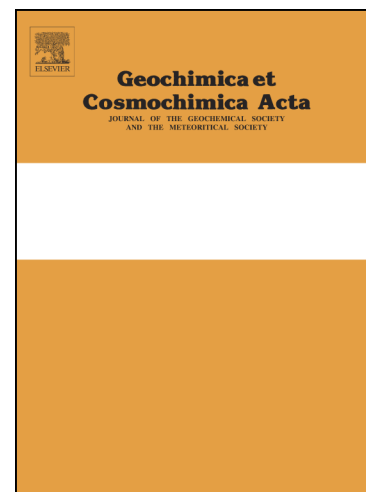


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Calcite Mg and Sr partition coefficients in cave environments: implications for interpreting prior calcite precipitation in speleothems

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Abstract

Trace element to Ca ratios in speleothems have emerged as important proxies that reflect local environmental conditions. However, interpretations of speleothem trace element records can be challenging due to various processes. Positive correlations between speleothem Mg/Ca and Sr/Ca have often been interpreted to reflect prior calcite precipitation (PCP), a process potentially modulated by rainfall variability. For quantitative interpretation of PCP, the distribution coefficients for Mg and Sr (D_{Mg} and D_{Sr}) are required. Here, we use ten cave monitoring calcite and drip water datasets to investigate the influence of temperature and drip water and calcite Mg/Ca and Sr/Ca ratios on speleothem calcite D_{Mg} and D_{Sr} . The datasets cover a large range of climatic and geological settings resulting in a large range of drip water Mg/Ca ratios. Speleothem calcite D_{Sr} shows a positive correlation with the calcite Mg/Ca ratio. Furthermore, D_{Mg} shows a clear temperature dependence ($D_{Mg} = 0.013 * e^{0.035 * T}$).

Previous work proposed that the slope of a trend line through a plot of $\ln(Sr/Ca)$ versus $\ln(Mg/Ca)$ of a speleothem trace element dataset is between 0.709 and 1.003 if dominated by PCP. However, this only holds true if the initial drip water Mg/Ca and Sr/Ca ratios as well as D_{Sr} and D_{Mg} are constant for the whole dataset. We use an excel-based PCP model (see Electronic Annex) to assess the potential influence of PCP on drip water and speleothem Mg/Ca and Sr/Ca ratios and simulate different initial drip water Ca, Mg, and Sr concentrations corresponding to limestone, dolostone, and mixed host rock compositions. In the case of enhanced PCP and high Mg/Ca ratios, calcite D_{Sr} increases progressively with the mean Mg/Ca ratio of the speleothem time series resulting in steeper slopes of $\ln(Sr/Ca)$ versus $\ln(Mg/Ca)$ of up to 1.45.

We show that PCP can induce slopes ranging from 0.709 (or even shallower) up to 1.45. This large range suggests that the previously applied criteria to detect PCP in speleothem records were too strict and may lead to unjustified exclusion of PCP as a potential interpretation of speleothem and drip water trace element ratios. Thus, the number of speleothem Mg/Ca and Sr/Ca datasets that potentially reflect past changes in effective rainfall may be larger than previously suggested.

1. Introduction

Speleothems are cave CaCO_3 deposits and well-established continental climate archives (Cheng et al., 2016; Drysdale et al., 2009; Jo et al., 2014). Well-preserved specimens can be dated very precisely by the $^{230}\text{Th}/\text{U}$ dating technique and analyzed at high spatial and temporal resolution. Proxy data from speleothems shed light on temperature, local precipitation and atmospheric circulation patterns. The most frequently used proxies are carbon and oxygen isotopes as well as trace elements (Baldini et al., 2015; Griffiths et al., 2010; Moseley et al., 2014). Speleothem trace element variability, however, may depend on a complex set of processes, and may be affected by different sources or transport and incorporation mechanisms, such as the presence of colloids (Hartland et al., 2012), aerosols (Dredge et al., 2013) and volcanic ash (Jamieson et al., 2015). This makes their interpretation occasionally challenging (Fairchild and Treble, 2009). A solid understanding of the underlying processes and their effects on speleothem trace element variability are thus of utmost importance.

Despite the large range of factors that potentially affect speleothem trace elements, positive correlations between speleothem Mg and Sr concentrations are often interpreted as the result of variable degrees of prior calcite precipitation (Cruz Jr. et al., 2007; Griffiths et al., 2010; Johnson et al., 2006), or incongruent calcite dissolution (ICD; Sinclair et al., 2011). Prior calcite precipitation is defined as precipitation of calcite in the karst aquifer or on a stalactite before the drip water reaches the stalagmite surface. Incongruent calcite dissolution (ICD) is characterized by the dissolution of calcite host rock and near-simultaneous precipitation of calcite, which increases drip water Mg/Ca and Sr/Ca ratios with increasing water to rock interaction and, thus, water residence time. Importantly, both ICD and PCP have been shown to induce similar relationships between speleothem Mg/Ca and Sr/Ca ratios (Sinclair, 2011; Sinclair et al., 2012).

Prior precipitation of CaCO_3 , either PCP (Fairchild et al., 2000) or prior aragonite precipitation (PAP; Fairchild and Treble, 2009; Jamieson et al., 2016; Wassenburg et al., 2016b) may be enhanced under dry climate conditions due to low recharge or under low cave air CO_2 concentrations (Fairchild et al., 2006; Sherwin and Baldini, 2011). Both conditions promote CO_2 degassing from the precipitating solution and increase the CaCO_3 saturation index of the drip water. Prior calcite and aragonite precipitation affect the trace element/Ca ratio of the drip water because trace elements are incorporated disproportionately with respect to Ca. Trace element incorporation can be described by the concept of the trace element distribution coefficient (D_X), which is defined as:

$$D_X = \frac{(X/Ca)_{Solid}}{(X/Ca)_{Solution}} \quad (1)$$

where $(X/Ca)_{Solid}$ is the trace-element-to-Ca-ratio of the precipitate and $(X/Ca)_{Solution}$ is the trace element-to-Ca-ratio of the drip water. In order to qualitatively assess the effects of PCP/PAP on speleothem trace element concentrations, it is only required to know whether D_X is larger or smaller than one (Fairchild and Treble, 2009). When aiming for a quantitative description, accurate quantification of D_X is required. Where D_X is known, several “tests” can be applied to assess whether speleothem Mg and Sr concentrations are dominated by prior $CaCO_3$ precipitation (Sinclair et al., 2012; Stoll et al., 2012) and/or ICD (Sinclair, 2011). Sinclair et al. (2012) showed that the slope (S) of the trend line through a dataset of speleothem $\ln(Sr/Ca)$ versus $\ln(Mg/Ca)$ approximates:

$$S = (D_{Sr} - 1)/(D_{Mg} - 1). \quad (2)$$

These authors derived that the most likely slope should approximate 0.88. Sinclair et al. (2012) also demonstrated that the uncertainty of the slope arising from the various published trace element distribution coefficients is considerable. Stoll et al. (2012) introduced a quantitative model to delineate which flow parameters, drip water chemistries, and CO_2 concentrations are required to explain speleothem Mg, Sr, and Ba variability solely by PCP. However, the success of their model also largely depends on the correctness of the trace element distribution coefficients.

Calcite D_{Mg} and D_{Sr} have been determined using a variety of different methods and experimental setups. The consequence is a wide range of estimates of D_{Mg} and D_{Sr} . Estimates for D_{Mg} range from 0.012 (Day and Henderson, 2013) to 0.057 (Gascoyne, 1983) (see also Tremaine and Froelich (2013) and references therein). Laboratory controlled precipitation experiments revealed that calcite D_{Mg} decreases with increasing fluid Mg/Ca ratios (Mucci and Morse, 1983). In addition, Gabitov et al. (2014) reported that an increase in precipitation rate is associated with lower D_{Mg} , whereas other studies demonstrated that D_{Mg} increases with increasing temperature (Day and Henderson, 2013; Huang and Fairchild, 2001; Oomori et al., 1987). Calcite D_{Sr} was shown to decrease with increasing calcite Sr/Ca ratios (Pingitore and Eastman, 1986), but to increase with increasing precipitation rates (Gabitov et al., 2014; Lorens, 1981; Tang et al., 2008) and calcite Mg/Ca ratio (Mucci and Morse, 1983). As a consequence, different D_{Sr} values should

be applied to speleothems derived from caves with limestone host rock and caves with dolostone host rock due to the large difference in drip water Mg/Ca. In summary, laboratory precipitation experiments demonstrated that Mg and Sr distribution coefficients are not constant, but depend on a variety of factors.

