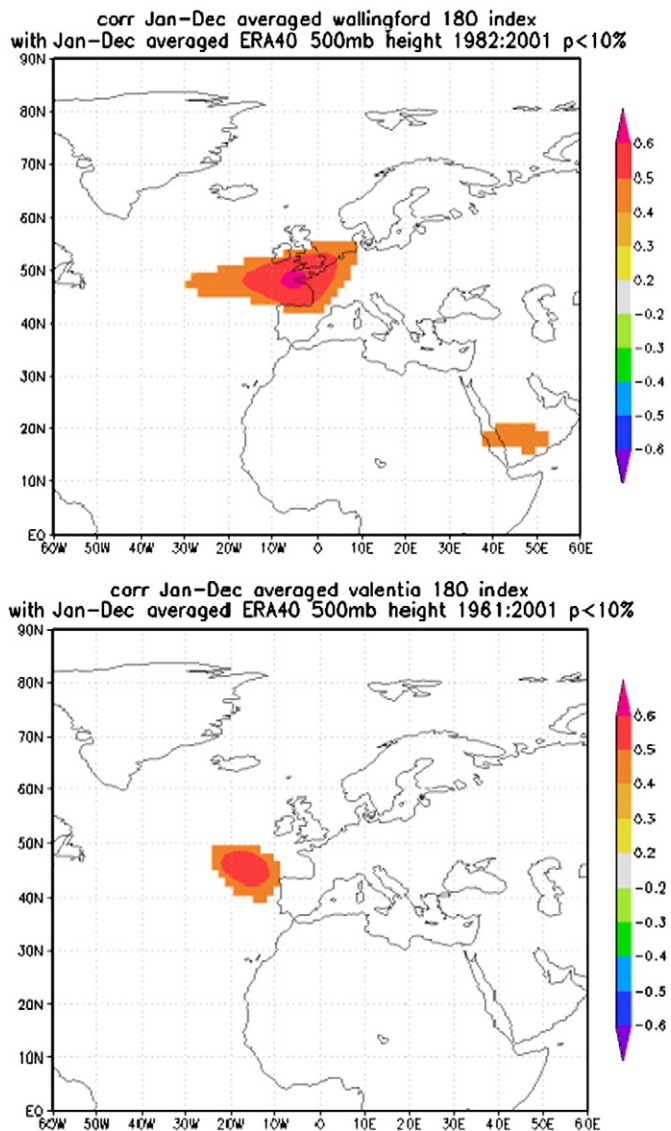
temperatures (which control the temperature dependent fractionation of both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ), this suggests that  $\delta^{18}\text{O}$  reflects greater source variability than  $\delta^{13}\text{C}$ . This agrees with our monitoring of  $\delta^{18}\text{O}$  of precipitation at the site (Fuller et al., 2008) that demonstrated substantial intra- and inter- annual variations in  $\delta^{18}\text{O}$  of precipitation (7.1‰) which was subsequently smoothed in the aquifer to a drip water variability of less than 1.2‰ from the annual weighted mean for all drip waters. In contrast,  $\delta^{13}\text{C}$  derives from the  $\text{CO}_2$  in the overlying peat water and bedrock carbon. The peat is isotopically homogenous ( $\delta^{13}\text{C} = -29.2 \pm 0.2\text{‰}$  over the last 2100 yrs—Charman et al., 2001), and the smoothed stalagmite  $\delta^{13}\text{C}$  suggests little intra-annual variation in recharged dissolved inorganic carbon.

Correlation between  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$  and annual lamina thickness over the period 1900–1995 AD is weak.  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  exhibit a positive relationship ( $r = 0.40$ );  $\delta^{13}\text{C}$  and growth rate a negative relationship ( $r = -0.48$ ) and  $\delta^{18}\text{O}$  and growth rate show no correlation ( $r = -0.13$ ). Over the last 1000 yrs, the correlation of  $\delta^{18}\text{O}$  against  $\delta^{13}\text{C}$  shows a stronger correlation ( $r = 0.65$ , significant at 99% with adjusted degrees of freedom to correct for autocorrelation in the time series (Trenberth, 1984)) but correlations between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  and annual lamina thickness are weak ( $\delta^{13}\text{C}$  versus growth rate:  $r = 0.02$ ;  $\delta^{18}\text{O}$  versus growth rate:  $r = 0.18$ ). The lack of strong correlations between the isotopic and lamina width proxies suggests that  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  are responding differently to annual lamina thickness; the correlation between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  is indicative of a common process affecting both these proxies.

### 3.2. Modern climate comparisons

Previously, annual growth rate data has been calibrated against instrumental temperature and rainfall series (Proctor et al., 2000, 2002).  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  series, however, are not amenable to instrumental calibration. Only thirty-eight samples, with 100  $\mu\text{m}$  resolution parallel to the growth direction, cover the last 100 yrs, with a variable temporal resolution of annual to biannual between 1934 and 1980 AD (when growth rates are highest, Fig. 2), but of only 4–6 yrs per sample before 1934 and after 1980 AD, when growth rates were slower. Coupled with the strong temporal autocorrelation in both series, which limits the number of degrees of freedom, linear regression-based temporal calibration is therefore not appropriate. Instead, for  $\delta^{18}\text{O}$ , we have explored the relationship between rainfall  $\delta^{18}\text{O}$  and instrumental climate data. The nearest IAEA rainwater  $\delta^{18}\text{O}$  stations to the site with relatively long  $\delta^{18}\text{O}$  rainfall records are at Wallingford, UK (760 km to the south), and Valentia, Ireland (770 km to the south-west). Using the IAEA Water Isotope System for data Analysis, Visualisation and Electronic Retrieval WISER; (<http://nds121.iaea.org/wiser/>) and KNMI Climate Explorer (<http://climexp.knmi.nl/>), we investigated the annual and seasonal correlations between rainfall  $\delta^{18}\text{O}$  at Valentia and Wallingford and rainfall, temperature and pressure fields over the North Atlantic–Europe region, using the European Centre for Medium range Weather Forecasts (ECMWF) ERA-40 reanalysis data. ERA-40 reanalysis data covers the period 1957–2002, whilst the Wallingford and Valentia data are shorter (1979–2005; and 1957–2005, with significant early data gaps; respectively), giving ~20 and ~40 yrs of overlap. Over this region, only pressure fields exhibit statistically significant correlations with rainfall  $\delta^{18}\text{O}$ . The spatial pattern persists for both annual-average and monthly averaged data and is strongest with 500 mb height.

