Mg records of two stalagmites from B7-Cave (northwest Germany) indicating long-term precipitation changes during Early to Mid-Holocene

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Abstract: Two stalagmites from B7-Cave in northwest Germany, which is part of the same cave system as the intensively studied Bunker Cave, were re-dated by multi collector inductively coupled plasma mass spectrometry (MC-ICPMS) $^{230}$Th/U-dating. Furthermore, the concentration of Mg, Sr, Ba, P, Y, Zn, and Al were determined at high-resolution by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). Stalagmite B7-1 grew from 10.8 to 5.8 ka BP. Stalagmite B7-7 grew during three growth phases from 11.0 to 6.2, 3.13 to 2.86 (late Bronze Age), and 1.27 to 1.15 ka BP (early Medieval Period). Aluminium is a proxy for detrital material and corresponds very well with the visible detrital layers in stalagmite B7-1 and the oldest growth phase of stalagmite B7-7. The two younger growth phases of stalagmite B7-7 are very clean and show very low Al concentrations. Phosphorus, Y, and Zn show positive correlations in both stalagmites and all growth phases, but do not show a relationship to temperature or precipitation. This may be related to the elevated detrital content in both stalagmites. Barium and Sr also show a positive correlation in both stalagmites and all growth phases, which is related to their dependency on growth rate. Magnesium is most probably influenced by prior calcite precipitation and therefore a proxy for past precipitation/infiltration. The Mg records of stalagmite B7-1 and of the oldest growth phase of stalagmite B7-7 show decreasing Mg concentration with time reflecting decreasing prior calcite precipitation and therefore increasing precipitation during the Early to Mid-Holocene. This is consistent with other climate reconstructions from Central Europe.

Keywords: $^{230}$Th/U-dating, trace elements, prior calcite precipitation, growth rate, soil and vegetation activity

INTRODUCTION

The precise dating of speleothems with the $^{230}$Th/U-method (e.g., Richards & Dorale, 2003; Scholz & Hoffmann, 2008) is a necessary prerequisite for the interpretation of speleothem proxy records. In the last two decades, this dating technique was further developed due to the improvement in mass spectrometry from thermal ionisation mass spectrometry (TIMS) to multi collector inductively coupled plasma mass spectrometry (MC-ICPMS), which has a significantly higher sensitivity (e.g., Scholz & Hoffmann, 2008; Cheng et al., 2013).

The most commonly used palaeoclimatic proxies from speleothems are $\delta^{13}$C and $\delta^{18}$O values, which can be influenced by temperature and/or precipitation, (e.g., Drysdale et al., 2004; Boch et al., 2009; Jex et al., 2010; Baker et al., 2011; Wainer et al., 2011; Moseley et al., 2015; van Rampelbergh et al., 2015; Cheng et al., 2016; Demény et al., 2017), and their signals can be modified in the soil and karst zone by infiltration, evaporation, mixing, open/closed system conditions, and prior calcite precipitation (e.g., McDermott, 2004; Lachniet, 2009). However, elemental concentrations in speleothems, such as Mg, Sr, P, and further elements, are also used as palaeoclimatic proxies for precipitation/infiltration, vegetation activity, soil microbial activity, and soil weathering (e.g., Cruz et al., 2007; Fairchild & Treble, 2009; Frisia et al., 2012; Wassenburg et al., 2012; Mischel et al., 2017b; Warken et al., 2018; Riechelmann et al., 2020). Magnesium is one of the
best understood elements, often influenced by prior calcite precipitation (PCP) induced by drier climate conditions leading to more air filled cavities above the cave with lower pCO$_2$, where calcite can be precipitated from the seeping water (Fairchild et al., 2000; Fairchild & Treble, 2009). Magnesium can also be influenced by further factors such as incongruent calcite and/or dolomite dissolution (e.g., Fairchild et al., 2000; Sinclair et al., 2012; Wassenburg et al., 2020). All these processes drive the Mg concentration in the drip water and the corresponding speleothem in the same direction (in case of drier climate conditions to higher values and vice versa). This makes Mg a valuable proxy for past precipitation/infiltration.

Bunker Cave, very close to B7-Cave, is one of the best monitored and investigated caves worldwide (Immenhauser et al., 2010; Kluge et al., 2010; Wackerbarth et al., 2010; Riechelmann et al., 2011; Fohlmeister et al., 2012; Münsterer et al., 2012; Riechelmann et al., 2012a; Riechelmann et al., 2012b; Kluge et al., 2013; Riechelmann et al., 2013; Riechelmann et al., 2014; Riechelmann et al., 2017; Weber et al., 2018; Riechelmann et al., 2019; Waltgenbach et al., 2020; Wassenburg et al., 2020; Waltgenbach et al., 2021; Riechelmann et al., 2022). Bunker Cave, B7-Cave, Hüttenbläserschacht Cave, and Dechencave belong to the same large cave system and it is of interest to analyse Holocene stalagmites, such as those from Bunker Cave, to determine if they all reflect supra-regional climate variability (Fohlmeister et al., 2012; Waltgenbach et al., 2020, 2021; Waltgenbach et al., 2021). Previous studies interpreted higher δ$^{18}$O values of Bunker Cave stalagmites as reflecting colder and drier winter conditions (Fohlmeister et al., 2012). Furthermore, the δ$^{13}$C and Mg records were interpreted as proxies for past precipitation with higher values during phases with drier climate and vice versa (Fohlmeister et al., 2012; Waltgenbach et al., 2020; Waltgenbach et al., 2021). A recent study has shown that the stalagmites from Hüttenbläserschacht Cave, which is also close to B7-Cave, do not show such a supra-regional climate signal during the Holocene because their proxy records are strongly influenced by in-cave and site-specific processes, such as disequilibrium stable isotope fractionation, increasing drip intervals, and/or PCP. These processes are probably induced by changes in hydrological pathways in the karst aquifer, which in this case seem to be independent of supra-regional climate variability (Weber et al., 2021). Therefore, it is of interest to re-investigate stalagmites from B7-Cave using state-of-the-art analytical techniques that were not available when the stalagmites were first analysed approximately 20 years ago (Niggemann, 2000; Niggemann et al., 2003).

The aims of this study are thus: (i) precise re-dating of two stalagmites from B7-Cave with state-of-the-art U-Series dating techniques and (ii) measuring high-resolution trace element records to compare them to the nearby records from Bunker Cave (Fohlmeister et al., 2012; Waltgenbach et al., 2021) and Hüttenbläserschacht Cave (Weber et al., 2021).

CAVE SETTING

B7-Cave (51°22´N, 7°39´E) is located in the Rhenish Slate Mountains in northwest Germany (Fig. 1). It is part of a large cave system in the area of Iserlohn also containing, Bunker Cave, Hüttenbläserschacht Cave, Dechencave and several other small caves. The entrance of Bunker Cave is located approximately 100 m east of the entrance of B7-Cave, and the entrance of Hüttenbläserschacht Cave is located approximately 800 m west of the entrance of B7-Cave. The host rock of these caves is 700 m thick upper Middle Devonian massive limestone partly containing dolomitic veins (von Kamp & Ribbert, 2005). The glacial-interglacial climate changes and the corresponding mountain uplift during the Quaternary (von Kamp, 1972) resulted in several river terraces, which can be related to different cave levels (Dreyer et al., 2008). The cave passages are mainly developed along the predominant fracture orientation of NNW-SSE and WSW-ENE. B7-Cave was discovered in AD 1965 during road works, and the full length of 5100 m was discovered after AD 1987. The two stalagmites analysed in this study were sampled at the end of the 1990s from the Candle Hall in the north of B7-Cave with an approximately 50 m thick rock overburden (Niggemann et al., 2003), which is covered by up to 70 cm inceptisol/alfisol soil (Riechelmann et al., 2011) developed from loess (Wirth, 1972).

![Fig. 1. Map of the Remscheid-Altena-Anticline in the northern part of the Rhenish Slate Mountains of northwest Germany (area represented by box in topographic inset map of Germany; https://i.imgur.com/cmKD6UJ.jpg). The upper Middle Devonian massive limestone (grey shaded area in the map) and the location of B7-Cave are indicated. Modified from Riechelmann et al. (2011).](Image)
MATERIAL AND METHODS

Stalagmites B7-1 and B7-7
The stalagmites B7-1 and B7-7 grew on cave loam, which made the sampling quite easy by just tipping the stalagmites. Both stalagmites were cut longitudinally in two halves along their growth axes. The half of stalagmite B7-1 analysed in this study has a height of approximately 44 cm, and the half of stalagmite B7-7 has a height of approximately 62 cm (Fig. 2). The drip site above stalagmite B7-1 was inactive, and the drip site of stalagmite B7-7 was active at the time of sampling (Niggemann et al., 2003). Both stalagmites were dated with the $^{230}$Th/U-method using TIMS at the Heidelberg Academy of Sciences with 11 ages (B7-1) and 10 ages (B7-7) (Niggemann et al., 2003). Furthermore, the $\delta^{13}$C and $\delta^{18}$O values of both stalagmites were analysed at low-resolution with approximately 115 years per data point for B7-1 and 25 to 130 years per data point for stalagmite B7-7.

