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Reconstruction of climate variation for the last millennium in the Bükk Mountains, northeast Hungary, from a stalagmite record

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Abstract—This paper presents the high-resolution stable isotope and trace element records from a stalagmite from Hungary (Kiskőhát Shaft, Bükk Mts.). Based on the variation of the isotopic and chemical composition of the carbonate deposit along the growth axis, changes in temperature and precipitation amount are assumed.

Our first results on the younger part (ca. last 1100 years) of the deposit suggest that not only major changes but several short period cycles can be recognized within the stalagmite, which are partly caused by temperature, precipitation amount, and vegetation changes. The oxygen isotope variation of the stalagmite can be explained mainly by the changes of the temperature, while carbon isotope ratios mainly reflect the changes in water recharge or precipitation amount. Combined trace element (Mg, Sr, and P) variations were used to reconstruct evapotranspiration changes.

The stalagmite recorded a generally wet and warm Medieval Warm Period, a colder but humid Little Ice Age, and several variably dry periods between.

Key-words: stalagmite, cave, paleoclimate, stable isotopes, trace elements, last millennium, Hungary

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1. *Introduction*

During the past four decades, the majority of the paleoclimatological studies was concerned either with investigating marine records and/or polar ice cores. Efforts in reconstructing climate change from continental records have renewed interest in the use of speleothems as climatic proxies (e.g., *Gascoyne*, 1992; *Lauritzen*, 1995).

These deposits have specific advantages: stalagmites are widespread in continental area, they develop in relatively protected environments, practically free from re-deposition and alteration, and can be dated by absolute radiometric methods at relatively high precision. TIMS or ICP-MS uranium series dating of only a few 100 milligrams allow dating speleothem calcite with a precision better than 1% (*Shen et al.*, 2002).

Carbonate speleothems are formed when water saturated in CO_2 from the soil zone enters a cave where the CO_2 degasses. If degassing proceeds slowly in a stable-temperature environment, calcite can be precipitated in isotopic equilibrium with the parent drip water (*Hendy*, 1971). In this case, the reconstruction of environmental conditions existing during the formation of the calcite can be possible mostly based on the stable isotope analyses of speleothems.

Recently published preliminary studies in Hungary have reported significant isotopic and chemical variations within stalagmites related to interglacial/glacial climate transitions (Marine Isotope Stage 5e-5d; *Siklósy et al.*, 2008a) or volcanically induced climate changes (*Siklósy et al.*, 2007; *Siklósy et al.*, 2009). Speleothems that record decadal-scale environmental changes in the Carpathian Basin during the last millennium are of particular interest, as this time range is not fully covered by historical and/or instrumental climate records (e.g., *Réthly*, 1962; *Rácz*, 1989; *Kiss*, 2009). Although tree-ring growth series may preserve climatically induced climate proxy signals (*Kern* and *Popa*, 2007; *Kern et al.*, 2009) the lack of corresponding series further back in the past prevents the establishment of detailed studies. Ground-surface temperature (GST) may reflect past climate conditions, but the resolution and precision of the reconstruction for Hungary (*Bodri* and *Dövényi*, 2004) need to be improved for direct comparison with other records. Biostratigraphic evidences for Holocene climate changes (based on vertebrate paleontology) cover several localities in northeast Hungary (*Kordos*, 1977; *Kordos* and *Ringer*, 1991), however, the precise age control and the lack of continuous records prevent the establishment of high-resolution reconstruction for the last thousands of years.

There is a need, therefore, for well-dated climate records from this continental area to increase the input for general climate models. High-resolution geochemical data on speleothems may fill the gap also for this period.

In this study, we conducted complex trace element and stable C and O isotope analyses on a speleothem from Hungary (*Fig. 1*) acquired at high spatial and temporal resolution using various mass spectrometric techniques in order to test and validate independently recognized climate changes (e.g., Little Ice Age [LIA]) and to apply *geochemical results as a climate driven proxies* for future research.

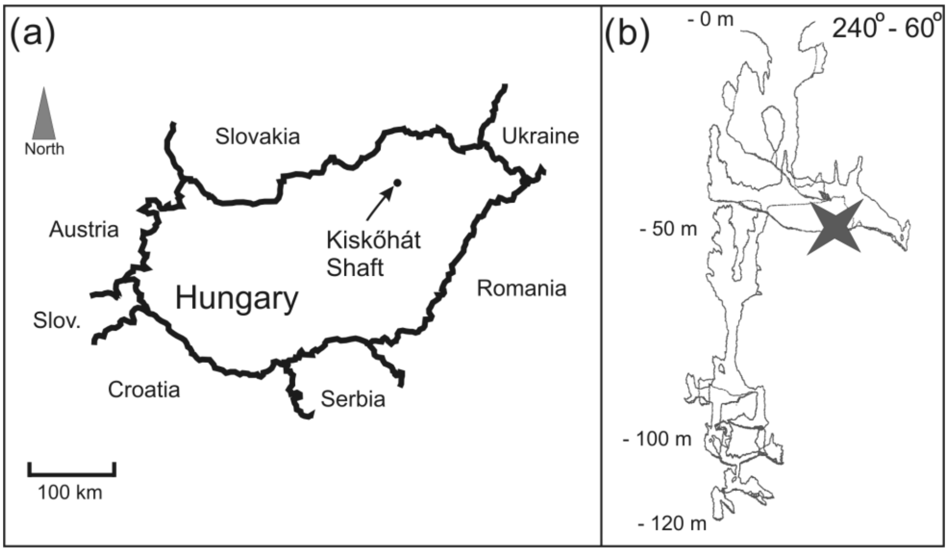

Fig. 1. Location of Kiskőhát Shaft in northeast Hungary (a) and vertical cross-section of the Kiskőhát Shaft with the sample location, indicated by a cross (mapped and created by the BEAC cave explorer group) (b).