With the exception of the experiments performed by Day and Henderson (2013), most previous laboratory experiments, however, are not comparable to the environmental parameters that typify cave environments. In particular, drip waters in cave environments are characterized by low ionic strength and contain organics in particulate or colloidal form (Fairchild and Treble, 2009; Hartland et al., 2012). Some laboratory experiments were conducted under constant pH, which is not always the case for cave drip water. Drip water pH is an important parameter controlling the dehydration of Mg and Sr ions prior to their incorporation into the calcite crystal lattice, where Mg binds stronger to water molecules than Sr (Rodriguez-Cruz et al., 1999). Furthermore, the trace element composition of the drip water is of importance because different trace elements may compete for non-lattice sites (Borsato et al., 2007). It is thus very likely that distribution coefficients determined by laboratory experiments cannot be applied to the interpretation of speleothem trace element records. Cave monitoring experiments with watch glasses or glass plates to collect recent precipitates and data from the associated drip waters have significantly enhanced our understanding of cave calcite D_{Mg} and D_{Sr} (Riechelmann et al., 2014; Tremaine and Froelich, 2013). Similarly, combined analysis of drip water and the topmost layer of actively growing stalagmites provided values for cave calcite D_{Mg} and D_{Sr} (Fairchild et al., 2010; Huang et al., 2001; Karmann et al., 2007). However, these data have not yet been compiled and systematically evaluated to quantify the effects of drip water and calcite composition on speleothem D_{Mg} and D_{Sr} .

Here we compile new Sr/Ca data and published Mg/Ca data of calcite collected from watch glass precipitation experiments performed in six different caves in Europe and North Africa and their associated drip waters (Riechelmann et al., 2014). The dataset is complemented by additional data from other cave monitoring programs (Fairchild et al., 2010; Huang et al., 2001; Karmann et al., 2007; Tremaine and Froelich, 2013), and the cave analogue precipitation experiments from Day and Henderson (2013). This extensive dataset of Mg/Ca and Sr/Ca ratios of both calcite and drip waters is ideal to study the relationship between solution composition, calcite composition and D_{Mg} and D_{Sr} in cave environments.

We aim to enhance our understanding of speleothem calcite trace element partitioning and to better constrain the partitioning coefficients, which provides the foundation for more accurate interpretations in terms of PCP/ICD and thus past climate variability.

2. Cave settings

The data presented in this study represents a compilation derived from ten caves located in Germany (Riechelmann et al., 2011), Morocco (Riechelmann et al., 2014; Wassenburg et al., 2016a; Wassenburg et al., 2012; Wassenburg et al., 2013), USA (Tremaine and Froelich, 2013), Brazil (Karmann et al., 2007), Italy (Frisia et al., 2011; Huang et al., 2001), and Austria (Fairchild et al., 2010; Spötl et al., 2005). These caves cover a wide variety of climatic and geological settings with different relative amounts of dolomite in the respective host rocks. This, among other factors, leads to variable drip water Mg/Ca and Sr/Ca ratios. Table 1 provides detailed information on locations, cave air temperatures, and host rock for all cave sites.

Table 1 Cave site and monitoring characteristics

Cave site	Coordinates	Altitude cave entrance (m asl)	Cave air temperature (°C)	Main host rock lithology	Substrate	Monitoring frequency (drip water / calcite)	Reference
Grotte de Piste, Morocco	34°N/4°W	1260	11.6 ± 0.5	Dolomite	Watch glass	3-monthly / 3-monthly	This study / Riechelmann et al. (2014) ^a
Grotte Prison de Chien, Morocco	34°N/4°W	360	14.0 ± 1	Dolomite / limestone mix	Watch glass	3-monthly / 3-monthly	This study / Riechelmann et al. (2014) ^a
Grotte Bab Mafraque, Morocco	35°/05°W	1500	12.5 ± 0.1	Dolomite	Watch glass	3-monthly / 3-monthly	This study / Riechelmann et al. (2014) ^a
Bunker Cave, Germany	51°N/07°E	184	10.9 ± 0.6	Limestone	Watch glass	1-monthly / 3-monthly	This study / Riechelmann et al. (2014) ^a
Zoolithen Cave, Germany	49°N/11°E	455	8.5 ± 0.4	Dolomite	Watch glass	3-monthly / 3-monthly	This study / Riechelmann et al. (2014) ^a
Kleine Teufels Cave, Germany	49°N/11°E	405	9.1 ± 0.5	Dolomite	Watch glass	3-monthly / 3-monthly	This study / Riechelmann et al. (2014) ^a
Hollow Ridge Cave, USA	30°N/85°W	28	19.5	Dolomite / limestone mix	Glass plate		Tremaine and Froelich (2013)
Obir Cave, Austria	46°N/14°E	1100	5.8	Limestone	Stalagmite		Fairchild et al. (2010)
Ernesto Cave, Italy	45°N/11°E	1167	6.6	Dolomite / limestone mix	Stalagmite and soda straw		Huang et al. (2001)
Santana-Pérola Cave system, Brazil	24°S/48°W	Approx. 270	19	Limestone	Coating on discharge counter		Karmann et al. (2007)

^aMg/Ca data is published in Riechelmann et al. (2014)

3. Materials and methods

3.1. Trace element analysis

We add new Sr/Ca data from the calcite and the drip waters from Bunker Cave, Zoolithen Cave and Teufels Cave from Germany and from Grotte de Piste, Grotte Prison de Chien and Grotte Bab Mafraque from Morocco in addition to published Mg/Ca ratios (Riechelmann et al., 2014). After collection in the cave, 10 ml subsamples of the drip waters were acidified with 100µl 65% HNO₃. Before January 2013, cation concentrations of the drip water subsamples were analyzed with a VISTA MXP ICP-OES (Varian) at Heidelberg University, Germany. Internal 1σ-standard deviation is <1% for Ca²⁺ and Sr²⁺, whereas external standards, NIST1643e and SPS SW2, indicate a long-term reproducibility of 3.6 and 4.3% for Ca and 3.0 and 3.4% for Sr, respectively. From January 2013 onwards the drip water samples were analysed with an Agilent ICP-OES 720, with

a long term reproducibility of 2.0% for Ca and 3.1% for Sr as based on the SPS SW2 external standard.

Calcite (1.5 mg) was sampled from the watch glasses with a scalpel from random positions. Considering that there is probably some spatial variability in the calcite composition, this might induce uncertainty in the distribution coefficient, as also acknowledged by Tremaine et al. (2013). Element concentrations of the calcite were analyzed with an ICP-OES (Thermo Fisher Scientific iCAP 6500 DUO) at the Ruhr-University Bochum, Germany. Internal 1σ -reproducibility based on the CRM512 (dolomite) and CRM513 (limestone) standards is 0.081 and 0.002% for Ca^{2+} , and 22 and 1 ppm for Sr, respectively. Throughout the text, drip water and calcite Sr/Ca ratios are given as mmol/mol and Mg/Ca ratios as mol/mol.

3.2. Carbonate materials and approach

Drip waters were collected every month for Bunker Cave, and every 3 months for the other caves at the start and end of the period that calcite was collected on the watch glass. Based on Eq. (1), calcite D_{Sr} and D_{Mg} were calculated for every individual watch glass using the Sr/Ca and Mg/Ca ratios of the calcite and the corresponding drip water. Riechelmann et al. (2014) observed watch glasses with both calcite and aragonite precipitates. Because aragonite has a very different trace element composition compared to calcite (Wassenburg et al., 2016b), the data from these watch glasses were not included in our dataset in order to be confident that the measured Mg/Ca and Sr/Ca ratios represent pure calcite.

The uncertainties of the calcite and drip water trace-element-to-Ca-ratios as well as the trace element partitioning coefficients were calculated by error propagation taking into account the analytical uncertainties of all elemental concentrations for the Moroccan and German caves. In order to propagate the uncertainties for Mg/Ca and Sr/Ca ratios and D_{Mg} and D_{Sr} we used the most conservative errors (i.e., the largest errors) of Mg, Ca and Sr concentrations in drip water and calcite. For the calcite uncertainty, we used the internal standard deviations, which are larger than the 1σ -reproducibility of the standards. For the drip water uncertainty, we used the long-term reproducibility of the external standards. In addition, drip water trace element to Ca ratios may not be stable over the time that the calcite is collected. Therefore, we include the standard deviation of all drip water samples for each drip site in our error propagation. Uncertainties for drip water trace element to Ca ratios were calculated with the following equation:

$$\Delta^X/Ca = \sqrt{\sigma_1^2 + \sigma_2^2 + \sigma_3^2} * X/Ca \quad (3)$$

where σ_1 refers to the relative uncertainty of Mg or Sr, σ_2 refers to the relative uncertainty of Ca, and σ_3 refers to the relative standard deviation of the Mg/Ca or Sr/Ca ratios from all drip water samples for each specific drip site. Similarly, the uncertainties for the distribution coefficients were calculated with the following equation:

$$\Delta D_X = \sqrt{\sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \sigma_4^2 + \sigma_5^2} * D_X \quad (4)$$

where σ_1 and σ_2 (σ_3 and σ_4) refer to the relative uncertainty of Mg or Sr and Ca of the calcite (drip water), and σ_5 refers to the relative standard deviation of the Mg/Ca or Sr/Ca ratios from all drip water samples for each specific drip site, respectively.

