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# Seasonality in cave dripwater and air properties – implications for speleothem palaeoclimatology, Nova Grgosova Cave (Croatia)

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## Abstract

Due to the wealth of climate-sensitive properties, speleothems have been propelled into prominence as one of the most powerful continental archives of past climate changes. However, the multitude of processes that operate in the unsaturated karst zone and in the cave atmosphere can make palaeoclimate interpretations of the speleothem proxies challenging and site specific. Hence, to better understand the climate-proxy relationship, cave monitoring studies are usually undertaken. Here, we present the first results of an ongoing cave monitoring study in the Nova Grgosova Cave in Croatia covering an eighteen-month long monitoring period. The driving mechanisms for Mg/Ca and Sr/Ca variability in dripwater samples that feed ten stalagmites are discussed. The results reveal high variability in infiltration among the monitored sites as well as strong seasonal variability in cave air carbon dioxide ($CO_2$) concentrations. A strong positive correlation between dripwater Mg/Ca and Sr/Ca suggests that prior calcite precipitation (PCP) is taking place at this site affecting the chemical composition of dripwater. Principal component analysis furthermore reveals that dripwater Mg/Ca and Sr/Ca are in strong negative correlation with cave air $CO_2$ concentrations, while there is a weak correlation with dripwater quantity. Cave ventilation is a primary process leading to the PCP at the Nova Grgosova Cave. The seasonality revealed in this study suggests the possibility that the Mg/Ca and Sr/Ca ratio in the speleothems from this cave site can be used to aid seasonal reconstructions of past climate conditions in central Croatia and beyond.

## 1. INTRODUCTION

Speleothems, cave carbonate deposits that decorate many karst caves around the world, are valuable continental natural archives of past climate changes. The vast majority of palaeoclimate studies dealing with speleothems utilised their geochemical properties, (also known as proxies), to explore the causes and timing of past climate variability at sub-annual to orbital timescales (TREBLE et al., 2003; BORSATO et el., 2007; DRYSDALE et al., 2009; CHENG et al., 2016; WARKEN et al., 2018). Among all the geochemical properties, the isotopic composition of oxygen and carbon are the most often used, while an increasing number of studies apply a multi-proxy approach by combining these two commonly used proxies with other geochemical properties, including for example trace element ratios, fluorescence, and petrography.

Although a multi-proxy approach generally improves the reliability of palaeoclimate reconstructions from speleothems, the underlying climate signal is not always straightforward to interpret because the proxy-climate relationship can be affected by site specific processes. These site-specific processes may occur in the soil and epikarst zone above the cave or within the cave itself, including for example changes in hydrological routing (TREBLE et al., 2022), cave ventilation (SPÖTL et al., 2005; MATTEY et al., 2010), or evaporation in the epikarst and/or cave environment (MICKLER et al., 2004) all of which may mask the ingenious climate signal. To better understand how the climate signal is transferred into speleothem proxies at a particular cave site, it is common nowadays to perform complex monitoring campaigns. These monitoring studies, particularly when performed for longer time periods, (TREBLE et al., 2015; TADROS et al., 2016; RIECHELMANN et al., 2022) sometimes almost over a decade (TREBLE et al., 2015; TADROS et al., 2019), are often of paramount importance for reliable palaeoclimate interpretation of the studied speleothem proxies.

Magnesium and strontium easily substitute calcium in the carbonate crystal lattice, and they are the most often utilised trace elements (TE) in speleothem palaeoclimatology. The uptake of these elements into carbonate is described by the partition coefficient (K) defined as $K_{TE} = [TE/Ca]_{carbonate} / [TE/Ca]_{dripwater}$. Partition coefficients for both elements are experimentally determined and relatively well understood (DAY & HENDERSON, 2013; WASSENBURG et al., 2020). Magnesium and strontium in dripwater may be sourced from atmospheric dust and overlying soil, but in most of the cases the main source is the bedrock (FAIRCHILD & TREBLE, 2009; RIECHELMANN et al., 2022). Numerous studies reveal that the trace element to calcium (TE/Ca) ratio of cave

dripwaters, and hence of speleothems is not constant through time and that it may be responsive to several climate and environmental processes operating in the unsaturated karst zone above the cave (MCDONALD et al., 2004; NAVA-FERNANDEZ et al., 2020; WORTHAM et al., 2021; BERNAL et al., 2023) as well as the processes occurring within the cave itself (MATTEY et al., 2010; TREBLE et al., 2015; LYU et al., 2023). The predominance of a particular process affecting the dripwater TE/Ca ratio can be cave specific (TREBLE et al., 2015; TADROS et al., 2016), but it can also vary among the observed drip sites within a single cave (WONG et al., 2011; TREMAINE & FROELICH, 2013).

Here, we present the first results of an ongoing cave monitoring campaign undertaken at Nova Grgosova Cave in central Croatia. The isotopic composition of oxygen and carbon in two speleothems from this site has already been used to explore climate variability throughout the Holocene (SURIĆ et al., 2021), underpinned by 12 consecutive months of cave monitoring results (SURIĆ et al., 2018). The results published in SURIĆ et al. (2018) revealed seepage flow for two drip sites and a seasonal flow type for one monitored dripsite. The stable isotope composition record for this 12 month period implies well homogenised groundwater for three monitored dripsites (SURIĆ et al., 2018). In this new research, we expand the monitoring into more detailed investigations of the processes occurring in the atmosphere, soil, cave air and modern speleothems, in order to gain better understanding of the proxy climate relationship at this cave site. Here, we discuss the variations in dripwater elemental ratios (Sr/Ca and Mg/Ca) and explore their potential for palaeoclimate research of speleothems from this site. We provide the first interpretations for the observed patterns by combining hydrochemistry data with monitoring results of cave air microclimate properties, (i.e., the carbon dioxide concentration of cave air) and dripwater recharge data. The results presented in this study will support palaeoclimate interpretations of geochemical proxies in speleothems from this cave site which is the subject of ongoing research.