The correlations between annual mean 500 mb pressure and Valentia and Wallingford rainfall  $\delta^{18}\text{O}$  are shown in Fig. 5. These demonstrate positive correlations between  $\delta^{18}\text{O}$  and 500 mb height over areas to the south and west of each site. Therefore, over this timescale, rainwater  $\delta^{18}\text{O}$  records moisture source rather than temperature or rainfall amount. This confirms the findings of Fuller et al. (2008) who show that  $\delta^{18}\text{O}_p$  at Wallingford has a negative correlation with monthly precipitation and positive correlation with



**Fig. 5.** Relationship between  $\delta^{18}\text{O}_p$  and atmospheric circulation. Correlation between Jan-Dec averaged  $\delta^{18}\text{O}_p$  from Wallingford (top) and Valentia (base) and Jan-Dec averaged 500 mb pressure height for the periods 1982–2001 AD and 1961–2001 AD respectively. Contours show regions where probability of the correlation being significant is  $>90\%$ . Figures produced using KNMI Climate Explorer.

monthly temperature for the data series as a whole, but over shorter time periods can have correlations of opposite sign with each of these climate parameters. Stalagmite  $\delta^{18}\text{O}_c$  over the modern period, if deposited at or close to equilibrium, should reflect the  $\delta^{18}\text{O}_p$  at the time of recharge, modified by the temperature-dependency of the fractionation of  $\delta^{18}\text{O}$  between water and calcite (0.24‰ per degree) at the time of deposition. Temperatures within the cave have a seasonal variability of 4.7 °C; strong seasonal biases in stalagmite deposition would permit the imprinting of this temperature signature in  $\delta^{18}\text{O}_c$ , superimposed on the signature from variations in mean annual temperature ( $\pm 0.4$  °C within a total range of mean annual temperature of 2.3 °C). The observed range in  $\delta^{18}\text{O}_c$  over the last 100 yrs of  $\sim 0.7\%$  is therefore within that explicable by a combination of moisture source and temperature variations.

The hypothesis that the  $\delta^{18}\text{O}$  signal in the stalagmite could be influenced by the  $\delta^{18}\text{O}$  of precipitation at the time of groundwater recharge, and is therefore potentially related to the source region of the precipitation and thus to atmospheric circulation, encouraged us to further explore this relationship in the stalagmite record. Due to the

relatively high temporal resolution (2–10 yrs) and small dating uncertainties of the proxy record, we can observe significant variations in the  $\delta^{18}\text{O}$  signatures over the instrumental period. However, these occur on the decadal timescale, inhibiting a comparison with the relatively short duration ERA-40 reanalysis data for 500 mb atmospheric pressure. Hence, to reveal if the relationship between  $\delta^{18}\text{O}_w$  and geopotential height patterns holds true for  $\delta^{18}\text{O}_c$ , the proxy record was compared to smoothed (30-yr spline) versions of the HADSLP2 dataset (Allan and Ansell, 2006) and SLP reconstructions of Luterbacher et al. (2002) and Küttel et al. (2010). Correlations were calculated with annually and seasonally averaged geopotential height fields at various time lags (1 season to 5 yrs) to account for water storage in the soil and groundwater, but no statistically significant results were found. To explore if variability in  $\delta^{18}\text{O}_c$  is determined by temperature or precipitation we conducted a similar correlation analysis with gridded CRU TS 3 (Mitchell and Jones, 2005) datasets and temperature (Xoplaki et al., 2005) and precipitation (Paulling et al., 2006) reconstructions. Theoretically, temperature could also influence the  $\delta^{18}\text{O}$  signal through summer evaporation and fractionation of soil water, and precipitation could have an impact through variations in the timing of the hydrologically effective precipitation. Our results, however, do not reveal statistically significant correlations, and a composite analysis showed no significant differences in geopotential height, temperature, or precipitation in years (10% of the total time series) with lowest versus highest  $\delta^{18}\text{O}_c$  values. The processes governing the transfer of  $\delta^{18}\text{O}$  from precipitation to stalagmite formation thus appear too temporally and mechanistically complex to be captured by our one-dimensional statistical analyses.