2. *Site and sample*

The speleothem analyzed in this study originates from the Kiskőhát Shaft (*Fig. 1*), northeast Hungary (N 48° 4.086’ and E 20° 29.422’). The cave is located at the southern rim of the Bükk Highland, at 915 m a.s.l. The 117 m deep inactive sinkhole opens up the cave with a total length of 479 m, situated in the Bükk National Park, under the Kiskőhát peak (938 m) at 915 m elevation, in Triassic limestone. The interior of the cave where the sample was located has a constant temperature of 5.5 °C, with only a minor variability over a year, except the shaft, close to the cave entrance, where freezing can occur during winter. In situ CO_2 measurements at the site revealed that the air masses within the cave can only change during wintertime because of the general, temperature dependent atmospheric circulation of sacklike chambers. When cold and dry winter air sinks into the cave, the environment may become totally dry and, therefore, the growth rate of the deposits becomes practically zero.

The stalagmite consists of dense, well-laminated dark crystalline and milky-colored calcite. Apparently, deposition has been continuous along the length of the sample (ca. 250 mm), except the top part of the stalagmite where hiatus in deposition are marked by small changes in crystal structure and layers of detrital inclusions (*Fig. 2*, shown by dotted lines). A polished section of the studied section of the stalagmite (ca. top 65 mm) was examined for calculating the number of growth bands along the growth direction.

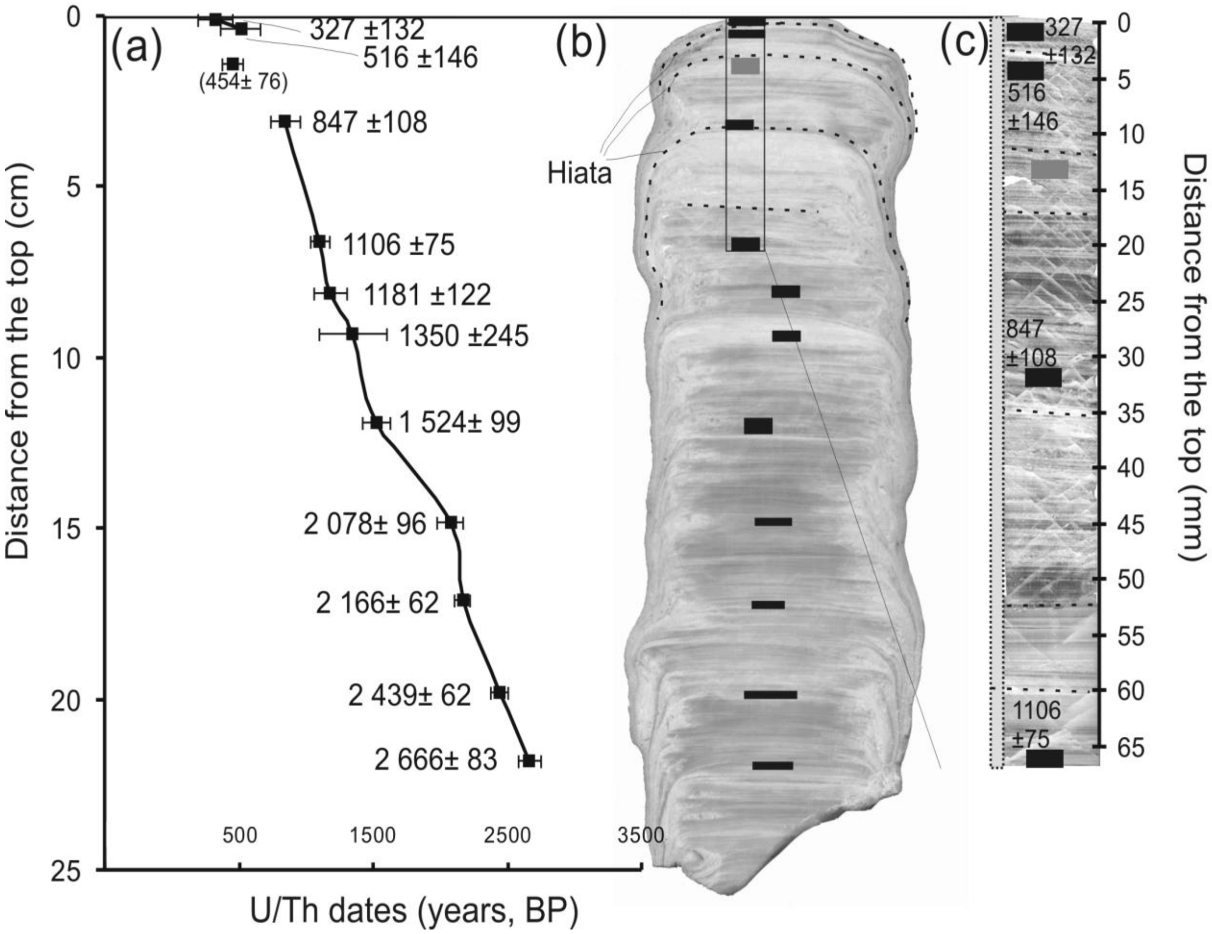

Fig. 2. The determined U-Th data series vs. the depth (a) of the studied Kiskőhát Shaft stalagmite (b), and the selected part for this study (c). Vertical gray bar shows the position of the stable isotope profile (c). Position of the Multi Collector-Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS) age data are indicated by the black regions (b and c). Dotted line represents textural changes and/or hiata during the deposition of the stalagmite. Errors of the age data are also indicated.

3. *Methodology*

3.1. Age determination

To place the observed isotopic changes into a time frame for comparison with other records, *precise age determinations* of the cave deposits is required. The technique is based on the precipitation of small amounts of uranium at the moment of deposition of natural samples (e.g., calcite speleothems) in the absence of thorium. After carbonate deposition, a gradual increase of the ^{230}Th concentration occurs in the speleothem through radioactive decay of ^{234}U. The ratio ^{230}Th/^{234}U is a function of the speleothem age, which can be determined by chemical separation of ^{230}Th and ^{234}U from the sample and by measuring each nuclide (*Edwards et al.*, 1987; *Richards* and *Dorale*, 2003).

Subsamples (ca. 0.1–0.3 g) were drilled for U-Th chemistry (*Shen et al.*, 2003) and ^{230}Th-dated isotopic measurements on a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS), Thermo Electron Neptune in the High-precision Mass Spectrometry and Environment Change Laboratory (HISPEC), Department of Geosciences, National Taiwan University. A triple-spike, ^{229}Th-^{233}U-^{236}U, isotope dilution method was employed to correct mass bias and determine uranium concentration (*Shen et al.*, 2002). A protocol, using one newly-developed MasCom secondary electron multiplier (SEM) with repelling potential quadrupole (RPQ), was employed. Only 1–4 ng of U is required to earn the 2-sigma reproducibility of 1–2‰. No significant difference between measurements of standards and carbonate samples on ICP-sector-field-MS (*Shen et al.*, 2002) and on MC-ICP-MS certify the developed MC-ICP-MS methodology.