## 2. STUDY SITE LOCATION, CLIMATE AND GEOLOGICAL SETTING

The Nova Grgosova Cave is located in the Samobor hills in northwestern Croatia (45º49'7" N, 15º40'42" E, 239 m asl) about 30 km to the west of the capital city of Zagreb (Fig. 1). The explored sections of the cave have a relatively simple morphology, featuring a few chambers linked by a single passage with a total length of 97 m, depth of 14 m and no active river flow (Fig. 1A). It is important to note, however, that these passages were predominantly filled with sediments, including both clastic materials and speleothems. It is likely that the explored portion represents only a small fragment of the entire network of passages. Slightly less than one hundred metres

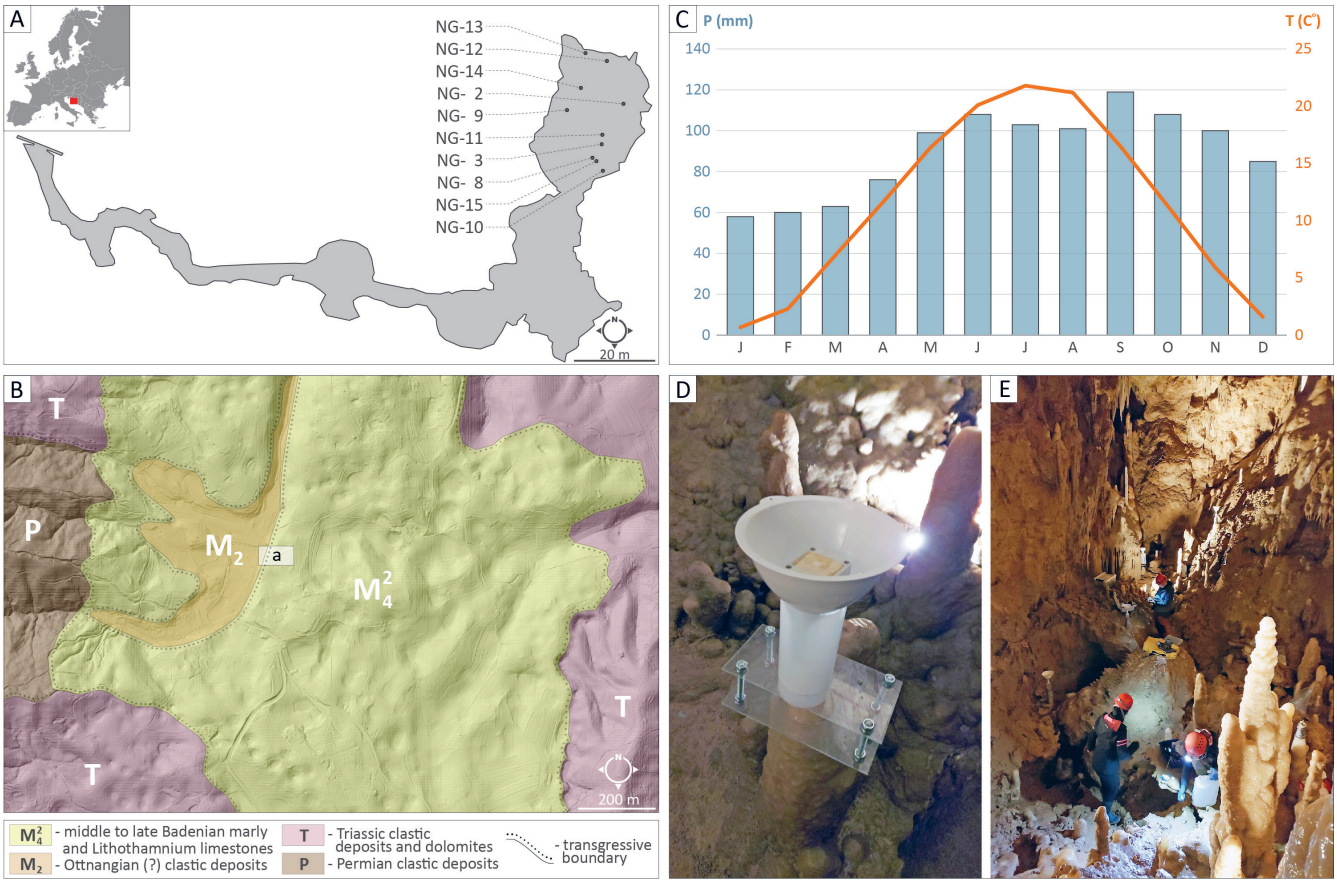


**Figure 1.** Geographic, geological and climate setting of the Nova Grgosova cave. Plan of the cave with marked positions of ten sampling locations (A). Local geological setting with basic chronostratigraphic units (ŠIKIĆ et al., 1978, 1979; VRSALJKO et al., 2005). Position of the cave is marked with letter a (B). Climate of the area is characterised as temperate humid continental with warm summers according to Köppen classification (C). Photographs of cave monitoring set up in Nova Grgosova Cave (D and E).

away, there is an entrance to another cave (the Stara Grgosova Cave), with passages developed on two levels. Both caves lacked natural entrances and were only discovered during quarrying and construction works in the hill slope. While no direct connection between them has been found, it is highly probable that these caves are parts of the same interconnected system. The Nova Grgosova Cave was sealed with metal doors soon after discovery in 2004. It is open for touristic visits throughout the year. Cave monitoring has been conducted at the far end of the cave, in a lower chamber not accessible to tourists.