In the present study, both stalagmites were re-dated by the $^{230}$Th/U-method using a MC-ICPMS and their element concentrations were determined by LA-ICPMS. Furthermore, the thin sections of both stalagmites, which are available from the previous studies (Niggemann, 2000; Niggemann et al., 2003), were checked for their calcite fabric and any evidence of diageneis.

Fig. 2. Scans of stalagmites B7-1 (a) and B7-7 (b). The hiatuses indicated by the age model are marked. In addition, the lower part of stalagmite B7-7 (below the lowermost black line) is not included in the age model and has not been analysed for trace elements. Sampling locations and their corresponding $^{230}$Th/U-ages are indicated on both stalagmites.

$^{230}$Th/U-dating
Samples (120 to 300 mg) for $^{230}$Th/U-dating of stalagmites B7-1 and B7-7 were drilled with a handheld dental drill. They were dissolved in 7N HNO3 and a mixed $^{229}$Th-$^{231}$U-$^{236}$U spike was added (see Gibert et al., 2016, for details of the calibration of the spike). We used the same spike solution for all analyses with both MC-ICPMS machines and at both institutes. The U and Th fractions were separated by ion-exchange column chemistry (Edwards et al., 1987;
Yang et al., 2015). All 44 ages of stalagmite B7-7 and 7 ages of stalagmite B7-1 were analysed using a Nu Plasma MC-ICPMS at the Max Planck Institute for Chemistry, Mainz. Thirteen samples of stalagmite B7-1 were analysed using a Neptune Plus MC-ICPMS at the Institute for Geosciences, Mainz University. For technical MC-ICPMS details, see Obert et al. (2016). All ages are given in ka BP, referring to AD 1950. All 20 ages of B7-1 and 40 ages of B7-7 were used to generate the new age models using the StalAge algorithm (Scholz & Hoffmann, 2011). Four ages of B7-7 in the lowermost part (Fig. 2b) were not included in the age model due to no clear stratigraphic growth in this section of the stalagmite, which is probably related to growth of this calcite in a drip water pool within the cave loam.

LA-ICPMS analysis of trace element concentrations
The element concentrations of the two stalagmites B7-1 and B7-7 were determined with an Element 2 ICPMS equipped with a high-energy Nd:YAG UP213 laser ablation system with a wavelength of 213 nm at the Max Planck Institute for Chemistry, Mainz. The synthetic glass NIST SRM 612 was used as reference material for calibration (Jochum et al., 2011), and the USGS MACS-3, a pressed carbonate powder, for quality control (Jochum et al., 2012). The measured values of the USGS MACS-3 for the analysed elements are in agreement within uncertainty with the values in the GeoReM database (Jochum et al., 2005). The measurements along the growth axis of the stalagmites were performed as line scans with a laser beam spot size of 110 µm. The laser repetition rate was 10 Hz and the scan speed was 10 µm/s. The measured isotopes were \(^{25}\text{Mg}, ^{88}\text{Sr}, ^{137}\text{Ba}, ^{31}\text{P}, ^{67}\text{Zn}, ^{89}\text{Y}, \) and \(^{27}\text{Al}, \) which were normalised to \(^{43}\text{Ca} \) as an internal standard. The reproducibility based on the analyses of the homogeneous NIST SRM 612 was 6.5% for Mg, 1.8% for Sr, 3.3% for Ba, 6.0% for P, 4.0% for Zn, 4.4% for Y, and 5.8% for Al (1 RSD). For details of the method, see Jochum et al. (2012) and Mischel et al. (2017a).

Data processing
The element data series were smoothed with a 40-point running median to improve the signal-to-noise ratio. The smoothed data were standardised prior to principal component analysis (PCA) (von Storch & Zwiers, 2002; Navarra & Simoncini, 2010), which was performed with the software PAST3 (Hammer et al., 2001).

RESULTS
230Th/U-dating and growth of stalagmites B7-1 and B7-7
The StalAge model (Scholz & Hoffmann, 2011) for stalagmite B7-1 shows growth from 10.8 to 5.8 ka BP with an average 2σ-error of ± 0.4 ka and an average growth rate of 120 µm/a (Fig. 3a). Four ages in the upper 15 cm of the stalagmite have larger 2σ-errors between 1.4 and 4.0 ka BP (Fig. 3a), which is related to the correction accounting for detrital contamination. The generally low \(^{230}\text{Th}/^{232}\text{Th} \) activity ratios of stalagmites B7-1 and B7-7 reflect the elevated detrital content of these stalagmites (Supplementary Table S1).