In the context of the wet temperate climate and vegetation of NW Scotland, stalagmite  $\delta^{13}\text{C}$  is a function of the proportion of biogenic to bedrock  $\delta^{13}\text{C}$  derived from large scale climate changes (Genty et al., 2001; 2003) and non-equilibrium deposition processes (Baker et al., 1997; Scholz et al., 2009). Stalagmite  $\delta^{13}\text{C}$  derives from both the soil carbon pool, predominantly from the respired  $\text{CO}_2$  of soil microbes which forms the soil-water dissolved  $\text{CO}_2$ , as well as limestone derived carbon derived from dissolution. The age of the soil derived carbon can be substantially older than the age of the water, as shown by  $^{14}\text{C}$  analyses of peat,  $\text{CO}_2$  and dissolved organic carbon (Clymo and Bryant, 2008), and the  $^{14}\text{C}$  profiles of modern stalagmites (Genty et al., 1998). The  $\delta^{13}\text{C}$  signal contained in the dissolved  $\text{CO}_2$  is a function of both the composition of original peat and fractionation processes that occur as the soil carbon is microbially processed. At our site, the peat  $\delta^{13}\text{C}$  is constant through time (Charman et al., 2001). Only a small proportion of this carbon is decomposed to give carbon dioxide, and the observed changes in stalagmite  $\delta^{13}\text{C}$  through time, if organically mediated, must therefore be due to fractionation processes during decomposition which are independent of carbon age, such as variations in the rate of lignin degradation, variations in the soil heterotroph population and the effects of temperature on microbial processing of soil organic matter (Benner et al., 1987; Andrews et al., 2000; Biasi et al., 2005). The fractionation process that is likely to be most important is that more microbially available (labile) carbon has been shown to be isotopically heavier than less available (recalcitrant) carbon (Andrews et al., 2000; Biasi et al., 2005). Under colder, less favourable climate conditions, the more labile and isotopically heavy isotope fraction is preferentially processed, whereas in warmer conditions the more recalcitrant but isotopically light fraction can also be accessed. Biasi et al. (2005) reported a 3–4‰ difference in  $\delta^{13}\text{C}$  between the most labile and recalcitrant fractions in different organic soils. This process, along with variations in the proportion of biogenic to bedrock derived carbon, could be used to infer a negative correlation between temperature and stalagmite  $\delta^{13}\text{C}$ , as commonly observed over glacial-inter glacial timescales (Genty et al., 2003; Genty et al., 2006).

In competition with these phenomena are non-equilibrium deposition processes. Their applicability to the study site is illustrated by

previously unpublished  $\delta^{13}\text{C}$  data on drip water (Fig. 6). Data have a distinctive distribution in which there is a relationship between  $\delta^{13}\text{C}$  and drip rate. Faster drips ( $>0.01$  drips per second) have  $\delta^{13}\text{C}$  signatures between  $-16$  and  $-13\%$ , whereas the slower drips have compositions between  $-14.5$  and  $-10.2\%$ . Two drip sites, S12 and S13 (site code from Fuller et al., 2008), characterized by significant variation in drip rate, show an inverse relationship to  $\delta^{13}\text{C}$ . Our observations of a relatively weak build-up of cave air  $\text{CO}_2$  concentration above atmospheric values, and a seasonal variation in cave air temperature, can both be linked to an open connection between the speleothem chamber and an underlying chamber containing a stream. Data presented in Fuller (2007) demonstrates that the drip waters are supersaturated and degassing  $\text{CO}_2$ . Modelled addition of  $\text{CO}_2$  to reverse this process (using MIX4 software, Fairchild et al., 2000) indicates that the waters originally attained saturation with calcite at  $\text{PCO}_2$  values between  $10^{-1.9}$  and  $10^{-2.1}$ . This result is independent of season and implies a fairly well-mixed epikarstic reservoir for carbon as has been observed at other cave sites (Fairchild et al., 2000; Spötl et al., 2005). Drip waters have Mg/Ca ratios close to that of the overlying dolomite bedrock, indicating that prior calcite precipitation (Fairchild et al., 2000) is not a major process, consistent with the limited development of calcite in straw stalactites and slow speleothem growth rates. Hence we need only consider degassing to explain the spreading of  $\delta^{13}\text{C}$  by within-cave processes. Unlike the study of Spötl et al. (2005), sampling logistics required that the water samples for  $\delta^{13}\text{C}$  measurement were collected over relatively short time periods, and so they are not expected to have completely equilibrated with cave air. The spread of data therefore will represent a range of states of degassing.

A degassing model has been constructed as follows. Firstly, the similar bulk chemistry of all the drips, including the  $\text{PCO}_2$  at which they equilibrated with calcite implies a similar primary  $\delta^{13}\text{C}$  value. This is taken to be  $-16\%$ , close to the lowest observed values. Secondly, equilibrium degassing is simulated as a Rayleigh fractionation process (following Bar-Matthews et al., 1996 using fractionation factors of Mook and de Vriess, 2000).  $\text{PCO}_2$  falls from  $10^{-1.9}$  to  $10^{-3.05}$ , corresponding to a loss of about 12% of the total dissolved inorganic carbon (DIC), by removal of isotopically light  $\text{CO}_2$ . This leads to a linear increase in  $\delta^{13}\text{C}$  with decrease in DIC in the water. The rate of degassing is assumed to follow first order kinetics such that:

$$dC/dt = -\lambda(C_0 - C_{\text{eq}})$$

where  $C_0$  is the initial DIC and  $C_{\text{eq}}$  is the DIC at equilibrium with cave air  $\text{PCO}_2$ ,  $\lambda$  is a kinetic constant (characteristic of the geometry of the degassing surface and the rate of cave ventilation) and  $t$  is the time during which water is free to degas before sample collection. Inspection of Fig. 6 shows that degassing is complete by around 1000 s (discharge of 0.001 drips per second). This allows  $\lambda$  to be calculated as  $0.00257 \text{ s}^{-1}$ . Kinetically enhanced degassing corresponds to a simple multiple of the gradient  $d(\delta^{13}\text{C})/dt$ .

