Mg, Sr and Sr isotope geochemistry of a Belgian Holocene speleothem: implications for paleoclimate reconstructions

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Abstract

In this study, variations in Mg/Ca, Sr/Ca and 87Sr/86Sr ratios in a Holocene Belgian speleothem (cave secondary carbonate deposit) are interpreted in terms of changes in water residence time and changes in weathering processes, possibly induced by changes in West European climate. A stalagmite from the Père Noël cave (Belgium) was dated with the TIMS U/Th method and was deposited between ~ 13 and ~ 2 ka BP. The 1000 Mg/Ca ratio varies between 4.9 and 26, and displays short-term changes but no significant long-term trend. The 1000 Sr/Ca ratio varies between 0.09 and 0.31 and displays both short-term changes and a long-term decreasing trend from 12.9 to 3.5 ka. In parallel, the Sr isotopic composition of the speleothem decreases from 0.7090 at 12.9 ka to 0.7088 at 3.5 ka. The Sr isotope ratio is higher than expected from the overlying limestone (87Sr/86Sr = 0.7081) which implies an external source of radiogenic Sr, most probably from a silicate phase. Short-term and long-term changes in Mg/Ca, Sr/Ca as well as long-term changes of 87Sr/86Sr ratios can be explained by changes in the dissolution and precipitation processes of the host limestone. These processes are controlled by changes in water residence times linked to changes in the water excess (precipitation minus evapo-transpiration).

Keywords: Holocene; Speleothem; Stalagmite

1. Introduction

Holocene continental climatic and environmental records of ice volume, air temperature, amount of precipitation and vegetation are available from studies of ice cores (Johnsen et al., 1972; Oeschger et al., 1984; Taylor et al., 1993; Stuiver et al., 1995), lake levels (Street-Perrott and Harrison, 1985; Magny,
Hendy and Wilson, 1968; Gascoyne et al., 1981; Labeyrie et al., 1967; Talma and Vogel, 1992. Attempts have also been made to interpret paleoclimate from the chemical composition of speleothems. Earlier studies (Gascoyne, 1983, 1992; Goede and Franke, 1970; Hennig et al., 1980; Genty and Massault, 1997). They can therefore contribute to our understanding of the timing of paleoclimatic events on the continents. Paleoclimatic studies on speleothems can be performed with a very high time resolution, since the seasonal character of visible or UV-fluorescent growth layers have been identified in some stalagmites (Broecker et al., 1960; Shopov and Dermendjiev, 1990; Genty, 1993; Railsback et al., 1994; Genty and Quinif, 1996; Baker et al., 1993, 1998, 1999). Speleothems may record surface air temperatures through \( \delta^{18}O \) and floral composition through \( \delta^{13}C \), provided they are deposited in isotopic equilibrium with the seepage water (Labeyrie et al., 1967; Hendy and Wilson, 1968; Gascoyne et al., 1981; Talma and Vogel, 1992). Attempts have also been made to interpret paleoclimate from the chemical composition of speleothems. Earlier studies (Gascoyne, 1983, 1992; Goede and Vogel, 1991) interpreted changes in Mg/Sr ratios in a stalagmite as reflecting temperature changes. Later studies emphasize the importance of paleohydrology (Roberts et al., 1998; Fairchild et al., 1996, 2000). Recently, there has also been interest in the Sr isotopic composition of speleothems (Avigour et al., 1990; Banner et al., 1996; Goede et al., 1998; Ayalon et al., 1999, Bar-Matthews et al., 1999). Since overlying limestone typically releases a significant amount of Sr, transported downward by the seepage water, the Sr in speleothems is expected to be derived mainly from the overlying limestone. Changes in the Sr content of a stalagmite can be controlled by dissolution–precipitation processes in the unsaturated zone due to differences in residence time, reflecting effective precipitation (Roberts et al., 1998; Bar-Matthews et al., 1999; Fairchild et al., 2000). However, in semi-arid and arid regions considerable amounts of Sr can be added to the stalagmite by deposition of terrestrial dust at the surface above the cave (Goede et al., 1998). The \( ^{87}\text{Sr}/^{86}\text{Sr} \) ratio can change significantly if even only small quantities of Sr with a very different \( ^{87}\text{Sr}/^{86}\text{Sr} \) ratio are added as shown by Banner et al. (1996). Avigour et al. (1990) attributed the high Sr isotopic ratios in an Israeli stalagmite, in comparison to the host rock, to rainwater Sr with a higher \( ^{87}\text{Sr}/^{86}\text{Sr} \) ratio. Banner et al. (1996) related variations in the Sr isotopic composition of a Holocene stalagomite from Barbados to changes in groundwater composition as a function of rainfall recharge in the area. Goede et al. (1998) interpreted the changes in Sr isotopic composition in a Tasmanian speleothem as changes in Sr input from \( ^{87}\text{Sr} \) enriched terrestrial dust, due to changes in the wind directions. Finally, Ayalon et al. (1999) and Bar-Matthews et al. (1999) interpreted changes in the Sr content and the \( ^{87}\text{Sr}/^{86}\text{Sr} \) ratio in speleothems from the Soreq Cave in the Eastern Mediterranean region as changes in weathering intensity due to changes in rainfall intensity and temperature. Ayalon et al. (1999) argued that mixed exogenic sources such as sea spray and aeolian dust had a role in generating the more radiogenic ratios at Soreq Cave. All these studies relate variations in the Sr content and Sr isotopic composition of speleothems to climatic or environmental changes. However, Roberts et al. (1999) observed no similarities between Sr content time-series of three coeval Holocene speleothems from a GB Cave. They suggest that the trace element variations reflect hydrological mixing of waters in the epikarstic zone above the cave.