The climate of the wider area is classified as belonging to the type Cfb – continental temperate humid with warm summers (PEEL et al., 2007). The mean annual temperature of the area is 11.4 °C and the mean annual precipitation is 1089 mm, both based on meteorological data collected from 1981 to 2023 at the Samobor meteorological station located 3 km away from the cave site, (data provided by Croatian Meteorological and Hydrological Service – CMHS, 2024). The annual distribution of rainfall is uniform with the maximum in September and a minimum recorded in January (Fig. 1C). Maximum temperatures are recorded in July and minimum in January (Fig. 1C). Potential evapotranspiration is at its maximum during the summer months (SURIĆ et al., 2018) causing the main infiltration season to coincide with the colder part of the year (i.e., from October to March).

The Nova Grgosova Cave is formed in the so called "Lithothamnium limestones" (Fig. 1B, M4), shallow-marine carbonates deposited from the middle to upper Badenian (ŠIKIĆ et al., 1978, 1979; VRSALJKO et al., 2005). These biolithic limestones were formed in reef to lagoonal (rhodolitic and back reef bioclastic facies) paleoenvironments, in a temperate to subtropical climate zone of the southwestern part of Central Paratethys. Vertical and lateral distributions of these deposits shows diversification of the depositional conditions followed by synsedimentary tectonic movements (MAGYAR et al., 1999; VRSALJKO et al., 2005). The Nova Grgosova Cave area tectonically belongs to the border zone between the Eastern and Southern Alps, Dinarides and the Pannonian basin, south of the Periadriatic line, with highly deformed pre-Neogene units (TOMLJENOVIĆ & CSONTOS, 2001). These deposits are most commonly in tectonic and transgressive contact with Mesozoic carbonates of the Žumberak Mt. (ŠIKIĆ et al., 1978, 1979).

## 3. METHODOLOGY – SAMPLING, ANALYSES AND DATA PROCESSING

The dripwater results we present here were collected between October 2022 and February 2024 at 10 monitoring locations positioned above stalagmites spread around the cave chamber (Fig. 1). The monitoring set up is composed of a drip logger, above which a watch glass is placed for harvesting recent carbonate samples. The drip logger is positioned in the funnel firmly attached to a bottle which is in some cases connected with the tubing to the canister of various sizes. The water from the bottle and canister is collected and analysed monthly usually at the end of the calendar month.

The $CO_2$ concentrations in the cave air were measured with a handheld Vaisala MI70 meter attached to the GMP252 $CO_2$ probe (manufacturer's accuracy: +/- 2% for readings in the range 3000 - 10 000 ppm) during monthly cave visits. Another Vaisala MI70 meter with GMP252 $CO_2$ probe is kept in the cave chamber for monitoring of $CO_2$ concentrations at hourly resolution and the results replicate well (unpublished data).

Temperature and relative humidity were recorded at hourly intervals by a HOBO Onset PRO v2 temperature and relative humidity logger beginning from December 2022. The logger was mounted in a holder off the cave wall, next to the position of the NG-2 stalagmite (Fig. 1).

The amount of infiltrated water at ten drip locations was monitored by Stalagmate acoustic driploggers (COLLISTER & MATTEY, 2008) at an hourly resolution. For this study, we calculated the number of drips corresponding to the time periods between the dripwater sample collection dates so that the resolution is comparable to other parameters discussed (i.e., trace metal to calcium ratios and $CO_2$ in the cave air). We used a 0.05 conversion factor for converting the number of drips to litres. The factor was selected based on the cross check of the total calculated volume with field notes of the approximate amount of water collected in containers between the two visits. As the volume of the collected water exceeded the canister capacity in some cases (i.e., NG-2 and NG-11), we were not able to do the comparison for those data.

A 20 mL aliquot of dripwater was filtered with a Chromafill Xtra PFTE 1 µm filter, subsampled to an acid-clean HDPE bottle, and acidified in the cave with 20 µL of 60% suprapure $HNO_3$ in order to prevent carbonate precipitation pre-analyses. The samples were stored in a refrigerator (≈ 4 °C) and analysed within a few days at the Croatian Institute for Public Health in Zagreb. A total of 176 dripwater samples were analysed throughout the study period. A larger number of elements was analysed, but here we focus on Mg, Sr and Ca results. Sample analysis was undertaken on an ICP-qMS system (Agilent Technologies, ICP-MS 7900). Calibration was performed with standard element calibration solutions 1000 mg/L for Ca and Mg (Certified Reference Material, CPA chem) and a multi-element calibration solution 10 µg/mL (Multi-element Calibration Standard 2A, Agilent Technologies) for Sr. Estimated measurement uncertainties for Mg, Sr and Ca were 11%, 8% and 20% respectively.