The modelled degassing lines follow a sigmoidal form (Fig. 6) because of the logarithmic scale on the y axis. The main change in  $\delta^{13}\text{C}$  occurs over the time period of tens to hundreds of seconds, corresponding to the discharges where the range of observed  $\delta^{13}\text{C}$  values increases. Equilibrium degassing can only account for a small change in  $\delta^{13}\text{C}$  of the order of 1.3% (see modelled line on Fig. 6). This is inconsistent with the present-day composition of speleothems in the cave and specifically the  $-10.5\%$  composition of the top of stalagmite SU96-7 (fractionation between  $\text{HCO}_3^-$ , which makes up most of the DIC, and calcite is much smaller than the other factors considered here). Kinetically enhanced degassing by a factor of 4.3 (kinetic line of Fig. 6) leads to DIC (and hence calcite) with the composition observed at the top of SU96-7. This degree of kinetic enhancement is about twice as great as that observed in the dynamically ventilated Obir cave (Spötl et al., 2005), but in the Obir

case the observed processes were an equal mixture of (fast) simple degassing and (slow) degassing accompanying calcite precipitation and the kinetic effect should relate mainly to the simple degassing. Significant kinetic degassing effects are also observed at Ernesto Cave, Italy (Frisia et al., 2011).

Sampling site S12 shows strong changes in  $\delta^{13}\text{C}$  at higher discharges than most of the data (corresponding to a smaller value of  $\lambda$ ), whereas a higher value of  $\lambda$  should apply for example to drip sites S4 and SU96-7. The implications of these data are that a significant change in discharge and/or degree of ventilation could result in a corresponding change in  $\delta^{13}\text{C}$  with a potential range of several per mil. Higher  $\delta^{13}\text{C}$  would thus correspond to lower discharge (drier conditions) whereas stronger ventilation is likely to be a feature of enhanced winter circulation (e.g. more prolonged winters, Spötl et al., 2005). Over a two year monitoring period, drip-site SU967 displays very limited variation in discharge (Fuller et al., 2008), consistent with the lack of high-frequency variability in  $\delta^{13}\text{C}$  in stalagmite SU96-7. However, it has been demonstrated elsewhere that gradual multi-year trends of variation in drip rate can occur (Spötl et al., 2005; Baldini et al., 2006) and also it was not possible to collect drip data during the wettest periods of the year. Overall, therefore, for constant overlying soil conditions and a relatively small temperature range over the last 1000 yrs,  $\delta^{13}\text{C}$  in SU-96-7 is likely to be a mixed signal of water supply and temperature, with more positive  $\delta^{13}\text{C}$  in colder and drier conditions.

### 3.3. Last millennium SU-96-7 proxies and comparison with other archives

Fig. 7 presents a comparison of the climate proxies obtained from stalagmite SU-96-7; annual lamina thickness, which has been used to reconstruct a winter NAO series ( $\text{NAO}_{\text{ms}}$ ) from the combined annual lamina thickness and Moroccan tree ring reconstruction (Trouet et al., 2009), the record of 'double laminae' which reflects years with a second 'snowmelt-like' recharge (Baker et al., 2002), along with our new  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  records. Also shown are other proxy records which are relevant to the region, two ice core  $\delta^{18}\text{O}$  records from Svalbard (Isaksson et al., 2005) which are interpreted as winter temperature records, Stockholm winter temperatures (Leijonhufvud et al., 2008, 2010), Low Countries winter temperature (Shabalova and van Engelen, 2003) and the Central England Temperature series (Parker et al., 1992). Notable is the good visual correlation between the temperature proxies, and the comparative lack of correlation with the

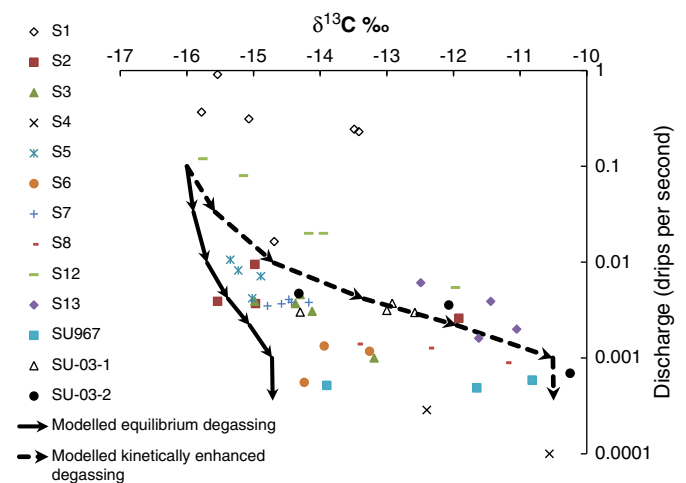


Fig. 6. Relationship between drip rate (drips/s) and  $\delta^{13}\text{C}$  of drip water in UAT. Data collected on a maximum of six occasions over the period Dec 2003–July 2005; for further details of the wider cave monitoring programme see Fuller et al. (2008). Modelled degassing lines are shown as discussed in the text.

stalagmite SU-96-7 growth rate,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  proxies. Table 1 presents the correlation matrix of all bivariate pairs over the periods of mutual overlap using the 30 yr smoothed series, with the degrees of freedom adjusted for 1st order autocorrelation of the series, and the 1-tailed p-values calculated. Despite the visual correlations observed in Fig. 7, especially between the ice core, Stockholm, Low Country and Central England series, these do not result in statistically significant correlations.

Stalagmite growth rate at Uamh an Tartair has previously been interpreted as being primarily determined by the water level in the overlying bog, which limits the amount of soil  $\text{CO}_2$  produced and therefore limestone dissolved. Low growth rates until the 14th century AD are interpreted as high annual rainfall totals and a persistent positive wNAO (Trouet et al., 2009). A marked increase in annual growth rate, and therefore a decrease in precipitation and the strength of the NAO are observed from ~1350 AD, at the end of the Medieval Climate Anomaly (MCA).

Baker et al. (2002) presented data on a small number of years where fine soil-derived colloidal material was observed, often associated with a second, weaker fluorescence lamina (shown here as triangles above the  $\text{NAO}_{\text{ms}}$  series in Fig. 7). These were always found to be following rather than preceding the more prominent annual fluorescent lamina, which forms during an ‘autumn flush’ of organic matter. It is thought that the fine soil-derived colloidal material is related to years that caused the cave to flood. Stalagmite SU-96-7 is situated <10 m from the current river baseflow level in the cave, and the cave chamber floods every winter during snowmelt, but normally to a level below that of stalagmite formation. Evidence to support a snowmelt flooding hypothesis comes from the observation that events over the last ~350 yrs correlate with some of the coldest winters in the Central England Temperature series (Baker et al., 2002). No events have occurred since 1850 AD, indicative of increased warmth in the 20th century. Likewise, few events occurred throughout the period of sustained positive  $\text{NAO}_{\text{ms}}$  between 1080 and

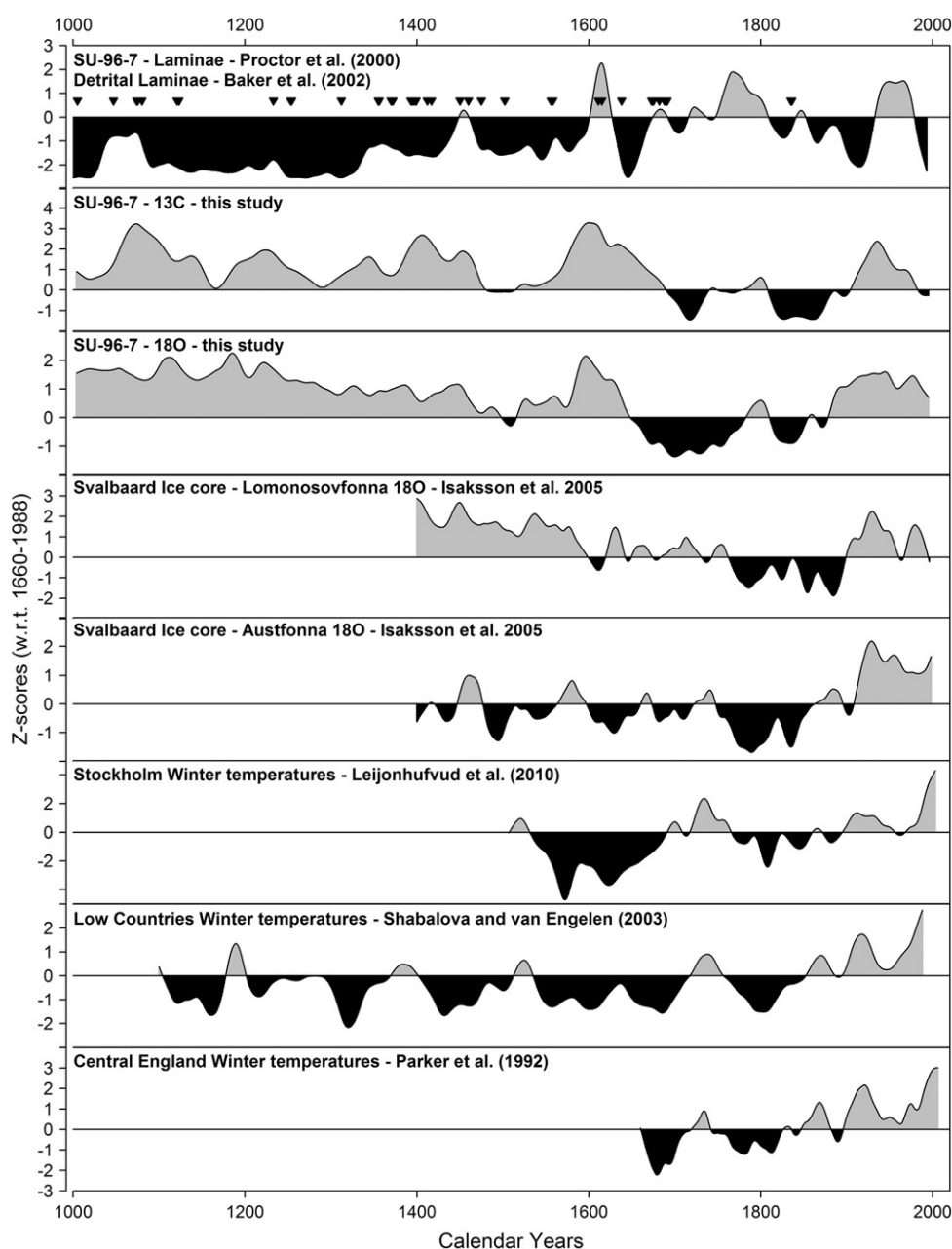


Fig. 7. Comparison of a variety of winter based proxy records. The raw data have been smoothed with a 30 yr cubic smoothing spline and normalised to the common period.

**Table 1**  
Correlations between regional climate series: for locations see Fig. 1. Values shown are the r value, the adjusted degrees of freedom, and the 1 tailed p-value. Significance cannot be calculated when the degrees of freedom <3 and is shown in those cases as 'na'.

	SU-96-7 $\delta^{13}\text{C}$	SU-96-7 $\delta^{18}\text{O}$	$\delta^{18}\text{O}$ Lomonosovfonna	$\delta^{18}\text{O}$ Austfonna	Stockholm Winter T	Low Countries Winter T	Central England Winter T
SU-96-7 Lamina width	−0.12 6.1 p = 0.41	−0.39 6.1 p = 0.22	−0.40 3.6 p = 0.30	−0.03 3.6 p = 0.49	0.03 3.0 p = 0.49	0.03 5.4 p = 0.48	−0.42 2.0 na
SU-96-7 $\delta^{13}\text{C}$		0.65 6.1 p = 0.08	0.44 3.6 p = 0.28	0.28 3.6 p = 0.36	−0.49 3.0 p = 0.34	−0.21 5.4 p = 0.37	0.15 2.1 na
SU-96-7 $\delta^{18}\text{O}$			0.33 3.6 p = 0.34	0.40 3.6 p = 0.30	−0.22 3.0 p = 0.43	0.05 5.4 p = 0.47	0.59 2.1 na
$\delta^{18}\text{O}$ Lomonosovfonna Svalbaard Ice Core			0.33 3.7 p = 0.34	0.02 3.0 p = 0.49	0.03 3.6 p = 0.49	0.03 3.6 p = 0.49	0.41 2.1 na
$\delta^{18}\text{O}$ Austfonna Svalbaard Ice Core				0.37 3.0 p = 0.38	0.51 3.6 p = 0.25	0.69 2.9 p = 0.26	0.71 2.1 na
Stockholm Winter T							0.71 2.1 na
Low Countries Winter T							0.90 2.0 na