Dating of the youngest part of the stalagmite was possible by applying the U-Th method due to its low detrital Th content. Age corrections are applied anyway, as even small amount of U-derived Th may have effect on the U/Th age for young samples. Thus, we used the corrected values for all dated subsamples (*Table 1*). The obtained ages are absolute ones and given as years BP (before present; here: before the chemistry date 2007 AD).

3.2. Stable isotopes

Carbon and oxygen isotope compositions of drilled calcite samples at a spatial resolution of ~0.5 mm were determined using the conventional H_3PO_4 digestion method (*McCrea*, 1950; *Spötl* and *Venneman*, 2003) at 72 °C and an automated GasBench II preparation unit attached to a Thermo Finnigan delta plus XP continuous flow mass spectrometer at the Institute for Geochemical Research in Budapest. Standardization was conducted using laboratory calcite standards calibrated against the NBS-19 standard. The results are expressed according to the following equation:

$$\delta^{18}\mathrm{O} \ \text{or} \ \delta^{13}\mathrm{C} = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \cdot 1000 \quad (‰). \tag{1}$$

The variations of stable ^{18}O and ^{16}O or ^{13}C and ^{12}C are measures by a mass spectrometer relative to a standard, therefore expressed in a „delta" (‰) notation, here, relative to the carbonate standard named Vienna Pee Dee Belemnite (V-PDB). Reproducibilities for C and O isotope analyses are better than ±0.15‰.

In temperate regions, cave air is characterized by high-humidity (typically 95–99%), minimizing the evaporation that might otherwise cause kinetic isotope fractionation by preferred loss of easier water molecules ($H_2{}^{16}O$). In this case the variations in δ^{18}O value of a carbonate reflects primarily the changes in oxygen isotopic composition of precipitation in the area ($\delta^{18}O_{water}$) and the temperature of formation (*McDermott*, 2004 and references therein). Since the isotopic composition of dripping water is closely related to the meteoric precipitation at the studied region (*Harmon et al.*, 1979; *Yonge et al.*, 1985) and the cave temperature reflects the mean annual temperature at the surface (*Fairchild et al.*, 2006), the O isotope compositions of meteoric water that infiltrates into the cave, and from which the carbonate precipitates, reflect regional climate conditions. However, in order to interpret the $\delta^{18}O$ value of the stalagmite correctly, the factors that may influence the O isotope compositions of infiltrating water have to be listed here. As mentioned above, the $\delta^{18}O$ in cave seepage waters reflect the $\delta^{18}O$ of the local precipitation but may reflect evaporative processes that modify the $\delta^{18}O$ of the infiltrating water along the flow path from the surface across the vadose zone into the cave. The oxygen isotope composition of precipitation is temperature and site dependent.

Over the mid and high latitudes, *Rozanski et al.* (1993) calculated an average modern-day $\Delta\delta^{18}O_{precipitation}/\Delta T$ of approximately $+0.6‰/°C$. This value may have been different in the past, however, we may assume that the positive correlation remained. The equilibrium fractionation (*Friedman* and *O'Neil*, 1977) that accompanies calcite deposition from drip-waters inside the cave ($\Delta\delta^{18}O_{calcite}/\Delta T$) is approximately $-0.24‰/°C$ at 25 °C (*O'Neill et al.*, 1969). Since the temperature dependence of $\delta^{18}O$ in rainfall (ca. $+0.6‰/°C$) exceeds the calcite-water fractionation ($-0.24‰/°C$), in principle the *temperature dependency* of the O isotope compositions of meteoric water define the $\delta^{18}O$ value of the calcite (i.e., a positive correlation between $\delta^{18}O$ in the calcite and temperature).

The $\delta^{13}C$ values of the stalagmites can also provide important palaeoenvironmental information. The carbon isotopic composition of the drip water is the most important factor determining the $\delta^{13}C$ of speleothem carbonates. Carbon dissolved in drip water mainly derives from three sources: atmospheric CO_2, soil CO_2, and dissolution of the karstic host rock. Among these, the *amount of soil* CO_2 has a major factor. Thus, changes of the vegetation activity or in the microbial activity within the oxidation process of soil organic matter plays a key role in the CO_2 production. Part of the precipitation will penetrate plant cover and pass through the soil and epikarst zone, where it takes up the CO_2, produced by plant respiration. The CO_2 uptake produces carbonic acid, which in turn dissolves limestone (Eq. (2)). The $\delta^{13}C$ value of soil CO_2 varies according to the photosynthetic pathway of plants (C3 and C4-types), however, the C4-type drought-adapted grasses can be ruled out for this region at the time range for this study (*Sümegi*, 2007). The $\delta^{13}C$ values of the stalagmite may become more positive also in case of above or within-cave phenomena, mostly related to rapid *outgassing* of CO_2, caused by stronger *ventillation* or *evaporation* which leads to kinetic fractionation, thus the enrichment of calcite precipitation (i.e., stalagmite) in isotopically heavier carbon isotope.