The StalAge model (Scholz & Hoffmann, 2011) for stalagmite B7-7 results in three growth phases. Two ages are excluded by StalAge from the calculation and were determined as outliers. Furthermore, the four ages in the lower part of B7-7 were not utilised for the age model (Fig. 3b). The oldest growth phase of stalagmite B7-7 was from 11.0 to 6.2 ka BP with an average 2σ-error of ± 0.3 ka and an average growth rate of 110 µm/a. The youngest section of stalagmite B7-7 grew from 1.27 to 1.15 ka BP with an average
Elemental concentrations

The Mg and Sr records of stalagmite B7-1 show commonly decreasing long-term trends (Figs. 4a and b). Barium does not show this pronounced long-term trend, but does exhibit a positive correlation with Sr of $R^2 = 0.22\ (p < 0.001)$ (Figs. 4b and c). Phosphorus, Y, and Zn show positive correlations: $P$ and Zn $R^2 = 0.42$, $P$ and Y $R^2 = 0.37$, and $Z$ and Y $R^2 = 0.26$ (all p-values < 0.001) and exhibit common features, such as increased variability between 7.4 and 6.9 ka BP (Figs. 4d, e, and f). Aluminium shows pronounced spikes (Fig. 4g), which are partly also visible in the other elemental records (Fig. 4). The PCA of the element data of stalagmite B7-1 shows three groups, one with Mg, Sr, and Ba, the second with Al, and the third with Y, P, and Zn (Fig. 5a), which corresponds well with the patterns in the elemental records (Fig. 4).
Stalagmite B7-7 shows three growth phases, which do not show pronounced differences in the elemental concentrations except for Al (Fig. 6). The two younger growth phases of stalagmite B7-7 do not show detrital layers and are very clear (Fig. 2b), which is reflected by the very low Al concentration (Fig. 6g). As also seen in the element records of stalagmite B7-1, the spikes in the Al record in the oldest growth phase (Fig. 6g) are partly also occurring in the other element records (Fig. 6). The two younger growth phases of stalagmite B7-7 are too short to identify long-term trends (Fig. 6). In the oldest growth phase commonly decreasing long-term trends in Mg, Sr, and Ba are identified (Figs. 6a, b, and c). Strontium and Ba show positive correlations overall three growth phases ($R^2 = 0.69$, $p < 0.001$) (Fig. 6b and c), similarly as P, Y, and Zn ($p$ and Zn $R^2 = 0.28$, P and Zn $R^2 = 0.15$, Y and Zn $R^2 = 0.83$, all $p$-values $< 0.001$) (Fig. 6d, e, and f). The PCA of stalagmite B7-7 shows the same grouping as the PCA of stalagmite B7-1 (Fig. 5b).

**DISCUSSION**

**Comparison between the old and the new age model**

The age model of Niggemann et al. (2003) for stalagmite B7-1, based on 11 $^{230}$Th/U-ages measured by TIMS, indicated growth between 12.6 and 12.4 ka BP and between 9.6 and 6.0 ka BP with a hiatus in between (Fig. 3a). The $\sigma$-errors of these ages are relatively small, which is due to a different error propagation, which did not consider the uncertainty of the detrital correction. The re-dating of stalagmite B7-1 with 20 $^{230}$Th/U-ages measured by MC-ICPMS, in contrast, suggests continuous growth from 10.8 to 5.8 ka BP (Fig. 3a). The difference in the top ages is most probably due to the different calculation of the age models. The age model in this study is calculated with StalAge (Scholz & Hoffmann, 2011) and the age model in Niggemann et al. (2003) was calculated by linear interpolation. The hiatus indicated in B7-1 by Niggemann et al. (2003) corresponds with the lowest couple of detrital layers below the white/milky part in the lower quarter of the stalagmite (Fig. 2a). However, the new age below these detrital layers is 10.8 ± 1.7 ka BP, and the age above is 10.3 ± 0.3 ka BP, which does not indicate a hiatus within uncertainty (Fig. 3a). The ages below and above this couple of detrital layers in the study of Niggemann et al. (2003) are 12.4 ± 0.4 ka BP below and 9.6 ± 0.2 ka BP above, which indicated a hiatus. These samples in both studies were aligned to each other by the stratigraphy of stalagmite B7-1. The differences in distance from top (Fig. 3a) between the two studies are due to the sampling on different halves of the stalagmites, which have different total lengths. The half used in the study of Niggemann et al. (2003) has a total length of 46 cm, and the one used in this study only has a total length of 44 cm. This is because the slice used for the thin sections was cut from the half used in this study.

The age model of stalagmite B7-7 conducted by Niggemann et al. (2003) by linear interpolation shows growth from 17.6 to 16.7 ka BP, from 9.6 to 5.4 ka BP, and from 4.0 ka BP until sampling at the end of the 1990s (Fig. 3b). For these ages, the errors are relatively small due to the reasons explained above. We also measured one age with 17.6 ka BP in this “root”-like part of stalagmite B7-7. We excluded this lower part of the stalagmite from the age model and the interpretation (Figs. 2b, 3b) because this part of the stalagmite most probably grew below the cave loam level. It probably grew in a drip water induced depression (pool) in the cave loam, which then filled with calcite over time and later evolved to a candle like stalagmite. Such a formation may be associated with some carbonate rims growing at the water surface, carbonate rafts from the water surface subsiding to the ground of the pool, and carbonate growing from the irregular walls into the pool, which is not in agreement with the stratigraphic growth of a candle like stalagmite. Therefore, the ages in this part highly depend on the very complex growth structure and where the samples for dating were taken. Thus, we decided to use only the part of stalagmite B7-7 in which no cave loam is attached at the sites of the stalagmite (lowermost line in Fig. 2b) indicating a stratigraphic growth of the stalagmite above the cave loam level. The lowermost age above the “root”-like part of stalagmite B7-7 dated by Niggemann et al. (2003) was 16.7 ± 0.7 ka BP. The age determined herein at the corresponding distance from top is 11.2
± 0.9 ka BP. Furthermore, the hiatus detected above this age by Niggemann et al. (2003) is not visible in the new age model (Fig. 3b). The upper hiatus detected by Niggemann et al. (2003) corresponds with the hiatus we detected between 6.2 ka BP and 3.13 ka BP. However, these ages differ from those of Niggemann et al. (2003), most probably due to the differences in the calculation of the age models. In the uppermost section, Niggemann et al. (2003) analysed three ages and assumed constant growth until the day of sampling due to the active drip site above B7-7. We analysed six ages in this section, and the resulting age model indicates a further hiatus and cannot be brought in line with constant growth until the sampling date (Fig. 3b). Niggemann et al. (2003) assumed growth until sampling time because the corresponding drip site was monitored for one year and was continuously dripping and supersaturated with respect to calcite.

This particular case, that a stalagmite does not grow under an active and supersaturated drip site was also observed in the nearby Bunker Cave. Stalagmite Bu1 stopped growing at 0.14 ka BP (Fohlmeister et al., 2012) although the corresponding drip site TS 5 was actively dripping over seven years of monitoring and was always supersaturated with respect to calcite (Riechelmann et al., 2022). Why the stalagmites under these two drip sites do not grow further is unclear.

We conclude that in the older parts of the stalagmites, the previously published ages of Niggemann et al. (2003) have a tendency to be too old, whereas they have the tendency to be too young in the late Holocene part. The new age models presented in this study for the stalagmites B7-1 and B7-7 are based on a much higher number of \(^{230}\)Th/\(^{230}\)U-ages, increasing our confidence in the revised age model.

Fig. 6. Element proxy records of stalagmite B7-7 plotted against age for Mg (a), Sr (b), Ba (c), P (d), Y (e), Zn (f), and Al (g).
Trace element variations of the two speleothems and proxy identification

Aluminium is a proxy for detritus in speleothems, which is transported as particles, such as clay minerals, into the cave (e.g., Fairchild & Treble, 2009; Wassenburg et al., 2012). This is also obvious in the correlation of the detrital layers in stalagmites B7-1 and the oldest growth phase of stalagmite B7-7 (Fig. 2) with the peaks in the Al records (Figs. 4g and 6g).

Phosphorus, Y, and Zn form dense groupings in the PCAs (Fig. 5) and are positively correlated (see section elemental concentrations for R² values) in both stalagmites and all growth phases (Figs. 4 and 6 each d, e, and f). These three elements are predominantly transported as colloids, such as humic acid and organic substances, from the soil to the cave drip water (Borsato et al., 2007; Fairchild & Treble, 2009). Phosphorus originates from microbial breakdown of organic matter in the soil, and Y and Zn are adsorbed to these organic compounds (Borsato et al., 2007). Therefore, these three elements are often interpreted as vegetation productivity and soil microbial activity with increasing values of these elements induced by higher temperatures and/or more humid climate conditions and vice versa (Treble et al., 2003; Borsato et al., 2007; Fairchild & Treble, 2009; Wassenburg et al., 2012).

The NGRIP δ¹⁸O record representing northern hemisphere temperature (Fig. 7a) (Svensson et al., 2008) and the pollen concentrations from two Eifel maar lakes represent precipitation reconstructions (Fig. 7b) (Litt et al., 2009). For the first half of the Holocene, the NGRIP record (Svensson et al., 2008) is interpreted to reflect increasing temperatures from 11.0 to 9.0 ka BP whilst the pollen records are interpreted to reflect increasing precipitation from 11.0 to 8.5 ka PB (Fig. 7a and b). These increases in temperature and precipitation at the beginning of the Holocene should lead to an increase in vegetation density, vegetation productivity, and soil microbial activity. However, a potentially expected increasing long-term trend is not visible in the P records of both stalagmites (Figs. 4d and 6d). This may be related to the high number of detrital layers in the lower part of both stalagmites (Fig. 2) between 11.0 and 10.0 ka BP. In this section, the Al concentrations are also higher in both stalagmites (Figs. 4g and 6g). Phosphorus, as well as Y and Zn, could also be incorporated within detritus, which would result in detrital contamination of these element proxy records, overwhelming the other signals (Riechelmann et al., 2020). Furthermore, a lag in transport, storage in the soil, and complex recycling of P makes it complicated to interpret.

The second group of elements in the PCA analyses are Mg, Sr, and Ba, which do not group very closely (Fig. 5). These three elements are often interpreted as proxies for PCP, which occurs during drier conditions in air filled cavities above the cave and at stalactites where calcite precipitates (e.g., Fairchild et al., 2000; Treble et al., 2003; Johnson et al., 2006; Fairchild & Treble, 2009; Smith et al., 2009; Wassenburg et al., 2012, 2020). During this process, the Mg, Sr, and Ba to Ca ratios increase in the drip water and subsequently in the speleothem calcite (Fairchild et al., 2006). To test whether PCP is the major controlling factor for Mg and Sr in the speleothems, ln(Mg/Ca) can be plotted versus ln(Sr/Ca) and the regression calculated (Sinclair et al., 2012). The corresponding slopes should be between 0.71 and 1.45 (Sinclair et al., 2012; Wassenburg et al., 2020) if PCP was the major influencing factor for both elements. The calculation of these slopes results in 0.52 for stalagmite B7-1 and 0.37 for stalagmite B7-7. Although, the slopes are too shallow for a positive “Sinclair -test” (Sinclair et al., 2012; Stoll et al., 2012; Regattieri et al., 2016; Riechelmann et al., 2020; Wassenburg et al., 2020), PCP can still has an influence on Mg, Sr, and Ba, which is probably visible in the common long-term trends in Mg and Sr in B7-1 as well as Mg, Sr, and Ba in the oldest growth phase of B7-7 (Figs. 4a and b and 6a, b, and c).

In both stalagmites and all growth phases, Sr and Ba show a positive correlation with each other (see section elemental concentration for R² values) (Figs. 4 and 6 each b and c). This is most probably related to the dependency of the distribution coefficients of Sr and Ba on growth rate (Huang & Fairchild, 2001; Treble et al., 2005; Borsato et al., 2007; Warken et al., 2018). Since the distribution coefficient of Mg does not depend on growth rate, no correlation is detected between Mg and Sr as well as Mg and Ba (Figs. 4 and 6 each a, b, and c). Furthermore, the two fast growth phases of stalagmite B7-7 do not show higher Sr concentrations than the oldest growth phase of B7-7 (Fig. 6b), which would be expected due to their higher growth rate. This could be related to a change of the Sr supply from the soil (Fohlmeister et al., 2012) or, more probably, due to a stronger influence of PCP on the Sr in the first half of the Holocene increasing the Sr/Ca ratio in the stalagmite more than during the two younger, faster growing phases. This is supported by the common long-term trends of Mg and Sr in stalagmite B7-1 (Fig. 4a and b) and of Mg, Sr, and Ba in the oldest growth phase of stalagmite B7-7 (Fig. 6a, b, and c). However, these analyses show that Sr and Ba are both influenced by more than one factor, growth rate and PCP, and the contribution of both is possibly not stable over time. The growth rate relation of Sr and Ba and the decoupling from Mg was also identified in other speleothems studies (Treble et al., 2003; Regattieri et al., 2016; Mischel et al., 2017b; Warken et al., 2018) and especially in the stalagmites from nearby Bunker Cave (Waltgenbach et al., 2020, 2021). In the seven-year monitoring study from Bunker Cave, it is clearly visible in the Ca, Mg, and Sr concentrations of the drip waters that PCP is a major controlling factor for these elements for most of the drip sites. The increasing Mg/Ca and Sr/Ca ratios over the seven-year monitoring period are clearly related to decreasing drip rates and therefore, more PCP in the karst system (Riechelmann et al., 2022). During precipitation of stalagmite calcite in this cave system, growth rate seems to outcompete the PCP influence for Sr and Ba (Waltgenbach et al., 2020, 2021). However, Mg could still be influenced to a major extent by PCP and serve as a strong proxy for past precipitation/infiltration as indicated by the studies from nearby Bunker Cave (Fohlmeister et al.,...
temperatures from 11.0 to 9.0 ka BP (Svensson et al., 2012; Weber et al., 2018; Waltenbach et al., 2020, 2021) and other caves (Treble et al., 2003; Regattieri et al., 2016; Mischel et al., 2017b; Warken et al., 2018). Furthermore, Mg could also be influenced by other factors, such as incongruent calcite and/or dolomite dissolution. Incongruent dolomite dissolution was identified in the long-term monitoring of nearby Bunker Cave, due to the dolomitic veins in the host rock (Riechelmann et al., 2022). During drier climate conditions, the seeping water has a longer residence time in the host rock, which allows to dissolve more dolomite and, therefore, Mg from the dolomite because dolomite has a much higher dissolution capacity than limestone (Fairchild et al., 2000). This increases the Mg concentration in the drip water and subsequently in the stalagmite. Incongruent dolomite dissolution cannot be detected with the PCP Sinclair test (Sinclair et al., 2012) because both processes produce similar slopes (Wassenburg et al., 2020). Therefore, it is not possible to disentangle the different processes from each other. As discussed above, Sr is also influenced by the growth rate. However, in case of drier climate conditions, all these factors drive the Mg concentration to higher values (e.g., Fairchild et al., 2000; Sinclair et al., 2012; Wassenburg et al., 2020) and to conclude, the Mg records of the B7-Cave stalagmites are a proxy for past precipitation/infiltration.

Interpretation of past climate variability

Fast growth phases of stalagmite B7-7 during Early Medieval Period and Late Bronze Age

The youngest growth phase of stalagmite B7-7 from AD 682 to 804 (123 years) falls within the early Medieval Period, and the second growth phase from 1177 to 910 BCE (267 years) falls within the Late Bronze Age. Why stalagmite B7-7 just grew during these short time intervals with a fast growth rate is most probably due to drip site specific effects, which are hard to solve. In contrast, stalagmite Bu4 from nearby Bunker Cave grew continuously over more or less the last 8.2 ka BP (Fohlmeister et al., 2012) under the same climate conditions as the B7-Cave stalagmites. However, such short and fast-growing phases as these two of stalagmite B7-7, cannot give profound insights into past climate due to their short duration and large age uncertainties, which span half of their growth interval. On the other hand, their short growth periods do not provide a longer context of proxy records.

Early to Mid-Holocene

The oldest growth phase of stalagmite B7-7 from 11.0 to 6.2 ka BP and the growth phase of stalagmite B7-1 from 10.8 to 5.8 ka BP span nearly the first half of the Holocene. Both show decreasing long-term trends in their Mg records with time (Fig. 7e). This decrease is about 45% for stalagmite B7-1 and about 30% for stalagmite B7-7, which is significantly higher than the analytical uncertainty. This indicates increasing precipitation/infiltration over this time period. The NGRIP record (Fig. 7a) shows increasing temperatures from 11.0 to 9.0 ka BP (Svensson et al., 2008), which coincides with the pollen precipitation reconstructions from Meerfelder Maar and Holzmaar (Eifel) showing increasing precipitation from 11.0 to 8.5 ka BP (Fig. 7b). The stacked δ18O record (Fig. 7a) from nearby Bunker Cave also reflects this change from colder and drier to warmer and wetter winter climate from 10.7 to 8.5 ka BP (Fohlmeister et al., 2012). Furthermore, the Mg/Ca records of stalagmites Bu2 and Bu4 from Bunker Cave also show the decreasing long-term trend with time (Fig. 7d) as the Mg records of the B7-Cave stalagmites. Fohlmeister et al. (2012) interpreted this decreasing trend as a gradual leaching of Mg due to decalcification of the loess covering the cave during the last Glacial, even if they emphasized that, it cannot prove that the Mg/Ca ratio of the loess was higher than that of the Devonian limestone host rock. Due to the same decreasing trend with time recorded in the Mg records of the two B7-Cave stalagmites and the agreement with other records showing changes to warmer and wetter climate conditions during this time, it is likely that the decreasing long-term trend with time in the Mg records is induced by decreasing PCP related to the increase of precipitation/infiltration.

The Mg record of stalagmite HBSH 4 from nearby Hüttenbläserschacht Cave shows an opposite increasing long-term trend with time (Fig. 7c). The substantially higher Mg concentrations in this stalagmite are probably due to a larger dolomite lens above Hüttenbläserschacht Cave (von Kamp & Ribbert, 2005). Weber et al. (2021) analysed several speleothem proxy records from Hüttenbläserschacht Cave and compared them with the Bunker Cave records and found that they show opposite trends during the Holocene. They concluded that the proxies of the stalagmites from Hüttenbläserschacht Cave are strongly influenced by cave or even drip site-specific factors and not by super-regional climate variability. Such site-specific factors could also have an influence on the Mg records of the two B7-Cave stalagmites because they show differences in the short-term variability even if considering the uncertainties of the age models ± 0.4 ka for B7-1 and ± 0.3 ka for B7-7. Furthermore, the analytical uncertainty of the Mg concentrations of 6.5% (1 RSD) has to be taken into account when the short-term variability is considered.

Comparing the results of this study with a speleothem record from northern Spain, which is influenced by the North Atlantic, this Spanish speleothem record also shows a general wetting trend from the beginning of the Holocene until 8.8 ka BP (Smith et al., 2016). In addition, a gridded pollen data set, covering the whole of Europe, indicates an increase in winter and annual precipitation in Central Europe during the early Holocene (Mauri et al., 2015). They also compared their findings (nearest grid point) with the Bunker Cave 818O record and concluded a good agreement for winter precipitation. Therefore, the Mg records of the B7-Cave stalagmites confirm this picture of increasing precipitation during the early Holocene. To conclude, the Mg records of the two B7-Cave stalagmites show decreasing long-term trends with time, which are interpreted as decreasing PCP induced by increasing precipitation/infiltration during Early to Mid-Holocene, which is in line with other precipitation records.
Fig. 7. a) The $\delta^{18}$O stack record from Bunker Cave (Fohlmeister et al., 2012) and the NGRIP $\delta^{18}$O record (Svensson et al., 2008). b) Pollen records from two Eifel maar lakes (Litt et al., 2009). c) The Mg record of stalagmite HBSH 4 from Hüttenbläserschacht Cave (Weber et al., 2021). d) The Mg/Ca ratio records of two stalagmites from Bunker Cave (Fohlmeister et al., 2012). e) The Mg records of stalagmite B7-1 and the oldest growth phase of stalagmite B7-7. Please note that the Mg axes are inverse.
CONCLUSIONS

The re-dating of the two B7-Cave stalagmites with a state-of-the-art mass-spectrometer and considerably more ages highly improved the age model of both stalagmites. However, the relatively high content of detrital material in stalagmite B7-1 and in the oldest growth phase of B7-7 still causes considerable age uncertainties in some parts of the stalagmites.

Trace elements (Mg, Sr, Ba, P, Y, Zn, Al) were measured at high resolution for both stalagmites. Aluminium is a proxy for detritus, and high concentrations of Al in both stalagmites corresponds with visible detrital layers. Phosphorus, Y, and Zn can be influenced by various parameters, and the signal is affected by detrital contamination. Therefore, none of these three elements can be considered as a clear climate proxy. Sr and Ba show positive correlations in all growth phases of both stalagmites. This indicates that Sr and Ba are influenced by growth rate. The negative result for the PCP Sinclair test suggests that it is unlikely that both Mg and Sr are influenced by PCP. For Sr the growth rate outcompetes the PCP influence. However, Mg is related to PCP and/or incongruent dolomite dissolution and is therefore a proxy for past changes in precipitation/infiltration.

The Mg records of the two short growth phases of stalagmite B7-7 are not easy to interpret in terms of past climate variability due to their short growth and the relatively large age uncertainties. The Mg records of stalagmite B7-1 and of the oldest growth phase of B7-7 show decreasing long-term trends from Early to Mid-Holocene indicating a progressive increase in precipitation. This is in line with the Mg record from nearby Bunker Cave as well as precipitation reconstructions based on pollen records from Eifel Maar lakes and other stalagmite and pollen studies from Central Europe.

ACKNOWLEDGMENTS

D. F. C. Riechelmann and D. Scholz are grateful to the Deutsche Forschungsgemeinschaft (DFG) for funding of the projects RI 2136/2-1, RI 2136/2-2, ScoH 1274/11-1, and INST247/889-1. We thank the “Speläogruppe Letmathe e.V.” for their support during LA-ICPMS measurements by multi-collector inductively coupled plasma mass spectrometry. Earth and Planetary Science Letters, 371-372, 82-91. https://doi.org/10.1016/j.epsl.2013.04.006


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