Because D_{Mg} is temperature dependent (Day and Henderson, 2013), we corrected the calcite Mg/Ca ratios and the corresponding D_{Mg} values such that all values are representative of a temperature of 12°C (arbitrary value). Based on the relationship between D_{Mg} and temperature from Day and Henderson (2013), a theoretical D_{Mg} can be calculated. We then calculated the difference between the theoretical D_{Mg} for the real cave air temperature and the theoretical D_{Mg} at 12°C. This difference was then subtracted from the D_{Mg} derived from the real calcite and drip water Mg/Ca ratio. Similarly, a theoretical calcite Mg/Ca ratio can be calculated from the theoretical D_{Mg} and real drip water Mg/Ca ratio. The difference between the theoretical calcite Mg/Ca at the real cave air temperature and at 12°C was subtracted from the real calcite Mg/Ca ratio. This temperature correction was not applied when we examined the relationship between D_{Sr} and the calcite Mg/Ca ratio because the temperature correction may mask a potential effect. Clearly, uncorrected D_{Mg} were used for examining the relationship between D_{Mg} and cave air temperature within our compiled dataset. In general, the effect of the temperature correction on the calcite Mg/Ca ratio and D_{Mg} is small, with maximum corrections of 10 to 15% for one sample from the coldest cave (Ernesto Cave) and three samples from the warmest cave (Hollow Ridge Cave). All other corrections are much smaller than 10%.

4. Results

Calcite Sr/Ca ratios (mmol/mol) range from 0.021 to 0.314, with a mean of 0.053, whereas drip water Sr/Ca ratios range from 0.11 to 3.33 (Fig. 1a), with a mean of 0.56. Calcite Mg/Ca ratios (mol/mol) range from 0.00059 to 0.029, with a mean of 0.0087, whereas drip water Mg/Ca ratios range from 0.044 to 1.41, with a mean of 0.46 (Fig. 2a). Calcite and drip water trace element ratios are highly correlated for the respective elements (Figs. 1a, 2a). The slopes of the trend lines represent the corresponding D_X value and are 0.018 and 0.072 for D_{Mg} and D_{Sr} , respectively. The temperature correction for the calcite Mg/Ca has no significant effect on the slope or the correlation. The high correlation for the Sr plot ($r = 0.88$, $p < 0.001$, $n = 46$) is mainly due to two high Sr values from the Santana-Pérola cave system and the experimental data from Day and Henderson (2013). If these values are discarded, the correlation decreases to 0.75 ($p < 0.001$, $n = 44$), and the slope is substantially shallower (0.046; Fig. 1b). Many values do not plot on the trend lines suggesting that the corresponding D_{Mg} and D_{Sr} values are different compared to those values that plot close to the trend line.

Table 2 Drip site characteristics

Cave site	Drip site	Monitoring period	Mean drip water Mg/Ca ratio (mol/mol) ^a	Mean drip water Sr/Ca ratio (mmol/mol)	Total nr. of drip water samples	Mean calcite Mg/Ca ratio (mol/mol) ^a	Mean calcite Sr/Ca ratio (mmol/mol)	Total nr. of calcite samples	Mean growth rate ($\mu\text{m/yr}$)	Drip interval (s)
Grotte de Piste	GP6	02-10 / 08-12	0.649 \pm 13%	0.236 \pm 12%	11	0.014	0.031	2	79	123 \pm 138
Grotte Prison de Chien	GC5	11-09 / 08-12	0.435 \pm 5%	0.422 \pm 4%	11	0.010	0.062	2	10	9 \pm 6
Grotte Bab Mafrage	BM8	02-10 / 08-12	1.055 \pm 9%	0.191 \pm 6%	10	0.022	0.030	4	16	57 \pm 17
Bunker Cave	U I	07-11 / 06-13	0.053 \pm 8%	0.406 \pm 4%	8	0.001	0.038	3	29	10 \pm 6
	U IV	07-11 / 06-13	0.116 \pm 7%	0.697 \pm 7%	8	0.002	0.060	4	8	1380 \pm 276
Zoolithen Cave	Zoo1	02-10 / 01-12	1.007 \pm 8%	0.133 \pm 8%	5	0.011	0.037	1	6	6 \pm 5
	Zoo2	07-12 / 07-13	1.334 \pm 6%	0.133 \pm 7%	5	0.025	0.030	4	24	142 \pm 72
Kleine Teufels Cave	Teu4	04-11 / 07-13	0.897 \pm 19%	0.153 \pm 17%	7	0.017	0.023	1	51	1117 \pm 955
	Teu5	10-10 / 01-12	0.684 \pm 9%	0.182 \pm 7%	5	0.009	0.031	3	86	12 \pm 9
	Teu6	07-11 / 04-13	1.010 \pm 11%	0.105 \pm 11%	7	0.014	0.021	1	6	11 \pm 16

^aPublished in Riechelmann et al. (2014)

4.1. Calcite D_{Sr} and D_{Mg}

The calculated D_{Sr} values range from 0.037 to 0.34. The correlation between calcite D_{Sr} and calcite Sr/Ca is not significant ($r = -0.22$, $p > 0.1$, $n = 46$; Fig. 1c). However, a significant positive linear

correlation between D_{Sr} and calcite Mg/Ca ($r = 0.72$, $p < 0.001$, $n = 46$; Fig. 1d) is observed, which is described by the following equation:

$$D_{Sr} = 5.0 (\pm 0.7) * Mg/Ca + 0.082 (\pm 0.008) \quad (5)$$

This indicates that D_{Sr} increases with increasing calcite Mg/Ca and confirms the earlier findings from Mucci and Morse (1983).