The carbon isotopic values, therefore, mainly reflect the influence of biogenic activity of soil above the cave and the degree of limestone dissolution. The driving force of karstification and speleothem deposition is the meteoric water circulation system in combination with soil carbon dioxide production, as expressed by the following equation:

$$CaCO_3(s) + CO_2(g) + H_2O(l)_{(precipitation)} <=>_{(dissolution)} Ca^{2+}(aq) + 2HCO_3^{-}(aq). \qquad (2)$$

Table 1. U/Th isotopic compositions and ^{230}Th ages for Kiskőhát Shaft on MC-ICP-MS

	Dis-tance (cm)	Weight	^{238}U	^{232}Th	δ^{234}U	[^{230}Th/^{238}U]	[^{230}Th/^{232}Th]	Age		Age		δ^{234}U initial	Growth rate
Sample ID	**From the top**	**g**	**ppb**	**ppt**	**Measured^{a}**	**Activity^{b}**	**ppm^{c}**	**Uncorrected**	**Error**	**Corrected^{b,d}**	**Error**	**Corrected^{e}**	**δm/yr**
Kiskőhát 12.	0.1	0.298	35.7	356	317	0.0051	8.5	427	± 86	327	± 132	317	16
Kiskőhát 11.	0.4	0.249	33.9	334	335	0.0075	12.5	614	± 108	516	± 146	336	
Kiskőhát 10.*	1.4	0.352	41.8	100	374.6	0.0060	41	477	± 73	454	± 76	375	43
Kiskőhát 9.	3.1	0.222	38.7	58	349	0.0106	116.5	862	± 107	847	± 108	350	135
Kiskőhát 8.	6.6	0.332	39.4	115	358	0.0140	79.8	1135	± 70	1106	± 75	360	199
Kiskőhát 7.	8.1	0.221	34.0	60	349	0.0147	137.3	1199	± 121	1181	± 122	350	71
Kiskőhát 6.	9.3	0.159	27.1	171	366	0.0176	45.8	1412	± 240	1350	± 248	367	150
Kiskőhát 5.	11.9	0.416	35.4	47	374.6	0.0192	238	1537	± 98	1524	± 99	376	52
Kiskőhát 4.	14.8	0.116	37.4	177	391.9	0.0268	93.4	2123	± 85	2078	± 96	394.2	260
Kiskőhát 3.	17.1	0.197	35.0	98	396.0	0.0278	164.5	2193	± 56	2166	± 62	398.4	99
Kiskőhát 2.	19.8	0.171	128.1	215	420.3	0.0316	310.2	2455	± 60	2439	± 62	423.2	88
Kiskőhát 1.	21.8	0.143	340.0	2584	420.6	0.0352	76.5	2737	± 43	2666	± 83	423.7	

Analytical errors are 2s of the mean.

[a] $d^{234}U = ([^{234}U/^{238}U]_{activity} - 1) \times 1000$.

[b] $[^{230}Th/^{238}U]_{activity} = 1 - e^{-\lambda_{230}T} + (\delta^{234}U_{measured}/1000)[\lambda_{230}/(\lambda_{230} - \lambda_{234})](1 - e^{-(\lambda_{230} - \lambda_{234})T})$, where T is the age.

Decay constants are 9.1577×10^{-6} yr^{-1} for ^{230}Th, 2.8263×10^{-6} yr^{-1} for ^{234}U, and 1.55125×10^{-10} yr^{-1} for ^{238}U (*Cheng et al.*, 2000).

[c] The degree of detrital ^{230}Th contamination is indicated by the [^{230}Th/^{232}Th] atomic ratio instead of the activity ratio.

[d] Age corrections were calculated using an ^{230}Th/^{232}Th atomic ratio of 2 (± 2) ppm.

[e] $\delta^{234}U_{initial}$ corrected was calculated based on ^{230}Th age (T), i.e., $\delta^{234}U_{initial} = \delta^{234}U_{measured}\ X\ e^{\lambda_{234} * T}$, and T is corrected age.

*: U fraction lost during chemistry; estimate age using ”Kiskőhát 11.” U data.

3.3. Trace elements

As the speleothem grows, it incorporates trace elements into its structure, and their concentrations and ratios reflect environmental conditions at the time of deposition, e.g., temperature and water throughput (rainfall at the surface).

Trace element compositions were determined by laser-ablation (LA-)ICP-MS technique using a Perkin-Elmer ELAN 6100 DRC ICP-MS coupled with a LAMBDA PHYSICS excimer laser (193 nm) at the University of Lausanne. The measurements were performed using the following settings: laser: 7 Hz, 28 kV, energy ~170 mJ, fluency ~13 J/cm^2; spot size 60 μm, acquisition time: gas blank ~30s, data ~60s. Data were reduced using the CONVERT and LAMTRACE programs. NIST612 glass was used as external standard and Ca electron microprobe measurements served as an internal standard. BCR-2 glass was monitored during all analytical sessions for phosphoros and treated as unknowns during data reduction. The error is estimated to lie between 5–10% on a relative basis. With the applied method, elements incorporated into the structure of the calcite with low concentration and high spatial resolution could be followed along the growth axis.

In this paper we focus on prominent changes and cycles of the following trace elements: Mg, Sr, and P.

Mg can substitute Ca in the calcite lattice (*Mucci* and *Morse*, 1983). The main factors that can modify the Mg-signal in stalagmites are the following:

- Experimental results have demonstrated that Mg partitioning into calcite from water is temperature-dependent (*Mucci*, 1987; *Burton* and *Walter*, 1991). *Gascoyne* (1983, 1992) calculated that a 1 °C increase would increase the Mg content of the stalagmite with 7%, however, the long-term (millennial) temperature control on Mg abundance have proved to be over-simplified (*Fairchild et al*., 2006).
- Under isothermal conditions or during short-term changes (yearly or decadal), variation in solution composition is much more important, hence Mg variation on decadal time scales reflects variations in solution Mg. This mostly reflect changes in hydrological parameters, with solution Mg/Ca tending to be lower under high flow-rate (i.e., wet) conditions, as a result of dilution.
- Furthermore, the enrichment of Mg in cave waters can be explained by prior low-Mg calcite precipitation from the cave waters along the flow path, which are consequently enriched in Mg. The partition coefficients (Kd) for Mg (and also for Sr) between cave waters and cave calcite are $<<1$ (*Katz*, 1973; *Mucci* and *Morse*, 1983), therefore, Mg/Ca and Sr/Ca ratios increase in solutions that have precipitated calcite ("prior calcite precipitation"). This can explain co-variations of Mg and Sr in the seepage waters and consequently in the speleothem.

- Prolonged water residence time in the vadose zone linked to the reduced amount of precipitation may also enhance the Mg concentration in the solution and stalagmite due to the dissolution of the host rocks.

In the case of Sr variability, the increase in the speleothems can be interpreted by:

- Increased water residence time in the vadose zone and /or by an increase in prior calcite deposition caused by an increase in calcite saturation of the waters.
- In addition to varying solution Sr/Ca, the growth rate, or more specifically crystallographic changes can also influence Sr incorporation at higher growth rates (*Huang* and *Fairchild*, 2001). Higher Sr at a given Mg content represents faster growth rate of the stalagmite (*Huang et al*., 2001).

