

Article

StalGrowth—A Program to Estimate Speleothem Growth Rates and Seasonal Growth Variations

Rolf Vieten ^{1,*} and Francisco Hernandez ²¹ Department of Marine Sciences, University of Puerto Rico, Mayaguez 00680, Puerto Rico² Department of Geology, University of Puerto Rico, Mayaguez 00680, Puerto Rico; Francisco.Hernandez@upr.edu

* Correspondence: rolf-martin.vieten@upr.edu

Abstract: Speleothems are one of the few archives which allow us to reconstruct the terrestrial paleoclimate and help us to understand the important climate dynamics in inhabited regions of our planet. Their time of growth can be precisely dated by radiometric techniques, but unfortunately seasonal radiometric dating resolution is so far not feasible. Numerous cave environmental monitoring studies show evidence for significant seasonal variations in parameters influencing carbonate deposition (calcium-ion concentration, cave air pCO₂, drip rate and temperature). Variations in speleothem deposition rates need to be known in order to correctly decipher the climate signal stored in the speleothem archive. StalGrowth is the first software to quantify growth rates based on cave monitoring results, detect growth seasonality and estimate the seasonal growth bias. It quickly plots the predicted speleothem growth rate together with the influencing cave environmental parameters to identify which parameter(s) cause changes in speleothem growth rate, and it can also identify periods of no growth. This new program has been applied to multiannual cave monitoring studies in Austria, Gibraltar, Puerto Rico and Texas, and it has identified two cases of seasonal varying speleothem growth.

Keywords: speleothem; software; cave monitoring; carbonate precipitation; seasonal bias; seasonality



Citation: Vieten, R.; Hernandez, F. StalGrowth—A Program to Estimate Speleothem Growth Rates and Seasonal Growth Variations. *Geosciences* **2021**, *11*, 187. <https://doi.org/10.3390/geosciences11050187>

Academic Editors: Philippe Claeys and Jesus Martinez-Frias

Received: 31 December 2020
Accepted: 21 April 2021
Published: 27 April 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Speleothems (e.g., stalagmites) are secondary deposits occurring in karst settings. Most speleothems are made of carbonate which precipitates after CO₂-enriched soil waters have entered an open interior space such as a cave, and diffusive CO₂ degassing causes the solution to become oversaturated in calcium carbonate. Speleothems are important geochemical deposits to reconstruct paleoclimate changes [1–3] because they provide long (>100 ky) environmental records that can be sampled at very high resolutions and are generally unaffected by post-depositional diagenetic alteration [1]. Highly reliable growth-age models are based on accurate and precise absolute ²³⁰Th/U-dating [4–7]. A wide range of geochemical proxies, e.g., stable oxygen isotope ratios and trace element ratios, have been interpreted as paleoclimate proxies in many settings [8–14].

However, interpretation of these proxies is not always straightforward and the timing of carbonate precipitation has to be known. State of the art radiometric dating methods do not allow sub-annual resolution. Drip site monitoring inside the cave system prior to speleothem based paleo-climate reconstruction plays a key role in investigating seasonal effects on speleothem deposition [3,15–17]. Many studies have shown that seasonality is a common cave climate feature [18–24]. Seasonal variations can occur in the cave atmosphere, hydrology and in the drip water chemistry, and they can cause seasonal variations in speleothem growth rates [1,25–29]. A global cave ventilation model predicts that speleothem growth varies by season at most sites [15]. Seasonal speleothem growth can bias the recorded climate signal towards the season of fast growth (seasonal bias—the fraction of speleothem growth occurring during the fast growth season) and might lead

to aliasing, if not resolved at sufficiently high resolution [15,24,30,31]. In extreme cases, speleothems might only grow during one season (fast growth season), similar to tree rings, showing a seasonal bias of 100%.

Stalagmite growth is related to the oversaturation of the drip water. It depends on the water infiltration at the surface, the evolution of the seepage water from the surface into the cave, the cave atmosphere and the drip dynamic at the stalagmite's apex [3,32,33]. Variations in drip rate change the stalagmite growth rate as well. Decreasing drip rates slow the calcite growth [29]. Thus, the simplest interpretation is to relate faster stalagmite growth to higher drip rates during wetter climate conditions; however, the system is not this simple. Speleothem growth is a complex interaction of multiple parameters. A study in Florida highlights the growth rate complexity, identifying that stalagmites grow faster during drier conditions [34]. In certain locations, growth rate variations and hiatuses in speleothems are caused by climatic variations on the surface, e.g., changes in precipitation amount and the extension of permafrost [3,34–36]. It is obvious that the stalagmite growth rate response to surface processes is site dependent. The theory of carbonate precipitation inside a cave and speleothem formation is well understood, and parameters controlling the rate of speleothem growth are known [27,28]. In certain cases, the growth rate alone might be another climate proxy, providing valuable information to aid reconstruction of the past climate [27,35]. Numerous cave studies are monitoring these parameters at seasonal or higher resolution. However, presently, there is no straight-forward way to calculate theoretical speleothem growth rates based on cave monitoring observations. Programs have been developed to model the age depth relation in speleothems based on U-Th dates [37,38]. Another model [39] exists to reconstruct the three-dimensional shape of speleothems without accounting for detailed cave and drip parameter monitoring data. An earlier study [40] shows the difficulty of calculating speleothem growth rates based on cave monitoring observations using existing equations without a program to quickly calculate speleothem growth rates. StalGrowth is a new program filling this gap. StalGrowth uses cave monitoring observations as input data and quickly calculates the predicted growth rates, providing an easy to use tool to shed lights into the speleothem growth characteristics at every site of interest.

StalGrowth has many features to investigate speleothem growth characteristics. It calculates the seasonal and multi-annual growth rate time series, which allows correlation with surface processes such as rain amount, temperature or vegetation activity. Most settings are expected to have seasonal variations in carbonate precipitation [15]. StalGrowth can quantify a seasonal growth bias in speleothems, allowing the climate reconstruction to account for the depositional bias. In the case that the growth rates appear constant over time or vary without any relation to seasons, the analysis via StalGrowth can be used as evidence that there is no bias in the speleothem record related to seasonal growth.

2. Materials and Methods

The program StalGrowth is a free online program. It can be accessed at <https://github.com/RolfVieten/StalGrowth/releases/latest> (accessed on 23 April 2021). From there the source code can be downloaded. It is coded in C++ using the QT Framework which allows you to compile it for various different operating systems. It is free and open source under the LGPL License v2.1. The supplementary material provides a detailed instructions on how to use StalGrowth.

StalGrowth is a 3-step process to calculate the seasonal growth bias in speleothems. In the first step, StalGrowth computes theoretical growth rates based on cave monitoring measurements and illustrates cave measurement data and results graphically. In the second step, seasonal growth rates are calculated and tested for significant differences between the seasons. In the third step, the seasonal growth bias is estimated. The program features a fast calculation of theoretical speleothem growth rates and seasonal growth averages, significance testing of seasonal variations in growth rates, and quantification of the seasonal growth bias. The program is based on cave monitoring observations. The uncertainties of

individual measurements are propagated to the average seasonal growth rate calculation. Input parameters are: the CO₂ concentration in the cave atmosphere (pCO₂), the incoming concentration of Ca²⁺-ions in the drip water (cCa), drip water temperature (T), drip-interval (Δd) and water-film thickness (δ). StalGrowth is equipped with a graphic display of input parameters and calculated growth rates to aid the user's interpretation of cave monitoring results and growth rate variations. The user can set individual dates for summer and winter growth seasons to account for lag-times and dynamic cave systems which have variations that do not overlap with the common winter and summer season. A summer–winter season marker highlights data points belonging to each season. Data can be directly read from the graphic display using an interactive date and growth rate read-out assistant, and growth rate calculation results can easily be exported in common file formats. The advanced user can manipulate and improve the StalGrowth algorithm as future scientific advances promise better theoretical understanding of speleothem growth. To do so, StalGrowth is stored on GitHub which is an interactive platform that safeguards the original version of StalGrowth and allows the advanced user to add features and change the StalGrowth source code. Detailed instructions on how to use and prepare the input data can be found in the supplementary material of this paper.

2.1. Growth Rate Calculation

Growth rate calculation using StalGrowth accounts for known parameters affecting the carbonate growth rate (pCO₂, cCa, T, Δd and δ). Their chemo-physical relations have been well investigated [25–28]. All parameters necessary to calculate theoretical growth rates can be measured inside the cave and sophisticated cave monitoring programs document these parameters periodically [20,22,24,25,38–42].

StalGrowth calculates speleothem growth rates based on the growth rate Equation (1), [27]) for each time where cave monitoring observations exist. Equation (1) includes the apparent Ca concentration cCa_{app} and the kinetic reaction constant α. Baker et al. (2014) [25] provide an empirical equation to calculate cCa_{app} based on cave atmospheres pCO₂ and T (Equation (2)). A function has been fitted to kinetic rate constant values [26]. The fitted function (Equation (3); [26,43]) determines α for a given cave temperature. The equations are shown below:

Equations:

$$\text{Growth rate} = 1.17410^3 (c\text{Ca} - c\text{Ca}_{\text{app}}) \delta / \Delta d (1 - e^{(-\alpha/\delta \Delta d)}) \text{ m/yr (Dreybrodt, 1999)} \quad (1)$$

with:

$$c\text{Ca}_{\text{app}} = 1/2 ((5.872 p\text{CO}_2^{0.2526}) + (-0.0167T + 1.5146)) \text{ mol/m}^3 \text{ (Baker et al., 2014)} \quad (2)$$

and:

$$\alpha = (0.52 + 0.04T + 0.004T^2) \times 10^{-7} \text{ m/s}^1 \text{ (Baker et al., 1998, Dreybrodt, 2012)} \quad (3)$$

where: pCO₂ = partial pressure of CO₂ in cave atmosphere (atm)

cCa = incoming Ca²⁺-concentration (in mol/m³)

cCa_{app} = apparent Ca²⁺-concentration (in mol/m³)

δ = thickness water-film on top of stalagmite (in m)

Δd = drip interval (in s)

α = kinetic reaction constant (in m/s)

T = water temperature (°C)

2.2. Propagation of Uncertainties

StalGrowth considers uncertainties during the growth rate calculation. The uncertainties of each parameter (Equations (1)–(3)) are included in the growth rate calculation. They depend on the measurement technique and device used. The user can edit individual

uncertainty values for each measured parameter (see section in the Supplement: Input Data Preparation and Upload). The positive and negative growth rate errors are calculated via inserting the extreme values defined by the parameter's error in such a manner that StalGrowth calculates the minimal and maximal growth rate. The reported growth rate error is the deviation between the extreme and median values.

2.3. Seasonal Growth Rates and Significant Seasonal Differences

StalGrowth includes a test for significant differences between the seasons. Student's *t*-test for unequal variance and unequal sample size (also called Welch's *t*-test) is used to calculate the probability that differences between seasonal growth rate averages are due to chance. The *t*-test is calculated for unequal sample sizes because the number of site visits can vary per season, and it assumes unequal variances because variance per season is unknown and might be different. Ultimately, the user can decide which data point should be included in each season (see instructions in the supplement for more detail).

2.4. Outliers

Outliers should be removed from the starting data set or be excluded in the bias calculation (see Supplementary Material's section Statistics—Calculating the Seasonal Growth Bias) because they falsify the results. Outliers are data points which deviate strongly from the general trend of the data and usually result from contamination during sampling, during transport and/or during analysis of drip water samples or due to erroneous measurements of the cave atmosphere or other unknown error sources. The identification of outliers is difficult and has to be done with caution. In cases where there is considerable suspicion that the data set contains outliers, different techniques to identify outliers can be applied. The outlier identification can be based on the user's experience and the user's inspection of the input and results data. If a data point does not follow the continuous trend of the overall data it might be an outlier, especially if its absolute value significantly exceeds the rest of the data. Before removing the suspected outlier, the weather data of a nearby weather station should be checked, as extreme climate events such as droughts, heat waves or hurricanes, could be a natural cause for unexpected observations and might reach the cave with a known or unknown delay time. The user is advised to consider the use of sophisticated outlier detection methods to pretreat the input data. Possible methods to identify outliers can be found in the according literature [44–47].

2.5. Case Studies

Four cave monitoring studies have been chosen as case studies to show the applicability of StalGrowth. The case study sites needed to fulfill the following criteria: 1. A monitoring period of at least two years with seasonal or higher monitoring intervals to allow the study of reoccurring seasonal growth patterns; 2. The published cave monitoring studies needed to provide information about all parameters ($p\text{CO}_2$, $c\text{Ca}$, T , Δd) needed to run StalGrowth. Four cave sites were identified which fulfilled these requirements and which are located in different geographical settings. These caves are Obir Cave, Austria [19], located in an alpine environment at 2139 m, Inner Space Cavern, Texas [24], located in central Texas, St. Michaels Cave, located on Gibraltar [21] and Larga Cave, located on the tropical island of Puerto Rico [23,41]. Water film thickness on the top of the stalagmite's apex (δ , Equation (1)) is a difficult parameter to measure inside a cave, so we used a value of 0.01 cm for all cave StalGrowth models because it is a common value for water film thickness observed in speleothem-like situations [48].

3. Results

Cave monitoring provides key information to interpret speleothem records correctly. Over the past decades, many multiannual cave monitoring studies have documented cave environmental changes over time at different locations. Three multi-annual studies published all environmental parameters to calculate speleothem growth rates using StalGrowth.

The monitoring data comes from Obir Cave, Austria (Figure 1; [19]), Inner Space Cavern, Texas (Figure 2; [24]) and St. Michaels Cave, Gibraltar (Figure 3; [21]). StalGrowth results calculated for each cave are shown below, followed by the programs application to 2 drip sites inside Larga Cave, Puerto Rico (Figures 4 and 5; [23,41]).

- Obir Cave, Austria

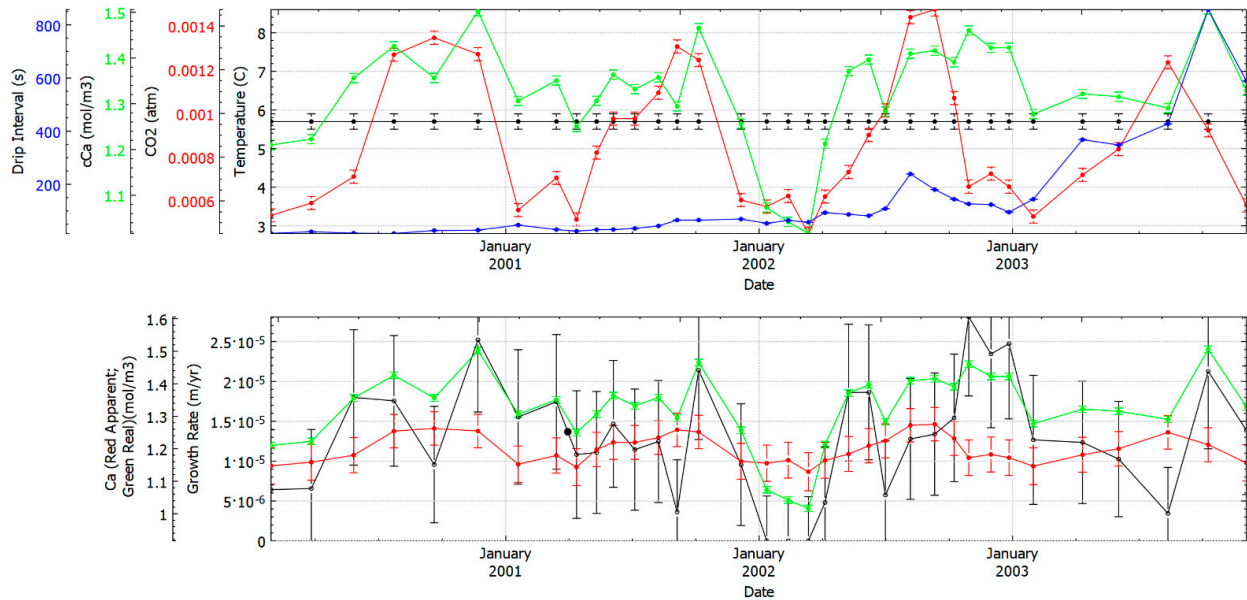


Figure 1. Growth rate calculation in Obir cave. The top plot shows the input parameters (temperature in black, cave pCO₂ concentration in red, drip water Ca concentration (cCa) in green and drip interval in blue). The bottom plot shows the output of StalGrowth: the calculated growth rate (black) and the apparent Ca-concentration (red), compared to the real calcium concentration (green).

- St. Michaels Cave, Gibraltar

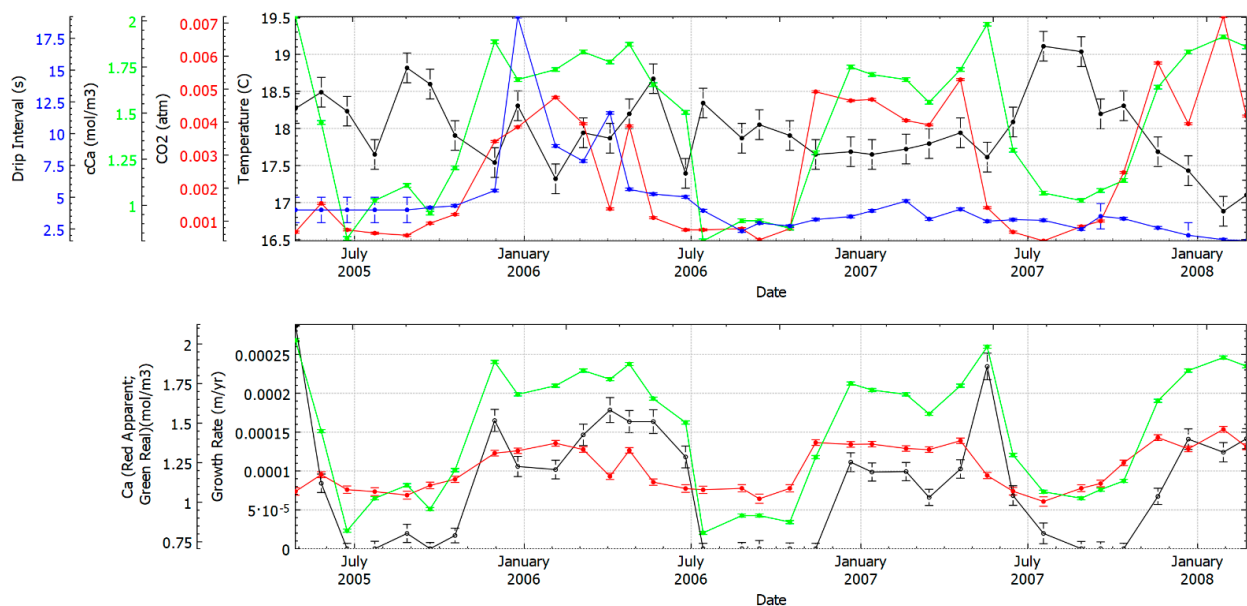


Figure 2. StalGrowth applied to St. Michaels Cave. The top plot shows the input parameters and the bottom plot shows the output of StalGrowth (see Figure 1 for more detail).

• Inner Space Cavern, Texas

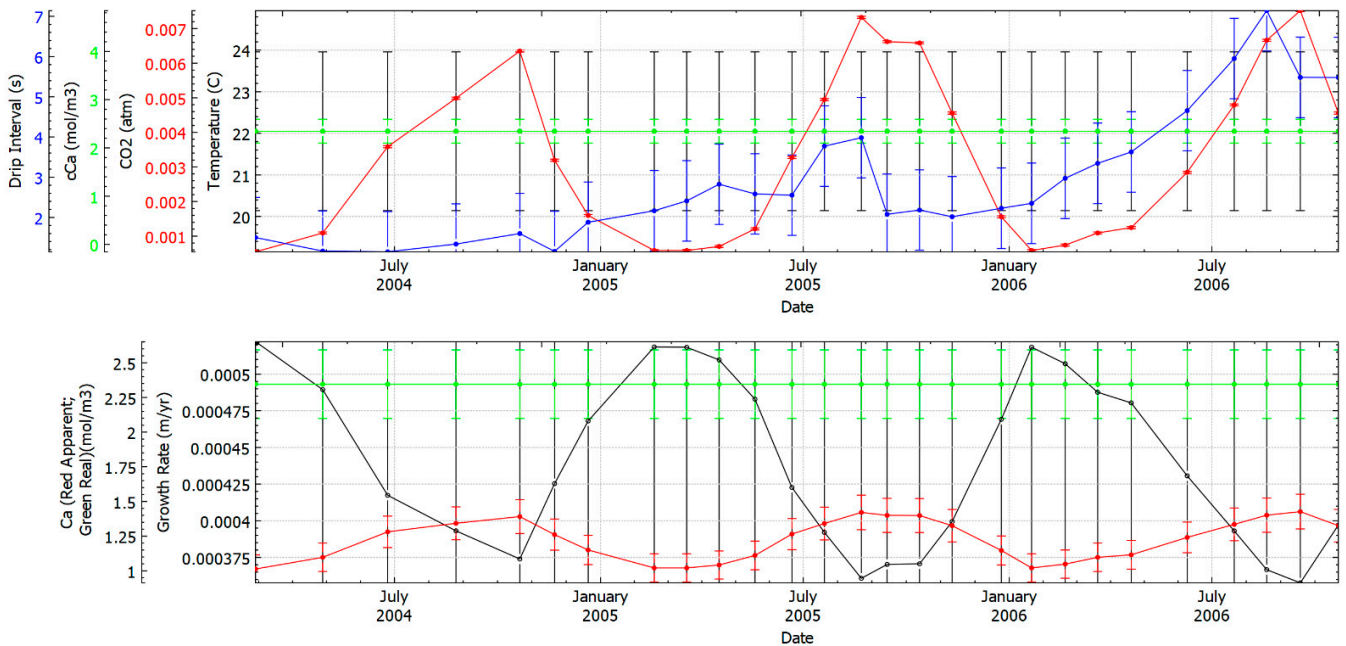


Figure 3. StalGrowth applied to Inner Space Cavern. The top plot shows the input parameters and the bottom plot shows the output of StalGrowth (see Figure 1 for more detail).

• Larga Cave, Puerto Rico

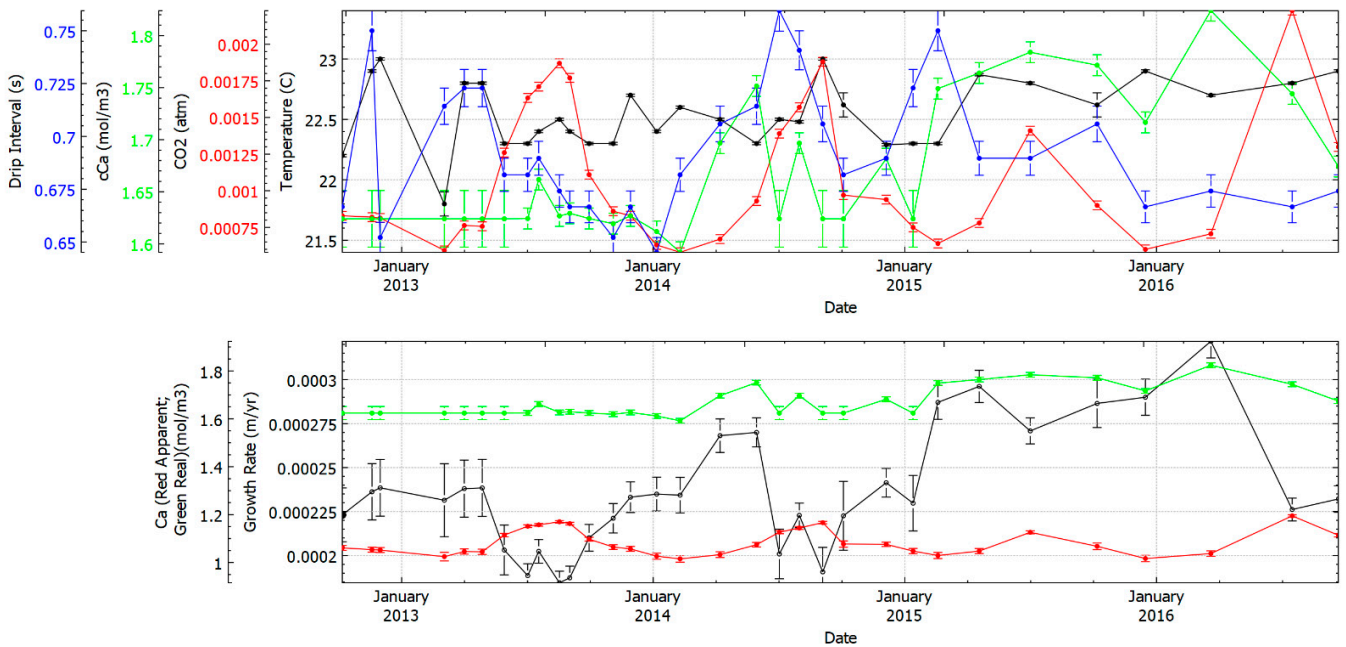


Figure 4. StalGrowth applied to Larga Cave drip site LA2. The top plot shows the input parameters and the bottom plot shows the output of StalGrowth (see Figure 1 for more detail).

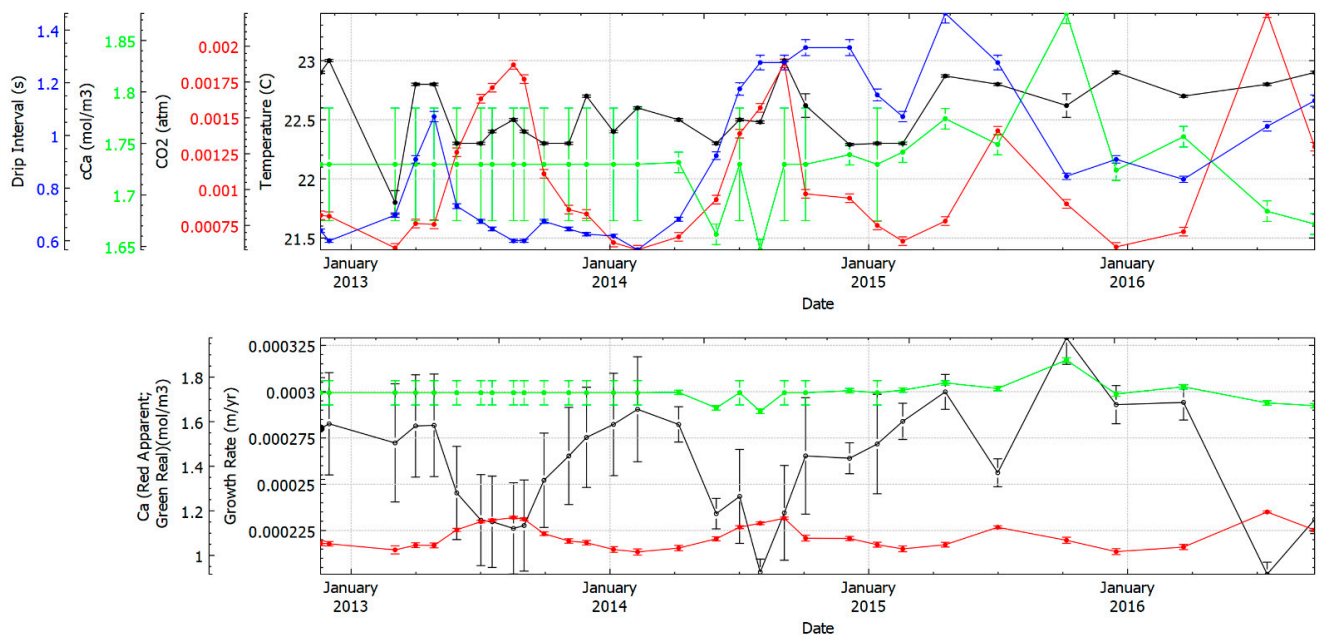


Figure 5. StalGrowth applied to Larga Cave drip site LA4. The top plot shows the input parameters and the bottom plot shows the output of StalGrowth (see Figure 1 for more detail).

In Obir Cave (Figure 1) the modeled growth rate usually varied between 0.8×10^{-5} to 2.8×10^{-5} m/yr. It closely followed the Ca concentration of the drip water (green line). In winter 2001/02 a period of no growth occurred. During this time period the drip water Ca-concentrations fell below the apparent Ca-concentration. In St. Michaels cave (Figure 2) no growth occurred in the late summer, while growth rates of 0.2×10^{-3} m/yr were reached during the rest of the year. Similar to Obir cave, the growth rate closely followed the Ca-concentration of the drip water. Inner Space Cavern (Figure 3) showed the fastest modeled growth of all chosen caves, varying between 0.35×10^{-3} to 0.52×10^{-3} m/yr. Here the Ca-concentration was constant at 2.3 mol/m^3 , the highest value of all monitored caves. Variations in modeled growth rates correlate to $p\text{CO}_2$ variations where low growth rates occurred during high $p\text{CO}_2$ concentrations. In Larga Cave (Figures 4 and 5) modeled growth rates varied between 0.18×10^{-3} to 0.32×10^{-3} m/yr. Both drip sites had similar variations in cave environment and modeled growth rates. From 2013 to 2015, seasonal growth occurred, closely following the seasonal $p\text{CO}_2$ cycle at drip site LA2 (Figure 4) and LA4 (Figure 5). Then, in 2016, the Ca-concentration increased while the maximal $p\text{CO}_2$ value was lower than in the years before and the seasonality of carbonate precipitation was not visible in the modeled StalGrowth result. The growth rate variability appeared to respond to both variations in cave air $p\text{CO}_2$ and Ca-concentration of the drip water.