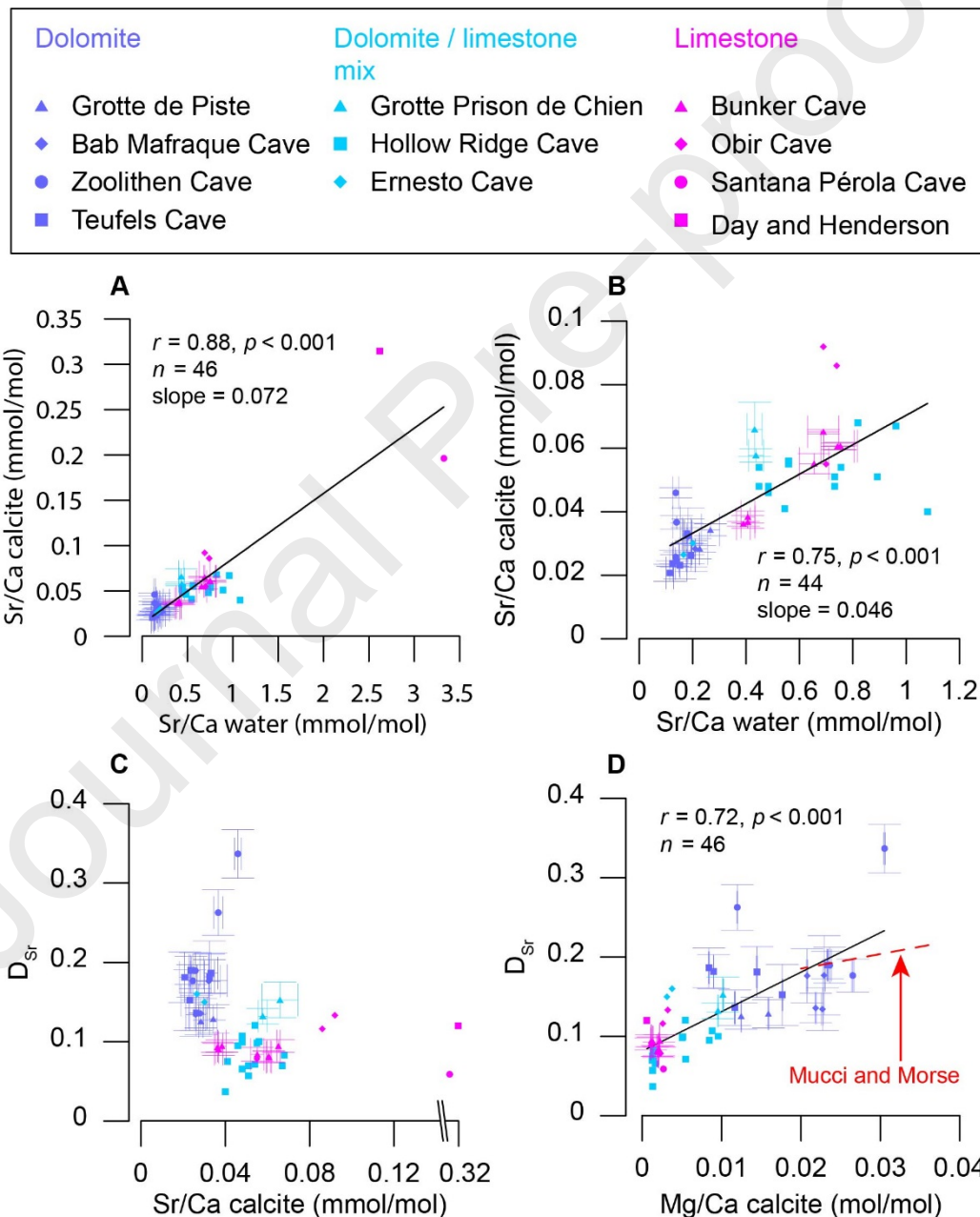


Fig. 1. a) Calcite Sr/Ca *versus* drip water Sr/Ca. b) Same as (a) but without the values from the precipitation experiments from Day and Henderson (2013) and Santana Perola Cave system (Karmann et al., 2007). c) D_{Sr} *versus* calcite Sr/Ca. d) D_{Sr} *versus* calcite Mg/Ca. Data corresponding to caves with a dolomite, limestone, and dolomite limestone mix host rock are indicated by different colors. Different symbols represent different cave sites: Ernesto Cave (Huang et al., 2001); Obir Cave (Fairchild et al., 2010); Santana Pérola Cave system (Karmann et al., 2007), Grotte de Pisté, Grotte Prison de Chien, Grotte Bab Maфраque, Kleine Teufels Cave, Zoolithen Cave (ZOO1-2), and Bunker Cave (Riechelmann et al., 2014), Hollow Ridge Cave (Tremaine and Froelich, 2013), and the value corresponding to the laboratory precipitation experiments from Day and Henderson (2013).

Values calculated for D_{Mg} range from 0.011 to 0.039. No significant relationship is observed between D_{Mg} and calcite Sr/Ca ($r = 0.11$, $p > 0.40$, $n = 46$; Fig. 2c).

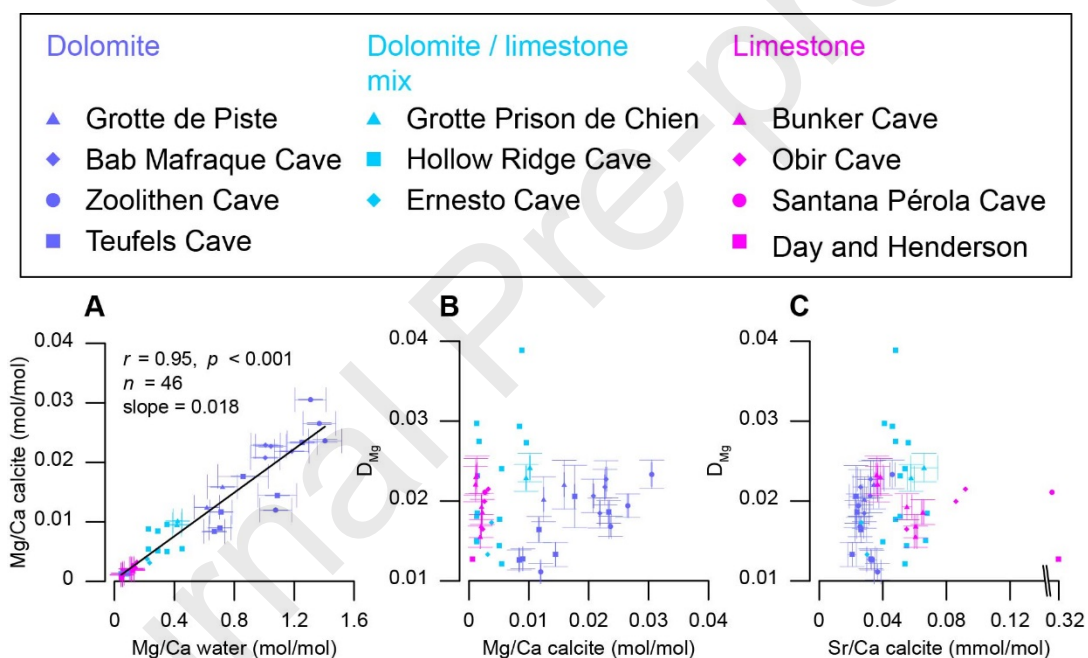


Fig. 2. a) Calcite Mg/Ca ratios *versus* drip water Mg/Ca ratios. b) D_{Mg} *versus* calcite Mg/Ca ratios. c) D_{Mg} *versus* calcite Sr/Ca ratios. Note the break in the x-axis between 0.12 and 0.32.

5. Interpretation and Discussion

5.1. Substrate

Calcite tends to follow the template of the underlying substrate and can grow at lower super saturation on stalagmite tips than on unseeded watch glasses. This is related to the nucleation energy that has to be overcome before calcite precipitation can initiate on the watch glasses. However, once calcite precipitates on the watch glass, growth rates should be comparable to that

of natural speleothems (Hansen et al., 2019). In our dataset we likely miss the low super saturation endmember, because we used unseeded watch glasses. Therefore, our results cannot be extrapolated to very low super saturation conditions as in Drysdale et al. (2019). To study low super saturation conditions with precipitation experiments it is advised to use seeded watch glasses that are spiked with rare earth elements as in Day and Henderson (2013). However, the distribution coefficients calculated from the watch glass experiments are comparable with those based on drip water and natural speleothems from Ernesto Cave (Huang et al., 2001) and Obir Cave (Fairchild et al., 2010). Therefore, we are confident that the substrate does not significantly affect our calculated distribution coefficients.

5.2. Rayleigh distillation *versus* apparent D_X

Rayleigh distillation taking place on the watch glass as a consequence of progressive CaCO_3 precipitation between two subsequent drips changes the trace element to Ca ratio of both the water film and the precipitating calcite. Especially in case of long drip intervals and high supersaturation, this may induce an apparent D_X that is higher than the real distribution coefficient (Johnson et al., 2006). The degree of Rayleigh distillation can be assessed by calculating the excess Ca (%) (Stoll et al., 2012) with the following parameters from the cave monitoring programs: calculated growth rates ($\mu\text{m/a}$), mean Ca deposition rates ($\text{mmol/cm}^2/\text{s}$) calculated using equation six from Wassenburg et al. (2016b), drip-intervals (s), and initial Ca concentrations of the drip water (mg/l). Growth rates are only available from the precipitation experiments from the German and the Moroccan caves published in Riechelmann et al. (2014).

The results show a Ca-excess ranging from 0.01 to 12.6% with only four watch glasses associated with a Ca-excess higher than 5%, including two from Bunker Cave, one from Grotte de Piste, and one from Teufels Cave (see Electronic Annex). With Ca-excess lower than 5% the apparent D_X that we rely on for our analysis approximates the true D_X . Considering that only two watch glasses with Ca-excess $>5\%$ are associated with higher calcite Mg/Ca ratios there is no significant influence on the relationship between calcite Mg/Ca ratio and D_{Sr} . Even a Ca-excess of 10% only results in an increase of approximately 5-7% in the D_{Mg} and D_{Sr} . Because the trace element to Ca ratio of the calcite that precipitates between two subsequent drips needs to be integrated over the entire drip interval. Therefore, we are confident that Rayleigh distillation only had a minor effect on the calculated values of D_X . Although we do acknowledge, that the calculated growth rates are associated with considerable uncertainties due to potentially variable growth rates

of single calcite crystals and the nucleation energy that has to be overcome before calcite precipitation can initiate on the watch glasses (Hansen et al., 2019).

5.3. D_{Sr} in speleothems

A relationship between calcite D_{Sr} and temperature is not observed in our dataset. Instead, we showed that speleothem calcite D_{Sr} increases with calcite Mg/Ca ratios (Fig. 1d). This relationship has been observed in laboratory experiments (Mucci and Morse, 1983), but so far not in natural cave environments. However, increases in speleothem trace element concentrations (including Mg) have also been suggested to result in lower D_{Sr} due to outcompeting Sr for non-lattice sites (Borsato et al., 2007). Furthermore, lower calcite growth rates under drier conditions may also cause lower D_{Sr} (Treble et al., 2003). Thus, the observed relationship seems to contradict earlier findings. The mechanism proposed by Mucci and Morse (1983) to explain this relationship involves the incorporation of the relatively small Mg cation replacing Ca in the calcite crystal lattice. They suggested that the associated lattice strain creates more space for larger cations, such as Sr, but back then, this hypothesis was difficult to prove. Recently, Littlewood et al. (2017) suggested that this relationship may be explained by the crystallization pathway involving amorphous calcium carbonate. In the following, we address these apparent contradictions in detail by discussing the above mentioned mechanisms in the context of our dataset.