Phosphate is one of the strongest adsorbents onto defect sites on the calcite surface (*Meyer*, 1984). It is directly linked

- to the vegetation productivity and its decay (*Fairchild et al*., 2001), and
- the P incorporation into the calcite structure is sensitive to phosphate concentration in seepage water and rate of supply of dripwater (dilution).

Therefore, P concentrations can be used as an indipendent proxy together with carbon isotope values to estimate the change of biogenic activity. A control on P incorporation by rate of supply of inorganic P, rather than by defects produced during faster growth, is inferred from the lack of correlation of P and Sr in this case.

4. *Results*

4.1. ^{230}Th-^{234}U results of age determinations

Uranium-series dating results indicate that the stalagmite growth started some 2700 years BP. We obtained a total of 12 U-Th series dating along the growth direction (*Table 1*) and all subsamples were in stratigrapic order (*Fig. 2a*). The section selected for this study (ca. top 65 mm of the stalagmite) cover ca. 1100 ±75 years.

The age data demonstrate that the growth rate varied in time, from ca. 199 μm/year at the bottom of the studied section to ca. 16 μm/year at the top. This change may be due to the (i) real decreased rate in continuous growth or (ii) the presence of hiata. The visible laminae counts and width calculations using the CAROTA software (*Popa*, 1999) revealed that regular, high-frequency cycles can be recognized along the studied section (*Fig. 3a*) with a sum of 373 laminae within the determined age ranges for the studied section (from the bottom to the top of the stalagmite, between 1106 ± 75 and 327 ± 132 years BP, respectively). For the majority of the deposition, therefore, the stalagmite suffers from the lack of visible laminae. Fewer counted laminae than expected may probably represents brake during the stalagmite deposition. The average thickness of the bands is ca. 173 μm (*Fig. 3a*).

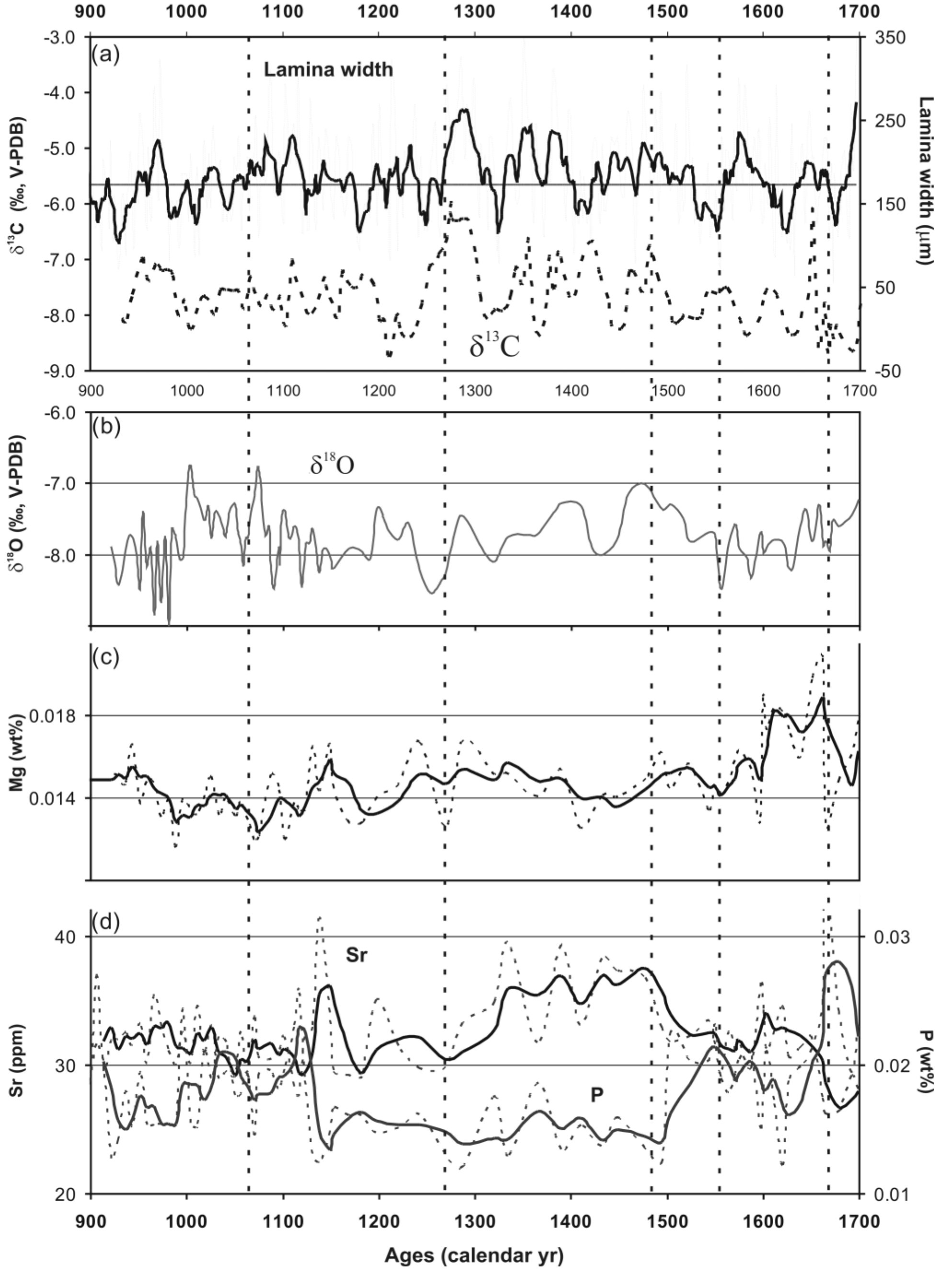

Fig. 3. Lamina thickness (upper) and $\delta^{13}C$ value (bottom) along the growth direction of the stalagmite. Horizontal line represents the average lamina width of 173 μm (a); Stable oxygen isotope composition of the studied section (b); Mg (c) and Sr-P (d) variations in the studied section of the Kiskőhát stalagmite. The thick line in each case shows smoothed data (3 running means). All data are plotted against the ages (calendar years or AD), based on the U-Th data. Vertical dotted lines mark the recognized textural changes and/or hiata (see *Fig. 2*).