A Holocene stalagmite from a Belgian cave, the Père Noël cave, was sampled as part of the EC project “Holocene/Late Pleistocene High Resolution Climate Reconstruction from Continental Carbonates (Speleothems)” based on geochemical and stable isotope studies on speleothems from Ireland, Belgium, France and Italy (McDermott et al., 1999).
In the Belgian stalagmite, long-term variations in Sr content occurred together with a pronounced similarity between the short-term changes of $\delta^{18}$O, $\delta^{13}$C, Mg/Ca and Sr/Ca (Verheyden et al., 1998) (Fig. 1).

Previous research has suggested that changes in the $^{87}$Sr/$^{86}$Sr ratio of the stalagmite might provide information about the different Sr sources involved and how their relative contributions changed during the stalagmite deposition as a result of paleoclimatic and paleo-environmental changes (e.g. Avigour et al., 1990; Banner et al., 1996; Goede et al., 1998; Ayalon et al., 1999; Bar-Matthews et al., 1999). This paper presents new data for the Mg and Sr content of the Père Noël cave waters and for the Mg and Sr content and the Sr isotopic composition in a Holocene Belgian stalagmite from the Grotte du Père Noël.

The paper discusses possible interpretations of these short and long-term changes in the context of possible links with climatic and environmental change.

2. Methodology

Our study was performed in the Belgian Père Noël cave, located in Han-sur-Lesse in the Ardennes massif (Fig. 2). The cave opens in the Devonian (Givetian) Fromelene Formation with subvertical limestone beds (Delvaux de Fenffe, 1985) that reach a thickness of ca. 70 m above the cave (Deflandre, 1986). Some of the beds are dolomitised. Since no impermeable formations are present above the cave and since the river no longer flows through the cave,
the water entering the cave consists only of local rain, seeping directly through the overlying limestone. An approximately 40-cm-thick woodland soil covers the host rock limestone. The soil consists of heavily rooted, unconsolidated brown earth comprising limestone fragments, small aggregates and residual clays. A Holocene stalagmite, ca. 65 cm long, was taken at 300 m from the entrance and at 30 m above the groundwater level. The stalagmite was dated at 10 different heights by TIMS U/Th method at the Department of Earth Sciences at Open University, UK, following the method described in McDermott et al. (1999). Calcite samples for U/Th dating (0.2–2 g) were dissolved and equilibrated with a mixed 232Th–236U spike. U and Th were separated on columns containing 2 ml of anion exchange resin (1 × 8 AG, 200–400 mesh Biorad). The total procedural blanks were negligible (ca. 15 pg of 232Th and 238U). Th and U fractions were loaded onto out-gassed graphite-coated Re-filaments, and the isotope ratios were measured using a Finnigan MAT 262 RPQ-2 mass spectrometer. The typical abundance sensitivity was 5 × 10−4 at mass 237 (1 amu below the major 235U peak, hence tail contributions at masses 230 and 234 from the large 232Th and 233U peaks were negligible. 230Th/232Th, 232Th/238U, 234U/238U and 235U/236U atomic ratios were measured in peak-switching ion-counting mode. Errors based on the counting statistics were <0.1% for all ratios except for 230Th/232Th, where the small number of 230Th ions result in a relative error of typically 0.4–1.0% (2σ) depending on the U content and age of the sample. Samples for Mg and Sr content were drilled from 1 mm pits every 5 mm along the central growth axis of the stalagmite in order to construct the Mg/Ca and Sr/Ca time-series. Aliquots of approximately 10 mg calcite were dissolved in dilute hydrochloric acid and analysed for Ca, Mg and Sr by inductively coupled plasma (ICP) atomic emission Spectrometry at the University of Birmingham. Within-run precision is around 2% for each of Ca and Mg and 3% for Sr. Since the stalagmite consists of pure low-Mg calcite, changes in Mg/Ca and Sr/Ca ratios are caused by changes in Mg and Sr content, respectively. Thirteen measurements of the Mg and Sr content of the host limestone (calcite and dolomite minerals) were also performed. Mg/Ca and Sr/Ca ratios of seepage waters, sampled in 1994–1998 were determined. Separate acidified and unacidified aliquots were taken for cation and anion analysis, respectively. Measurements were performed by ICP atomic emission spectrometry and ion chromatography at Keele University. Comparison of the Mg and Sr content of the host rock and of the seepage waters with that of the speleothem should give us a better knowledge about the dissolution–precipitation processes above the cave (Lohmann, 1988; Domenico and Schwartz, 1990).