5.3.1. Growth rate *versus* D_{Sr}

Growth rates are only available from the in-cave precipitation experiments documented in Riechelmann et al. (2014). These are based on the weight of the watch glasses determined before and after precipitation of $CaCO_3$. The growth rates presented in Riechelmann et al. (2014) are equivalents of speleothem extension rates in $\mu m/a$. As documented in Fig. 3, a relationship between D_{Sr} and growth rate cannot be observed within our dataset. This might be explained by the relatively low growth rates of 4-108 $\mu m/a$ for our dataset. Indeed, Gabitov et al. (2014) showed that calcite D_{Sr} increases for growth rates larger than 316 $\mu m/a$.

It may be argued that the large range of calcite Mg/Ca ratios masks the effect of the growth rate on D_{Sr} . However, this is not the case as a growth rate effect is not observed even if the dataset is divided into subsets with similar calcite Mg/Ca ratios (not shown). Moreover, the growth rates calculated with our approach are associated with considerable uncertainties, and represent minimum rates as the crystals need time to nucleate on the smooth surface of the watch glass.

Nevertheless, growth rates are controlled by drip rate, drip water Ca concentration, and the difference between cave-air and drip water $p\text{CO}_2$, factors that were not continuously monitored over the time of calcite precipitation on the watch glass. Therefore, the effect of the growth rate on D_{Sr} should be investigated with cave-analogue precipitation experiments with fixed drip water Mg/Ca ratios in order to verify our results.

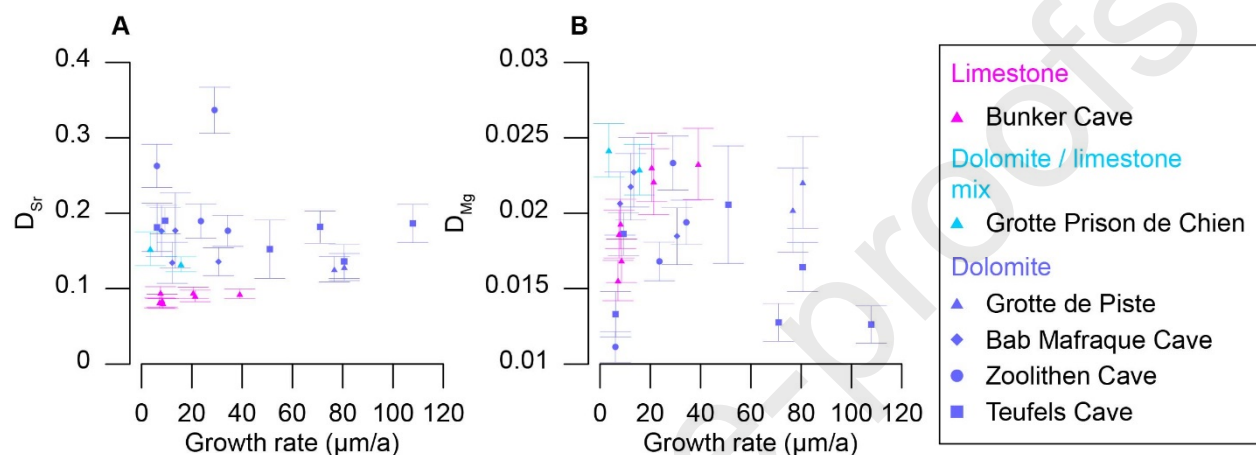


Fig. 3. a) D_{Sr} versus growth rate. b) D_{Mg} versus growth rate. Different colors correspond to different host rocks: dolomite, dolomite with limestone, and limestone, respectively. Squares, crosses and diamonds correspond to different cave sites.

5.3.2. Drip water composition and pH versus D_{Sr}

Although only Mg/Ca and Sr/Ca data from the drip water are presented, it has been suggested that other trace elements may outcompete Sr for non-lattice sites (Borsato et al., 2007), which would lead to a lower calcite D_{Sr} . Magnesium can be incorporated in the calcite crystal lattice, but it may also be incorporated at non-lattice sites and thus outcompete Sr. Another mechanism that would increase Mg incorporation with respect to Sr is related to the drip water pH that affects the bonding strength of Mg and Sr to water molecules. Water molecules need to be removed from Mg and Sr ions prior to their incorporation in the calcite crystal lattice (ion desolvation/dehydration; Ohtaki and Radnai, 1993; Pavlov et al., 1998). Mg bonds strongly to water molecules, whereas Sr bonds only weakly (Rodriguez-Cruz et al., 1999). An increase in drip water pH enhances the ion desolvation process, which results in more Mg available for incorporation. Therefore, we hypothesize that at higher drip water pH, Mg may outcompete Sr for crystal lattice sites, resulting in a lower D_{Sr} . Because higher drip water Mg/Ca ratios are associated with higher drip water pH (Riechelmann et al., 2014), variations in drip water pH cannot explain the strong positive

correlation between D_{Sr} and drip water Mg/Ca ratio ($r = 0.78$, $p < 0.01$, $n = 46$). This is a strong indication that D_{Sr} is indeed related to the calcite Mg/Ca ratio.

D_{Sr} also shows a negative correlation with drip water Sr/Ca ($r = -0.48$, $p < 0.01$, $n = 46$; Fig. 4a). Although this relation would be in line with the findings from Pingitore and Eastman (1986), 96% of the calcite Sr/Ca ratios are within a range of 0-0.1 mmol/mol, which is not comparable to the experiments of Pingitore and Eastman (1986), who used ratios of 0.19-1.88 mmol/mol. Instead, we argue that the relationship between drip water Sr/Ca and D_{Sr} is an artifact derived from the relationship between drip water Mg/Ca and Sr/Ca ratio, which is related to the variable balance between limestone and dolomite of the host rock of the different caves (Fig. 4b). Dolomite, $CaMg[CO_3]_2$, contains about 50% Mg, but has very low Sr concentrations, whereas limestone may have higher Sr concentrations, but lower Mg concentrations (Fairchild et al., 2000; Jacobson and Usdowski, 1976). Furthermore, the correlation between D_{Sr} and the drip water Sr/Ca ratio is much lower than the correlation with the calcite Mg/Ca ratio. Thus, we conclude that the calcite Mg/Ca ratio is the most important parameter affecting D_{Sr} in our dataset.

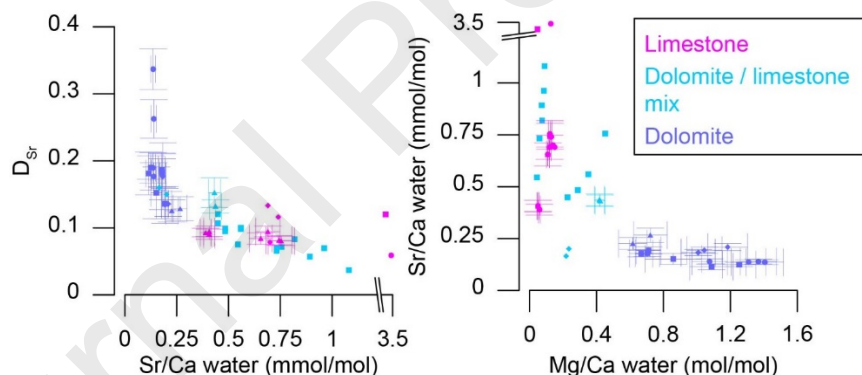


Fig. 4. a) Calcite D_{Sr} versus drip water Sr/Ca (same data as in Figs. 1 and 2). b) Drip water Sr/Ca versus drip water Mg/Ca. The relationship to the composition of the host rock is clearly visible. Symbols are colored according to the cave host rock of the drip site or stalagmite with the laboratory precipitation experiment from Day and Henderson (2013) labelled as “limestone”.

5.3.3. Calcite composition versus D_{Sr}

The relationship observed between D_{Sr} and calcite Mg/Ca ratios generally confirms the findings of Mucci and Morse (1983) (Fig. 1d). The intercept in the equation of Mucci and Morse (1983), however, is 0.146, whereas ours is 0.082 (± 0.008). The latter value is very similar to the lower range of published speleothem D_{Sr} values, which are representative for speleothem calcite

precipitated from drip water with low Mg/Ca ratios. This confirms that the D_{Sr} value estimated by our approach is applicable for cave environments.

Mucci and Morse (1983) explained the relationship between D_{Sr} and calcite Mg/Ca ratio by the different size of the cations, i.e., Mg (Sr) is small (large) relative to Ca. They argued that the incorporation of a small Mg cation deforms the crystal lattice such that more space is available to accommodate larger cations, such as Sr. However, Littlewood et al. (2017) examined this relationship in more detail and suggested that it can also be explained by the crystallization pathway of calcite. The precipitation of calcite may be preceded by an amorphous calcium carbonate precursor (ACC). Although parameters affecting the stability of ACC are debated (Purgstaller et al., 2017), high solution Mg/Ca ratios are associated with higher stability of ACC (Rodríguez-Blanco et al., 2012;) promoting the nucleation of calcite without vaterite as an intermediate phase. Under conditions of high supersaturation, the structure of amorphous calcium carbonate appears as a combination of aragonite and vaterite structures (Tribello et al., 2009). Since aragonite D_{Sr} is high and the trace element composition of amorphous calcium carbonate may be preserved, a crystallization pathway without vaterite may result in calcite with higher Sr/Ca ratios and thus higher D_{Sr} . However, the above experiments were conducted at much higher supersaturation than observed in cave environments. Therefore, we are cautious with assigning the observed positive correlation between Mg/Ca calcite and D_{Sr} in our dataset to the crystallization pathway.