The slowest growth rate based on the age-depth relationship (*Fig. 2a*) occurs at the top of the stalagmite, coinciding with the observed hiata. To put the observed changes in the isotopic composition and trace element concentration into the time-frame, U–Th ages along the growth direction were used to create time dependent proxy rather than distance.

In most speleothems from Hungary, growth rate changes and hiata during the deposition may indicate the occurrence of favorable (warm and humid) or unfavorable (cold and/or dry) conditions for calcite precipitation (*Siklósy et al.*, 2008a), thus, the observed features may represent climate changes.

4.2. Stable isotopes

The stable oxygen and carbon isotopic values were plotted against the ages (*Figs. 4a* and *4b*) according to the determined U-Th data of the selected section (ca. top 63 mm of the stalagmite). The profile consists of 125 samples obtained at ca. 0.5 mm increments. δ^{18}O values range between –9‰ and –6.7‰ (V-PDB) and δ^{13}C values range between –8.7‰ and –6‰ (V-PDB). The correlation between the two isotopes is very weak (0.13), and there is no systematic variation along a single growth layer, that suggest the sample deposited in isotopic equilibrium. However, distinct parts of the section studied (especially between ca. 1250 and 1500 AD) are characterized by fluctuations in both δ^{18}O and δ^{13}C values with higher correlation coefficient in response of possible kinetic fractionation. Processes including evaporation or rapid degassing of CO_2 from the cave dripwaters may explain this isotopic signal. In the case of δ^{18}O values (*Fig. 3b*), high-frequency cycles (with amplitudes of 1–1.5‰) are superimposed on low-frequency signals. Calcite at the bottom of the section exhibit δ^{18}O value of ca. –8‰ (V-PDB) with rapid fluctuations. Within a short period (at 1000 AD), a marked increase of >1‰ can be observed towards to less negative values of the section. These higher values remain and caracterize the section between 1000 and 1150 AD. Furter up-section, towards the younger part, lower averaged values were measured with some abrupt jumps towards higher δ^{18}O values, from which some coincide with similar δ^{13}C peaks. Between 1550 and 1680 AD there is a remarkable shift to lower δ^{18}O, while the very top of the stalagmite (>1680 AD) shows slightly higher values again.

The carbon isotope composition of the stalagmite (*Fig. 3a*) is characterized by similar high-frequency cycles with even more abrupt changes. Smaller variability can be observed at the bottom part of the section (before 1200 AD), while more variable values of δ^{13}C are present between ca. 1200 and 1500 AD. An abrupt change at ca. 1250–1300 AD resulted the highest δ^{13}C value of the stalagmite. From this point to the top, a trend towards lower values appear with another sharp peak at 1650 AD, which coincides with darker calcite just below the observed hiata at the top of the section (dotted lines in *Figs. 2* and *4*).