1350 AD, consistent with warmer winter conditions and a lack of snowmelt flooding to the level of the stalagmite.

Stalagmite  $\delta^{18}\text{O}$  not only depends on the composition of rainfall  $\delta^{18}\text{O}$ , but also has a temperature-dependent fractionation, with  $\delta^{18}\text{O}_c$  becoming higher with decreasing temperatures. Stalagmite  $\delta^{18}\text{O}_c$  will therefore depend on the synoptic situation at the time of recharge of the karst aquifer, the mixing of waters of different age, and finally the cave temperature at the time of deposition. Our comparisons with modern rainfall  $\delta^{18}\text{O}$  data and reconstructions of atmospheric circulation suggest that it is the synoptic situation at the time of recharge that dominates the precipitation  $\delta^{18}\text{O}$  record, but that this is not simply preserved in the stalagmite record. Fig. 4, presenting the stalagmite  $\delta^{18}\text{O}$  for the last 1000 yrs shows that higher  $\delta^{18}\text{O}_c$  occurred briefly at around 1500 AD and persistently between 1620 and 1880 AD, falling well outside the range of that observed in the last 100 yrs. For the latter period,  $\delta^{18}\text{O}_c$  is between 0.5 and 1.0‰ higher than the highest  $\delta^{18}\text{O}_c$  in the last 100 yrs. A short period of relatively low  $\delta^{18}\text{O}_c$  between 1590 and 1610 AD is intriguing.

Stalagmite  $\delta^{13}\text{C}$  is dependent on the overlying vegetation  $\delta^{13}\text{C}$  and the extent to which this is fractionated during microbial breakdown and respiration in the soil, and fractionation during calcite precipitation due to the rate of degassing and drip rate, as well as the relative proportions of biogenic and bedrock derived carbon.  $\delta^{13}\text{C}$  has less high-frequency variability than  $\delta^{18}\text{O}$ , suggesting that both event and storage flow waters have the same  $\delta^{13}\text{C}$  signature due to a low variability of  $\delta^{13}\text{C}$  in soil respired  $\text{CO}_2$ , whereas  $\delta^{18}\text{O}$  high frequency variability in part reflects variations in the seasonality of recharge. Over the last 1000 yrs, stalagmite  $\delta^{13}\text{C}$  is mostly within the range of variability of the last 100 yrs (Fig. 4), with the periods 1700–1740 AD and 1810–1880 AD exhibiting higher values, and 1590–1610 AD lower values, than the 20th century. We interpret  $\delta^{13}\text{C}$  as a mixed signal of water supply and temperature, however  $\delta^{13}\text{C}$  exhibits no clear correlation with winter or annual temperature reconstructions across central and northern Europe (Fig. 7), tentatively suggesting that a moisture signal might dominate.

#### 4. Conclusions

For stalagmite SU-96-7, calibration of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  has proven problematic. For  $\delta^{18}\text{O}$ , Fuller et al. (2008) demonstrated variations in strength and signal of correlation between regional rainfall  $\delta^{18}\text{O}$  and temperature and precipitation due to variations in synoptic conditions. Here, we observed a relationship between monthly rainfall  $\delta^{18}\text{O}$  and

500 mb height for the last ~40 yrs. However, this was not integrated into the stalagmite  $\delta^{18}\text{O}_c$  record in such a way as to allow correlation with atmospheric pressure reconstructions over longer time periods. Fischer and Treble (2008) and Treble et al. (2005) similarly observed complex relationships between rainfall  $\delta^{18}\text{O}$ , synoptic conditions, and modern stalagmite  $\delta^{18}\text{O}$ . Their site was at an equivalent mid-latitude location (W Australia, ~34° S) and we suggest that such locations are not ideal for the calibration and interpretation of relatively low amplitude (<1 per mil), high frequency (annual to decadal) variations in stalagmite  $\delta^{18}\text{O}$ , at least over periods of relatively stable inter-glacial climate. Despite our inability to calibrate the stalagmite  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  record, both proxy series clearly show a signal (rather than noise), and that  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  correlating with each other ( $r = 0.65$  over the last 1000 yrs) suggests that one process might be the main driver of the isotopic composition of SU-96-7. Non-equilibrium deposition processes would be a likely cause, the very slow mean drip rate feeding SU-96-7 gives ample time for degassing and ventilation-related disequilibria of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  to occur within the cave environment. The proxies can be combined with those of lamina width and lamina doublets, and we note some periods of interesting isotopic composition which fall within the Little Ice Age. The period 1590–1610 AD is unusual, with very light  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  in contrast to the modern period. In contrast, 1680–1880 AD ( $\delta^{18}\text{O}$ ) and 1700–1740 AD and 1810–1880 AD ( $\delta^{13}\text{C}$ ) exhibit heavier isotopes compared to the modern period. A lack of correlation with temperature proxies from the region (Fig. 7) as well as the precipitation proxy contained within the annual growth rate proxy prevents us from interpreting how these periods were different from others during the last millennium.

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## References

- Allan, R.J., Ansell, T.J., 2006. A new globally complete monthly historical mean sea level pressure data set (HadSLP2): 1850–2004. *Journal of Climate* 19, 5816–5842.
- Andrews, J.A., Matamala, R., Westover, K.M., Schlesinger, W.H., 2000. Temperature effect on the diversity of soil heterotrophs and the  $\delta^{13}\text{C}$  of soil-respired  $\text{CO}_2$ . *Soil Biology and Biochemistry* 32, 699–706.
- Baker, A., Ito, E., Smart, P.L., McEwan, R., 1997. Elevated  $^{13}\text{C}$  in speleothem and implications for palaeovegetation studies. *Chemical Geology (Isotope Geoscience)* 136, 263–270.
- Baker, A., Proctor, C.J., Barnes, W.L., 2002. Stalagmite lamina doublets: a 1,000 year record of extreme winters in NW Scotland. *International Journal of Climatology* 22, 1339–1345.
- Baker, A., Fuller, L., Genty, D., Fairchild, I.J., Jex, C., Smith, C.L., 2008. Annually laminated stalagmites: a review. *International Journal of Speleology* 37, 193–206.
- Baldini, J.U.L., McDermott, F., Fairchild, I.J., 2006. Spatial variability in cave drip water hydrochemistry: implications for stalagmite paleoclimate records. *Chemical Geology* 235, 390–404.
- Bar-Matthews, M., Ayalon, A., Matthews, A., Sass, E., Halicz, L., 1996. Carbon and oxygen isotopic study of the active water-carbonate system in a karstic Mediterranean cave: implications for palaeoclimate research in semiarid regions. *Geochimica et Cosmochimica Acta* 60, 337–347.
- Benner, R., Fogel, M.F., Sprague, E.K., Hodson, R.E., 1987. Depletion of  $^{13}\text{C}$  in lignin and its implications for stable carbon isotope studies. *Nature* 329, 708–710.
- Biasi, C., Rusalimova, O., Meyer, H., Kaiser, C., Wanek, W., Barsukov, P., Junger, H., Richter, A., 2005. Temperature-dependent shift from labile to recalcitrant carbon sources of arctic heterotrophs. *Rapid Communications in Mass Spectrometry* 19, 1401–1408.
- Charman, D.J., Caseldine, C.J., Baker, A., Gearey, B., Hatton, J., 2001. Palaeohydrological records from peat profiles and speleothems in Sutherland, NW Scotland. *Quaternary Research* 55, 223–234.
- Clymo, R.S., Bryant, C.L., 2008. Diffusion and mass flow of dissolved carbon dioxide, methane, and dissolved organic carbon in a 7-m deep raised peat bog. *Geochimica et Cosmochimica Acta* 72, 2048–2066.
- Colman, A., 1997. Prediction of summer central England temperature from preceding North Atlantic winter sea surface temperature. *International Journal of Climatology* 17, 1285–1300.
- Fairchild, I.J., Borsato, A., Tooth, A.F., Frisia, S., Hawkesworth, C.J., Huang, Y., McDermott, F., Spiro, B., 2000. Controls on trace element (Sr–Mg) compositions of carbonate cave waters: implications for speleothem climatic records. *Chemical Geology* 166, 255–269.
- Fairchild, I.J., Baker, A., Borsato, A., Frisia, S., Hinton, R.W., McDermott, F., Tooth, A.F., 2001. Annual to sub-annual resolution of multiple trace-element trends in speleothems. *Journal of the Geological Society of London* 158, 831–841.
- Fischer, M.J., Treble, P.C., 2008. Calibrating climate- $\delta^{18}\text{O}$  regression models for the interpretation of high-resolution speleothem  $\delta^{18}\text{O}$  time series. *Journal of Geophysical Research* 113, D17103.
- Frisia, S., Fairchild, I.J., Fohlmeister, J., Miorandi, R., Spötl, C., Borsato, A., 2011. Carbon mass-balance modelling and carbon isotope exchange processes in dynamic caves. *Geochimica et Cosmochimica Acta* 75, 380–400.
- Fuller, L., 2007. High resolution multiproxy geochemical Holocene climate records from 1000-year old Scottish stalagmites. Unpublished PhD, University of Birmingham.
- Fuller, L., Baker, A., Fairchild, I.J., Spötl, C., Marca-Bell, A., Rowe, P., Dennis, P.F., 2008. Isotope hydrology of dripwaters in a Scottish cave and implications for stalagmite palaeoclimate research. *Hydrology and Earth System Sciences* 12, 1065–1074.
- Genty, D., Baker, A., Massault, M., Proctor, C., Gilmour, M., Pons, E., Hamelin, B., 2001. Stalagmite dead carbon proportion variation: paleodissolution process and soil organic matter dynamics recorder—implications for  $^{13}\text{C}$  variations in stalagmites. *Geochimica et Cosmochimica Acta* 65, 3443–3457.
- Genty, D., Blamart, D., Ouhadi, R., Gilmour, M.A., Baker, A., Jouzel, A., Van-Exter, S., 2003. Greenland ice core chronologies constrained by Dansgaard-Oeschger events preserved in a SW-France stalagmite (32–83 ka). *Nature* 421, 833–836.
- Genty, D., Blamart, D., Ghaleb, B., Plagnes, V., Causse, Ch., Bakalowicz, M., Zouari, K., Chkir, N., Hellstrom, J., Wainer, K., Bourges, F., 2006. Timing and dynamics of the last deglaciation from European and North African  $\delta^{13}\text{C}$  stalagmite profiles—comparison with Chinese and South Hemisphere stalagmites. *Quaternary Science Reviews* 25, 2118–2142.
- Genty, D., Vokal, B., Obelic, B., Massault, M., 1998. Bomb  $^{14}\text{C}$  time history recorded in two modern stalagmites—importance for soil organic matter dynamics and bomb  $^{14}\text{C}$  distribution over continents. *Earth and Planetary Science Letters* 160, 795–809.