Pingitore and Eastman (1986) examined the relationship between D_{Sr} and calcite Sr/Ca ratios and showed that D_{Sr} decreases with increasing Sr content of the calcite. Their experiments were performed with calcite Sr/Ca ratios ranging from 0.19 to 1.88 mmol/mol. In the cave datasets, we do not see a significant effect (Fig. 1c). However, Pingitore and Eastman (1986) performed experiments with fixed Mg/Ca ratios, in our dataset the Mg/Ca ratios covers a large range, which is ideal to study the effect of changes in Mg/Ca, but not for Sr/Ca. Furthermore, calcite Sr/Ca ratios are very low in our dataset, and the range is small compared to the experiments of Pingitore and Eastman (1986). The results can thus not be compared directly.

5.4. D_{Mg} in speleothems

5.4.1. Temperature *versus* calcite D_{Mg}

Calcite D_{Mg} is well known to be dependent on temperature with higher D_{Mg} corresponding to higher temperatures (Day and Henderson, 2013; Mucci, 1987). Temperature is considered to have little effect on speleothem Mg/Ca ratios due to relatively stable cave air temperatures all year round.

However, our dataset is compiled from caves with a large range in temperature and allows us to assess the D_{Mg} -temperature relationship. A significant positive correlation with temperature can be observed ($r = 0.54$; $p < 0.01$; $n = 46$; Fig. 5a), which increases when mean cave D_{Mg} values are taken into account ($r = 0.84$; $p < 0.01$; $n = 10$; Fig. 5b). The relationship is described by the following equation:

$$D_{Mg} = 0.013 * e^{0.035 * T} \quad (6)$$

Our dataset shows a slightly stronger dependency of D_{Mg} on temperature and an overall higher D_{Mg} compared to Day and Henderson (2013). In fact, our data plot closer to an exponential fit through the data from Rimstidt et al. (1998) (Fig. 5b). The exponential fit through the data from Rimstidt et al. (1998) is based on both natural biogenic as well as abiogenic and lab-controlled experimental calcites, whereas the experimental conditions from Day and Henderson (2013) were adjusted to mimic cave environments. This better agreement with the data of Rimstidt et al. (1998) is thus unexpected. There may be several explanations for this observation.

Day and Henderson (2013) use glass plates with carbonate seeds to mimic speleothem calcite surfaces, whereas in our compilation, unseeded watch glasses were used. Nevertheless, the D_{Mg} values derived from drip waters and speleothem calcite from Obir Cave and Ernesto Cave seem consistent with the watch glass and glass plate experiments (Fig. 5). Therefore, this is unlikely to be the cause for the observed difference. Interestingly, Day and Henderson (2013) included the elements Co and Cd in their solutions, which are not often measured in speleothems or drip water. Thus, “typical” Co/Ca and Cd/Ca ratios in cave environments are unknown. Both D_{Co} and D_{Cd} are larger than one, especially D_{Cd} varies from 37 to 27 for 7°C and 15°C, respectively (Day and Henderson, 2013). In the presence of Cd, the number of crystal lattice sites available for Mg may be smaller because D_{Mg} is three orders of magnitude lower than D_{Cd} . However, Day and Henderson (2013) only used low concentrations of Cd, and typical values for cave environments are unknown. Thus, it is unclear whether this explains the relatively low D_{Mg} values in their experiments. Finally, the presence of organic compounds in cave drip water may have an effect on calcite crystal morphology (Riechelmann et al., 2014), which in turn may affect speleothem calcite D_{Mg} . However, this remains to be explored.

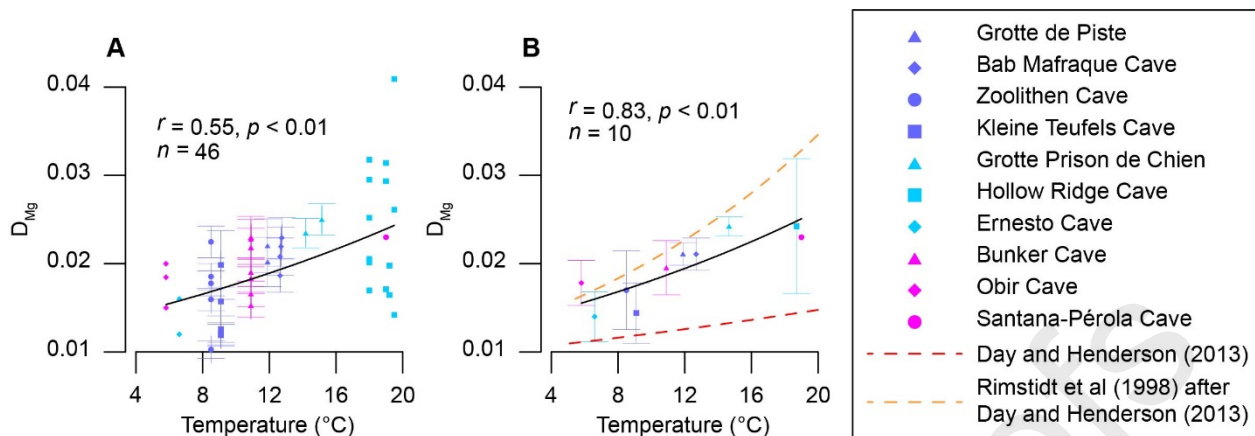


Fig. 5. Calcite D_{Mg} versus temperature. A) All data except Day and Henderson (2013) with exponential fit ($D_{Mg} = 0.013 * e^{0.034 * T}$). Uncertainties are as in Fig. 2 conform the error propagation explained in the method section. b) Mean cave D_{Mg} values with exponential fit ($D_{Mg} = 0.013 * e^{0.035 * T}$) and comparison with exponential fit from Day and Henderson (2013) ($D_{Mg} = 0.01 * e^{0.02 * T}$), and an exponential fit through the data of Rimstidt et al. (1998) as published in Day and Henderson (2013) ($D_{Mg} = 0.012 * e^{0.023 * T}$). Uncertainties reflect standard deviations of all D_{Mg} from the specific cave sites.

5.4.2. Growth rate and calcite and drip water composition versus D_{Mg}

We neither observe a relationship between D_{Mg} and calcite Mg/Ca or Sr/Ca ratio (Fig. 2b-c) nor with drip water Mg/Ca or Sr/Ca ratios in our dataset (not shown). Furthermore, calcite growth rate does not seem to affect D_{Mg} either (Fig. 3b). This is most likely related to the relatively low growth rate of the calcite because laboratory experiments only show an effect for growth rates higher than $316 \mu\text{m/a}$ (Gabitov et al., 2014).

5.5. Implications for the interpretation of Mg/Ca and Sr/Ca ratios in speleothem calcite

Sinclair et al. (2012) presented a compilation of Mg/Ca and Sr/Ca data from speleothems from six caves from the Western Pacific. They document that if both speleothem Mg/Ca and Sr/Ca ratios are dominated by PCP or ICD, the slope of the trend line of a graph of $\ln(\text{Sr/Ca})$ versus $\ln(\text{Mg/Ca})$ depends on D_{Sr} and D_{Mg} (Eq. 2). Importantly, the slope is independent from the initial drip water Mg/Ca and Sr/Ca ratios or host rock composition as long as the initial ratios are constant. The uncertainty associated with D_{Sr} and D_{Mg} directly translates into the uncertainty of the slope. Sinclair et al. (2012) account for these uncertainties and provide a range of slopes (0.709 – 1.003) based on different combinations of D_{Mg} and D_{Sr} based on a literature review of Huang and Fairchild (2001). In all following paragraphs, the word “slope” refers to the slope of the trend line on a plot of $\ln(\text{Sr/Ca})$ versus $\ln(\text{Mg/Ca})$.

The most relevant type of ICD increases Mg/Ca and Sr/Ca ratios in the drip water with increasing water-to-rock interaction and thus water residence times. Increased water residence times occur under drier climate conditions when PCP is also enhanced. Prior calcite precipitation also increases Mg/Ca and Sr/Ca ratios, and therefore ICD and PCP force drip water Mg/Ca and Sr/Ca ratios in the same direction under drier climate conditions. In the following, we discuss how changes in the drip water Mg/Ca and Sr/Ca ratios are modified by PCP, the potential effect on D_{Sr} and the consequences on the slopes.