Thirteen calcite samples for 87Sr/86Sr analysis, between 28.3 and 61.3 mg in weight, were drilled along the longitudinal axis of the stalagmite. They were chosen carefully in the light of the δ18O time-series and Sr/Ca curve to represent significant trends and very specific samples (i.e. top of stalagmite, lowest and highest δ18O, etc.). Samples of the overlying host rock, a limestone and a dolomite sample which is present in small quantities, were also analysed. Each sample was carefully checked for purity and lack of foreign particles such as clays. The fine powdered samples were dissolved in 2.5 N HCl, which concentration was increased slowly and left overnight to assure complete dissolution of the carbonate phase. No residue was observed. Sr was separated on anion exchange columns, following the procedure described in Weis et al. (1987). The total
blanks were < 0.3 ng, which were negligible in comparison to the Sr content of the samples (> 200 ng). Sr isotopic compositions were analysed on a VG Sector 54 multicollector mass spectrometer at the Université Libre de Bruxelles (Belgium). For each run, $^{87}\text{Sr}/^{86}\text{Sr}$ was normalised to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and 120 ratios were taken. Repeated analysis of NBS 987 during this study gave $0.710272 \pm 9 \times 10^{-6}$ ($2\sigma_m$ on 48 analyses). The $2\sigma$ on individual runs is presented in Table 3 and is typically $< 1.5 \times 10^{-3}$. The sample “50 cm” was sampled and measured three times in order to test the reproducibility and the homogeneity of the speleothem. The maximum difference is $1.7 \times 10^{-5}$ for analyses on different powders. The sample “0 cm” was measured twice in order to confirm its surprising $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Sr isotope analyses of 6.2 N hydrochloric acid leachates left overnight of clayey cave sediments, collected in the cave were also performed. The sediments were collected nearby the sampled speleothem within a radius of 30 m on the floor of the cave.

### 3. Results

1000 Mg/Ca and 1000 Sr/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 (Table 1). 1000 Mg/Ca ratios of seepage waters vary between 62 and 1118 with a mean of 324. 1000 Sr/Ca ratios vary between 0.98 and 4.46 with a mean of 1.88. The water samples exhibit an important variability within the cave, but a more narrow range at one drip place (Fig. 3). The 1000 Mg/Ca vs. 1000 Sr/Ca diagram suggests a general sympathetic correlation ($R^2 = 0.3$), which is highly significant at a single drip location ($R^2 = 0.9$, data enclosed by ellipses, Fig. 3). These results will be discussed more in detail in a following publication.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Minerals</th>
<th>1000 Mg/Ca</th>
<th>1000 Sr/Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>calcite</td>
<td>17.1</td>
<td>0.74</td>
</tr>
<tr>
<td>1b</td>
<td>dolomite</td>
<td>309.4</td>
<td>0.78</td>
</tr>
<tr>
<td>1c</td>
<td>calcite</td>
<td>11.5</td>
<td>1.28</td>
</tr>
<tr>
<td>2</td>
<td>calcite + dolomite</td>
<td>8.0</td>
<td>0.61</td>
</tr>
<tr>
<td>3</td>
<td>calcite + minor dolomite</td>
<td>10.0</td>
<td>1.10</td>
</tr>
<tr>
<td>4</td>
<td>calcite</td>
<td>13.0</td>
<td>1.20</td>
</tr>
<tr>
<td>5</td>
<td>calcite + dolomite</td>
<td>13.4</td>
<td>0.93</td>
</tr>
<tr>
<td>6</td>
<td>dolomite</td>
<td>320.0</td>
<td>0.64</td>
</tr>
<tr>
<td>7</td>
<td>dolomite + minor calcite</td>
<td>315.4</td>
<td>0.77</td>
</tr>
<tr>
<td>8</td>
<td>dolomite + minor calcite</td>
<td>310.4</td>
<td>0.66</td>
</tr>
<tr>
<td>9</td>
<td>calcite</td>
<td>8.5</td>
<td>0.85</td>
</tr>
<tr>
<td>10</td>
<td>calcite + minor dolomite</td>
<td>11.1</td>
<td>1.09</td>
</tr>
<tr>
<td>11</td>
<td>calcite</td>
<td>16.4</td>
<td>1.12</td>
</tr>
</tbody>
</table>

U/Th dating indicates that the Père Noël stalagmite started growing a short time before 12,671 a BP (+ 70 a) and stopped growing at about 2024 a BP (+ 11 a) (Table 2, Fig. 4). Because of changing growth rates (Fig. 4), the time interval between two Mg and Sr content measurements along the central growth axis of the stalagmite varies between 20 and 200 a for the same stalagmite length. Fast-growing parts of the stalagmite will therefore display more short-term variations than slow-growing parts. In order to eliminate this growth rate-effect, the 1000 Sr/Ca data are given as averages of 200 a time slices through the Holocene (Fig. 5). Accordingly, between 1 and 10 analyses contribute to each of the 200 a time slice data points.

1000 Mg/Ca values in the speleothem vary between 4.7 and 25.6 with a mean of 9.5. No long-term trend is observed in Mg/Ca. By contrast, 1000 Sr/Ca, between 0.09 and 0.31, displays a long-term
Table 2
Mass-spectrometric U/Th age data for the Pere Noel speleothem

<table>
<thead>
<tr>
<th>Distance from top of stalagmite (mm)</th>
<th>U (ppm)</th>
<th>234U/238U</th>
<th>230Th (pg/g)</th>
<th>230Th/232Th</th>
<th>230Th/234U</th>
<th>Age in years BP ± 2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.2339</td>
<td>2.3657</td>
<td>0.1666</td>
<td>30</td>
<td>0.01847</td>
<td>12671 ± 71</td>
</tr>
<tr>
<td>45</td>
<td>0.2971</td>
<td>2.3914</td>
<td>0.4100</td>
<td>59</td>
<td>0.03540</td>
<td>10303 ± 55</td>
</tr>
<tr>
<td>115</td>
<td>0.1985</td>
<td>2.4656</td>
<td>0.4664</td>
<td>980</td>
<td>0.05846</td>
<td>9185 ± 21</td>
</tr>
<tr>
<td>190</td>
<td>0.1680</td>
<td>2.4973</td>
<td>0.4196</td>
<td>1216</td>
<td>0.06134</td>
<td>7853 ± 45</td>
</tr>
<tr>
<td>250</td>
<td>2.7809</td>
<td>2.4961</td>
<td>0.7259</td>
<td>2345</td>
<td>0.06414</td>
<td>7164 ± 22</td>
</tr>
<tr>
<td>365</td>
<td>0.2275</td>
<td>2.5064</td>
<td>0.6520</td>
<td>1902</td>
<td>0.07013</td>
<td>6843 ± 37</td>
</tr>
<tr>
<td>435</td>
<td>0.3037</td>
<td>2.5779</td>
<td>1.0420</td>
<td>724</td>
<td>0.08163</td>
<td>6515 ± 37</td>
</tr>
<tr>
<td>520</td>
<td>0.2528</td>
<td>2.6538</td>
<td>0.9978</td>
<td>299</td>
<td>0.09121</td>
<td>3907 ± 16</td>
</tr>
<tr>
<td>635</td>
<td>0.1790</td>
<td>2.7290</td>
<td>0.8857</td>
<td>161</td>
<td>0.11122</td>
<td>2024 ± 11</td>
</tr>
</tbody>
</table>

Decay constants used to calculate activity ratios from measured atomic ratios are as follows: λ238U = 1.551 × 10⁻¹⁰, λ234U = 2.835 × 10⁻⁸, λ230Th = 9.915 × 10⁻⁶, λ232Th = 4.948 × 10⁻¹¹. Age uncertainties are reported at the 2σ level.

A decreasing trend from ~0.25 at 12.9 ka BP to ~0.10 at 3.5 ka BP (Fig. 5). Significant shorter-term changes (on a ca. 500 a time-scale) can be observed in both trace element ratios. The changes of Mg and Sr show a significant similarity, especially the change around 10.5 ka BP, the perturbation between 9 and 8.5 ka BP, the three peaks between 6 and 4 ka BP and the important increase at the top of the stalagmite. Overall, the correlation between Mg/Ca and Sr/Ca has an R² value of 0.54 for the time period between 11 and 2 ka BP, but is not significant at the base of the stalagmite (R² = 0.03).

The ⁸⁷Sr/⁸⁶Sr time-series displays a long-term decreasing trend from 0.70899 at 12.9 ka BP to 0.70881 at 3.5 ka BP (Table 3, Fig. 6). The top of the stalagmite has an ⁸⁷Sr/⁸⁶Sr of 0.70889, which is considerably higher than that expected from the long-term trend. The high ⁸⁷Sr/⁸⁶Sr ratio of the top of the stalagmite matches the behaviour of the 1000 Sr/Ca ratio, which is also higher than expected from

![Fig. 4. U/Th dating and growth rate of the Père Noël stalagmite. The Père Noël stalagmite was deposited between ~13 and 2 ka BP. Large points represent the measured U/Th ages, while the age of intervening points between two measurements are interpolated. Each point represents one subsample taken every 0.5 cm along the growth axis of the stalagmite for geochemical and isotopic analysis. Higher growth rates are observed between ~6.5 and ~7.8 ka BP.](image-url)
Fig. 5. The 1000 Mg/Ca and 1000 Sr/Ca time-series of the Pere Noel stalagmite. Both short-term and long-term fluctuations in Mg/Ca and Sr/Ca ratio can be interpreted as changes in water residence times. Low values represent periods of shorter residence times (humid conditions). Crosses indicate which samples were analyzed for \(^{87}\)Sr/\(^{86}\)Sr. Mean values of 1000 Mg/Ca and 1000 Sr/Ca in the speleothem are given by the horizontal lines.

The long-term 1000 Sr/Ca trend. A relationship exists between the Sr isotopic composition and the Sr content of the analysed samples (Fig. 7). The 1/Sr vs. \(^{87}\)Sr/\(^{86}\)Sr diagram seems to display three end-members (Fig. 7): a radiogenic component with intermediate Sr contents and two low radiogenic end-members with high and low Sr contents, respectively. The lowest \(^{87}\)Sr/\(^{86}\)Sr ratio of the stalagmite (0.70881) is still far above those measured in the overlying slightly dolomitised Givetian limestone.

Table 3
Sr/Ca and \(^{87}\)Sr/\(^{86}\)Sr ratios in the Pere Noel stalagmite

<table>
<thead>
<tr>
<th>Sample (in cm from top of stalagmite)</th>
<th>Age of the sample (in years BP)</th>
<th>1000 Sr/Ca ratio</th>
<th>Sr content (ppm)</th>
<th>(^{87})Sr/(^{86})Sr ratio</th>
<th>2(\sigma_m) (x 10(^{-6}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–1</td>
<td>1789</td>
<td>0.24</td>
<td>96</td>
<td>0.708893</td>
<td>15</td>
</tr>
<tr>
<td>0–2</td>
<td>1789</td>
<td>0.24</td>
<td>96</td>
<td>0.708877</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>3672</td>
<td>0.12</td>
<td>49</td>
<td>0.708809</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>5211</td>
<td>0.29</td>
<td>115</td>
<td>0.708850</td>
<td>7</td>
</tr>
<tr>
<td>11.5</td>
<td>6515</td>
<td>0.15</td>
<td>60</td>
<td>0.708837</td>
<td>10</td>
</tr>
<tr>
<td>14</td>
<td>6624</td>
<td>0.15</td>
<td>59</td>
<td>0.708829</td>
<td>9</td>
</tr>
<tr>
<td>25</td>
<td>7164</td>
<td>0.20</td>
<td>80</td>
<td>0.708913</td>
<td>16</td>
</tr>
<tr>
<td>28</td>
<td>7344</td>
<td>0.15</td>
<td>60</td>
<td>0.708879</td>
<td>8</td>
</tr>
<tr>
<td>32</td>
<td>7583</td>
<td>0.17</td>
<td>68</td>
<td>0.708904</td>
<td>10</td>
</tr>
<tr>
<td>43</td>
<td>9090</td>
<td>0.20</td>
<td>80</td>
<td>0.708911</td>
<td>8</td>
</tr>
<tr>
<td>50–1</td>
<td>10,040</td>
<td>0.22</td>
<td>88</td>
<td>0.708922</td>
<td>11</td>
</tr>
<tr>
<td>50–2</td>
<td>10,040</td>
<td>0.22</td>
<td>88</td>
<td>0.708906</td>
<td>13</td>
</tr>
<tr>
<td>50–3</td>
<td>10,040</td>
<td>0.22</td>
<td>88</td>
<td>0.708905</td>
<td>14</td>
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<tr>
<td>55</td>
<td>10,921</td>
<td>0.23</td>
<td>92</td>
<td>0.708919</td>
<td>8</td>
</tr>
<tr>
<td>60</td>
<td>11,950</td>
<td>0.23</td>
<td>92</td>
<td>0.708947</td>
<td>7</td>
</tr>
<tr>
<td>64.5</td>
<td>12,877</td>
<td>0.16</td>
<td>64</td>
<td>0.708991</td>
<td>10</td>
</tr>
</tbody>
</table>

Notice that the \(^{87}\)Sr/\(^{86}\)Sr ratio of sample “50 cm” was measured three times, sample “0 cm” was measured two times.
Fig. 6. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Père Noël stalagmite displays a long-term decreasing trend from ~13 to ~3 ka BP. The long-term decreasing trend can be interpreted as a progressive shift to better climatic conditions, when the contribution of host rock Sr ($^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7081) is relatively more important compared with Sr from a silicate phase ($^{87}\text{Sr}/^{86}\text{Sr}$ ratio of ~0.72).

(0.70808 for calcite and 0.70818 for dolomite). The latter values are in agreement with the $^{87}\text{Sr}/^{86}\text{Sr}$ range predicted for Givetian ocean water (Burke et al., 1982). The 6.2 N hydrochloric acid leachates of the cave sediments have a measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio between 0.70860 and 0.70894 (Table 4).