Two samples of the host rock were sampled for elemental analysis. One sample (NG ROCK 1) was sampled from the surface outcrop above the cave. Another sample (NG-WR-1) was taken from the weathered zone at 30 to 40 cm depth and is composed of 5 to 10 cm large fragments of host rock. Microwave digestion of samples was performed in a closed microwave digestion system (Multiwave GO, Anton Paar). Approximately 50 mg large subsamples were weighed with the addition of 2 mL Mili-Q water (18,2 MΩ at 25 °C), 5 ml nitric acid ($HNO_3$, TraceSelect$^{TM}$ ≥ 69%) and 2 ml hydrogen peroxide ($H_2O_2$, Suprapure® 30%) into teflon digestion vessels. Sample blanks were prepared using the same amount of reagents. The microwave digestion programme was set as follows: $t_{max}$ = 185 °C (ramp = 10 min, hold = 10 min). After digestion,

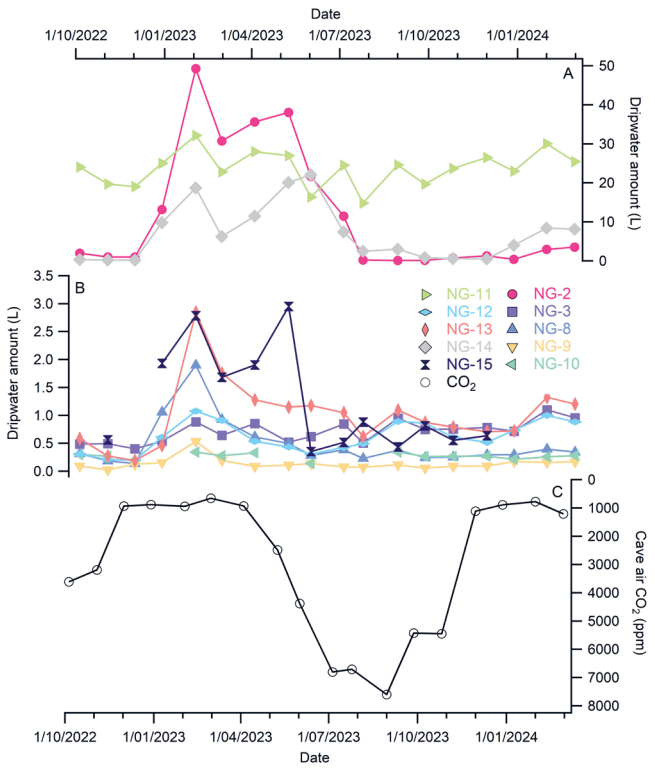


**Figure 2.** Dripwater amount (A i B) and cave air $CO_2$ concentration (C) results. While $CO_2$ shows strong seasonal variability, dripwater amount data reflective of discharge at particular monitoring positions reveal a large range in data as well as differences in variability between the monitored sites.

each sample aliquot was quantitatively transferred to a 50 ml PP sample cup and diluted with Mili-Q water to approximately 50 g. No precipitate or residue was observed. Samples were analysed on an ICP-qMS system (Agilent Technologies, ICP-MS 7900) at the Croatian Institute for Public Health in Zagreb. Calibration was performed with standard element calibration solutions: 1000 mg/L for Ca and Mg (Certified Reference Material, CPA chem) and multi-element calibration solution 10 µg/mL (Multi-element Calibration Standard 2A, Agilent Technologies) for Sr. Estimated measurement uncertainties for Mg and Ca were both 5% and 6% for Sr.

To unravel the underlying patterns and relationships among the collected dataset, Principal Component Analysis (PCA) was employed. The parameters used in analysis included cave air $CO_2$ concentrations, dripwater amount and dripwater Mg/Ca and Sr/Ca ratios. In the statistical programming language R (R CORE TEAM, 2024), the FactoMineR and factoextra packages were utilized for the PCA analysis, tailored to the specific requirements of the study. Before conducting PCA, all the variables were standardized individually for each sampling location, except for the NG-9 sample as explained further below. The standardization ensured that the data were on a comparable scale and retained information about spatial variability across the study area.

## 4. RESULTS

Magnesium, strontium and calcium concentrations, Mg/Ca and Sr/Ca molar ratios, dripwater amount, cave air temperature and $CO_2$ concentrations are all listed in Supplement Table 1.

Dripwater quantity results reveal high variability between the sites. Due to the large spread in the data, they are presented on two separate y-axes in Figs. 2A and 2B. The minimum monthly amount of 25 mL was recorded in the sample collected in November 2022 at the site NG-9 and a maximum monthly amount of > 49 L was registered in February 2023 at site NG-2. The time series analyses of the monthly data presented here, demonstrate that some sites display uniform drip rates (e.g., NG-3, NG-9, NG-10 and NG-11) with no seasonal variability, while others show higher variability in dripwater quantities throughout the investigated period (e.g., NG-2, NG-8, NG-12, NG-13, NG-14 and NG-15).

Monthly data on $CO_2$ concentration in the cave air (Fig. 2C) show large seasonal variations with lower $CO_2$ values observed from November to April, and higher $CO_2$ throughout the rest of the year. A minimum of 658 ppm was measured during the cave visit on the 1st of March 2023 (winter), and a maximum of 7600 ppm was recorded on the 30th of August 2022 (summer). Although exploring the mechanisms responsible for seasonal fluctuations in the cave air $CO_2$ is beyond the scope of this publication, it is likely that the observed seasonality in cave air $CO_2$ in Nova Grgosova Cave is caused by ventilation of the cave driven by strong outside temperature seasonality (Fig. 1). Seasonal temperature variability at the surface leads to differences in density between surface and cave air, a process often observed in other mid-latitude cave sites (SPÖTL et al., 2005; FRISIA et al., 2011; VAN RAMPELBERGH et al., 2014; TREBLE et al., 2015; GABROVŠEK, 2023). Our results demonstrate effective cave ventilation during periods of colder air outside the cave compared to the cave air, which leads to a decrease in cave air $CO_2$ concentration.

The monthly average data on cave air temperature and relative humidity are presented in Supplement Table 2. The average monthly cave air temperature is 11.42 +/–0.01 °C, throughout the monitoring period. The cave temperature is stable throughout the year and corresponds to the average surface temperature of 11.4 °C as measured at Samobor meteorological station (CMHS, 2024) for the period 1981–2023.

Results on relative humidity reveal 100% saturation throughout the monitoring interval. However, these data should be taken with caution due to the possibility of instrument malfunction when the saturation of 100% is reached.

Dripwater magnesium results (Fig. 3A) reveal low and rather stable concentrations throughout the monitoring period and most of the samples are within the range from 600 to 1500 ppb. The maximum Mg concentration is observed at site NG-9, which also shows the largest variability in Mg concentration in the whole dataset. The higher variability in NG-9 data compared to all other sites may be a result of different hydrogeological characteristics of the preferential flow paths feeding this particular stalagmite. To confirm this particularity, a longer time series and higher resolution data are needed.

Dripwater strontium data (Fig. 3B) do not display seasonal variability, similar to the Mg results. Most of the samples range in between 70 ppb and 110 ppb. The maximum of 165 ppb is recorded in sample NG-10 collected in July 2023. Indeed, all samples collected in July 2023 show an unusual systematic increase in Sr concentrations, accompanied by a systematic increase in Mg and a decrease in Ca concentrations. This sug-

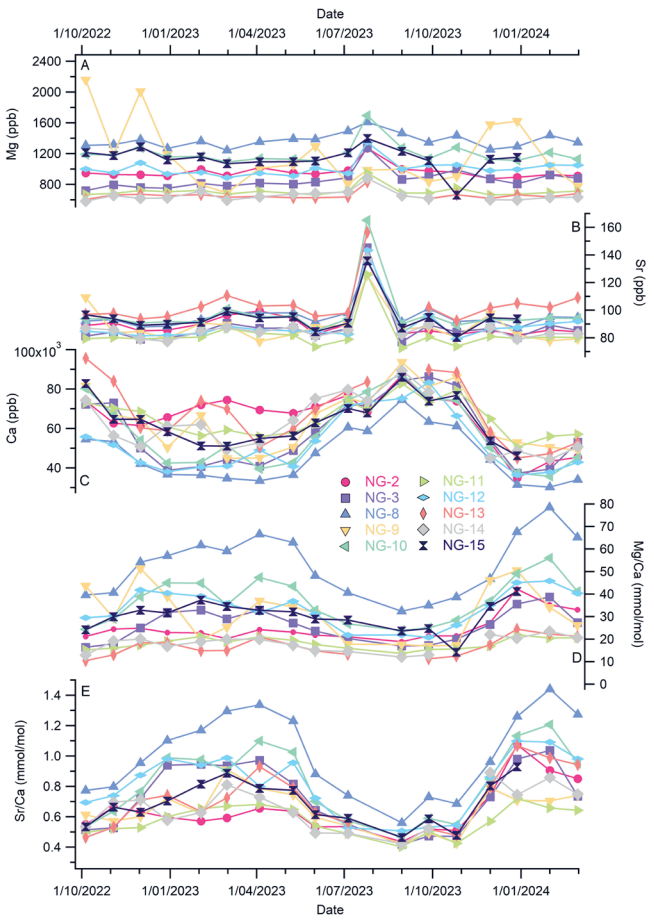


**Figure 3.** Magnesium (A), strontium (B) and calcium (C) contents in dripwater; magnesium to calcium (D) and strontium to calcium (E) ratios. Samples from July 2023 are identified as outliers (for explanation please see the text) and they are not included in the plot with Mg/Ca and Sr/Ca molar ratios.

gests a possible analytical problem with this dataset. Therefore, the results from samples collected in July 2023 are considered as outliers and were not included in further statistical treatment of the data nor their discussion.

Unlike Mg and Sr, Ca results (Fig. 3C) reveal strong seasonal variability with higher values measured in the Summer and Autumn while lower Ca concentrations are generally observed in samples from the Winter and Spring seasons. A maximum of 95 630 ppb was observed in sample NG-13 in October 2022, and a minimum of 30 239 ppb was recorded in January 2024 at site NG-8.

The majority of the observed sites reveal seasonal variability in their trace elements to calcium ratios, although seasonality is more pronounced in the Sr/Ca than in the Mg/Ca data (Figs. 3D and 3E). A minimum of Mg/Ca of 10.431 mmol/mol (NG-13) was recorded in October 2022, and a/maximum of 78.542 mmol/mol (site NG-8) in January 2024. A minimum in Sr/Ca of 0.40157 mmol/mol (site NG-11) was observed in August 2023, and a maximum of 1.4398 mmol/mol (site NG-8) in January 2024.

## 5. DISCUSSION

Results of our study indicate a strong positive correlation between Mg/Ca and Sr/Ca with the Pearson correlation coefficient (r) ranging from 0.89 (NG-15) to 0.98 (NG-2), ($p<0.001$) for all samples except NG-9 (Supplement Table 2). A positive correlation between Mg/Ca and Sr/Ca in cave dripwaters and in speleothems is often interpreted as an indication of prior carbonate precipitation (PCP) (FAIRCHILD et al., 2000; TOOTH & FAIRCHILD, 2003; RIECHELMANN et al., 2022). PCP is defined as a process of carbonate precipitation from percolation solution enroute, within the unsaturated karst zone or in the cave, but prior to the dripwater collection site (FAIRCHILD et al., 2000). SINCLAIR et al. (2012) proposed that the slope of a trendline through ln(Mg/Ca) versus ln(Sr/Ca) in speleothems or dripwater samples spanning from 0.709 to 1.003 is indicative of PCP affecting the TE/Ca ratio at the monitored location. WASSENBURG et al. (2020) showed that an even larger range (up to 1.45) in the slope is possible if PCP plays a main role in infiltration by considering variable partition coefficients for Mg and Sr as well as accounting for variable host rock composition. Our ln(Mg/Ca) vs ln(Sr/Ca) (Fig. 4A) shows slopes ranging from 1.01 to 1.15 and this indicates a strong effect of PCP in the infiltration dynamics at all the monitored locations, apart for site NG-9. The slope for site NG-9 is only 0.33. This different behaviour of NG-9 data compared to other sampling locations might be related to a high variability of Mg content in groundwater feeding this drip site but is yet to be resolved in more detail in future research.

PCP may be driven by two processes, often operating at the same time: 1) variability in water residence time in the epikarst because of seasonal variations in the infiltration process (WORTHAM et al., 2021; RIECHELMANN et al., 2022; BERNAL et al., 2023) and 2) seasonal variability in cave air $CO_2$ concentrations (TREBLE et al., 2015; LYU et al., 2023). During dry periods, the infiltration amount is usually low and the infiltrated water will equilibrate with a lower $pCO_2$ in the unsaturated zone, causing calcite (or aragonite) precipitation in the air-filled voids. Since the partition coefficient of Mg and Sr is much smaller than 1, Mg/Ca and Sr/Ca in the remaining water solution, and hence in dripwater will increase. Drier periods will also result in a lower drip rate in the cave, additionally enhancing the PCP on the cave ceiling (JOHNSON et al., 2006). Conversely, during wet periods, the epikarst is saturated with water and few air-filled voids are available. Therefore, an earlier degassing process in the epikarst is unlikely to occur, leading to a lower influence of PCP on Mg/Ca and Sr/Ca ratios in cave dripwater.

Mg/Ca and Sr/Ca ratios in dripwater can additionally be influenced by variations in the water-rock interaction including processes such as recrystallization or the incongruent dissolution of calcite/dolomite (TOOTH & FAIRCHILD, 2003). The role of incongruent dissolution of dolomite can be excluded from this study site, because the host rock is mainly limestone with no observed dolomite. This is additionally evidenced in low Mg and Sr concentrations and the low Mg/Ca ratio of the analysed host rock samples (Supplement Table 1, Fig. 4B), as well as in the analysed dripwater samples (Fig. 4B), compared to other studies where dolomite is present within the cave host rock (TREMAINE & FROELICH, 2013; WASSENBURG et al., 2020).

Recrystallization and incongruent dissolution of calcite (ICD) is another possible process which could lead to positive

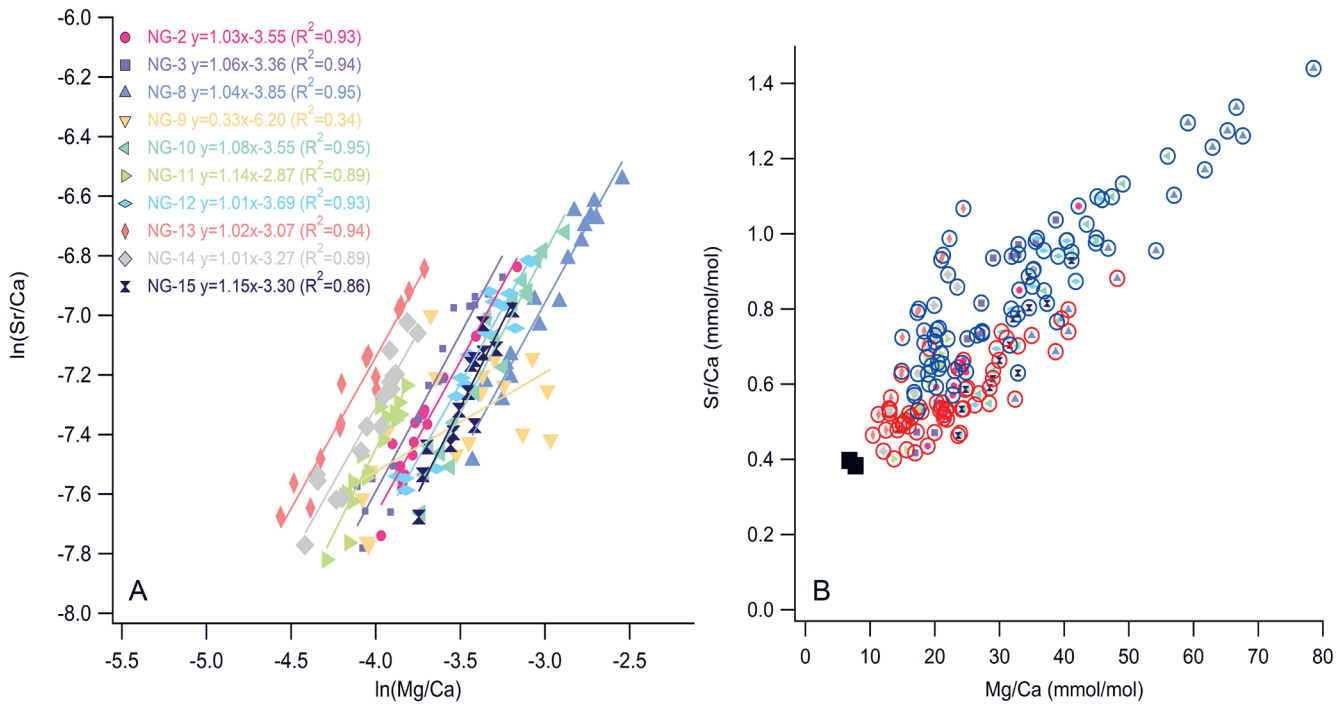


**Figure 4.** Dripwater ln(Mg/Ca) versus ln(Sr/Ca) data for each of ten monitored locations with linear fits. Slopes of the fit lines span from 1.01 to 1.15 indicating prior carbonate precipitation influence at nine out of ten dripwater sites (A). Mg/Ca vs Sr/Ca data plotted with respect to the two host rock samples. Red circles present samples corresponding to the May to October collection period, and blue circles indicate samples collected from November to April (B).

dripwater Mg/Ca and Sr/Ca correlation, but to make the distinction between PCP and ICD, additional methods should be applied including Sr isotopic composition of dripwater (WONG et al., 2011). However, both processes PCP and ICD would have the same effect on the Mg/Ca and Sr/Ca ratios in the dripwater (WONG et al., 2011) and would increase the Mg/Ca and Sr/Ca ratios during drier periods. This is unlikely to occur in the Nova Grgosova Cave, because higher Mg/Ca and Sr/Ca ratios correspond to seasons with higher infiltration, rather than drier periods.

Another driving process for PCP is the variability in $CO_2$ concentration of the cave air. This is particularly evident in mid-latitude ventilated caves, where seasonal changes in surface air temperature a density difference between air at the surface and within the cave, leading to stronger ventilation during the cooler period of the year. Such a process would lead to lower cave air $CO_2$ concentrations during the cooler part of the year, and weaker or no ventilation during warmer periods resulting in higher cave air $CO_2$ concentrations (SPÖTL et al., 2005; FRISIA et al., 2011.; KUKULJAN et al., 2021). In the Nova Grgosova Cave, the cave air temperature is stable throughout the year and it is very close to the mean annual surface temperature. However, the cave air $CO_2$ concentration is highly sensitive to the seasonal difference between surface and cave air temperatures, thus depicting a ventilation process occurring in the studied cave. Lower cave air $CO_2$ concentrations during the cooler season would increase the in-cave PCP process through the increase of degassing and the precipitation of carbonate in the form of stalactites or soda straws on the cave ceiling. An increase of Mg/Ca and Sr/Ca ratios in the remaining dripwater seems to follow such a process. In contrast, increased cave air $CO_2$ concentrations during warmer seasons would suppress the in-cave PCP, leading to a decrease in dripwater Mg/Ca and Sr/Ca ratios. Numerous stalactites and soda straws observed on the ceiling of the Nova Grgosova Cave, as well as a disproportionate number of stalagmites on the cave floor also indicate the important role of in-cave PCP at this cave site.

To further distinguish between hydrological and cave atmosphere effects on PCP evidenced in the strong positive correlation of Mg/Ca and Sr/Ca ratios, principal component analysis (PCA) was utilised. The analysis was undertaken for data from all the monitored locations, except for site NG-9 where PCP was not identified as a major influencing factor, according to the criteria of SINCLAIR et al. (2012) and WASSENBURG et al. (2020). The results of PCA analysis are presented in Figure 5.

On the PCA biplot (Fig. 5), Sr/Ca and Mg/Ca are positioned close to each other confirming the strong correlation between both parameters, because of the influence of PCP. The inverse relationship of the Mg/Ca and Sr/Ca ratios with respect to the cave air $CO_2$ concentrations on the PCA biplot, indicate a strong negative correlation between Mg/Ca (Sr/Ca) and $CO_2$. In contrast, the position of Mg/Ca and Sr/Ca with respect to the dripwater amount on the PCA biplot, indicate a weak correlation between Mg/Ca and Sr/Ca ratios and dripwater quantity.

The PCA analysis results reveal that two principal components explain a total of 92% of the variance in the dataset. PC1 explains a substantial portion of the variance (68%), while PC2 accounts for an additional 24% of the variance. In the context of our study, PC1 most likely reflects the dominant influence of cave ventilation on the seasonal variability in cave air $CO_2$ concentrations and consequently, dripwater Mg/Ca

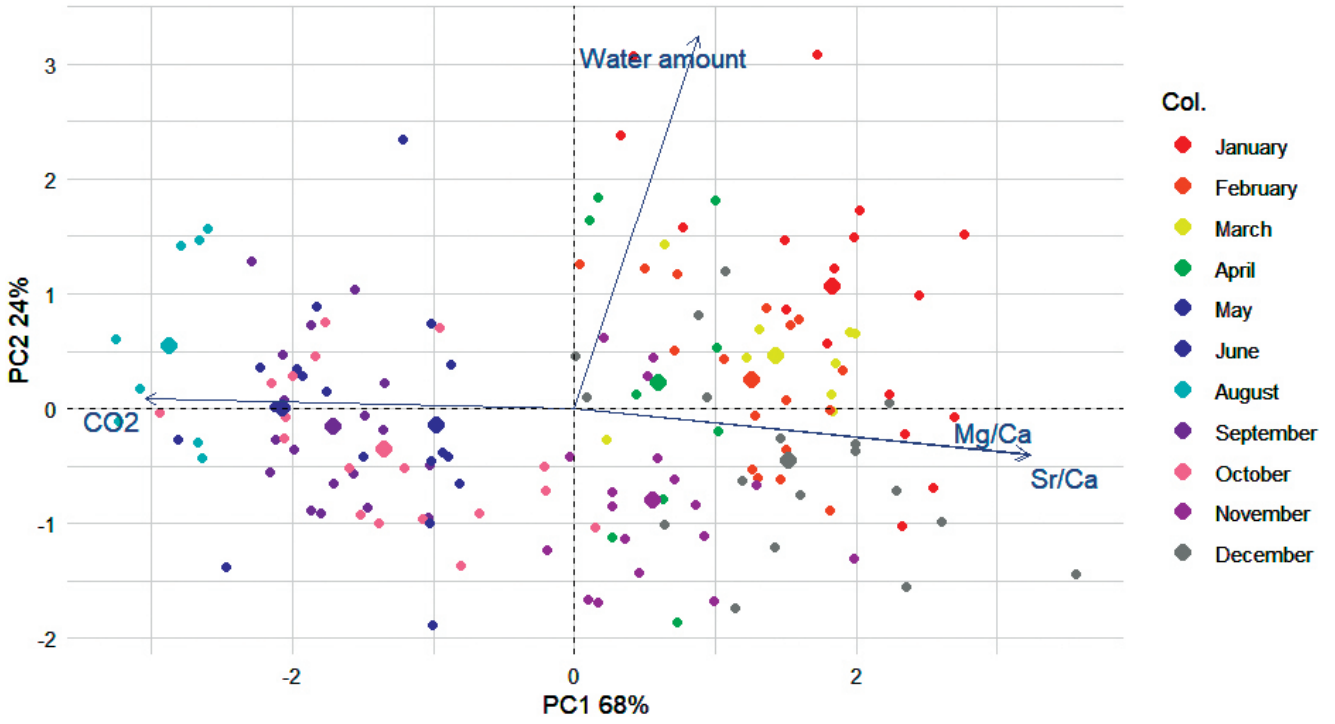


**Figure 5.** Results of principal component analysis confirm the strong positive correlation between Mg/Ca and Sr/Ca indicative of PCP and strong negative correlation between TE/Ca ratios and cave air $CO_2$ concentrations but weak correlation to dripwater amount. The arrow lines are used to reflect the variables of the dataset (parameters), and dots are used to show the observations (samples). The different colours correspond to the samples taken at different months throughout the monitoring period.

and Sr/Ca ratios. PC2, although explaining a smaller portion of the total variance (24%), represents an additional mode of variation, distinct from PC1. In our study, PC2 most likely reflects the influence of dripwater amount on the dripwater Mg/Ca and Sr/Ca ratios. However, the Mg/Ca and Sr/Ca are positioned almost under 90º with respect to the dripwater amount, indicating a weak correlation between Mg/Ca and Sr/Ca and dripwater amount.

Taken together, the analyses reveal that seasonal changes in cave air $CO_2$ is the main driver of PCP observed in this dataset. Low air $CO_2$ concentrations during the cooler period (from November to April), will increase the degassing process and calcite precipitation on soda straws and stalactites, thus increasing the PCP influence on dripwater trace element composition. In contrast, higher $CO_2$ concentrations from May to October, due to low ventilation conditions, will suppress the PCP effect. The dripwater composition is closer to the bedrock values (Fig. 4B) during this warmer part of the year.

The results of this ongoing study show the role of seasonal changes in cave air $CO_2$ in modifying Mg/Ca and Sr/Ca ratio in cave dripwater of the Nova Grgosova Cave. If the dripwater is supersaturated with calcite throughout the year, it is likely to expect that the seasonality observed in dripwater TE/Ca would be captured in speleothems in this cave. Depending on the growth rate TE/Ca, particularly Sr/Ca, ratio in speleothems from Nova Grgosova Cave can then be used as a seasonality proxy in palaeoclimate studies from these speleothems.

## 6. CONCLUSIONS

Cave monitoring program over 18 months has been conducted in Nova Grgosova Cave (Croatia) encompassing dripwater chemical composition (Mg/Ca and Sr/Ca ratios) and dripwater amount at 10 drip sites as well as cave air properties ($CO_2$ concentration, temperature and relative humidity). Two host rock samples were additionally collected and analysed for their Mg/Ca and Sr/Ca ratios. The results of the cave monitoring program conducted in this cave so far show strong seasonal variability in cave air $CO_2$ concentrations. Water infiltration is generally higher in winter and spring, and lower in summer and autumn, but it is very variable among the monitored sites. Some of the observed sites do not show any seasonal variability in the dripwater amount. Mg/Ca and Sr/Ca ratios for nine drip sites reveal a strong positive correlation with a slope ranging from 1.01 to 1.15 on the ln(Sr/Ca) vs ln(Mg/Ca) plots. Such correlations imply the influence of PCP on Sr/Ca and Mg/Ca ratios in the cave dripwater. PCA analysis between TE/Ca ratios, $CO_2$ concentrations in the cave air and dripwater amount shows that the PCP at Nova Grgosova Cave is likely driven by the seasonal variability in cave air $CO_2$ due to cave ventilation. The role of dripwater amount related to the seasonal infiltration is probably of minor importance. Assuming continuous supersaturation of the dripwater throughout the year, it is likely that the seasonal change in dripwater chemical composition would be reflected in the Mg/Ca and Sr/Ca ratios of the calcite.

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