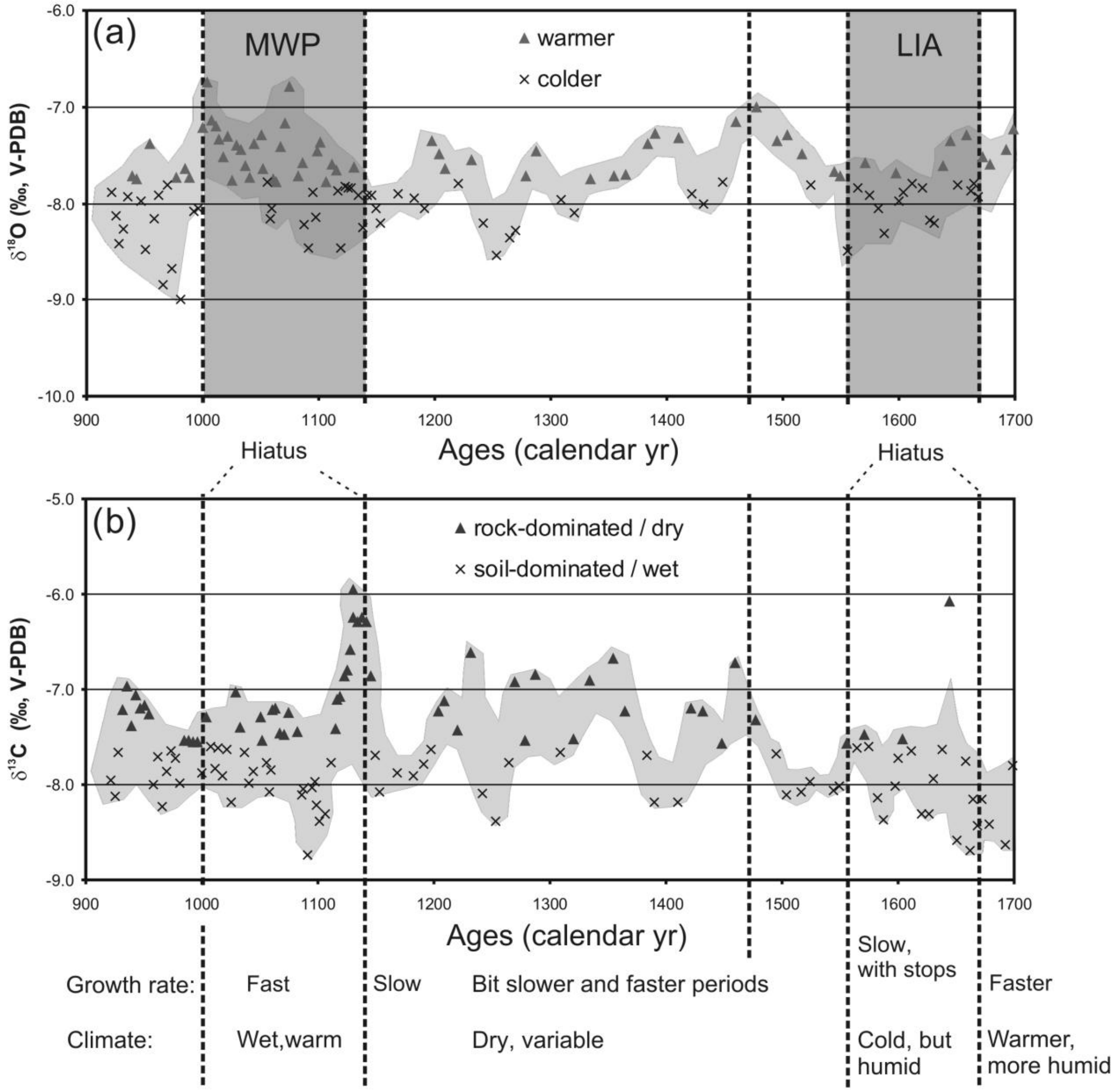

Fig. 4. Stable oxygen (a) and carbon (b) isotope record plotted against the age-relationship of the studied stalagmite. Vertical dotted line indicates hiata and/or marked textural changes during the selected growth period (see *Fig. 2*). See text for details.
(a) Triangles represent higher oxygen isotope values and crosses represent lower oxygen isotope values compared to the average of the total section.
(b) Triangles represent higher carbon isotope values and crosses represent lower carbon isotope values compared to the average of the total section.

4.3. Trace elements

Trace element data are plotted against the ages (AD) from the top of the sample (*Fig. 3c* and *d*). The stalagmite is practically free from detrital-derived impurities as the textural and prelimintary chemical scanning showed, therefore, they are not mentioned in this study or they are not responsible for the laminae observed in the stalagmite. The selected trace elements (Mg, Sr, and P) display similar oscillations along the studied section of the stalagmite, although there are some obvious differences (peaks and trends) at different parts of the concentration profiles.

Magnesium exhibits short-time cycles along the growth direction superimposed on a long-term increasing trend towards the top of the stalagmite (*Fig. 3c*). Low concentration appears between ca. 950 and 1100 AD, whereas the top part (between 1600 and 1680 AD) is characterized with higher Mg values. Mg shows no covariation with Sr or P.

Strontium displays high-frequency cycles superimposed on long-term changes as well. The highly variable Sr concentration clearly reveals a similar pattern as the δ^{13}C values in most of the section. The highest Sr values and peaks between 1300 and 1500 AD coincide with elevated δ^{13}C values, while there is a general decreasing trend between 1650 and 1700 AD for both profiles (*Fig. 3d*).

Phosphorus displays anticorrelation with Sr, but not with any other element (*Fig. 3d*). The overall anticorrelation is 0.61. The lowest values are observed between ca. 1150 and 1550 AD, with some troughs around 1600 AD. P peaks and elevated values (1000 – 1150 AD) generally encompass the lower values of Mg.

5. *Discussion on the stable isotopes and trace element records*

Before discussing the temperature and precipitation amount information obtained from the Kiskőhát Shaft, stable isotope data points were separated and colored according to their relative values to the averaged value of both (C and O isotope) datasets (*Fig. 4*), and plotted against the age.

As shown in *Fig. 2*, the older part of the studied section (35 – 40 mm to ca. 65 mm, which value represents ages between 847 and 1106 years BP) is characterized by faster growth rate (ca. 135 μm/year), opposit to the top of the stalagmite. In order to reconstruct the paleoenvironmental changes during this period, the δ^{18}O values of the stalagmite was first investigated. δ^{18}O of the seepage water is not controlled by the routing of the water but the composition of the local precipitation, thus the climate of the region (*Harmon et al.*, 1979; *Yonge et al.*, 1985). As abovementioned, higher δ^{18}O values of the precipitated carbonate primary reflect warmer climate. Evaporation may also have caused elevated δ^{18}O values, but this would be also indicated by the elevated Sr and Mg concentration. This period (between ca. 1000 and 1150 AD) is characterized by the highest values with positive shift of δ^{18}O (*Fig. 4)*, indicating warmer and/or arid climate conditions. This latter possibility can be ruled out, as the P and δ^{13}C show no systematic shifts towards low and high values, respectively, therefore towards drier conditions (*Fig. 3c* and *d*). Instead, the high P and the slight shift of δ^{13}C to more negative values imply increased soil biogenic activity, most probably due to the increased precipitation amount. Low Mg and decreasing Sr values can be also explained by dilution effect related to the elevated infiltration (i.e., wet conditions). According to the determined U–Th ages, this warmest period with the highest oxygen isotope values around 1000–1150 years may represent the Medieval Warm Period (MWP).

Just before this time period, the very bottom of the section (between ca. 900 and 1000 AD) represents colder and drier period, but the lack of interpretable data preceeding this time prevent the precise comparison.

In contrast to the MWP, the next few hundred years (ca. 1150–1500 AD) are characterized by highly variable geochemical parameters with sharp peaks of $\delta^{13}C$ values and Sr concentrations. In the case of Kiskőhát Shaft, the overall $\delta^{13}C$ values are determined by the contribution of biogenic CO_2 (plant respiration within the soil zone) and the degree of rock-water interaction. The resulted overall value is then modified or obscured by secondary processes as mentioned above (varying kinetic isotope effects, e.g., rapid degassing of CO_2 caused mostly by increased ventilation). In the case of the Kiskőhát Shaft, the $p(CO_2)$ of cave air falls strongly in winter because of the more ventilated system during cold seasons as a result of temperature dependent atmospheric circulation in sacklike chambers. This leads to a strong degassing of CO_2, therefore, a kinetic effect and an increase of $\delta^{13}C$ values in cave water. As the dissolved CO_2 degasses, the solution becomes supersaturated, and there is a tendency for $CaCO_3$ to precipitate. The maximum rates of $CaCO_3$ precipitation is, therefore, generated in the winter or cold periods, but only if the hydrologic system remains active for water infiltration.

As a result of slower flow rates within the karst system (i.e., dry climatic period), enhanced prior calcite precipitation along the flow-path may occur from waters due to Ca^{2+} supersaturations by CO_2-degassing. This prior calcite precipitation will lead to trace element enrichment (e.g., increased Sr and Mg concentration) of the dripping water and consequently in the stalagmite.