4. Interpretation and discussion

4.1. Mg- and Sr-content of the stalagmite

The incorporation of Mg and Sr in calcite depends on the initial composition of the precipitating solution and on their respective distribution coefficients (Mg/Ca<sub>calcite</sub>/Mg/Ca<sub>solution</sub>) (Banner, 1995; Mucci and Morse, 1990). The distribution coefficient of Mg depends mainly on temperature (Katz, 1973; Mucci, 1987; Burton and Walter, 1991), while the distribution coefficient of Sr depends mainly on the precipitation rate of the calcite (Lorens, 1981; Pingitore and Eastman, 1986) among other parameters. The Mg and Sr contents of the Père Noël stalagmite are comparable to values measured in other stalagmites (Gascoyne, 1977; Avigour et al., 1990; Goede et al., 1998; Bar-Matthews et al., 1999), but are slightly higher than those expected from the host rocks Mg and Sr. The higher Mg/Ca and Sr/Ca ratios of the speleothem reflect the higher ratios of the seepage water, taking into account a distribution coefficient between 0.005 and 0.03 for Mg for 10°C (Gascoyne, 1983; Mucci, 1987; Burton and Walter, 1991) and between 0.14 and 0.15 for Sr (Mucci and Morse, 1987).

Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$ ratio</th>
<th>2$sigma$ ($\times 10^{-6}$)</th>
</tr>
</thead>
<tbody>
<tr>
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Fig. 7. The 1/Sr vs. $^{87}\text{Sr}/^{86}\text{Sr}$ diagram is suggesting the existence of three end-members, a radiogenic low Sr end-member and two unradiogenic end-members with high and low Sr content. However, the appearance of a “dubble” low radiogenic end-member may be due to the short-term changes of the Sr/Ca ratios, while the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are controlled only by longer-term changes.
Since limestone releases important amounts of Mg and Sr and since it is estimated that only 2% of the Sr in Père Noël cave waters is seawater-derived (based on correction of cave water compositions using the marine aerosol Sr/Cl ratio), it seems unlikely that such important amounts of Mg and Sr are added by an external source. On the contrary, since partition coefficients of Mg and Sr in calcite are < 1 (Katz, 1973; Mucci and Morse, 1983; Mucci, 1987; Lorens, 1981), Mg/Ca and Sr/Ca ratios increase in solutions that have precipitated calcite. Mg and Sr are added to the fluid as calcite and dolomite dissolves because of calcite precipitation in the host rock prior reaching the cave (Lohmann, 1988; Fairchild et al., 2000). An increase in the Mg/Ca and the Sr/Ca ratios occurs in the seepage waters and consequently in the precipitated speleothem. This also explains the sympathetic variations of Mg and Sr in the seepage waters as well as in the speleothem (Figs. 1 and 3). Previous studies on the chemistry of karst waters in partly dolomitised host rocks observed an antipathetic correlation between Mg/Ca and Sr/Ca explained by the occurrence of differential dissolution of dolomite and calcite (Roberts et al., 1998; Fairchild et al., 1996, 2000). If this process was important at the Père Noël cave, an antipathetic relationship would be expected because the dolomite contains less Sr than the calcite (Table 1). However, in the Père Noël cave, prior calcite deposition seems to be the dominant process controlling the Mg and Sr chemical composition of the cave waters and of the speleothem.

4.2. Short-term changes in the Mg/Ca and Sr/Ca ratio

As explained above, the Mg and Sr contents in the speleothem seem to be controlled by dissolution–precipitation processes (such as prior calcite deposition) in the limestone (Lohmann, 1988). These observations seem in agreement with observations made by Huang and Fairchild (1998), Roberts et al. (1998), Bar-Matthews et al. (1999) and Fairchild et al. (2000). At the Père Noël cave site, one possible explanation is that a longer residence time of the seepage water in the limestone above the cave will increase the Mg/Ca and Sr/Ca ratios of the seepage waters due to an increase in prior calcite deposition caused by an increase in calcite saturation of the waters. As a consequence, these ratios will also increase in the calcite precipitated in the cave. We therefore conclude that the Mg/Ca and Sr/Ca changes in the speleothems can be interpreted by changes in water residence time in the vadose zone.

Changes in the water residence time may be linked to changes in effective rainfall. However, caution is required when interpreting short-term changes in only one stalagmite in terms of climate since changes in the chemical content of the seepage water could also be controlled by changes in the routing of the water when seeping down (Domenico and Schwartz, 1990; Roberts et al., 1999). A statistical study should therefore be done but is often impossible due to cave preservation requirements. However, δ¹⁸O of the seepage water is not controlled by the routing of the water (Harmon, 1979; Yonge et al., 1985). This is also the case in the Père Noël cave since δ¹⁸O values of the cave waters are rather constant (Verheyden et al., 1999b). Therefore, the similarity of the changes in δ¹⁸O, Mg/Ca and Sr/Ca ratios in the stalagmite (Fig. 1) (Verheyden et al., 1998, 1999a,b) suggest that these changes were not induced by changes in routing of the water. There also is a striking analogy between the generally lower and less variable values around 7000 ka BP and the rapid speleothem growth, probably due to a more humid and warm climate with an increase in the soil CO₂ production (Dreybrodt, 1988; Gewelt, 1986; Genty et al., 1992).

4.3. Long-term changes in the Mg/Ca and Sr/Ca ratio

Applying the same arguments as for short-term Sr content changes, the long-term decrease of the 1000 Sr/Ca ratio of the stalagmite from 0.25 to 0.10 between ca. 12.9 and ca. 3.5 ka BP is due to a general decrease of the effect of prior calcite deposition, possibly due to a decrease in water residence time, causing a decrease in the Sr/Ca ratio of the seepage water and consequently in the calcite. The long-term trend for younger ages is difficult to inter-
pret because of the poorer time resolution of the sampling due to lower growth rates of the speleothem. However, despite the poorer time resolution, an important variability is observed, suggesting important changes in water residence time. The gradual increase in Mg/Ca and Sr/Ca between ca. 3.5 and 2.0 ka BP suggests that the end of speleothem deposition was accompanied with an increase in prior calcite precipitation, possibly related to an increase in the water residence time. Poor speleothem deposition is observed in Belgium after ca. 2000 a BP (Gewelt, 1986), corresponding to the end of the Père Noël speleothem deposition. We expect Mg/Ca ratios to follow the same long-term trend as the Sr/Ca ratios. However, other factors, such as temperature could influence Mg incorporation and the Mg/Ca changes in the speleothem.

4.4. $^{87}$Sr/$^{86}$Sr isotopic composition of the stalagmite

Since no Sr isotopic fractionation occurs during dissolution, deposition or evaporation, the Sr isotopic composition of the stalagmite reflects the Sr isotopic composition of the precipitating solution. The Sr isotopic ratios for the Père Noël stalagmite vary between 0.70881 and 0.70899 (Fig. 6). These values are much higher than those expected from the Sr isotopic composition of the limestone (0.70808), implying an external source of Sr with a high $^{87}$Sr/$^{86}$Sr ratio. The Sr isotopic composition of the 6.2 N hydrochloric acid leachates of the cave sediments is in agreement with the values for the speleothem calcite and therefore probably reflect the Sr isotopic composition of carbonates precipitated on the cave floor between the clay particles (Table 4). Higher Sr isotopic compositions in stalagmites than in host rock limestones have also been reported by other authors as detailed earlier. As reported earlier, only 2% of the Sr in Père Noël cave waters are seawater-derived. Thus, seawater-derived Sr cannot influence significantly the Sr isotopic composition of the stalagmite because seawater-derived Sr (through rain or through aerosols) with a Sr isotopic signature of 0.70906 ± 0.00003 (Burke et al., 1982) cannot reasonably shift the carbonate host rock Sr isotopic composition from ~0.7081 to the ~0.7090 value observed in the stalagmite. Nevertheless, the observed deviation from the carbonate host rock Sr isotopic value can be obtained by contamination of even small amounts of high $^{87}$Sr/$^{86}$Sr leached from detrital phases, such as shales or clays, in fact any “old” Rb-rich and Sr-poor mineral assemblage. A mixture of, e.g. 7% Sr with an $^{87}$Sr/$^{86}$Sr ratio of 0.72 with the balance from the host-rock limestones could account for the Sr isotopic composition of the stalagmite. In order to determine the exact origin of the radiogenic Sr, a detailed study of the Sr isotopic signature of the rain, of the soil cover and of the detrital components around the limestone is needed. Highly radiogenic Sr could be derived from the soil or from detrital clay particles, contained in a recent terrigenous sediment cover, e.g. loess, terrestrial dust, volcanic tephra (Banner et al., 1996). Contribution of underlying groundwater and nearby shales (about 300 m away) seems very unlikely because of the distance from the speleothem and because of the rather vertical flow component due to subvertical limestone layering. It is not the purpose of this study to investigate the Sr isotopic composition of the siliciclastic mineral phases in and around the cave site in detail. We are interested in finding a possible explanation for the changes in $^{87}$Sr/$^{86}$Sr signature in the speleothem and their relation with other geochemical parameters. Two components with different $^{87}$Sr/$^{86}$Sr signature must control the $^{87}$Sr/$^{86}$Sr signature of the Père Noël speleothem, the host-rock limestone representing the low $^{87}$Sr/$^{86}$Sr ratio end-member (the great majority of the Sr, with an $^{87}$Sr/$^{86}$Sr ratio of ~0.7081) and a detrital phase representing the much higher $^{87}$Sr/$^{86}$Sr ratio end-member (at most 10% of the Sr with an $^{87}$Sr/$^{86}$Sr ratio of ~0.720 or more). The Sr isotopic composition of the speleothem is a result of variable contributions from these two end-members.