The slope is mainly determined by D_{Sr} because it is one order of magnitude larger than D_{Mg} (Sinclair et al., 2012). As a consequence, changes in D_{Mg} related to temperature only have a minor effect on the slope. However, our data show a clear increase of D_{Sr} with the Mg/Ca ratio of speleothem calcite. Equation (3) provides a means to correct for the potential effect of speleothem calcite Mg/Ca and, thus, to apply a more accurate D_{Sr} .

5.5.1. Modeling prior calcite precipitation

Generally, higher D_{Sr} values correspond to shallower slopes and *vice versa*. It can thus be inferred that speleothem records from dolostone host rock caves are associated with shallower slope values than speleothem records from limestone host rock caves. However, enhanced PCP progressively increases the calcite Mg/Ca ratios of the drip water and the precipitated $CaCO_3$ and, therefore, also D_{Sr} . Thus, D_{Sr} may even change within a single speleothem or drip water dataset. In order to assess the effect of progressively increasing D_{Sr} , we use a simple PCP model, in which we set the initial Ca, Mg, and Sr concentrations of the drip water, and subsequently calculate the change in the Mg and Sr concentrations as a consequence of taking out a certain percentage of Ca related to PCP. From this, we calculate the new trace element to Ca ratios corresponding to the new concentrations. We use the following equations:

$$\Delta Mg = \Delta Ca * \left(\frac{Mg}{Ca} \right)_i * D_{Mg} \quad (7)$$

$$\Delta Ca = Ca_i - Ca_x \quad (8)$$

$$D_{Mg} = \frac{(\Delta Mg / \Delta Ca)}{\left(\frac{Mg}{Ca} \right)_i} \quad (9)$$

where the subscript (i) refers to the initial values and (x) refers to the value corresponding to a specific percentage of Ca taken out from the drip water. These values are then used to calculate the calcite trace element to Ca ratios using equation (1). The modeling file is provided as an excel-file in the Electronic Annex that can be used to check whether drip water or speleothem calcite Mg/Ca and Sr/Ca datasets are dominated by PCP or not.

Four scenarios are considered with different initial drip water Sr and Mg concentrations corresponding to 100% limestone (low Mg, high Sr: scenario 1) and 100% dolostone (high Mg, low Sr: scenario 2) endmembers, a mix of 80% limestone and 20% dolostone (scenario 3), and a mix of 40% limestone and 60% dolostone (scenario 4). We set the corresponding initial concentrations as published by Tremaine et al. (2013). Because D_{Sr} depends on calcite Mg/Ca ratios (Fig. 1d), we model all scenarios with a variable D_{Sr} dependent on calcite Mg/Ca ratios. We acknowledge, however, that the calcite Mg/Ca ratio is not the only parameter that affects D_{Sr} because it only explains approximately 52% of the total variance. Therefore, we also model all scenarios with a constant D_{Sr} to show the full range of possible slopes related to the different scenarios. The constant D_{Sr} corresponds to the calcite Mg/Ca ratios calculated from the initial drip water Mg/Ca ratios such that both models with constant and variable D_{Sr} start with the same initial calcite Sr/Ca ratios. For the scenarios that involve mixed limestone/dolostone host rocks, we assume that both calcite and dolomite saturation indices are zero before CO_2 degassing creates a supersaturated solution with respect to calcite, which is then followed by PCP.

5.5.2. Slopes corresponding to different scenarios

If D_{Sr} is constant during the phase of speleothem growth, speleothem calcite derived from caves with (partly) dolostone host rocks (i.e., high drip water Mg/Ca ratios) result in shallower slopes compared to speleothem calcite formed in caves with limestone host rock (Table 3; Fig. 6a). However, all scenarios with constant D_{Sr} are associated with very similar slopes ranging from 0.90 to 0.93 (Table 3), i.e., comparable to the slopes presented by Sinclair et al. (2012).

Table 3
Slopes corresponding to different scenarios.

Scenario			1	2	3	4
Constant D_{Sr}	Drip water	Overall	0.93	0.9	0.93	0.91
	Calcite	Overall	0.93	0.89	0.93	0.91
Variable D_{Sr}	Drip water	Overall	0.93	0.86	0.92	0.89
		Min.	0.93	0.76	0.90	0.83
		Max.	0.93	0.90	0.93	0.91
	Calcite	Overall	0.95	1.31	1.08	1.23
		Min.	0.94	1.21	1.02	1.13
		Max.	0.97	1.45	1.22	1.4

For calcite, the slopes corresponding to model runs with variable D_{Sr} , dependent on the calcite Mg/Ca ratios, are steeper compared to the slopes of the corresponding model runs with constant D_{Sr} (Fig. 6a-b; Table 3). This can be explained by the fact that speleothem calcite with high Mg/Ca ratios is associated with a higher D_{Sr} and, thus, relatively enriched in Sr. These data points will thus plot above the trend line associated with a constant D_{Sr} although the initial elemental concentrations are the same (Fig. 6a). The difference is most (least) pronounced for the 2nd scenario (1st scenario). This results from the fast increase of the drip water Mg/Ca ratio as a consequence of PCP for the 2nd scenario. We also present the evolution of the slopes with respect to the mean Mg/Ca ratios, with D_{Sr} depending on calcite Mg/Ca (Fig. 6b). The slopes corresponding to scenarios with a constant D_{Sr} are by definition constant and thus not shown. It appears that the rate at which the slope increases is especially high for low mean Mg/Ca ratios, whereas a maximum slope of ≈ 1.45 is established for the 2nd (high Mg) scenario with a mean calcite Mg/Ca ratio of ≈ 0.035 .

If D_{Sr} depends on calcite Mg/Ca, the range of slopes for the drip water is within the range presented by Sinclair et al. (2012). However, a higher D_{Sr} at higher calcite Mg/Ca ratios causes the calcite to have a steeper slope than the range presented by Sinclair et al. (2012; Table 3; Fig. 6).