Sr incorporation into the calcite structure is dependent on precipitation rate. The overall good correlation between Sr, $\delta^{13}C$ (*Fig. 3a, d*) and – interestingly – also to lamina width, therefore, can be attributed to elevated precipitation rate most probably due to the temporal variations (i.e., sharp decrease) in $p(CO_2)$ in the cave air, which is mainly controlled by ventilation. We assume that both above mentioned processes, i.e., rapid degassing of CO_2 caused mostly by elevated, temperature dependent ventillation and prior calcite precipitation along the flow-path as a result of reduced precipitation amount occurred. Therefore, periods of low precipitation amount (dry conditions) and decrease in mean annual temperature (or longer winters) recorded during the deposition between ca. 1150 or 1200 and 1500 or 1550 AD. Low P concentration (*Fig. 3d*) supports our assumption, since the drier conditions prevent soil activity and, therefore, the biogenic production. Decreased soil biogenic CO_2 production via plant respiration and microbial activity leads to less negative $\delta^{13}C$ values, which, again record dry or drier conditions during the deposition of this part of the stalagmite. We assume that the increased δ^{18}O values may also represent drier conditions as a result of kinetic effect of evaporation events (e.g., at around 1280, 1400, and 1480 AD).

The rapid decrease of δ^{18}O values and change in trace element composition of the stalagmite imply remarkable change during the deposition at ca. 1500 AD. P shows rapid increase paralel to the decrease in Sr concentration, while Mg shifting towards more positive values. Textural studies indicate that there are small, but obvious variations in the petrographical features along the studied part of the stalagmite. The recognized hiata (vertical dotted lines in *Figs. 2* and *4),* represent ceased growth, especially near the top of the stalagmite (younger part). Non-uniform calcite growth rates were also shown by the age-depth relationship (*Fig. 2a*) and by the variable lamina width values (*Fig. 3a*). The lack of continuous growth reveals that the formation of the stalagmite suffer optimal conditions (i.e., warm and/or wet) in certain time period(s). The most remarkable hiatus can be seen close to the top of the stalagmite (ca. 1600 –1700 AD). As the recent mean annual temperature in the cave interior is ca. 5.5 °C, we could exclude solely the temperature decrease for widespread freezing of the cave system. A gradual cooling would inevitability resulted in significant δ^{18}O shift for the deposited carbonate (*Siklósy et al.*, 2008b), however, in the case of Kiskőhát Shaft, only minor variability were observed before and after the growth cessation. Restricted growth can be explained by reduced drip rate of infiltrating water in dry periods, or because of heavy water flows in the wet season within the cave, when the water is no longer supersaturated for $CaCO_3$. This latter option can be ruled out as the trace element composition (especially Mg) exhibit higher values rather than the diluted, low values. The rapid increase in Mg after between 1600 and 1700 AD is possibly due to an important increase in water residence time followed by the cessation of speleothem growth as indicated by hiata at the top. Decreasing Sr concentration values after 1500 AD and especially after 1650 AD also suggest reduced growth rate. By the end of this process, stalagmite growth ceased. Therefore, our data suggest that the lack of infiltrated water would explain the marked growth break. It is important to distinguish internal and external dryness, as the second option would definitely imply regional climate variability, and the P concentration and δ^{13}C values would reflect aridity induced changes in the vegetation and soil system. On the contrary, P concentration increases and δ^{13}C values decrease, representing prosperous conditions in the soil zone. We, therefore, argued that internal (”within cave”) dryness and, subsequently, the decrease in water availability during this period were responsible for the pausa of the growth. Water deficit in the interior can emerge by the advanced ventilation caused by enhanced winter (cold and dry) air masses entering the cave. In situ seasonal changes in p(CO_2) were recorded and supported our assumptions. Therefore, we suggest that elevated ventilation during this time period was caused by longer winters. Based on the determined ages, this section of the studied stalagmite deposited during the LIA. As a consequence of external cooling, $\delta^{18}O$ of the stalagmite during this period exhibits lower values, while averaged growth rate decreased (to ca. 16 – 40 μm/year), according to the determied U–Th ages and distances (*Fig. 2a*). As a first approach, the observed ca. 2‰ isotopic shift between the MWP and LIA can be translated into temperature change using the above mentioned temperature dependency factor of the local precipitation (ca. + 0.6‰ / °C) and the equilibrium fractionation that accompanies calcite deposition from drip-waters (– 0.24 ‰ / °C) inside the cave. These two factors would result a range of ca. 5 °C cooling, which is higher than the realistic value. Thus, more complex scenario required for the interpretation of the isotopic record, therefore, we need to consider additional factors than solely the temperature dependency that may modify the $\delta^{18}O$ values of the calcite. We assume that a combination of the following processes shifted the $\delta^{18}O$ values of the stalagmite towards less negative values during the MWP:

- a slight evaporation of the local precipitation and the infiltrating water resulted in elevated $\delta^{18}O$ value for the dripping water, thus for the precipitated calcite as well, or
- the decrease of the ratio between winter/summer precipitation resulted in positive shift of the annual infiltrating water.

To summarize, the coldest years (most probably longer or colder winters) spans around from 1550 to ca. 1700 AD. The missing periods (hiata) and the relatively bigger age errors around the top of the stalagmite prevent the better resolution of the LIA, however, the minimum growth rate and the complex geochemical record support our assumptions.

6. Conclusions

We investigated the textural characteristics, stable carbon and oxygen isotope composition, and the trace element content of the subrecent part of a laminated stalagmite from northeast Hungary (Kiskőhát Shaft) in order to reveal a climate induced geochemical record for the last millennium. The high-resolution record from the cave deposit revealed a number of paleoenvironmental proxy. We interpreted the changes in this speleothem as a result of complex changes in the environmental parameters:

1. Cold and/or arid years (lower annual mean temperature or longer winter) reduce the average growth rate or even stop the growth of the stalagmite, while warm and humid periods results in optimal conditions for the accretion (faster growth rate).
2. More positive $\delta^{18}O$ values represent warmer periods (Medieval Warm Period), with a favorable conditions (wet and warm) for biogenic activity in the soil zone.

3. Cooling at the end of the Medieval Warm Period resulted in a reduced soil biogenic activity revealed by the increased stable carbon isotope values.
4. The climate experienced several warmings and coolings and important changes in the precipitation amount over the Medieval Warm Period – Little Ice Age transition, both with slower and faster growth rates, compared to the previous time period (MWP).
5. During the Little Ice Age, the cave was colder, the growth rate of the deposits was practically zero (presence of hiata). In the case of growing, stalagmite recorded colder but humid conditions.

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