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Monitoring climatological, hydrological and geochemical parameters in the Père Noël cave (Belgium): implication for the interpretation of speleothem isotopic and geochemical time-series

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Abstract:

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Père Noël cave climatology (air and water temperature, P_{CO_2}), hydrology (drip rate, conductivity) and geochemistry of water and calcite deposits ($\delta^{18}O$, $\delta^{13}C$, Mg/Ca and Sr/Ca) were studied to better interpret stable isotopic and trace element variations of speleothems. Results of an automated monitoring station and of manual sampling between 1991 and 1998 have demonstrated the highly seasonal signal of drip rate, its control by water excess and rainfall, and, at a shorter scale to air pressure changes.

The modern calcite deposit study suggests a relationship between cave calcite isotopic composition ($\delta^{18}O$ and $\delta^{13}C$) and drip rate likely due to variations in degree of isotopic equilibrium during calcite precipitation. $\delta^{18}O$ and $\delta^{13}C$ of the calcite are therefore, through drip rate, linked to water recharge. Mg/Ca and Sr/Ca ratios of Père Noël cave calcite, depend closely on the residence time of the water, and therefore are also linked to drip rate and therefore to water recharge. This crossed link of $\delta^{18}O$ and $\delta^{13}C$ as of Mg/Ca and Sr/Ca to water recharge may explain the very similar variations of these four parameters along the longitudinal axis of a Holocene stalagmite, but it may also be the consequence of kinetic effects during calcite precipitation as suggested by similar variations of the four parameters along a single layer of the Holocene stalagmite.

Keywords: cave hydrology, isotopes (oxygen and carbon), palaeoclimatology, drip rate, monitoring, modern calcite, seepage water, Mg, Sr

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INTRODUCTION

The Père Noël cave was discovered in 1964 during Christmas time (hence the cave's name) by a group of cavers among which Guy Deflandre. It is part of the karstic system which encloses the well-known Belgian caves of Han-sur-Lesse (Quinif & Bastin, 1986; Deflandre et al., 1987).

A first automatic monitoring device was installed in the Père Noël cave in 1991, seepage water was then monitored until 1999. First results of seepage water drip rate, flow rate and conductivity were published in Genty & Deflandre (1998). Here, we first recall the main results obtained thanks to this monitoring, then we present additional information on the oxygen

isotopic composition of rain and seepage water and modern calcite precipitated in the cave, sampled between May 1995 and August 1998 at different sites in the Père Noël cave (Fig. 1 and 2). During three-monthly in-situ sessions, cave-air temperature and pCO_2 and seepage-water temperature and drip rate were measured. Samples of cave water and cave calcite including some months-old calcite were taken and analysed at the laboratory for respectively their $\delta^{18}O$, Mg/Ca and Sr/Ca, and $\delta^{18}O$, $\delta^{13}C$, Mg/Ca and Sr/Ca. The monitoring of the seepage water and modern calcite in the Père Noël cave gives a clear view of the hydrological and geochemical seasonal variations of the cave environment, it also brings precious information on the different controls (i.e. climatic, environmental) of the isotopic ($\delta^{18}O$ and $\delta^{13}C$) and chemical (Mg, Sr) composition of Père Noël speleothems. Besides the study of the modern environment, we present here isotopic and geochemical results obtained on a Holocene stalagmite that was sampled in May 1995.

CLIMATE AND VEGETATION

The Père Noël cave (50.0°N, 5.2°E, 230 m asl) (Fig. 1 and 2) is situated about 200 km inland in a temperate maritime climate. The mean annual precipitation of

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the nearby meteorological station (Lessive, 3 km NE of the cave), measured over the period 1980-1998, is 826 mm and the mean annual air temperature is 9.2°C (Royal Meteorological Institute, 1998). While the temperature displays a well marked seasonality, with cool summer and mild winter, the rainfall is spread all over the year (Fig 3). A C3 type vegetation consisting of mixed-leaf forest with oaks, beech and hazel trees covers the bedrock above the cave. The soil is ~40 cm thick and consists of heavily rooted, unconsolidated brown earth comprising limestone fragments and residual clays. The area above the cave is property

of the touristic caves and is preserved from direct human influence.

GEOLOGY AND SAMPLING LOCATION

The Père Noël cave opens in Givetian limestone (Delvaux de Fenffe, 1985) with partly dolomitised beds. Overlying host rock reaches a thickness of ca. 70 m (Fig 2 and 4) (Vandersleyen, 1967; Verheyden et al., 2000). The cave is a result of the meander cutting of the Lesse river through the Massif de Boine (Quinif & Bastin, 1986; Quinif, 1977) as shown by the presence of numerous pebbles of 10 to 20 cm diameter in the Salle du bivouac. The original river does not flow through the cave anymore since more than ~150,000 years B.P (Quinif & Bastin, 1986). The water entering the cave today consists only of local rain, seeping directly through the overlying limestone and a small water flow from unknown origin and visible at only two places in the cave. The narrow entrance, which is situated near the top of the hill, was closed with a door after its discovery to prevent vandalism. After a steep descend of ~25 meters, a small passage leads to a first small room. A second steep descend of ~20 meters leads to a second room, the *Salle du bivouac*. It is the biggest room of the cave which is ~50 meters large, ~200 meters long and ~30 meters high. Our study was performed in this place where six locations were regularly sampled: three at the entrance of the room (3,4 and 6 in Fig. 2) and three at the back of the room (1,2 and 5 in Fig. 2) and in the narrow sideways passage, the *Chambre à coucher*, in which the automatic monitoring was performed (Location M in Fig. 2). Most sites are actively dripping which is convenient for the water sampling, however other locations were sampled occasionally when water was

Fig. 1. Location of the Père Noël cave (50.0°N, 5.2°E, 230 m asl).

Fig.2. Map of the Père Noël cave with indication of the sampling locations. Slpl labels refer to the locations of the glass slabs for the sampling of nowadays precipitated calcite. The Holocene stalagmite was sampled at location 1. Based on map of P. Vandersleyen (1967).

Fig. 3. Mean temperature and mean rainfall for the period 1990-1996 at the Lessives station, located 3 km NE of the Père Noël cave (Royal Meteorological Institute).

Fig. 4. Geological cross section of the Père Noël cave area.

1: Frasnian black shales; 2: Givetian limestone – Formation de Fromelennes; 3: Givetian limestone – Formations de Trois Fontaines, Terre d'Hairs and Mont d'Hairs; 4 and 5: Eifelian limestone and calcareous shales; 6: Eifelian shales.

available. Most of speleothems of the Père Noël Cave are candle shaped calcite stalagmites (Fig. 5), others consist of huge columns, sometimes broken, rounded stalagmites and draperies (Fig. 6, 7).

SEASONAL CHANGES IN THE CAVE CLIMATOLOGY

The cave air temperature in the *Salle du bivouac* and *La chambre à coucher* sideway (measured with a thermocouple T type Testo thermometer with an accuracy of $\pm 0.3^\circ\text{C}$), varies between 8.5° and 9.3°C (Table 1). Despite the significant differences between measurements, there is no well marked seasonal variation in the cave air temperature (Fig. 8). The mean cave temperature (9.0°C) corresponds within uncertainty ($2\sigma \sim 0.2^\circ\text{C}$) to the mean annual temperature of the air (9.2°C) at the nearby Lessives

station over the sampling period 1988 – 1998 (Royal Meteorological Institute, 1998). Seepage water temperature is generally slightly warmer than the cave air temperature (Fig. 5). Highest temperatures (10.2°C) were measured in July 1996 while lowest temperatures occurred in August 1998. The water temperature is not location dependent.

The P_{CO_2} of the cave air measured using a Dräger pump system ($\sim \pm 30\text{ppmv}$) shows strong seasonal variations from 350 ppmv at the end of winter to 650 ppm with occasional maxima up to 1000 ppm at the end of summer (Table 1). This variation can be related to the seasonal production of CO_2 by the vegetation and bacterial activity in the soil, entering the cave through fractures and by degassing (Ek, 1979; Gewalt & Ek, 1983). Because CO_2 content of the cave air is not very high compared to other Belgian caves where concentrations up to $\sim 8000\text{ ppm}$ (Gewelt & Ek, 1986) and exceptionally up to 15000

Table 1. Cave air temperature (T_{ca}), seepage water temperature (T_{sw}) and driprate of the seepage water and P_{CO_2} of the cave air measured every two to three months between October 1995 and August 1998 in the Père Noël Cave (Han-sur-Lesse, Belgium).

	$T_{\text{ca}}, ^\circ\text{C} \pm 0.3$	$T_{\text{sw}}, ^\circ\text{C} \pm 0.3$	Driprate, drips/min	$\text{PCO}_2, \text{ppm} \pm 30$
Mean	9.0	9.2	10.6	514
Range	0.8	1.4	99.9	650
Minimum	8.5	8.8	0.1	350
Maximum	9.3	10.2	100.0	1000
Count	56	25	69	14

Fig. 5. Candle shaped stalagmites are very common in the Père Noël cave.

Fig. 6. Big stalagmites, sometimes broken, are present mainly in the Salle du Bivouac.

Fig. 7. Different types of speleothems are very close: older ones and present-day still active white deposits, candle shaped, rounded or huge stalagmites, sometimes broken give the impression of a chaotic ensemble.

ppm (Verheyden, 2001) are often observed, it is likely that exchanges between cave air and external air are relatively important.

The relative humidity, measured with a classical hair hygrometer, varied between 95% and 98% $\pm$ 5%, no seasonality was observed but may be due to the low accuracy of the measurement above 95% humidity.

SEASONAL CHANGES IN THE CAVE HYDROLOGY

Monitoring of cave hydrology

The drip monitoring of the Père Noël Cave was among the first in the world; it was installed by G. Deflandre, B. Bastin, S. Colet and J.M. Robert (RSH: Recherche Scientifique Han-sur-Lesse, Han-sur-Lesse, Belgium) during the summer of 1991 in the “Chambre à coucher” room, 70 m under the surface, just under a soda-straw stalactite. The drip rate was measured by electroluminescent diodes located a few centimeters below the tip of the stalactite. The water was then collected in a closed 100 ml glass where the conductivity and pH probes are situated. Besides drip counting, the water volume was also measured thanks to a tipping-bucket system (2x50 ml). Two other sensors measured the air temperature and pressure. All measurements: air temperature, air pressure, pH, conductivity, drops number and discharge volume were stored in RAM memory every 10 minutes and are transferred onto a PC computer with a specialised hardware board every 60 days at maximum. This automatic station was working from 1991 to 1999.

Main results of this monitoring are the following (Genty & Deflandre, 1998):

- demonstration of a well marked seasonal signal in the drip rate (Fig. 9) mainly controlled by the water excess changes during five studied hydrological cycles; the stalactite flow rate can be split into three stages: 1) a drip rate increase during late autumn; 2) a winter-spring wet period; 3) a recession period during summer and autumn; the occurrence of a seasonal variation in the stalactite drip rate might be the main cause of annual laminations found in speleothems;

- characterization of the autumn drip rate increase by a drastical increase of the water conductivity suggesting that the “autumn flush” brought a water rich in minerals and/or organic matter (OM) into the karst. These OM components such as fulvic and humic acids might be due to the intense biological activity of the spring and summer;

- at the day scale, anticorrelation between the air pressure changes and the drip rate wiggles was observed during some periods of the year; this was explained by a rock formation constraint, i.e. the atmospheric pressure reduces or widens the conduits diameter and fissures thickness.

- Other interesting features have been observed in this monitoring, for example, an “oscillatory regime” occurred, superimposed to the day-scale wiggles, during the wet periods. These instabilities were linked to a chaotic behaviour that occurs when the flow rate is above a threshold (Fig. 10). Thanks to both

Fig. 8 Temperature of Père Noël cave air and seepage water between May 1995 and August 1998. The vertical line at the left side gives the uncertainty on the measurement.

Fig. 9. Flow rate time series of the Père-Noël automatic station between 1991 and 1996. Note the well marked seasonality of the flow rate (estimated with the drip rate counting and the drop volume calibration) (from Genty & Deflandre, 1998).

drip counting and drip flow measurements, the drop volume could be measured and turned to be constant (0.14 ml) for more than 94% of the studied hydrological cycles. An interesting feature is that, for extreme drip rates, the drop volume varies significantly: at low drip rate it increases because of surface tension forces, but at high flow rate, the drop volume decreases possibly because satellite drops are then formed (Genty & Deflandre, 1998).

Manual monitoring : Seasonal changes in the seepage water isotopic and trace element composition.

Thanks to the continuous data of the automatic station, Genty and Deflandre (1998) showed that the interannual stalactite drip rate variation is controlled by the yearly water excess (rainfall minus evapo-transpiration). Is all the dripping water which flows through the stalactite

during one hydrological year derived from the rainfall of the same year ? Since the seepage-water drip-rate shows a strong seasonal signal but that water dripping never stops, the seepage water should be composed of reservoir water. Different processes can be suggested: 1. Most of the dripping water comes from the same year's rainfall, 2. The dripping water is a reservoir of water mixed and stored for more than one year in pores and the micro-fissure network, which is pushed by the yearly rainfall increase like a piston flow system and 3. The water is a mix of recent rainfall water and older reservoir water (Genty & Deflandre, 1998).

Isotopic composition

The $\delta^{18}\text{O}$ of the seepage water ($\delta^{18}\text{O}_{\text{sw}}$) varied from -8.0‰ to -6.8‰ ($\pm 0.2\text{‰}$) vsmow and lies within the $\sim 4\text{‰}$ variability of that of the rainwater samples from Han-sur Lesse ($\delta^{18}\text{O}_{\text{rw}}$) (Table 2, Fig 11 and 12).

Fig. 10. Time-delay graphs of the stalactite dripping flow rate for the 1992-1993 hydrological cycle suggesting a chaotic behaviour of the dripping. Note the well marked L-shaped structures which occur when the drip rate increases (from Genty & Deflandre, 1998).

Table 2. Mean $\delta^{18}\text{O}$, 1000Mg/Ca and 1000Sr/Ca of the Père Noël cave seepage water at all locations.

	$\delta^{18}\text{O}_{\text{sw}} \pm 0.2$	1000Mg/Ca $\pm 15\%$ on the value	1000Sr/Ca $\pm 15\%$ on the value
Mean	-7,51	324	2,32
Standard Error	0,03	45	0,15
Range	1,2	1056	3,48
Minimum	-8,0	62	0,98
Maximum	-6,8	1118	4,46
Count	73	40	40

The $\delta^{18}\text{O}_{\text{sw}}$ mean (on all stations during the 1995-1998 sampling period) is $-7.5 \pm 0.2\text{‰}$ VSMOW which is similar, within uncertainty, to the weighted regional annual mean rainwater $\delta^{18}\text{O}_{\text{rw}}$ of -7.3‰ (Verheyden, 2001). In contrast with $\delta^{18}\text{O}_{\text{rw}}$, the $\delta^{18}\text{O}_{\text{sw}}$ exhibits only a weak seasonal variation with maximum amplitude of 1.2‰ . For locations 1, 4 and M during the year 1996, and for slp11 during 1997, lowest values occurred in summer and the highest ones in winter which is in antiphase with the general pattern of rainfall $\delta^{18}\text{O}_{\text{rw}}$ (Rozanski, et al., 1993). Low $\delta^{18}\text{O}_{\text{rw}}$ observed for Han-sur-Lesse in August 1996 and during September 1997 (Fig. 11), may explain low values for the $\delta^{18}\text{O}_{\text{sw}}$ for August and September 1996 in locations 1, 4 and M, and for autumn 1997 in locations 1 and slp11. However, high values in winter for 1, M and 4 in 1996 and for 4 in 1997 are difficult to explain and suggest that the seepage water might have a time lag of ~ 6 months on the rainfall. Although the smaller range of $\delta^{18}\text{O}_{\text{sw}}$ compared to $\delta^{18}\text{O}_{\text{rw}}$ indicates that important mixing occurs in the vadose water, it seems not important enough to mix water of an entire year completely. The strong increase of drip rates in autumn is therefore at several places most likely

only due to the “piston effect” (i.e. new recharge water pushing down water stored into micro-fissures) with, at least for locations 1, M and 4 during the year 1996, preferentially summer waters reaching the cave in winter and vice-versa. The seasonal and shorter-term variability in the $\delta^{18}\text{O}_{\text{sw}}$ excludes the existence of a simple mixed vadose-water reservoir. The hydrological and isotopic data suggest that the water reservoir above the cave seems slightly stratified. However, since low $\delta^{18}\text{O}_{\text{sw}}$ values seem to occur in response to low $\delta^{18}\text{O}_{\text{rw}}$ values, and because uranine dye tests have shown the first arrival of the dye after one week at some places in the Salle du Bivouac (Deflandre, oral communication), other processes, including the occurrence of rapid transfers between surface and the cave, must be considered. The local differences in seepage water hydrology does not seem to affect the longer-term mean $\delta^{18}\text{O}$ of the seepage water, since three-year mean $\delta^{18}\text{O}_{\text{sw}}$ at each individual dripping site are similar within uncertainties, with values from -7.4 ± 0.2 to $-7.8 \pm 0.2\text{‰}$ VSMOW depending on the dripping location (Table 3).

Trace element concentrations

1000Mg/Ca and 1000Sr/Ca, i.e. the ratios of Mg or Sr to Ca concentrations (in ppm), display mean values of 324 and 2.32 respectively with an important spatial as well as temporal variability indicated by the range of measured 1000Mg/Ca and 1000Sr/Ca values of 1056 and 3.48 respectively (Table 2, Fig. 13). 1000Mg/Ca and 1000Sr/Ca ratios of the host limestone display a mean of 12.1 and 0.99, respectively for calcite minerals and of 313.8 and 0.71, respectively for dolomite minerals (see details in Verheyden et al., 2000).

The 1000Mg/Ca and 1000Sr/Ca ratios display a strong location dependence as shown in Figure 13 and 14. At single dripping locations, there are well marked variations in the concentrations, displaying significant sympathetic correlation ($R^2=0.9$) between 1000Mg/Ca and 1000Sr/Ca. With exception of location 4, the ratios seem to vary seasonally although highest values occur at summer, autumn or winter; depending on the location (Fig. 14). Since the host rock consists of partially dolomitised limestone, incongruent dissolution of dolomite in the presence of calcite may increase the Mg/Ca ratio in the seepage waters. When calcium saturation with respect to calcite is attained, continued dissolution of dolomite, generally richer in Mg than calcite, increases the Mg/Ca ratio, since Ca is kept constant through calcite precipitation. Dolomite generally contains less strontium than calcite and continuous dissolution of dolomite and precipitation of calcite will create an inverse relationship between Mg/Ca and Sr/Ca in seepage waters and consequently in precipitated cave calcite (Roberts et al., 1998), which is not the case here. According to Fairchild et al (2000), a covarying Mg/Ca and Sr/Ca or the sympathetic behavior of Mg and Sr is due to prior low Mg calcite precipitation enriching the precipitating water. The longer the

Fig. 11. Oxygen isotopic compositions of the Père Noël seepage water ($\delta^{18}\text{O}_{\text{sw}}$) and of local rainwater ($\delta^{18}\text{O}_{\text{rw}}$). Note that the $\delta^{18}\text{O}$ of the seepage water (water collected on day of sampling and water collected in bottles left between two samplings) displays a more constant trend throughout the sampling period (1995-1998) than Han-sur-Lesse rainwater $\delta^{18}\text{O}$ (weighted means of water collected between the sampling sessions). For comparison, the annual weighted mean $\delta^{18}\text{O}$ of rainwater from nearby places (source: GNIP database, <http://isohis.iaea.org>) is also given with Y-error bars displaying the range of the monthly weighted mean $\delta^{18}\text{O}$ of Liège (B) (50.7; 5.47; 200; '66-'70); Beek (NI) (50.9; 5.78; 111; '81-'99); Trier (DE) (49.75; 6.07; 273; '78-'00). Analyses were performed on a Delta E mass spectrometer at the University of Brussels using the CO_2 equilibration technique (Epstein and Mayeda, 1953). Results are given in ‰ VSMOW with an analytical uncertainty of $\sigma 0.2\text{‰}$ (2s)

Fig. 12 $\delta^{18}\text{O}$ of the seepage water at different locations and different times in the Père Noël cave.

water stays in the vadose zone, the more it is controlled by precipitation-redissolution processes which enriches the remaining water in both, Mg and Sr. Therefore, the Mg/Ca and Sr/Ca ratios of the Père Noël seepage waters seem to depend on

the residence time, which depends on the water recharge and should thus be linked to the drip rate. This is confirmed for the 1000Sr/Ca ratios where a strong relationship exists with drip rate (Fig. 15), but is less clear for the 1000Mg/Ca ratios.

Fig. 13. 1000Mg/Ca and 1000Sr/Ca ratios of the Père Noël seepage water. Note the quite good correlations between Mg/Ca and Sr/Ca for each individual station. Mg, Ca and Sr concentrations of the seepage water, acidified with a few drops of suprapur HNO_3 during sampling to avoid carbonate precipitation, were measured on a Fisons-VG PlasmaQuadII+ (ICP) mass spectrometer at the Belgian Royal Museum for Central Africa with an analytical uncertainty (1σ) of $\pm 10\%$.

Table 3 - Average seepage water $\delta^{18}\text{O}_{\text{sw}}$ and mean drip rate of the seven sampling sites of the Père Noël cave (Han-sur-Lesse – Belgium). The sampling period is between October 1995 to August 1998.

	$\delta^{18}\text{O}_{\text{sw}}$ in ‰ vsMOW $\pm 2\sigma$	n	mean driprate (drips/min)	n
1	-7.4 ± 0.2	12	0.067	12
2	-7.5 ± 0.2	12	0.067	12
3	-7.5 ± 0.2	11	0.075	11
4	-7.5 ± 0.3	12	4.48	12
5	ND		0.10	ND
6	-7.6 ± 0.2	5	19.76	5
m	-7.8 ± 0.2	13	40.46	13

Fig. 14. 1000Mg/Ca and 1000Sr/Ca ratios of the Père Noël seepage waters at individual locations.

Fig. 15. A clear relation is observed between the drip rate and the 1000Sr/Ca ratio of the seepage water. This relation is much less clear for the 1000Mg/Ca values.

MODERN CALCITE DEPOSITS

Present day calcite was collected on glass slabs at nine dripping places and removed after between two months and 1 year, as soon as enough calcite had precipitated to permit stable isotope analysis. At the same time, recent calcite was scratched at the top of active stalagmites and collected from tips of soda straws.

$\delta^{18}\text{O}_{\text{pc}}$ and $\delta^{13}\text{C}_{\text{pc}}$ vary between -6.0 and -3.8 ‰ VPDB and between -9.0 ‰ and -2.6 ‰ VPDB respectively. (Table 4, Fig 16). From the glass slabs experiment, we noted that where water dripped all the year, the seepage water deposited calcite the whole year through. There may exist a seasonal bias in isotopic composition of the calcite due

to seasonal growth rate variation (Verheyden, 2001). The important range in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of the present day calcite, deposited in similar climatic and hydrologic conditions suggests that non-equilibrium processes likely occur during calcite precipitation.

Deposits out of isotopic equilibrium

Present day calcite that precipitated on glass slides, displays a significantly wider $\delta^{18}\text{O}_{\text{pc}}$ range (2.3‰) and higher $\delta^{18}\text{O}$ values than expected from the $\delta^{18}\text{O}_{\text{sw}}$ (range: 1.2‰) and from the cave temperature variations (8.5°C to 9.2°C) (Fig. 17). The oxygen isotopic composition of calcite depends on the O isotopic composition of the precipitating water and on the fractionation of oxygen between water and calcite which is temperature dependent (e.g. Kim & O'Neil, 1997). If calcite is deposited in isotopic equilibrium, oxygen isotopes of water and calcite can be used to calculate calcite precipitation temperature. Since the oxygen isotopic composition of Pèrè Noël seepage water varies between -8.0‰ and -6.8‰ VSMOW and since that of present-day calcite displays values from -6.0 to -3.7‰ VPDB, calculated temperatures vary from -4.8 to 13.6°C (Table 5). Temperature calculations with the highest observed values of $\delta^{18}\text{O}_{\text{pc}}$, lead to invalid temperature values indistinctly the used temperature calculation formula, i.e. the Kim and O'Neil (1997) or the Craig (1965) formula. The calculated temperature closest to the nowadays Pèrè Noël cave temperature is obtained with the lowest observed $\delta^{18}\text{O}_{\text{sw}}$ values and $\delta^{18}\text{O}_{\text{pc}}$ values and using the Craig (1965) formula, referred to as giving the most accurate results in the cave environment by McDermott et al. (2005). Therefore, present-day calcite with a $\delta^{18}\text{O}$ value of -6‰ is probably deposited close to isotopic equilibrium. Note that present-day calcite with low $\delta^{18}\text{O}$ values also display low $\delta^{13}\text{C}$ values. Similarly to the $\delta^{18}\text{O}_{\text{pc}}$, $\delta^{13}\text{C}_{\text{pc}}$ values of the calcite are higher and display more important variations (up to 6.3‰) than expected from the presence of a dense C3 vegetation cover (between -13‰ and -9‰) (Hendy, 1971). The enrichment in both the $\delta^{18}\text{O}_{\text{pc}}$ and the $\delta^{13}\text{C}_{\text{pc}}$ is a first sign for a non-equilibrium precipitation. The second sign of a kinetic fractionation, is the positive and significant correlation between $\delta^{18}\text{O}_{\text{pc}}$ and $\delta^{13}\text{C}_{\text{pc}}$ ($R^2 = 0.94$ on the 99% confidence level) (Fig. 16).

$\delta^{18}\text{O}_{\text{pc}}$ and $\delta^{13}\text{C}_{\text{pc}}$ values of calcite deposited at the same place may vary along a $\delta^{18}\text{O}_{\text{pc}} - \delta^{13}\text{C}_{\text{pc}}$ correlation line, which, we suggest, is the consequence of a variation in the degree of equilibrium during calcite precipitation: higher isotopic values are from deposits far from the equilibrium while the lowest values are close to equilibrium (Fig. 12). This correlation suggests that the calcite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ are controlled by related processes: evaporation of the water and fast CO_2 degassing (Fornaca-Rinaldi et al., 1968; Gonzales & Lohmann, 1988). Fast CO_2 degassing will mainly affect the $\delta^{13}\text{C}$ (Inoue & Sugimura, 1985; Hendy, 1971) due to preferential removal of ^{12}C , while evaporation will mainly affect $\delta^{18}\text{O}$ by preferential removal of ^{16}O (Craig et al., 1963; Dansgaard et al., 1964) but also $\delta^{13}\text{C}$ since degassing will increase synchronously to evaporation. Calcite precipitated from fast dripping

Table 4. Oxygen and carbon isotopic composition of present-day calcite from the Pèrè Noël cave (Han-sur-Lesse – Belgium) deposited on glass slabs.

	$\delta^{18}\text{O}_{\text{pc}}$ ‰ VPDB ± 0.1	$\delta^{13}\text{C}_{\text{pc}}$ ‰ VPDB ± 0.06	drip rate (drips/min)
Mean	-4.9	-5.9	6.6
Range	2.3	7.1	35.1
Minimum	-6.0	-9.5	0.2
Maximum	-3.7	-2.5	35.3
n	24	24	34

Fig. 16. Oxygen and carbon isotopic composition of present day calcite deposited on glass slabs in the Pèrè Noël cave (Han-sur-Lesse, Belgium). Note the temporal as well as spatial variations (see figure 2 for the locations of the different stations). The oxygen and carbon isotopic composition are positively correlated with an R^2 of 0.94 at the 99% confidence level. Fast dripping water (more than 1 drip/minute, numbers between brackets) precipitates lighter calcite. Measurements of calcite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ were done the same way as for water samples after cryogenic purification of CO_2 (McCrea, 1950). The values are given in ‰ VPDB and analytical uncertainties are $\leq 0.1\text{‰}$ (2σ) for $\delta^{18}\text{O}$ and $\leq 0.06\text{‰}$ (2σ) for $\delta^{13}\text{C}$.

Table 5. Temperature calculations using the Craig (1965) and the Kim and O'Neil (1997) formulas

$\delta^{18}\text{O}_{\text{sw}}$ (VSMOW $\pm 0.2\text{‰}$)	$\delta^{18}\text{O}_{\text{pc}}$ (VPDB $\pm 0.1\text{‰}$)	Calculated T (°C) Craig (1965)	Calculated T (°C) Kim & O'Neil
-8.0 ‰ (min.)	-6.0 ‰ (min.)	9.0°C	4.8°C
	-3.7 ‰ (max.)	1.2°C	-4.8°C
-6.8 ‰ (max.)	-6.0 ‰ (min.)	13.6°C	10.0°C
	-3.7 ‰ (max.)	5.1°C	0.1°C

waters display a more negative isotope composition while calcite precipitated from slow dripping water exhibits more positive isotope compositions (Fig. 16). A higher drip rate will replace more rapidly the precipitating fluid and therefore limits the effect of degassing and of possible evaporation processes on the calcite isotopic composition. The low P_{CO_2} of the Pèrè Noël cave air (360-1000 ppm) likely favours fast CO_2 degassing. However, important evaporation seems unlikely in an overall humidity of 95 to 98%, therefore it remains unclear if the high and variable $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of nowadays calcite are due to evaporation and fast degassing processes or to other kinetic effects linked to precipitation dynamics

$\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of other recent calcite from the

Fig. 17. Oxygen and carbon isotopic composition of all the Père Noël cave calcite studied : nowadays calcite deposited on glass slabs, subsamples along the vertical axis of the Holocene stalagmite PN-95-5 and recent tips of soda straws and of tops of stalagmites. Note that all of these deposits display a positive covariation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ suggesting changes in the degree of isotopic equilibrium.

Père Noël cave, i.e. presumed recent tips of soda straws and tops of stalagmites, display the same trend ($R^2 = 0.64$ on the 99 % confidence level) (Table 6, Fig. 17) as observed in the present-day calcite. Therefore, variations in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ observed in recent calcite, deposited on a longer period (i.e. several years to several centuries) are likely also due to the degree of isotopic equilibrium, linked with drip rate and consequently, through recharge, with rainfall.

Measurements of the Mg/Ca and Sr/Ca ratios in recent calcite show a significant correlation (Table 6, Fig. 18), inherited from the already existing correlation in the seepage waters. The Mg/Ca and Sr/Ca ratios in the calcite are therefore, as the ratios in the seepage water, dependent on the seepage water residence time.

PALAEOCLIMATIC RECONSTRUCTION IN THE LIGHT OF THE PRESENT-DAY, EXAMPLE OF THE HOLOCENE STALAGMITE PN-95-5

Petrography, age and growth period

A Holocene calcite stalagmite, ca. 65 cm long and with a mean diameter of 10 cm, was sampled at 300 m from the entrance at location slp11 (Fig. 2). The stalagmite is composed of an alternation of dark brown and milky white calcite (Fig. 19). Growth layers

are visible over nearly the entire length, however not always easily countable. No hiatus is observed. The growth period, from 13 ka to 2 ka, was constrained by ten TIMS U-Th ages (Fig. 19).

Isotopic and Chemical Holocene records

Subsamples for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ analyses were drilled every 5 mm along the central growth axis of the speleothem. Mg/Ca and Sr/Ca measurements in the same stalagmite are reported by Verheyden et al. (2000) and are used here for comparison with the oxygen and carbon isotopic profiles. Sr isotopic measurements are reported and discussed in Verheyden et al. (2000) and are not considered here.

The $\delta^{18}\text{O}$ displays changes between -6.4‰ and -4.3‰ VPDB. $\delta^{13}\text{C}$ varies between -9.5‰ and -2.6‰ VPDB and displays parallel changes as $\delta^{18}\text{O}$ along the vertical axis of the stalagmite (Table 7, Fig. 17). $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ measurements along single growth layers were performed at ten different heights in order to check the isotopic equilibrium (Hendy, 1971).

Chemical and isotopic composition trends along a single growth layer

A significant covariation is observed between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in 6 layers, indicating non-equilibrium deposition (Fig. 20). As for the stable isotopes, we have tried to see the lateral variation of the Mg/Ca and Sr/Ca ratio along a single laminae of the PN-95-5 stalagmite where

Table 6. Oxygen and carbon isotopic composition of recent calcite (top of stalagmites and tip of soda straws) from the Père Noël cave (Han-sur-Lesse, Belgium).

	$\delta^{18}\text{O}_{\text{c}}$ ‰ VPDB ± 0.1	$\delta^{13}\text{C}_{\text{c}}$ ‰ VPDB ± 0.06	1000Mg/Ca $\pm 15\%$ on the value	1000Sr/Ca $\pm 15\%$ on the value
Mean	-4.6	-4.1	15.9	0.4
Standard	0.1	0.3	1.5	0.1
Range	3.0	9.6	47.9	2.4
Minimum	-6.1	-10.0	3.3	0.1
Maximum	-3.1	-0.3	51.3	2.5
Count	56	56	45	46

Table 7. $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, 1000Mg/Ca and 1000Sr/Ca changes along the longitudinal axis of the Père Noël stalagmite.

	$\delta^{18}\text{O}$ in ‰ VPDB	$\delta^{13}\text{C}$ in ‰ VPDB	1000Mg/Ca $\pm 15\%$ on the value	1000Sr/Ca $\pm 15\%$ on the value
Mean	-5.4	-7.2	9.5	0.2
standard deviation	0.5	1.4	3.5	0.0
Range	2.2	6.9	20.9	0.2
Minimum	-6.4	-9.5	4.7	0.1
Maximum	-4.3	-2.6	25.6	0.3
Count	130	130	130	130

Fig. 18. 1000Sr/Ca and 1000Mg/Ca of recent calcite and the PN-95-5 stalagmite. Measurements were made in the same way as for cave waters after dissolution in 10% suprapur HNO_3 . Mean error is $\pm 15\%$.

an isotope increase was observed towards the edges (Fig. 21). Results display a similar pattern between isotopes and Mg/Ca, Sr/Ca ratios: they all increase significantly towards the edges and they all show a significant correlation ($\delta^{18}\text{O}$ with $\delta^{13}\text{C}$ and Mg/Ca with Sr/Ca) (Fig 21). 1000Mg/Ca variation from the central axis and to about 2 cm/axis is ~ 4 which is in the range of the Mg/Ca variations observed during the stalagmite growth (Fig. 18). It is the same for the Sr/Ca ratio. It is thus possible that a kinetic effect during the calcite precipitation on the stalagmite might be the main cause of the synchronous changes observed in all these proxies, itself controlled by the drip rate.

Isotopic and chemical variations through time – link with climate.

1000 Mg/Ca values in the speleothem vary between 4.7 ± 0.7 and 25.6 ± 3.8 with a mean of 9.5 (Table 6, Fig. 17). At a high frequency, the changes of Mg and Sr show a striking and significant

similarity during most of the stalagmite growth (Fig. 19).

The positive Hendy tests and the isotopic and elemental covariation, suggest that the 14 ka old PN-95-5 stalagmite was deposited out of equilibrium during most of its growth.

The study of present day calcite suggests the existence of a link between isotopic equilibrium precipitation of calcite and drip rate (linked to recharge at the cave site) (Fig. 16). Therefore, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of the stalagmite may give some information on dry/wet variations in the past: the more enriched the $\delta^{13}\text{C}$ and the $\delta^{18}\text{O}$ of the calcite, the wetter the climate. No quantitative relation between drip rate and calcite $\delta^{18}\text{O}$ could be established. However, the time-series might give relative information on dry-wet episodes during the Holocene.

In contrast to other European speleothems (i.e. Villars and Chauvet speleothems, Genty et al. 2006), the Père Noël stalagmite does not display a characteristic geochemical signal for the Younger Dryas. During this period, temperature changes play a role and may “contaminate” the $\delta^{18}\text{O}$ change linked with changing isotopic equilibrium conditions, itself linked with drip rate.

The striking similarity between the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ time-series and the Mg/Ca and Sr/Ca time-series suggests a common control on these changes. Two processes may explain this relationship: 1) Mg/Ca and Sr/Ca ratios closely depend on the Mg/Ca and Sr/Ca ratios of the seepage waters, which on their turn depend on the residence time of the water in the vadose zone and consequently, through the recharge amount, on the rainfall amount. The dependence on the residence time might be due to the degree of “prior calcite precipitation” (PCP) that will increase (and covary) both Mg/Ca and Sr/Ca in the seepage water and consequently in the calcite (Fairchild et al., 2000). $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ variations, as observed on the present day calcite, are mainly controlled by the isotopic equilibrium state during precipitation of the calcite, which depends on the drip rate, and consequently, through recharge, on the rainfall amount too; 2) Chemical as well as isotopic composition depend on kinetic processes during calcite precipitation on the stalagmite, which are on their turn somehow linked with drip rate (as suggested by the present day calcite) and consequently with recharge. Therefore, chemical and isotopic ratios appear, in both cases, to be two proxies for the rainfall amount, independently in case 1 but linked to the same process in case 2.

CONCLUSION

The Père Noël cave exhibits a rather constant climatology (temperature, humidity) and only slight variations in the seepage water isotopic composition. In contrast, clear spatial and seasonal variations are observed for the stalactite drip rates and the chemical composition (Mg/Ca and Sr/Ca) of the cave water as well as the isotopic and chemical composition of the cave calcite. Most

Fig. 19. Isotopic and geochemical time-series of the Pèrè Noël stalagmite PN-95-5 in front of the polished section. Points at the bottom of the figure indicate TIMS U/Th dating with 2s errors. U-series datings were performed at the Department of Earth Sciences of the Open University, UK, following the procedure described in Verheyden et al, 2000.

Fig. 20. "Hendy tests" at ten different heights (in cm from the top) in the PN-95-5 Pèrè Noël stalagmite. Except at 0.5 and 20.5 cm from the top, the stalagmite was mostly deposited out of isotopic equilibrium as indicated by lateral $\delta^{18}\text{O}$ enrichment and covariation of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ along single deposition layers. (Note that at 6.5 cm, a plateau value seems to be reached around the drip impact place suggesting calcite deposition close to equilibrium at this place).

Fig. 21. Covarying trends of $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Mg/Ca and Sr/Ca along a single layer in the Holocene Père Noël stalagmite.

of the calcite deposited in the Père Noël cave is clearly not deposited in isotopic equilibrium but, nevertheless, may give information on water availability through possible relationships between i) water recharge, drip rate and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of the cave calcite and ii) recharge, residence time, prior calcite precipitation and Mg/Ca and Sr/Ca composition of the water and of the precipitated calcite. The similar patterns found in $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Mg/Ca and Sr/Ca along a single layer in a Holocene stalagmite as well as along its longitudinal axis suggest a possible overall control of kinetics during the precipitation at the stalagmite place.

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