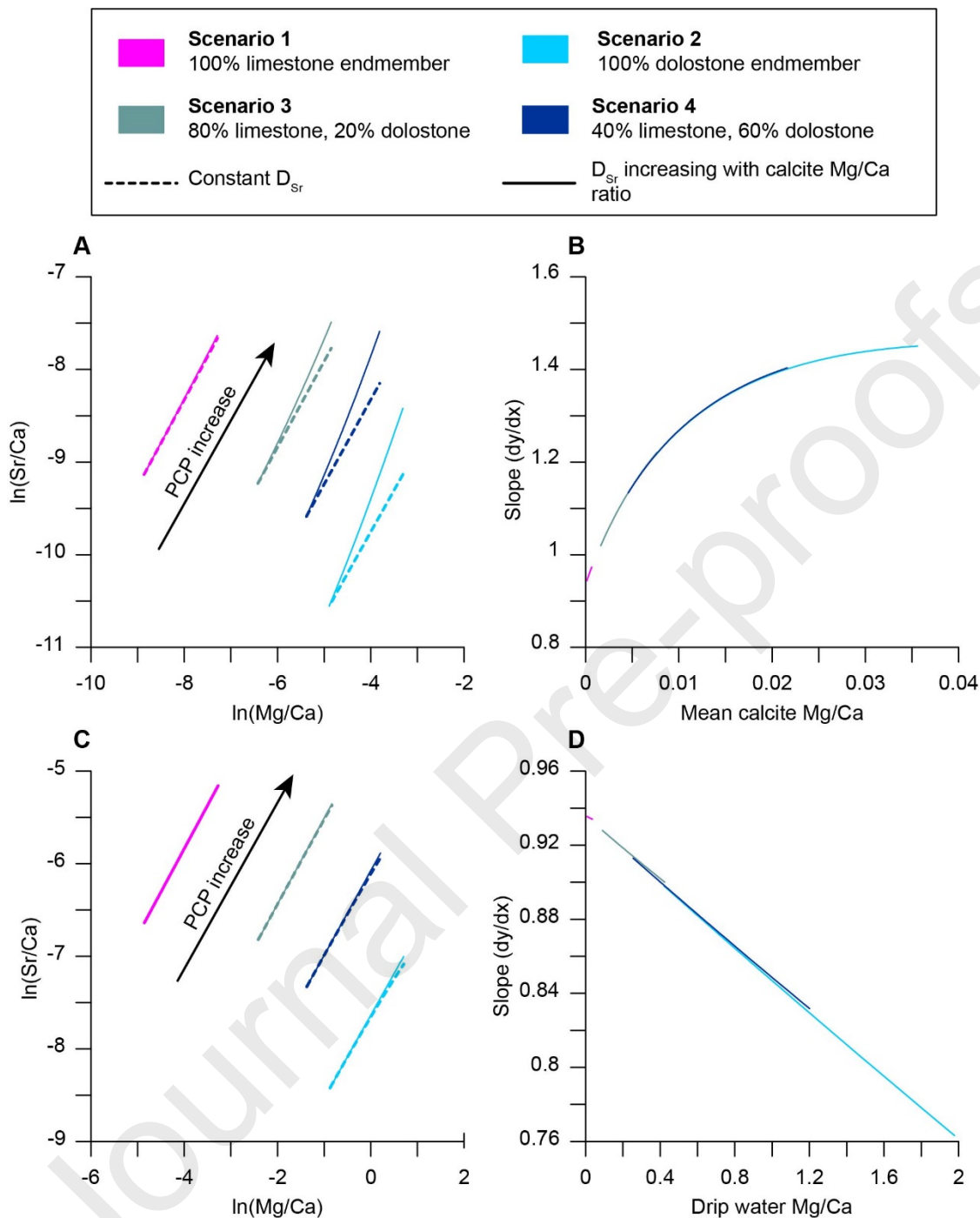


Fig. 6. a) Modeled evolution of speleothem calcite $\ln(\text{Sr}/\text{Ca})$ and $\ln(\text{Mg}/\text{Ca})$ forced by PCP for scenarios one to four outlined in the main text. Dashed lines correspond to model runs with constant D_{Sr} . These should be interpreted with caution because they can only be considered true if D_{Sr} is constant. b) Slope evolution with respect to the mean calcite Mg/Ca ratios for scenarios one to four with D_{Sr} depending on calcite Mg/Ca ratios. c) as (a) but for drip water. d) as (b) but for drip water. The model was forced by initial drip water Ca, Mg, and Sr concentrations as published by Tremaine et al. (2013; see Electronic Annex).

5.6. Changes in initial drip water trace element to Ca ratios

Initial drip water trace element to Ca ratios cannot be considered constant, especially if the cave host rock is a mixture of both limestone and dolostone. It is well known from computations and leaching experiments that it takes more time (up to several years) to reach full saturation with respect to dolomite compared to calcite (Fairchild et al., 2000). Variable water residence times may thus lead to different dolomite saturation states, which, in turn, have a large impact on the drip water Mg/Ca ratio (Fairchild et al., 2000), D_{Sr} and the slope of the trend line on a plot of $\ln(Sr/Ca)$ versus $\ln(Mg/Ca)$. Taking into account that the Mg/Ca (Sr/Ca) ratio is much higher (lower) in dolostone compared to limestone (Fig. 3), longer water residence times should be associated with higher Mg/Ca ratios and lower Sr/Ca ratios. Long but variable water residence times, could thus potentially explain negative correlations between speleothem Mg/Ca and Sr/Ca ratios. However, long water residence times may also be associated with PCP, which causes a positive correlation between speleothem calcite Mg/Ca and Sr/Ca ratios. The effect of a mixed limestone dolostone host rock may be particularly important for a low Mg limestone with a low percentage of dolostone host rock. Furthermore, the rate of dolomite dissolution determines how long PCP is accompanied by increasing initial drip water Mg/Ca ratios, which may have a profound effect on the slope. Modeling these effects is, however, beyond the scope of this paper.

In addition to mixed host rock cave settings, other sources may also contribute to changes in the initial Mg/Ca and Sr/Ca ratios of the drip water. Examples include volcanic ash deposits (Jamieson et al., 2015), aerosol settling under dry climate conditions within the cave (Dredge et al., 2013), wind-blown dust (Zhou et al., 2008), and the balance between Sr derived from the soil versus Sr derived from the host rock (Wortham et al., 2017). Mg- and Sr-isotope analysis is a valuable tool to identify different sources of these elements (Oster et al., 2010; Riechelmann et al., 2012; Weber et al., 2017). It is important to realize that positive correlations between Mg and Sr in speleothems may also be induced by changes in the sources of these elements.

5.7. Application to published datasets

Sinclair et al. (2012) presented an extensive survey of published drip water and speleothem calcite Mg/Ca and Sr/Ca ratios and indicated which datasets plot within their range of PCP-slopes (i.e. 0.709 – 1.003). From this survey, four speleothem calcite datasets from Clamouse Cave (McMillan et al., 2005), Botuvera Cave (Cruz Jr. et al., 2007), Aoufous Cave (Buhl et al., 2007),

and Liang Luar (Griffiths et al., 2010) showed slopes steeper than 1.003. However, when the uncertainties of these slopes are taken into account, they still overlap with the range of slopes presented by Sinclair et al. (2012), with the exception of the Liang Luar record (Table 4). Therefore, PCP may still be a possible mechanism to explain the variations in the calcite Mg/Ca and Sr/Ca ratios in these datasets. However, with constant D_{Mg} and D_{Sr} , a slope >1 can only occur if D_{Mg} is larger than D_{Sr} . Although this is possible, it is a very unlikely scenario (Sinclair et al., 2012). Our results show that slopes of >1 can be induced by progressively increasing D_{Sr} due to increasing Mg/Ca ratios of the solution and calcite.

In Table 4, we present a comparison between the observed slopes and the slopes according to our model for these four datasets taking into account the calcite Mg/Ca ratios. The modeled slopes are steeper than the observed slopes for Clamouse, Aoufous, and for Botuvera Cave, but shallower than the observed slope for Liang Luar. The steeper modeled slopes of the former caves can be potentially explained by a mixed (dedolomitized) limestone-dolostone host rock and different dissolution rates. Liang Luar is a special case as the host rock consists of reef carbonates of Miocene age mantled by Quaternary volcanic rocks (Griffiths et al., 2010). Volcanic rocks, consisting of silicate minerals, weather more strongly than carbonates under warm and dry climate, whereas carbonates weather more strongly under relatively cool and wet climate (Egli et al., 2008; Maher, 2010). In case of different Sr/Ca and Mg/Ca ratios of the volcanic rocks compared to the limestone host rock, the initial Mg/Ca and Sr/Ca ratios of the drip water depend on climate and might explain the much steeper slopes observed for Liang Luar.

Table 4. Examples of speleothems that exhibit average slopes higher than 1.003 as provided in Sinclair et al. (2012).

Cave site	Reference	Observed slope	Mg/Ca (mol/mol)		Modeled slope
Clamouse Cave	McMillan et al. (2005)	1.13 ± 0.14	Min.	0.026	1.42
			Max.	0.043	1.44
Aoufous Cave	Buhl et al. (2007)	1.13 ± 0.19	Min.	0.013	1.31
			Max.	0.041	1.45
Botuvera Cave	Cruz Jr. et al. (2007)	1.16 ± 0.21	Min.	0.033	1.44
			Max.	0.066	1.45
Liang Luar	Griffiths et al. (2010)	1.6-2.2 ^a	Min.	0.011	1.28
			Max.	0.041	1.45

^aSinclair et al. (2012) indicate a range, because the slope is variable.

We do acknowledge that we only take into account the effect of calcite Mg/Ca ratios in our PCP-model, which is not representative for the variety of processes potentially occurring in natural speleothems. It is well known that other factors, such as the number of non-lattice sites (Treble et al., 2005), abundance of other trace elements that may compete with Mg and Sr for crystal lattice and defect sites (Borsato et al., 2007), and varying growth rates may affect the distribution coefficients of Mg and Sr (Gabitov et al., 2014). However, the relationship between calcite Mg/Ca ratios and D_{Sr} shown in this study is statistically significant and provides a logical explanation for PCP-induced slopes that are steeper than one.

6. Conclusions

We compiled an extensive cave monitoring dataset including new and previously published calcite and dripwater Mg/Ca and Sr/Ca data to study the potential effects of solution and calcite composition on speleothem calcite D_{Sr} and D_{Mg} . We observe that calcite D_{Sr} increases with increasing speleothem calcite Mg/Ca ratios and present an equation describing this relationship ($D_{Sr} = 5.0 (\pm 0.7) * \text{Mg/Ca} + 0.082 (\pm 0.008)$). D_{Mg} is temperature dependent ($D_{Mg} = 0.013 * e^{0.035 * T}$). A relationship between D_{Sr} and precipitation rate or calcite Sr/Ca ratios is not observed, which might be explained by the large range in calcite Mg/Ca ratios in our dataset that may overprint these effects. We do not observe a relationship between D_{Mg} and precipitation rate either.

If D_{Sr} can be reasonably assumed as constant for a specific record, the slope of a trend line through a $\ln(\text{Sr/Ca})$ versus $\ln(\text{Mg/Ca})$ dataset approximates 0.93 for sites characterized by a pure limestone host rock (low Mg/Ca ratio) and 0.90 or even lower for sites characterized by a pure dolostone host rock (high Mg/Ca ratio). If D_{Sr} increases with speleothem Mg/Ca, the slope will become steeper (up to 1.45).

We show that PCP can induce slopes ranging from 0.709 up to 1.45 and that the criteria from Sinclair et al. (2012) to detect PCP in speleothem records were too strict. An important implication of this work is thus that the number of speleothem Mg/Ca and Sr/Ca records dominated by PCP reflecting rainfall variability may be larger than previously suggested.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: