

Mg isotopic composition of carbonate: insight from speleothem formation

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Abstract

Simultaneous high-precision measurement of ^{24}Mg , ^{25}Mg and ^{26}Mg isotopic compositions were made by multiple collector inductively coupled mass spectrometry (MC-ICP-MS) relative to the international standard SRM980. Data are presented on low-Mg calcite speleothems and their associated host rocks and waters from four caves, one in the French Alps and three in Israel, covering various climate conditions. In addition, data are presented on three dolostones and three limestones from the Himalaya. The overall variation is 4.13 ‰ and 2.14 ‰ in $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$, respectively. This is 35 times the uncertainty of the measurements and clearly demonstrates that the terrestrial isotopic composition of Mg is not unique. Each speleothem shows a characteristic range of $\delta^{26}\text{Mg}$ values that are attributed to the isotopic composition of the local water. Differences between the isotopic composition of Mg in the water dripping from stalactites and that of the modern speleothem are interpreted as being due to Mg isotopic fractionation during carbonate precipitation in the temperature range of 4–18°C. The low-Mg calcite is enriched in light isotopes by 1.35 ‰/AMU and the dependence on temperature has been found to be less than 0.02 ‰/AMU/°C. Despite various geological settings, the $\delta^{26}\text{Mg}$ of the studied dolostones is 2.0 ± 1.2 ‰ higher than the $\delta^{26}\text{Mg}$ of the limestones. All together, these results suggest a strong mineralogical control and a weak temperature effect on the Mg isotopic composition of carbonate. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Mg has three stable isotopes whose partitioning according to mass during physicochemical pro-

cesses, such as evaporation of molten rock at sub-atmospheric pressures, is large enough to be measurable [1]. In addition, Mg is a water-soluble element and hence mobile during weathering. By analogy with oxygen isotopes, Mg isotopic fractionation is anticipated during the incorporation of Mg at low temperatures into phases such as carbonates or clays. A preliminary survey of terrestrial Mg isotope ratios using thermal ionisation

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mass spectrometry showed very small isotopic variation [2], but little progress was made on the processes of Mg isotope fractionation because of the lack of a precise measurement technique. In this study, high-precision Mg isotopic measurements were made using multicollector inductively coupled mass spectrometry (MC-ICP-MS). This new method increases the precision by at least an order of magnitude relative to other techniques [3,4] and makes possible the search of mass-dependent variations of Mg isotopic ratios.

For the study, we use speleothems as a natural system to investigate Mg isotopic fractionation during precipitation of carbonates. This is evaluated from the difference between the isotopic composition of the dissolved Mg in the drip water (i.e. unsaturated zone water) and that of the modern speleothems. In addition, a possible systematic difference between limestone and dolostone has been investigated using the Mg isotopic com-

position of the host rock in which the caves are located and other limestone and dolostone samples from Himalayan formations [5].

Moreover, a preliminary study of temporal variations of Mg isotopic composition of the speleothems will be presented in the context of other geochemical and stable isotope parameters that have been widely used as a proxy for continental palaeo-environmental conditions, e.g. [6–13].

2. Sample location

Three cave sites from Israel (Soreq – SR, Mitzpe Shlagim – MS, Pekiin – PEK) and one from France (Trou du Glas – TDG) were studied (Fig. 1 and Table 1). The host rocks at all the cave sites are unmetamorphosed Mesozoic formations. SR and MS caves are located within Cenomanian and Jurassic dolostones respectively,

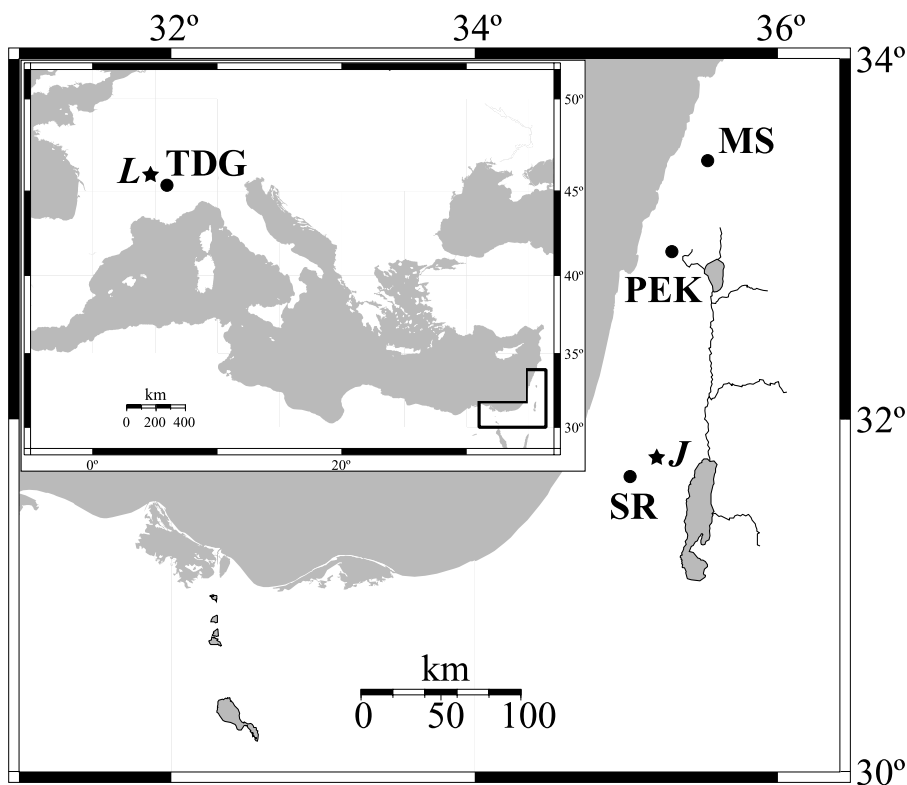


Fig. 1. Map of the Mediterranean basin and location of the four caves studied: Trou du Glas (TDG) near Lyon (L), Mizpe Shlagim (MS), Pekiin (PEK) and Soreq (SR) near Jerusalem (J).

Table 1
Climatic and lithological parameters of the caves

Cave	Elevation (m)	Annual rainfall (mm/yr)	Annual temperature (°C)	Country rock
Soreq	400	500	18	dolostone
Pekiin	800	700	16	limestone
Mizpe Shlagim	2000	> 1000	7	dolostone
Trou du Glas	1750	> 1000	4	limestone

while PEK cave is located in Turonian limestone. The TDG cave is located within the Cretaceous (Aptian) Urgonian limestone. The climatic conditions differ from one cave to the other (Table 1), and vary from semi-arid Mediterranean type cli-

mate for the Israel caves to a cold and humid climate in TDG cave, located in the Western Alps at an altitude of 1750 m. The range of mean annual temperature for the four caves is from 4 to 18°C [11,14].

Table 2
Isotopic composition of Mg in speleothem and water from four caves

Sample #	Type	Mineralogy ^b	Age (kyr)	$\delta^{26}\text{Mg}_{\text{SRM980}}$ (‰)	2 σ	$\delta^{25}\text{Mg}_{\text{SRM980}}$ (‰)	2 σ
<i>Soreq cave</i>							
Har-Tuv4	groundwater			1.71	0.06	0.88	0.01
SR-5-3-00-W	drip water			1.53	0.07	0.78	0.03
SR-8-5-00-W	drip water			1.35	0.03	0.70	0.06
SR-13-3-00-W	drip water			0.48	0.02	0.24	0.05
SR-5-3-00-S	speleothem	Ct	0	−1.24	0.12	−0.65	0.03
SR-8-5-00-S	speleothem	Ct	0	−1.22	0.02	−0.65	0.03
SR-13-3-00-S	speleothem	Ct+Dol	0	0.81	0.03	0.41	0.01
SR-2-8-B	speleothem	Ct	1.8	−1.01	0.12	−0.54	0.07
SR-2N-F	speleothem	Ct	8	−1.23	0.11	−0.66	0.07
SR-2-8-E3	speleothem	Ct	9	−0.76	0.11	−0.41	0.07
SR-2-8-G	speleothem	Ct	16	−1.28	0.12	−0.67	0.03
SR-2N-K	speleothem	Ct	20	−1.22	0.08	−0.65	0.04
SR-2-8-J	speleothem	Ct	25	−1.18	0.13	−0.63	0.09
SR-2-10-C1	speleothem	Ct	100	−1.38	0.03	−0.72	0.02
SR-2-10-C2	speleothem	Ct	101	−1.42	0.00	−0.75	0.01
SR-2-10-C2 ^a	speleothem	Ct		−1.44	0.04	−0.76	0.04
SR-2-10-D1	speleothem	Ct	124	−1.43	0.02	−0.75	0.02
<i>Pekiin cave</i>							
PEK-6-A	speleothem	Ct	24	0.60	0.09	0.26	0.01
PEK-9-A	speleothem	Ct	47	−0.92	0.02	−0.50	0.02
PEK-9-C	speleothem	Ct	123	−0.99	0.08	−0.51	0.03
PEK-9-D	speleothem	Ct	129	−0.92	0.04	−0.48	0.04
<i>Mizpe Shlagim cave</i>							
MSS	drip water			2.44	0.06	1.25	0.05
MSM	speleothem	Ct	0	−0.36	0.02	−0.21	0.02
MS-1D	speleothem	Ct	4	−0.12	0.03	−0.08	0.01
MS-2B	speleothem	Ct	70	−0.45	0.04	−0.24	0.02
<i>Trou du Glas cave</i>							
TDGW	drip water			0.98	0.12	0.47	0.05
TDGS	speleothem	Ct	0	−1.69	0.07	−0.89	0.05

^a Indicates duplicate analysis.

^b Dol indicates dolomite; Ct indicates calcite.

The most detailed study was performed on the speleothems of the SR cave for which high-resolution mineralogical and time-series records of the isotopic and trace element compositions have been determined [11–13,15–20]. To evaluate Mg isotope fractionation during calcification, we sampled the youngest portion of growing straw stalactites (the last few mm). Three sites were sampled in the SR cave: 5, 8 and 13, shown on a detailed map in Bar-Matthews et al. [11]. The dripping water was collected in HDPE bottles during the beginning of winter 2000. The stalactites at sites 5 and 8 are composed only of low-magnesium calcite (LMC; 0.5–7.5 mol% MgCO_3), but the mineralogy of the stalactites from site 13 is more complex and includes LMC, high-magnesium calcite (HMC), protodolomite, dolomite and hydroxyl Mg silicate minerals [15]. We sampled dripping water and modern stalactites also from MS and TDG caves but at the end of the winter when the snow melts. Dripping water from PEK cave could not be collected because the cave was closed to the public because of its archeological importance. In addition, groundwater (Har-Tuv4) from the nearby local aquifer of SR cave was collected and measured for its Mg isotope composition.

In order to determine if Mg isotopic variations can be recognised during the last 130 000 yr (Table 2) time period, which includes several glacial–

interglacial transitions, we studied three speleothems (2N, 2-8 and 2-10b) for which $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles versus time show large isotopic variations [12,19]. Mg isotope composition was also determined on two speleothems each from MS and PEK caves (Table 2) for which $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ time-series have also been determined [21].

The search for any systematic difference between limestone and dolostone from various ages (Early Proterozoic to Cretaceous) and various geological settings (sedimentary or metamorphic) has been carried out using the host rock in which the caves are located complemented with sample from the Himalaya (Table 3). The Tethyan sedimentary series (TSS) are composed primarily of Palaeozoic–Mesozoic carbonate and clastic sediments while the lesser Himalaya (LH) is composed of variably metamorphosed Precambrian sediments dominated by quartzo-pelitic schists with minor dolomitic carbonates. The $\delta^{18}\text{O}$ and Sr isotopic composition suggest that all of these carbonates have been affected by metamorphic reaction [5], but the metamorphic grade was not high enough to form marbles.

3. Materials and methods

Waters were filtered through 0.4 μm nylon Millipore filter, acidified by adding one drop of

Table 3
Mg isotopic composition of carbonate rocks

Sample #	Location	Formation ^b	$\delta^{26}\text{Mg}_{\text{SRM980}}$ (‰)	2 σ	$\delta^{25}\text{Mg}_{\text{SRM980}}$ (‰)	2 σ
Limestone						
PEK-HOST	Pekiin ^a	Bi'na	−0.69	0.07	−0.38	0.00
DDC	Trou du Glas ^a	Urgonian	−1.07	0.02	−0.59	0.03
NL 251	Central Nepal	TSS	−0.09	0.04	−0.08	0.04
NL 252	Central Nepal	TSS	0.73	0.02	0.37	0.06
XP 210	Central Nepal	TSS	0.38	0.08	0.16	0.04
Dolostone						
SR-D-1	Soreq ^a	Weradim	1.12	0.10	0.56	0.03
MSR	Mizpe Shlagim ^a	Hermion	2.32	0.04	1.19	0.02
AP 74-207	Central Nepal	LH	2.03	0.08	1.04	0.11
AP 75-867	Central Nepal	LH	2.07	0.19	1.07	0.09
AP 75-865	Central Nepal	LH	1.75	0.12	0.90	0.06

^a Those rocks are from the host rock formations of the four caves studied here and are unmetamorphosed Mesozoic formations.

^b LH, lesser Himalaya; and TSS, Tethyan sedimentary series. Sample locations are in [5].

strong distilled HNO_3 and dried. Speleothems and rocks were powdered to a uniform size and dissolved in 2 N HNO_3 . The residue after dissolution was separated by centrifuging. The supernatant liquid was evaporated to dryness and the nitrate salts were converted to chloride salts. A chemical separation of Mg has to be made before the measurement on the MC-ICP-MS. Chemical separation of Mg can be accomplished by liquid chromatographic methods but these introduce an isotopic fractionation. Our method uses Bio-Rad AG50W-X12 resin on which >99% recovery of Mg is achieved. The induced isotopic shift is <0.02‰ on $\delta^{26}\text{Mg}$, which is less than the MC-ICP-MS analytical uncertainty. Once Mg is purified, chloride salts are redissolved in 0.1 N HNO_3 and this Mg solution is introduced into the MC-ICP-MS (Nu Instruments) via a Cetac MCN-6000 nebuliser. Measurement of Mg is accomplished using three Faraday collectors (out of 12 collectors) over a mass range of 24–26 allowing direct measurement of ^{24}Mg , ^{25}Mg and ^{26}Mg . Instrumental peak shapes are carefully controlled throughout the run. The instrumental discrimination has been determined on an international isotopic standard: SRM980. We use a standard sample bracketing technique [4,22]. In this protocol, standard and sample isotope values are measured eight and six times, respectively for 200 s each. A negligible cross-contamination between the sample and the standard is achieved by washing the analytical instrumentation system and the cones with 0.1 N HNO_3 for 5 min between analyses. Results are expressed as a permil deviation from the isotopic composition of the standard:

$$\delta^x\text{Mg} = \left\{ \left(\frac{{}^x\text{Mg}}{{}^{24}\text{Mg}} \right)_{\text{sample}} / \left(\frac{{}^x\text{Mg}}{{}^{24}\text{Mg}} \right)_{\text{SRM980}} - 1 \right\} \times 1000 \text{ (where } x = 25 \text{ or } 26).$$

The internal reproducibility is between 0.01 and 0.14‰/AMU (2σ) and includes counting statistics for the sample and the standard as well as the drift for the standard between two measurements of the sample. The external reproducibility of the MC-ICP-MS obtained on pure Mg solutions is 0.06‰/AMU (2σ , $n = 167$) [4]. All figures that are reported in Tables 2 and 3 correspond to

average and standard deviations of at least triplicate measurements on the MC-ICP-MS of the same Mg solution. A full duplicate (dissolution, chromatographic separation and spectrometry) measurement of one speleothem (SR-2-10-C2, Table 2) has been performed and Mg isotopic composition agreed within 0.01‰/AMU.

4. Results

Results obtained are listed in Tables 2 and 3. The overall variation is 4.13 and 2.14‰ in $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$, respectively. This is 35 times the uncertainty of the measurements and clearly demonstrates that the terrestrial isotopic composition of Mg is not unique. The Mg isotopic compositions define a single mass fractionation curve on an Mg three-isotope plot (Fig. 2). Within the uncertainties, waters and carbonates fall along the same curve as other terrestrial samples [3]. This single correlation between $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ strongly supports a mass-dependent process. Following the terminology adopted for O isotopes in terrestrial environments, we will thereafter only refer to $\delta^{26}\text{Mg}$.

On average, the isotopic composition of dis-

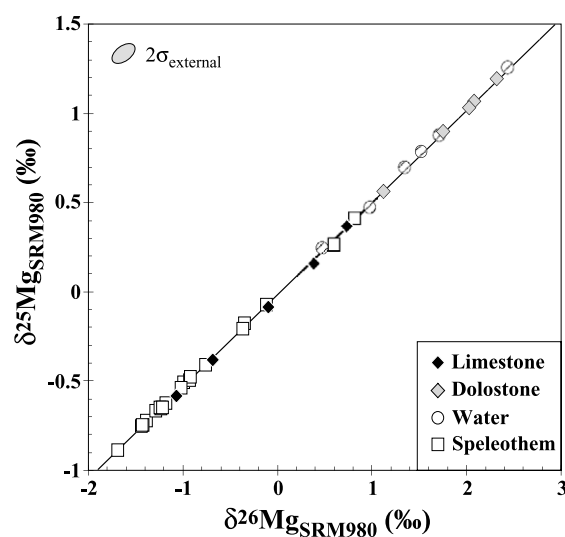


Fig. 2. Three-isotope representation of the Mg isotope ratios, expressed in δ units. The solid line corresponds to the terrestrial fractionation curve [3].

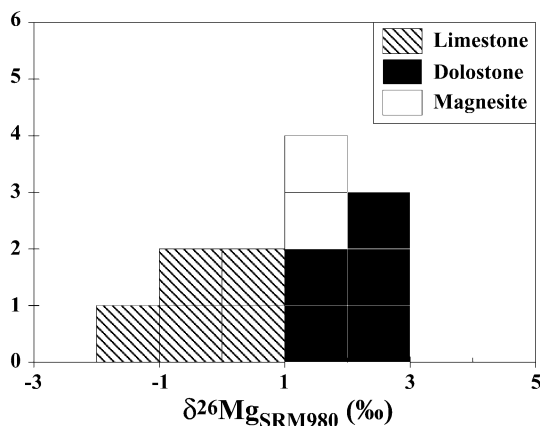


Fig. 3. Histogram showing $\delta^{26}\text{Mg}$ distribution in carbonate rock (this study) and magnesite [4]. Despite various geological settings, the $\delta^{26}\text{Mg}$ of the studied dolostones is $2.0 \pm 1.2\text{‰}$ higher than the $\delta^{26}\text{Mg}$ of the limestones.

solved Mg in water is higher than that of the stalactites, suggesting that Mg isotopes fractionate between aqueous solution and the precipitating carbonate at low temperature. The speleothems LMC have the lowest isotopic composition of Mg measured so far [3,4]. In addition, we looked at the isotopic composition of carbonate rocks from various ages and various geological settings (Table 3). Despite the small number of samples the $\delta^{26}\text{Mg}$ of the dolostone sample is systematically $\sim 2\text{--}3\text{‰}$ higher than that of the studied limestones (Fig. 3). By analogy with O and C isotope systematics, the variations in the $\delta^{26}\text{Mg}$ of the different carbonate rocks imply that the Mg isotopic fractionations are a function of several parameters including the mineralogy of the carbonate, the chemistry of the solution and the temperature.

5. Isotopic composition of dissolved Mg in karstic environment

The $\delta^{26}\text{Mg}$ of dissolved Mg (noted as $\delta^{26}\text{Mg}_{\text{water}}$ in the following) is variable, with a range of nearly 2‰ (Table 2). In karstic environments, the chemistry of waters is affected by (1) the chemistry and mineralogy of the local lithology (i.e. host rock), (2) the chemistry of the rain, (3) weathering processes and (4) the carbon-

ate phase deposited in the speleothem, e.g. [23–25]. The host rock in SR and MS caves is dolostone and although the $\delta^{26}\text{Mg}$ of the host rock at the two sites differs by 1.2‰ , the $\delta^{26}\text{Mg}_{\text{water}}$ is comparable to that of the host rock.

In SR, dripping water from the tips of three modern stalactites was analysed. $\delta^{26}\text{Mg}_{\text{water}}$ of two water samples precipitating calcite are slightly enriched in ^{26}Mg relative to the host dolostone (sites 5-3 and 8-5), whereas the $\delta^{26}\text{Mg}_{\text{water}}$ of water precipitating dolomite (site 13) is much lower than the host rock (Tables 2 and 3). Where dolomitic formations represent a significant proportion of the catchment area, nearly all the dissolved Mg comes from the dissolution of dolomite, e.g. [26], suggesting that the control of the $\delta^{26}\text{Mg}_{\text{water}}$ is governed by the local dolomitic lithology. At site 13 an unusual precipitation of dolomite occurs in the cave. The dissolved Mg of the dripping water is not the same as the initial isotopic composition of the host rock because there is additional evolution of the water chemistry in a closed system within the cave due to prior precipitation of LMC and HMC [15]. The $\delta^{26}\text{Mg}_{\text{water}}$ of groundwater (Table 2) is in the range of the isotopic composition of SR drip water, and the difference of 0.3‰ is likely related to a larger spread of lithologies averaged by the groundwater.

On the other hand, the host rock of the TDG cave is limestone composed of LMC (Mg $< 0.5\text{ mol\%}$, [27]) and for this cave the dripping water is enriched in the heavy isotopes by about 2‰ (Tables 2 and 3). Thus, there is very little isotopic difference between the host dolomite and the dripping waters when the precipitating mineral is calcite, whereas larger isotopic difference exists when the host rock is calcite. The first steps of limestone weathering correspond to the preferential leaching of HMC [23,28]. HMC may not have the same Mg isotopic composition as the whole limestone and its preferential dissolution may introduce a difference between the $\delta^{26}\text{Mg}_{\text{water}}$ and the $\delta^{26}\text{Mg}$ of the whole limestone. In addition, the budget of dissolved elements in dripping water from speleothems in cave that are formed into limestone formations suggests that up to 50% of the dissolved Mg come from the rain [29]. We suggest that be-

cause of the low Mg content of the carbonate in limestone, the Mg in waters percolating through limestone is more sensitive to additional external Mg sources (e.g. sea spray, dust) and other minor sources, such as silicate weathering and soil processes. A higher $\delta^{26}\text{Mg}$ between the dissolved Mg and the limestone clearly shows that a significant fraction of dissolved Mg in TDG originates from other sources than the carbonate or has been involved in chemical reactions fractionating the Mg isotopes. Such reactions can be the precipitation of Mg-bearing minerals in the soil or the incorporation of Mg in the biosphere.

6. Fractionation of Mg isotopes during carbonate precipitation

The $\delta^{26}\text{Mg}_{\text{water}}$ values in water that drips from stalactites have been compared with the $\delta^{26}\text{Mg}$ of the corresponding speleothems in Fig. 4. The speleothem in SR cave partly composed of dolomite (SR-13) is slightly enriched in ^{26}Mg (+0.33‰), whereas all the other LMC speleothems have $\delta^{26}\text{Mg}$ values lower by 2.57–2.77‰. The complex mineralogy and a closed system evolution in SR-13 do not allow straightforward interpretation of this result, but do suggest a smaller $\Delta^{26}\text{Mg}_{\text{dolomite-water}}$ than $\Delta^{26}\text{Mg}_{\text{calcite-water}}$ at room temperature.

The $\Delta^{26}\text{Mg}_{\text{calcite-water}}$ fractionation varies from −2.80‰ in MS, −2.57 to −2.77‰ in SR and −2.67‰ in TDG, despite differences in $\delta^{26}\text{Mg}_{\text{water}}$ of 1.46‰ between the two caves. The overall difference in $\Delta^{26}\text{Mg}_{\text{calcite-water}}$ values is less than 0.23‰. This essentially constant $\Delta^{26}\text{Mg}_{\text{calcite-water}}$ with changing $\delta^{26}\text{Mg}_{\text{water}}$ values is a strong argument that the measured fractionation factor could represent an equilibrium value. The small variations in $\Delta^{26}\text{Mg}_{\text{calcite-water}}$ could be the result of minor differences in precipitation conditions (temperature, evolution of the reaction) which the speleothem formed.

The oxygen isotopic fractionation between the water and the LMC in SR corresponds to the isotopic equilibrium at the mean annual temperature [11]. Therefore, the $\Delta^{26}\text{Mg}_{\text{calcite-water}}$ determined from SR is probably measured under near

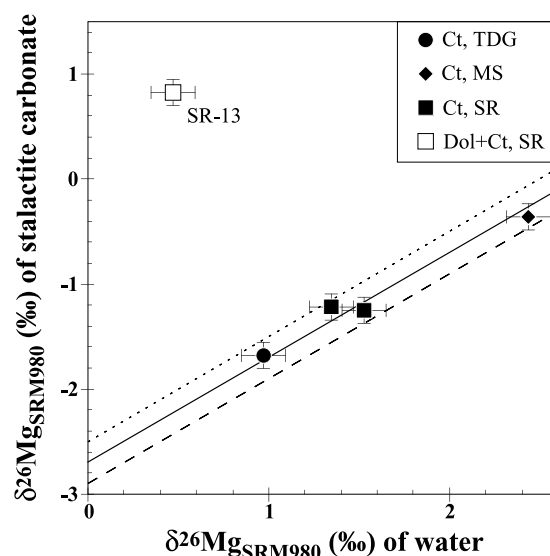


Fig. 4. Mg isotopic composition of modern stalactite versus Mg isotopic composition of dissolved Mg in the water falling from stalactite. Open symbols indicate water precipitating a mixture of calcite and dolomite while water precipitating LMC speleothems are shown by solid symbols. Error bars are $2\sigma_{\text{external}}$. SR, MS and TDG correspond to Soreq, Mizpe Shlagim and Trou du Glas caves, respectively. The solid line corresponds to an isotopic fractionation of −2.7‰ during low-Mg calcite precipitation. The dotted and dashed lines correspond to an isotopic fractionation of −2.5 and −2.9‰, respectively.

equilibrium conditions at temperatures between 18 and 20°C [11]. TDG and MS have been sampled during the end of the rainy season and fast-dripping speleothems are less affected by the evolution of the chemistry of the water by precipitation in a closed system [11]. Moreover, the precipitation of LMC in speleothems induces a depletion of Ca in the dripping water, while Mg is less affected. For instance, when 10% of the initial Ca carried by the water is precipitated in the speleothem, only 1% of the dissolved Mg is incorporated in LMC, and the $\delta^{26}\text{Mg}$ of speleothem remains constant (Fig. 5). Speleothems from MS and TDG are likely to represent the precipitation of LMC in thermodynamic equilibrium at average cave temperature much lower than SR cave (Table 1). The small variations in $\Delta^{26}\text{Mg}_{\text{calcite-water}}$ found in this study are likely to result from variations in the temperature of calcite formation.

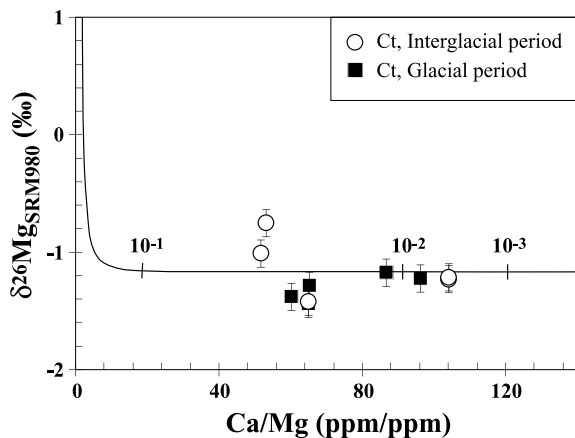


Fig. 5. Mg isotopic composition of low-Mg calcite stalactite versus Ca/Mg ratios of speleothems from Soreq cave. The curve represents the evolution of the overall chemical and isotopic composition of the speleothem in a closed system by a Rayleigh distillation. The initial composition of the water is an average of the modern water in site 5-3 (Ca/Mg=1.87 ppm/ppm; $\delta^{26}\text{Mg} = +1.53\text{‰}$). A distribution coefficient for Mg between water and low-Mg calcite (D_{Mg}) of 0.025 and a Mg isotopic fractionation ($\Delta^{26}\text{Mg}_{\text{calcite-water}}$) of -2.7‰ were used. The graduations give the fraction of Ca initially present in the water and which has been incorporated in the calcite.

When reported against the mean annual temperature of the cave (Fig. 6), the $\Delta^{26}\text{Mg}_{\text{calcite-water}}$ can be modelled with the conventional temperature dependence of stable isotopic fractionations such as $\Delta = a + b \times (1000/T)$. The small range of temperature investigated and the overall uncertainties induce a poor constraint on b . The values (-0.3 ± 0.8 or -1.3 ± 0.6 , whether the data were weighted by the uncertainties listed in Table 2 or by the external uncertainty) are, however, consistent with a decrease of the isotopic fractionation for an increasing temperature (Fig. 6). Several theoretical approaches give an explanation of the temperature dependence of mass-dependent isotopic fractionations in a thermodynamic system [30,31]. They consider isotopic fractionation to result from the difference of vibrational frequencies of a covalent bond. The thermal dependency of the mass-dependent isotopic fractionation simply reflects the thermal sensitivity of vibrational frequency. Since Mg bonds are dominantly ionic in character, isotope variations and the temperature dependence of $\Delta^{26}\text{Mg}_{\text{calcite-water}}$

are, therefore, difficult to predict on these theoretical bases.

Very little difference has been found between chondrite and terrestrial basalts [32], suggesting a smaller isotopic fractionation of Mg at high temperature between silicates than between carbonate and solution at low temperature. This behaviour of Mg isotopes is very similar to that described for O isotopes. Our finding of an apparent slight decrease of the isotopic fractionation when the temperature increases further highlights the analogy with O isotopes. Higher temperature experiments are clearly needed for the exact determination of the temperature dependence of the $\Delta^{26}\text{Mg}_{\text{calcite-water}}$. The dependence on the temperature is, however, less than 0.02‰/AMU/°C between 4 and 18°C , and the variations in Earth's surface temperature are, therefore, not the cause for the differences found in $\delta^{26}\text{Mg}$ among speleothems.

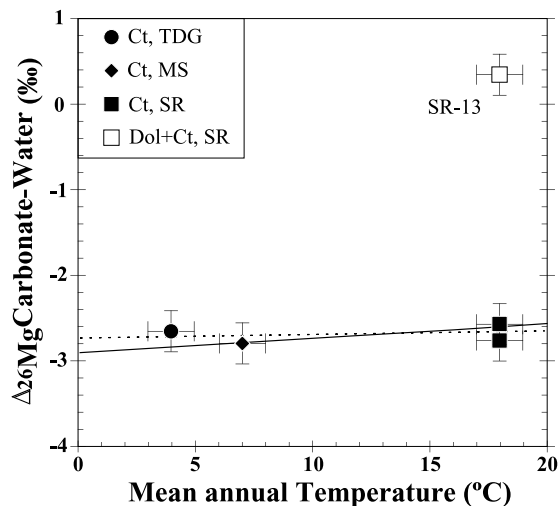


Fig. 6. Mg isotopic fractionation during speleothem formation versus the mean annual temperature in the cave. Symbols are the same as those in Fig. 4. The solid line represents the equation: $\Delta^{26}\text{Mg}_{\text{calcite-water}} = 2 - 1.34 \times (1000/T)$, corresponding to the best fit of the data weighted by the uncertainties listed in Table 2 for the isotopic measurements and an uncertainty of 2°C for the mean annual temperature. The dashed line represents the equation: $\Delta^{26}\text{Mg}_{\text{calcite-water}} = -1.6 - 0.3 \times (1000/T)$, corresponding to the best fit of the data weighted by the external uncertainty.

7. Significance of $\delta^{26}\text{Mg}$ in speleothems

The variable isotopic compositions of Mg in speleothems are mainly related to their provenance and to their mineralogy. If we restrict the mineralogy to LMC and look at each cave, the difference in $\delta^{26}\text{Mg}$ between the modern and the older speleothems is 0.33, 0.68 and 1.59‰ for MS, SR and PEK, respectively. In the latter, the variability is mainly between speleothems taken from different parts of the cave interior (Fig. 7). These two PEK speleothems have very different trace element contents. For instance, the [U] is 650 ppb in PEK-6-A while the [U] of PEK-9 varies between 1160 and 1570 ppb. Since trace element concentrations in speleothems are related to the source of the water [13,17], the $\sim 1.5\text{‰}$ difference in $\delta^{26}\text{Mg}$ between PEK-6 and PEK-9 is likely to correspond to the difference in the isotopic composition of the water forming these two speleothems. Using a constant $\Delta^{26}\text{Mg}_{\text{calcite-water}}$ of -2.7‰ , the $\delta^{26}\text{Mg}_{\text{water}}$ would have been $+3.30$ and $+1.76\text{‰}$ in PEK-6 and PEK-9, respectively. This is more than 2‰ heavier than the isotopic composition of the local limestone (Tables 2 and 3). A similar discrepancy between the $\delta^{26}\text{Mg}_{\text{water}}$ and the $\delta^{26}\text{Mg}$ of the limestone has been found in TDG. Together with the variability in $\delta^{26}\text{Mg}_{\text{water}}$ at a local scale, this suggests that dissolved Mg in karst developed in limestone has a more complex cycle, involving non-carbonate origins and/or chemical reactions fractionating the Mg isotopes. The $\delta^{26}\text{Mg}$ of clays occurring in the limestone and of Mg-bearing minerals in the soil are clearly needed to further interpret the $\delta^{26}\text{Mg}_{\text{water}}$ in limestone environments.

In dolostone environments (MS and SR), the variability in $\delta^{26}\text{Mg}$ of the speleothem is smaller ($<0.7\text{‰}$), but differences in $\delta^{26}\text{Mg}$ have been found between speleothems (SR-2-N versus SR-2-10) and within a speleothem (SR-2-8). If we assume a common source for the water feeding all the speleothem in SR, a closed system evolution cannot account for the chemical and isotopic variations (Fig. 5). Moreover, the glacial–interglacial temperature variation would neither explain the whole variation found in SR-2-8 (Fig. 7). In addition, there is no systematic difference in the

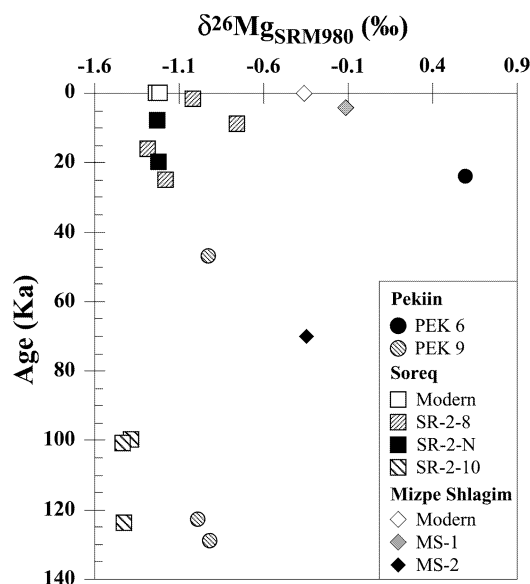


Fig. 7. Mg isotopic composition of low-Mg calcite stalactite versus age of speleothems from Soreq, Pekiin and Mizpe Shlagim caves. Each speleothem has been distinguished by a particular symbol. In dolostone environments (MS and SR), the main difference corresponds to different $\delta^{26}\text{Mg}$ of the host carbonate between each cave site.

isotopic composition of Mg between the glacial and interglacial periods (Figs. 5 and 7). As in limestone environments and following the interpretation of trace elements, Sr and U isotopic variations [17], changes in the local hydrological regime may be responsible for the main variations recorded in a given speleothem.

8. Conclusion

In this study, the overall variation of $\delta^{26}\text{Mg}$ is 4.13‰ , about 35 times the uncertainty of the measurements and clearly corroborates our previous results [3,4] implying that the terrestrial isotopic composition of Mg is not unique. Several points about the behaviour of Mg isotopes can already be drawn out:

- The $\delta^{26}\text{Mg}$ of dolostone is $\sim 2\text{--}3\text{‰}$ higher than the $\delta^{26}\text{Mg}$ of limestone, and the $\delta^{26}\text{Mg}$ of speleothem containing dolomite is also $\sim 2\text{‰}$ higher than the $\delta^{26}\text{Mg}$ of speleothem

composed only of LMC. This suggests an isotopic fractionation of Mg between calcite and dolomite.

- The $\Delta^{26}\text{Mg}_{\text{calcite-water}}$ has been estimated using the difference between the $\delta^{26}\text{Mg}$ of dissolved Mg in the water dripping from the stalactite and the $\delta^{26}\text{Mg}$ of the corresponding speleothem. The low-Mg calcite is enriched in light isotope by 1.35‰/AMU and the dependence on the temperature has been found to be less than 0.02‰/AMU/°C between 4 and 18°C. Precipitation under controlled conditions is clearly needed to better quantify the temperature dependence and to study the effect of the mineralogy.
- Each speleothem shows characteristic $\delta^{26}\text{Mg}$ values attributed to the Mg isotopic composition of the local water. The time-series variations are less than 0.52‰, but the glacial–interglacial temperature variation can account for only 20% of them. Changes in the local hydrological regime may be responsible for the main variations recorded in a given speleothem.

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