Two examples of seasonal growth are St. Michaels Cave (Figure 2) and Inner Space Cavern (Figure 3). Here we applied the seasonal growth function to show how a seasonal growth bias can be estimated using StalGrowth. The simple summer–winter period does not represent the seasonal growth in both caves, because in both caves seasonality appears to be shifted by about 2 months compared to the seasons defined by the equinoxes. Thus, the custom season function has been applied to investigate the seasonal growth cycle. With the manual read out tool we estimated the turning point to be around the 1st of December and defined the growth season for both caves to be similar from 1st of December to 1st of June as shown in Figures 6 and 7. In St. Michaels cave we used the user option to change two data points to the fast growing season (November 2005 and June 2006, blue points in Figure 6) because their values belonged to the fast growth season, which appeared to last longer in 2005/06 than the custom user defined season (Figure 6).

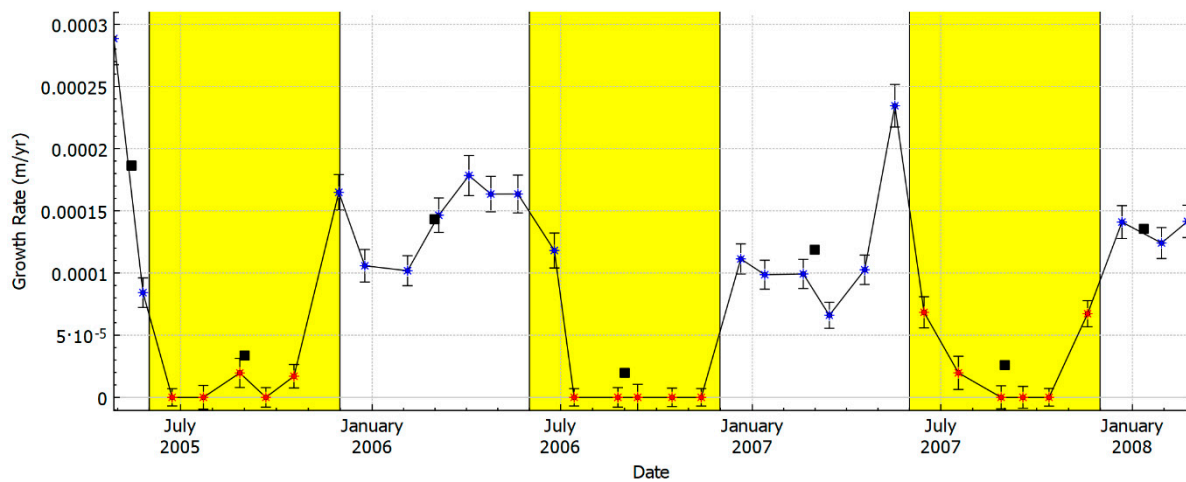


Figure 6. The user specified seasons for St. Michaels Cave, Gibraltar. Yellow shows the season of slow growth. See supplementary material for details.

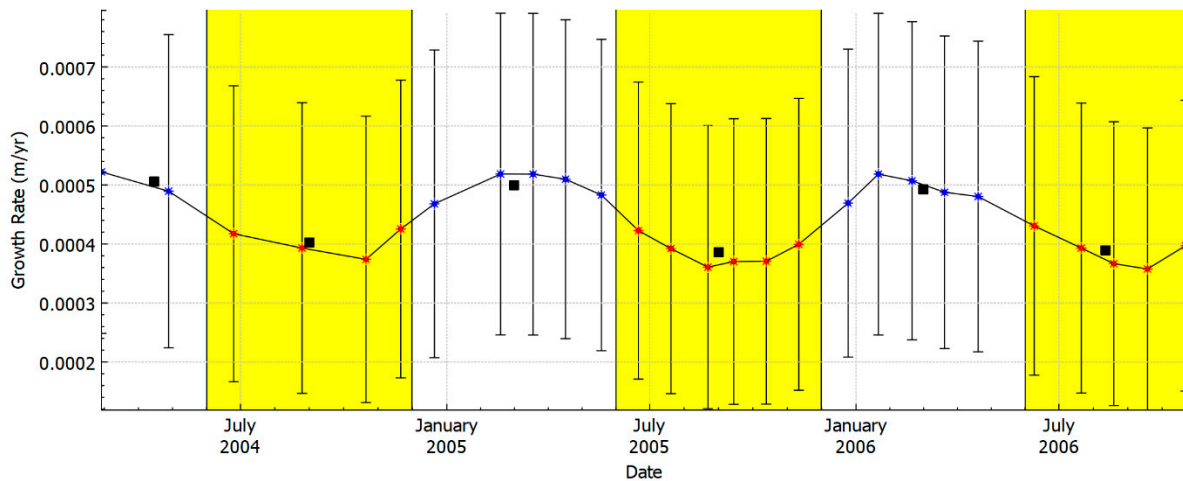


Figure 7. The user specified seasons for Inner Space Cavern, Texas. Yellow shows the season of slow growth. See supplementary material for details.

The statistical analysis performed by StalGrowth shows that speleothem growth was seasonal in St. Michaels Cave and Inner Space Cavern. The user defined fast growing season was significantly different from the slow growing season in both cases, because the p -value (1.9×10^{-10} and 2.9×10^{-12} , respectively) is smaller than 0.05; we can reject the hypothesis that both means are similar and can conclude that there are seasonal differences in speleothem growth rate. Using the Seasonal Bias calculation tool, we estimated the seasonal growth fraction at both locations. In St. Michaels Cave the mean growth rate during the fast growth season was 0.14 mm/yr while during the slow growing season no growth occurred. Here, 99% of the growth took place during the fast growth season. In Inner Space Cavern, growth occurred during both seasons; the mean value during the fast-growing season was 0.49 mm/yr and the mean value for the slow growing season was 0.39 mm/yr. Using the seasonal bias function of StalGrowth we estimated the seasonal growth bias to be 55%, meaning that in Inner Space Cavern 55% of calcite precipitation occurred during the fast growth season, while in St. Michaels Cave 91% of the carbonate growth occurred during the fast growth season.

4. Discussion

StalGrowth results have shown that speleothem growth can be seasonal, similar to other climate archives such as tree rings. The seasonal bias is well known in the tree ring climate records because they do not record during the time of non-growth [49]. Thus, tree ring climate records are biased towards the climatic signals occurring during the growth season, and do not record any climate signals during winter, which corresponds to the no growth season. Similarly, speleothems can be biased towards the growth season. If this is not considered, climate reconstructions are biased, possibly leading to wrong conclusions. In the case of speleothems, growth seasonality is rarely considered in climate reconstructions, possibly because the growth rate variations are linked in a complex way to the cave conditions. Secondly, the seepage water transport is another complex system because it can be stratified or fast. Transmitting individual rain events into the cave or the seepage water can be well mixed. In the scenarios of fast or stratified seepage flow, it is important to know when the speleothem is growing to identify if rain events belonging to one season are dominantly recorded by the seasonal growing speleothem. Using StalGrowth and detailed cave observations it is now possible to quickly see whether or not a speleothem has a seasonal growth pattern. Previously, more unsophisticated approaches were used, e.g., increased drip rates alone have been related to increased stalagmite growth [29,50]. This assumption cannot be made without additional information such as cave monitoring and calculation of growth rate variations. In many settings, drip rate maxima are related to the wet-summer season [16,22]. Simultaneously, in many caves the summer season might be the season of high $p\text{CO}_2$ and slow growth [15], showing the complexity of speleothem growth and the need to use a sophisticated growth rate model, such as StalGrowth. We show that StalGrowth is capable of the following:

- calculation of speleothem growth rates
- quick evaluation of growth influencing parameters
- identification of seasonal growth bias

The growth influencing parameters vary at different cave sites. Drip water Ca-concentration can be the parameter primarily driving variations of carbonate precipitation, as seen in Obir Cave and St. Michaels cave. In winter 2001/02 the real Ca-concentration in Obir drops below the apparent Ca-concentration, inhibiting carbonate precipitation. This appears to be a true feature in Obir cave (personal communications). In St. Michaels cave the Ca-ion concentrations appear to be the primary driver as well. The highest Ca-concentrations correlate to the fast growth season. This opposes the general understanding of cave ventilation-controlled speleothem growth [3], because the low $p\text{CO}_2$ season in St Michaels Cave occurs during the slow growth season: the summer [22]. In Inner Space Cavern, StalGrowth shows a seasonal cycle as well. Here, the seasonal $p\text{CO}_2$ cycle inside the cave appears to be the primarily controlling parameter, where high growth rates occur during times of low $p\text{CO}_2$. This seasonal growth pattern is also observed inside the cave [24]. Ca-concentration and temperature remain constant, thus here the strong seasonal variation in $p\text{CO}_2$ dominates the speleothem growth variation. Two caves show clear seasonal growth rate variations. Inner Space Cavern shows seasonal $p\text{CO}_2$ variations, which cause seasonal variation in speleothem growth both observed [24] and predicted by StalGrowth. Here the difference between average seasonal growth rates predicted by Stal Growth is small (0.49 mm/yr during the fast growth season and 0.39 mm/yr during the slow growth season) causing only a small seasonal bias of 55% of carbonate precipitated during the fast growth season. This will not lead to a large seasonal bias because carbonate from speleothems at this site will grow during both seasons. Carbonate precipitation experiments on glass plates in Inner Space Cavern show that there is no precipitation on glass plates during the time of maximal $p\text{CO}_2$ values (July to October). During this time, StalGrowth predicted carbonate growth rates in Inner Space cavern are minimal, but do not reach 0. Possibly, StalGrowth overestimates the growth rate during the high $p\text{CO}_2$ season in Inner Space Cavern. Another cause might be that we used average temperature and calcium concentration in Inner Space Cavern, because the detailed monthly observations

are not published in [24]. The large error bars in Figure 7 represent this uncertainty in the input data. Including the uncertainty, the lowest modeled growth rate during the slow growth season in Inner Space Cavern is 0.1 mm/yr, very close to no growth. Using the carbonate mass and glass plate surface area allows to roughly estimate the precipitation rate in mm/yr. During the fast growth season, the glass plate experiments in Inner Space Cavern [24] indicate precipitation rates between 0.17 and 0.49 mm/yr, similar to the StalGrowth prediction (predicted growth rate in fast growth season: 0.49 mm/yr). In Inner Space Cavern the precipitation experiments use glass plates. This surface is different than the apex of a speleothem. Some authors point out that glass plates need higher oversaturation to promote carbonate precipitation compared to the rough carbonate surface found on a speleothem [48]; if this is true, it might explain why there is no carbonate precipitation observed on glass plates inside Inner Space Cavern, while StalGrowth predicts some speleothem growth during the slow growth season. Inside Larga cave predicted growth rates compare well to observations. During the last 100 years, one actively growing specimen reveals an average growth rate around 0.20 mm/yr (Vieten unpublished data U/Th dating), very similar to the StalGrowth results (varying between 0.20 and 0.30 mm/yr, Figures 4 and 5). St. Michaels cave has a large seasonal growth bias because speleothem growth halts during the slow growth season and 99% of the carbonate is precipitated during the fast growth season. Thus, the application of StalGrowth to cave settings similar to St. Michael, where speleothem growth is discontinuous through the year, will improve the climate reconstruction based on speleothems from such locations significantly. Not accounting for the growth bias, the climate reconstruction might discuss changes in climate signals, in this case for St. Michaels cave during the springtime, which would not have been recorded by the speleothem due to drip water's geochemical tracer signals arrival at the speleothem's apex during a time of no growth. StalGrowth is the first tool available to identify such situations and quantify the seasonal growth bias.

Changes in cave pCO₂ influence the growth rates of stalagmites and the recorded paleoclimatic signal [19,50]. A global model [15] predicts that cave pCO₂ variations could be the main driver of calcite growth seasonality. The application of StalGrowth shows that in some caves other parameters dominate growth rate changes. Variations in Ca-ion-concentration have been identified as a parameter which can overprint seasonal pCO₂ changes. The new StalGrowth program allows a detailed investigation of changes in speleothem growth rate. It also allows to identify if growth rate changes repeat each year, causing annual growth seasonality or if growth rate changes are more complex showing no seasonal oscillation. StalGrowth also shows that speleothem growth depends on each cave system and it remains important to study each cave site in detail to guarantee a conclusive interpretation of speleothem proxy values. Modeled growth rates differ in all caves, highlight the importance of taking all parameters into account before making conclusions about growth rates, because ultimately the speleothem growth rate is controlled by the solutions supersaturation [33,51].

In the future StalGrowth could be used to understand causes of growth rate changes. Every paleoclimate reconstruction based on speleothems produces a growth rate–age model. StalGrowth provides a new tool to test which scenarios (changes of one or more parameters) are plausible causes of changes in speleothem growth rate in the past. Testing realistic paleo cave parameter combinations could be used to better reconstruct the past cave conditions. Furthermore, StalGrowth will aid to understand the formation of hiatuses (time periods of no growth) in speleothems. StalGrowth could identify growth thresholds which possibly caused hiatuses during the record formation. To do so, one single parameter needs to be changed to study its influence on the speleothem growth until the growth rate is zero. For example, the threshold pCO₂ value, the pCO₂ value above which carbonate precipitation does not occur, could be identified. In St. Michael's cave no growth occurred from July to October (Figure 6), related to low Ca values of about 1 mol/m³. This appears to be near the Ca-ion-growth threshold. Identifying growth thresholds can help to understand

the occurrence of times of no-growth (hiatus) in speleothem records and link this to past environmental conditions.

5. Conclusions

StalGrowth proves to be a tool to evaluate cave measurements quickly. It is the first algorithm to calculate speleothem growth rates. It can detect how changes in the cave-speleothem-growth-parameters (calcium-ion concentration, cave air pCO₂, drip rate and temperature) affect the speleothem growth rate. It can plot time series of input and output parameters. Based on the time series, slow growth and fast growth seasons can be specified and it can be tested if these growth seasons are significant. For seasonal speleothem growth scenarios, the seasonal growth bias can be calculated. This knowledge will lead to better reconstructions of climatic conditions using speleothems.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/geosciences11050187/s1>, Instructions StalGrowth.

Author Contributions: Conceptualization, R.V. and F.H.; Investigation, R.V. and F.H.; Methodology, R.V. and F.H.; Project administration, R.V. and F.H.; Software F.H.; Visualization F.H.; Validation, R.V. Writing—original draft, R.V.; Writing—review & editing, R.V. and F.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: StalGrowth is available at <https://github.com/RolfVieten/StalGrowth/releases/latest> (accessed on 23 April 2021).

Acknowledgments: This research was supported by grant AGS 1003502 from the National Science Foundation. We thank the University of Puerto Rico and especially the Marine Science and Geology department. We thank the AlgLib Community (<https://www.alglib.net/> (accessed on 23 April 2021)) and the QT Community (<https://qt-project.org/> (accessed on 23 April 2021)) and Emanuel Eichhammer for QCustomPlot (<https://www.qcustomplot.com> (accessed on 23 April 2021)). We thank Amos Winter and Wolfgang Dreybrodt for discussing the program with us. We thank the unknown reviewers. We also thank Sea Grant, Puerto Rico and the International Association of Sedimentologists for their support to present the preliminary program during the second speleothem summer school in Oxford, and for their support to continue cave monitoring in Cueva Larga.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Fairchild, I.J.; Baker, A. *Speleothem Science: From Process to Past Environments*, 1st ed.; John Wiley & Sons: Chichester, UK, 2012.
2. Fairchild, I.J.; Smith, C.L.; Baker, A.; Fuller, L.; Spötl, C.; Matthey, D.; McDermott, F. Modification and preservation of environmental signals in speleothems. *Earth Sci. Rev.* **2006**, *75*, 105–153. [[CrossRef](#)]
3. Lachniet, M.S. Climatic and environmental controls on speleothem oxygen-isotope values. *Quat. Sci. Rev.* **2009**, *28*, 412–432. [[CrossRef](#)]
4. Edwards, R.L.; Chen, J.; Wasserburg, G. 238U/234U/230Th/232Th systematics and the precise measurement of time over the past 500,000 years. *Earth Planet. Sci. Lett.* **1987**, *81*, 175–192. [[CrossRef](#)]
5. Richards, D.A. Uranium-series Chronology and Environmental Applications of Speleothems. *Rev. Miner. Geochem.* **2003**, *52*, 407–460. [[CrossRef](#)]
6. Pourmand, A.; Tissot, F.L.H.; Arienzo, M.; Sharifi, A. Introducing a Comprehensive Data Reduction and Uncertainty Propagation Algorithm for U-Th Geochronometry with Extraction Chromatography and Isotope Dilution MC-ICP-MS. *Geostand. Geoanal. Res.* **2014**, *38*, 129–148. [[CrossRef](#)]
7. Scholz, D.; Hoffmann, D. 230Th/U-dating of fossil corals and speleothems. *E&G Quat. Sci. J.* **2008**, *57*, 52–76. [[CrossRef](#)]
8. Lachniet, M.S.; Burns, S.J.; Piperno, D.R.; Asmerom, Y.; Polyak, V.J.; Moy, C.M.; Christenson, K. A 1500-year El Niño/Southern Oscillation and rainfall history for the Isthmus of Panama from speleothem calcite. *J. Geophys. Res. Space Phys.* **2004**, *109*, 1–8. [[CrossRef](#)]
9. Wang, Y.J.; Cheng, H.; Edwards, R.L.; An, Z.S.; Wu, J.Y.; Shen, C.-C.; Dorale, J.A. A High-Resolution Absolute-Dated Late Pleistocene Monsoon Record from Hulu Cave, China. *Science* **2001**, *294*, 2345–2348. [[CrossRef](#)] [[PubMed](#)]
10. Spötl, C.; Mangini, A. Stalagmite from the Austrian Alps reveals Dansgaard-Oeschger events during isotope stage 3: Implications for the absolute chronology of Greenland ice cores. *Earth Planet. Sci. Lett.* **2002**, *203*, 507–518. [[CrossRef](#)]

11. Fairchild, I.J.; Treble, P.C. Trace elements in speleothems as recorders of environmental change. *Quat. Sci. Rev.* **2009**, *28*, 449–468. [[CrossRef](#)]
12. Cruz, F.W.; Vuille, M.; Burns, S.J.; Wang, X.; Cheng, H.; Werner, M.; Edwards, R.L.; Karmann, I.; Auler, A.S.; Nguyen, H. Orbitally driven east–west antiphasing of South American precipitation. *Nat. Geosci.* **2009**, *2*, 210–214. [[CrossRef](#)]
13. Voarintsoa, N.R.G.; Barkan, E.; Bergel, S.; Vieten, R.; Affek, H.P. Triple oxygen isotope fractionation between CaCO₃ and H₂O in inorganically precipitated calcite and aragonite. *Chem. Geol.* **2020**, *539*, 119500. [[CrossRef](#)]
14. Li, H.; Sinha, A.; André, A.A.; Spötl, C.; Vonhof, H.B.; Meunier, A.; Kathayat, G.; Duan, P.; Voarintsoa, N.R.G.; Ning, Y.; et al. A multimillennial climatic context for the megafaunal extinctions in Madagascar and Mascarene Islands. *Sci. Adv.* **2020**, *6*, eabb2459. [[CrossRef](#)] [[PubMed](#)]
15. James, E.W.; Banner, J.L.; Hardt, B. A global model for cave ventilation and seasonal bias in speleothem paleoclimate records. *Geochem. Geophys. Geosyst.* **2015**, *16*, 1044–1051. [[CrossRef](#)]
16. Riechelmann, D.F.C.; Schröder-Ritzrau, A.; Scholz, D.; Fohlmeister, J.; Spötl, C.; Richter, D.K.; Mangini, A. Monitoring Bunker Cave (NW Germany): A prerequisite to interpret geochemical proxy data of speleothems from this site. *J. Hydrol.* **2011**, *409*, 682–695. [[CrossRef](#)]
17. Riechelmann, D.F.; Deininger, M.; Scholz, D.; Riechelmann, S.; Schröder-Ritzrau, A.; Spötl, C.; Richter, D.K.; Mangini, A.; Immenhauser, A. Disequilibrium carbon and oxygen isotope fractionation in recent cave calcite: Comparison of cave precipitates and model data. *Geochim. Cosmochim. Acta* **2013**, *103*, 232–244. [[CrossRef](#)]
18. Frisia, S.; Fairchild, I.J.; Fohlmeister, J.; Miorandi, R.; Spötl, C.; Borsato, A. Carbon mass-balance modelling and carbon isotope exchange processes in dynamic caves. *Geochim. Cosmochim. Acta* **2011**, *75*, 380–400. [[CrossRef](#)]
19. Spötl, C.; Fairchild, I.J.; Tooth, A.F. Cave air control on dripwater geochemistry, Obir Caves (Austria): Implications for speleothem deposition in dynamically ventilated caves. *Geochim. Cosmochim. Acta* **2005**, *69*, 2451–2468. [[CrossRef](#)]
20. Baldini, J.U.; McDermott, F.; Hoffmann, D.L.; Richards, D.A.; Clipson, N. Very high-frequency and seasonal cave atmosphere PCO₂ variability: Implications for stalagmite growth and oxygen isotope-based paleoclimate records. *Earth Planet. Sci. Lett.* **2008**, *272*, 118–129. [[CrossRef](#)]
21. Matthey, D.P.; Fairchild, I.J.; Atkinson, T.C.; Latin, J.-P.; Ainsworth, M.; Durell, R. Seasonal microclimate control of calcite fabrics, stable isotopes and trace elements in modern speleothem from St Michaels Cave, Gibraltar. *Geol. Soc. London Spéc. Publ.* **2010**, *336*, 323–344. [[CrossRef](#)]
22. Matthey, D.; Atkinson, T.; Barker, J.; Fisher, R.; Latin, J.-P.; Durrell, R.; Ainsworth, M. Carbon dioxide, ground air and carbon cycling in Gibraltar karst. *Geochim. Cosmochim. Acta* **2016**, *184*, 88–113. [[CrossRef](#)]
23. Vieten, R.; Winter, A.; Warken, S.F.; Schröder-Ritzrau, A.; Miller, T.E.; Scholz, D. Seasonal temperature variations controlling cave ventilation processes in cueva larga, Puerto Rico. *Int. J. Speleol.* **2016**, *45*, 259–273. [[CrossRef](#)]
24. Banner, J.L.; Guilfoyle, A.; James, E.W.; Stern, L.A.; Musgrove, M. Seasonal Variations in Modern Speleothem Calcite Growth in Central Texas, U.S.A. *J. Sediment. Res.* **2007**, *77*, 615–622. [[CrossRef](#)]
25. Baker, A.J.; Matthey, D.P.; Baldini, J.U. Reconstructing modern stalagmite growth from cave monitoring, local meteorology, and experimental measurements of dripwater films. *Earth Planet. Sci. Lett.* **2014**, *392*, 239–249. [[CrossRef](#)]
26. Dreybrodt, W. Speleothem Deposition. In *Encyclopedia of Caves*; White, W.B., Culver, D.C., Eds.; Elsevier BV: Amsterdam, The Netherlands, 2012; pp. 769–777. ISBN 9780123838322.
27. Dreybrodt, W. Chemical kinetics, speleothem growth and climate. *Boreas* **1999**, *28*, 347–356. [[CrossRef](#)]
28. Kaufmann, G. Stalagmite growth and palaeo-climate: The numerical perspective. *Earth Planet. Sci. Lett.* **2003**, *214*, 251–266. [[CrossRef](#)]
29. Kaufmann, G.; Dreybrodt, W. Stalagmite growth and palaeo-climate: An inverse approach. *Earth Planet. Sci. Lett.* **2004**, *224*, 529–545. [[CrossRef](#)]
30. Weedon, G.P. *Time-Series Analysis and Cyclostratigraphy: Examining Stratigraphic Records of Environmental Cycles*; Cambridge University Press: Cambridge, UK, 2003.
31. Casteel, R.C.; Banner, J.L. Temperature-driven seasonal calcite growth and drip water trace element variations in a well-ventilated Texas cave: Implications for speleothem paleoclimate studies. *Chem. Geol.* **2015**, *392*, 43–58. [[CrossRef](#)]
32. Hansen, M.; Dreybrodt, W.; Scholz, D. Chemical evolution of dissolved inorganic carbon species flowing in thin water films and its implications for (rapid) degassing of CO₂ during speleothem growth. *Geochim. Cosmochim. Acta* **2013**, *107*, 242–251. [[CrossRef](#)]
33. Dreybrodt, W. Evolution of the isotopic composition of carbon and oxygen in a calcite precipitating H₂O–CO₂–CaCO₃ solution and the related isotopic composition of calcite in stalagmites. *Geochim. Cosmochim. Acta* **2008**, *72*, 4712–4724. [[CrossRef](#)]
34. Van Beynen, P.E.; Soto, L.; Polk, J. Paleo-Precipitation Determination as Derived from Speleothems in Central Florida, USA. *J. Cave Karst Stud.* **2008**, *70*, 25–34.
35. Vaks, A.; Gutareva, O.S.; Breitenbach, S.F.M.; Avirmed, E.; Mason, A.J.; Thomas, A.; Osinzev, A.V.; Kononov, A.M.; Henderson, G. Speleothems Reveal 500,000-Year History of Siberian Permafrost. *Science* **2013**, *340*, 183–186. [[CrossRef](#)]
36. Cruz, F.; Karmann, I.; Magdaleno, G.; Coichev, N.; Viana, O. Influence of hydrological and climatic parameters on spatial-temporal variability of fluorescence intensity and DOC of karst percolation waters in the Santana Cave System, Southeastern Brazil. *J. Hydrol.* **2005**, *302*, 1–12. [[CrossRef](#)]
37. Scholz, D.; Hoffmann, D.L. StalAge—An algorithm designed for construction of speleothem age models. *Quat. Geochronol.* **2011**, *6*, 369–382. [[CrossRef](#)]

38. Breitenbach, S.F.M.; Rehfeld, K.; Goswami, B.; Baldini, J.U.L.; Ridley, H.E.; Kennett, D.J.; Prufer, K.M.; Aquino, V.V.; Asmerom, Y.; Polyak, V.J.; et al. CONstructing Proxy Records from Age models (COPRA). *Clim. Past* **2012**, *8*, 1765–1779. [[CrossRef](#)]
39. Tortelli, D.M.; Walter, M. Modeling and rendering the growth of speleothems in real-time. In Proceedings of the 13th International Joint Conference on Computer Vision, Imaging and Computer Graphics Theory and Applications, Rome, Italy, 27–29 February 2009; Volume 2, pp. 27–35.
40. Sherwin, C.M.; Baldini, J.U. Cave air and hydrological controls on prior calcite precipitation and stalagmite growth rates: Implications for palaeoclimate reconstructions using speleothems. *Geochim. Cosmochim. Acta* **2011**, *75*, 3915–3929. [[CrossRef](#)]
41. Vieten, R.; Warken, S.; Winter, A.; Scholz, D.; Miller, T.; Spötl, C.; Schröder-Ritzrau, A. Monitoring of Cueva Larga, Puerto Rico—A First Step to Decode Speleothem Climate Records. In *Karst Groundwater Contamination and Public Health*; White, W., Herman, J., Herman, E., Rutigliano, M., Eds.; Springer: Cham, Germany, 2017. [[CrossRef](#)]
42. Vieten, R.; Warken, S.; Winter, A.; Schröder-Ritzrau, A.; Scholz, D.; Spötl, C. Hurricane Impact on Seepage Water in Larga Cave, Puerto Rico. *J. Geophys. Res. Biogeosci.* **2018**, *123*, 879–888. [[CrossRef](#)]
43. Baker, A.; Genty, D.; Dreybrodt, W.; Barnes, W.L.; Mockler, N.J.; Grapes, J. Testing Theoretically Predicted Stalagmite Growth Rate with Recent Annually Laminated Samples: Implications for Past Stalagmite Deposition. *Geochim. Cosmochim. Acta* **1998**, *62*, 393–404. [[CrossRef](#)]
44. Aggarwal, C.C.; Yu, P.S. Outlier detection for high dimensional data. *ACM SIGMOD Rec.* **2001**, *30*, 37–46. [[CrossRef](#)]
45. Barnett, V.; Lewis, T. *Outliers in Statistical Data*, 3rd ed.; John Wiley & Sons: Hoboken, NJ, USA, 1994.
46. Crosby, T.; Iglewicz, B.; Hoaglin, D.C. How to Detect and Handle Outliers. *Technometrics* **1994**, *36*, 315. [[CrossRef](#)]
47. Knorr, E.M.; Ng, R.T.; Tucakov, V. Distance-based outliers: Algorithms and applications. *VLDB J.* **2000**, *8*, 237–253. [[CrossRef](#)]
48. Hansen, M.; Scholz, D.; Schöne, B.R.; Spötl, C. Simulating speleothem growth in the laboratory: Determination of the stable isotope fractionation ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) between H_2O , DIC and CaCO_3 . *Chem. Geol.* **2019**, *509*, 20–44. [[CrossRef](#)]
49. Fritts, H.C. Growth-Rings of Trees: Their Correlation with Climate. *Science* **1966**, *154*, 973–979. [[CrossRef](#)] [[PubMed](#)]
50. Mühlinghaus, C.; Scholz, D.; Mangini, A. Modelling stalagmite growth and $\delta^{13}\text{C}$ as a function of drip interval and temperature. *Geochim. Cosmochim. Acta* **2007**, *71*, 2780–2790. [[CrossRef](#)]
51. Dreybrodt, W. Deposition of calcite from thin films of natural calcareous solutions and the growth of speleothems. *Chem. Geol.* **1980**, *29*, 89–105. [[CrossRef](#)]