4.5. Long-term changes in the $^{87}$Sr/$^{86}$Sr ratio

If the Sr isotopic composition in the Père Noël speleothem is a result of mixing between different Sr isotopic compositions, long-term changes in $^{87}$Sr/$^{86}$Sr ratios may reflect changes in the relative importance of the two end-members. If simple two-component mixing was the only process responsible for the Sr isotope variations, we would expect a
linear mixing line in an $^{87}\text{Sr}/^{86}\text{Sr}$ vs. 1/$\text{Sr}$ diagram. In practice, the data appear to define two trends, which could reflect variable contributions between a high radiogenic component (from a silicate phase) and two low radiogenic (limestone) end-members, characterised by high and low Sr contents (Fig. 7). The subdivision of the limestone low $^{87}\text{Sr}/^{86}\text{Sr}$ end-member is an artifact induced by comparing $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, controlled by a long-term change, and Sr contents controlled by both a long-term change and short-term changes. Our choice of the samples for the $^{87}\text{Sr}/^{86}\text{Sr}$ analysis accentuates this effect because the samples were chosen to coincide with particularly high and low Sr/Ca ratios in the speleothem. The $^{87}\text{Sr}/^{86}\text{Sr}$ signature of the Père Noël speleothem probably also displays short-term changes, however not responding to the same environmental changes as the Sr content or with a different intensity and/or time-resolution. A more extensive sampling with comparable resolution as for the trace element time-series is needed to check this hypothesis.

The general decrease of $^{87}\text{Sr}/^{86}\text{Sr}$ of the stalagmite coincides with the observed long-term Sr/Ca decrease over the same period. It seems likely that both the changes in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and the changes in Sr/Ca ratios are responses to different processes, even if they may have the same ultimate cause. The general decrease of the $^{87}\text{Sr}/^{86}\text{Sr}$ of the stalagmite from 0.7089 to 0.7088 (Fig. 5) might reflect (i) a decreased input of radiogenic Sr or (ii) an increased input of low radiogenic Sr. A decrease in the radiogenic Sr input can be induced by a lowering in atmospheric-derived Sr (terrestrial dust) or by changes in the weathering processes or by differential weathering in the overlying soil (Banner et al., 1996). An increased input of the low radiogenic Sr can be due to enhanced dissolution of the host-rock limestone. Limestone dissolution depends on several factors among which water availability and CO$_2$ availability are the most important (Ford and Williams, 1989; Dreybrodt, 1988). In regions (or in periods) with higher rainfall and higher vegetation activity, a higher rate of limestone dissolution occurs (Ford and Williams, 1989). An increased limestone dissolution rate together with a more constant detrital Sr input, both diluted in an increasing amount of water, would lower the Sr/Ca ratio of the speleothem (due to shorter water residence times) and would lower the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. The $^{87}\text{Sr}/^{86}\text{Sr}$ time-series suggests therefore a decreasing radiogenic Sr input and/or increasing limestone dissolution from 13 to 3.5 ka BP linked with changes in environmental and/or climatic conditions.

The shift to more radiogenic Sr values at the top of the stalagmite is interpreted as an increase in silicate-derived Sr relative to that derived from limestone. A longer residence time of the seepage water as suggested by the higher Mg/Ca and Sr/Ca ratios would ensure saturation of the water with calcite, while the input of radiogenic Sr would continue to increase, through contribution of atmospheric Sr or Sr from the overlying soil.

5. Conclusions

The long-term trend as well as the short-term changes in Mg and Sr content of the Père Noël speleothem may be explained by changes in water residence time. The long-term trend in Sr/Ca ratios can be related to a general decrease in water residence time from 12 to 3.5 ka BP. The rapid increase in Sr/Ca and Mg/Ca after 3.5 ka BP is therefore possibly due to an important increase in water residence time followed by the end of speleothem growth. The long-term decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ trend is due either to an increase in low radiogenic limestone host rock Sr contribution relative to the high radiogenic detrital Sr contribution or to a decrease in radiogenic Sr input from siliciclastic sources.

The linear trend in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vs. age, the similar long-term decrease in Sr content (Fig. 4) and the possible relation between changes in Mg and Sr content with climatic parameters are strong indicators that Mg and Sr geochemistry in Sr isotope geochemistry in speleothems are parameters which are not controlled only by the Mg and Sr contents and Sr isotopic composition of the host rock. A more systematic study of well-characterised speleothems in Western Europe is necessary to confirm the reproducibility of these observations and to strengthen Sr isotopic geochemistry as a reliable tool to trace climatic variations, especially in order to extend our conclusions to the scale of Northern Europe.
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References