- Hendy, C., 1971. The isotopic geochemistry of speleothems I. The calculation of the effects of different modes of formation on the isotope composition of speleothems and their applicability as palaeoclimate indicators. *Geochimica et Cosmochimica Acta* 35, 801–824.
- Hurrell, J.W., 1995. Decadal trends in the North Atlantic Oscillation: regional temperatures and precipitation. *Science* 269, 676–679.
- Isaksson, E., Divine, D., Kohler, J., Martma, T., Pohjola, V., Motoyama, H., Watanabe, O., 2005. Climate oscillations as recorded in Svalbard ice core delta O-18 records between AD1200 and 1997. *Geografiska Annaler Series A—Physical Geography* 87, 203–214.
- Küttel, M., Xoplaki, E., Gallego, D., Luterbacher, J., Garcia-Herrera, R., Allan, R., Barriendos, M., Jones, P.D., Wheeler, D., Wanner, H., 2010. The importance of ship log data: reconstructing North Atlantic, European and Mediterranean sea level pressure fields back to 1750. *Climate Dynamics* 34, 1115–1128.
- Leijonhufvud, L., Wilson, R., Moberg, A., 2008. Documentary data provide evidence of Stockholm average winter to spring temperatures in the eighteenth and nineteenth centuries. *Holocene* 18, 333–343.
- Leijonhufvud, L., Wilson, R., Moberg, A., Söderburg, J., Retsö, D., Söderlind, U., 2010. Five centuries of Stockholm winter/spring temperatures reconstructed from documentary evidence and instrumental observations. *Climatic Change* 101, 109–141.
- Luterbacher, J., Xoplaki, E., Rickli, R., Gyalistras, D., Schmutz, C., Wanner, H., 2002. Reconstruction of Sea Level Pressure fields over the eastern North Atlantic and Europe back to 1500. *Climate Dynamics* 18, 545–561.
- Mitchell, Jones, 2005. An improved method of constructing a database of monthly climate observations and associated high-resolution grids. *International Journal of Climatology* 25, 693–712.
- Mook, W. and de Vriess, J., 2000. *Environmental Isotopes in the Hydrological Cycle. Principles and Applications*. International Atomic Energy Agency. Volume 1: Introduction - Theory, Methods, Review.
- Parker, D.E., Legg, T.P., Folland, C.K., 1992. A new daily Central England Temperature Series, 1772–1991. *Int. J. Clim.* 12, 317–342.
- Pauling, A., Luterbacher, J., Casty, C., Wanner, H., 2006. Five hundred years of gridded high-resolution precipitation reconstructions over Europe and the connection to large-scale circulation. *Climate Dynamics* 26, 387–405.
- Proctor, C.J., Baker, A., Barnes, W.L., Gilmour, M.A., 2000. A thousand year speleothem proxy record of North Atlantic climate from Scotland. *Climate Dynamics* 16, 815–820.
- Proctor, C.J., Baker, A., Barnes, W.L., 2002. A three thousand year record of north Atlantic climate. *Climate Dynamics* 19, 449–454.
- Scholz, D., Mühlinghaus, C., Mangini, A., 2009. Modelling  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in the solution layer on stalagmite surfaces. *Geochimica et Cosmochimica Acta* 73, 2592–2602.
- Shabalova, M.V., van Engelen, A.F.V., 2003. Evaluation of a reconstruction of winter and summer temperatures in the Low Countries, AD 764–1998. *Climatic Change* 58, 219–242.
- Smith, C.L., Baker, A., Fairchild, I.J., Frisia, S., Borsato, A., 2006. Reconstructing hemispheric scale climates from multiple stalagmite records. *International Journal of Climatology* 26, 1417–1424.
- Spötl, C., Matthey, D., 2006. Stable isotope microsampling of speleothems for palaeoenvironmental studies: a comparison of microdrill, micromill and laser ablation techniques. *Chemical Geology* 235, 48–58.
- Spötl, C., Venemann, T.W., 2003. Continuous-flow isotope ratio mass spectrometric analysis of carbonate minerals. *Rapid Communications in Mass Spectrometry* 17, 1004–1006.
- Spötl, C., Fairchild, I.J., Tooth, A.F., 2005. Cave air control on dripwater geochemistry, Obir Caves (Austria): implications for speleothem deposition in dynamically ventilated caves. *Geochimica et Cosmochimica Acta* 69, 2451–2468.
- Tan, M., Baker, A., Genty, D., Smith, C., Esper, J., Cai, B., 2006. Applications of stalagmite laminae to paleoclimate reconstructions: comparison with dendrochronology/climatology. *Quaternary Science Reviews* 25, 2103–2117.
- Treble, P.C., Budd, W.F., Hope, P., Rustomji, P.K., 2005. Synoptic scale climate patterns associated with rainfall  $\delta^{18}\text{O}$  in southern Australia. *Journal of Hydrology* 302, 270–282.
- Trenberth, K., 1984. Some effects of finite sample size and persistence on meteorological statistics. Part I: autocorrelations. *Monthly Weather Review* 112, 2359–2368.
- Trouet, V., Esper, J., Graham, N.E., Baker, A., Scourse, J.D., Frank, D.C., 2009. Persistent positive North Atlantic Oscillation mode dominated the Medieval Climate Anomaly. *Science* 324, 78–80.
- Xoplaki, E., Luterbacher, J., Paeth, H., Dietrich, D., Steiner, N., Grosjean, M., Wanner, H., 2005. European spring and autumn temperature variability and change of extremes over the last half millennium. *Geophysical Research Letters* 32, L15713.