Late Cretaceous to early Cenozoic hydrothermal fluid migration and red calcite formation in the Transdanubian Range, Hungary

ATTILA DEMÉNY[1,2,✉], LÁSZLÓ RINYU[3] and YURI DUBLYANSKY[4]

[1]Institute for Geological and Geochemical Research, HUN-REN Research Centre for Astronomy and Earth Sciences, Budapest, Budaörsi út 45, H-1112, Hungary
[2]CSFK, MTA Centre of Excellence, Budapest, Konkoly Thege Miklós út 15-17., H-1121, Hungary
[3]Isotope Climatology and Environmental Research Centre, HUN-REN Institute for Nuclear Research, Debrecen, Bem tér 18/C, H- 4026, Hungary
[4]Institute of Geology, University of Innsbruck, Innrain 52, 6020 Innsbruck, Austria

Abstract: Red calcite veins are found in Mesozoic limestones at several locations within the Transdanubian Range, western Hungary. Opinions on the origin and the formation conditions of the red calcites vary widely, with concepts ranging from high-temperature hydrothermal processes to speleothemic formation. The present study aims to constrain the formation temperatures and determine the fluid origins of the red calcites. Samples were taken from three locations previously investigated in earlier studies: the Sintérlap quarry at Sümeg, the Keselő Hill quarry at Tatabánya, and the Piliscsaba–Jászfalu quarry at Piliscsaba. Formation temperatures for the dark red calcites, presumably the earliest, ranged between 30 and 37 °C, as determined by the clumped isotopes method. The oxygen isotope compositions ($\delta^{18}O$) of the calcite-forming water were calculated using clumped isotope temperatures and the $\delta^{18}O$ values of calcite. These calculations revealed a fluid that had either undergone high-temperature water–rock interaction or contained an ^{18}O-enriched component and the temperatures are much lower than thought previously, but higher than those of speleothems. The hydrogen isotope compositions of inclusion-hosted waters, along with the carbon and oxygen isotope values of red calcites, suggest that the three red calcite occurrences were caused by distinct fluid movements, likely at different times. This indicates that a single red calcite formation event can be ruled out.

Keywords: red calcite veins, fluid inclusion, stable isotope compositions, clumped isotope thermometry, hydrothermal fluids

Introduction

Red calcite veins are spectacular formations that decorate the of quarries mining Triassic and Cretaceous limestones in the Transdanubian Range of western Hungary. On the basis of their appearance, i.e. systematic changes from fine-grained dark red calcite at the margins to pale red sparry calcite in the centres with widths ranging from several cm to ca. 4 m, as well as on the basis of fluid inclusion homogenization temperatures (100 to 190 °C) and stable isotope compositions, Demény et al. (1997) interpreted the veins as hydrothermal formations related to ascending magmatic fluids. Considering the evidence for the Late Cretaceous age of the red calcite veins at Sümeg (the host rock is Aptian, the overlying marine breccia-conglomerate which contains pebble-sized red calcite clasts is Campanian, hence red calcite veins may have been formed during the Coniacian–Santonian; Haas et al. 1985) Demény et al. (1997) proposed the occurrence of a regional hydrothermal event during that time. Later, based on detailed field investigations as well as fluid inclusion petrography and microthermometric analyses, Győri et al. (2014) offered an alternative interpretation, suggesting that the red calcites formed as speleothems, infilling paleokarstic voids through precipitation from descending meteoric waters at temperatures below 50 °C. As the authors noted, hematite is the most abundant solid inclusion in the calcite veins giving them their distinctive red color, while gibbsite, goethite and kaolinite are also commonly found as inclusions. Based on these data, they suggested that the red colour of the calcites is due to water infiltration through karst bauxite deposits. They attributed the high homogenization temperatures reported by Gatter (1984; 135 to 155 °C in the Sümeg site) and Demény et al. (1997; 100 to 190 °C at three sites: Sümeg, Tatabánya and Piliscsaba) to stretching, leakage, or heterogeneous entrapment of fluid inclusions. These effects would result in erroneous (unrealistically high) temperature determinations using the microthermometric method, invalidating any further calculations of paleofluid isotope compositions based on these temperatures.

However, the 4-meter-wide calcite veins in Keselő Hill quarry in Tatabánya – studied by Demény et al. (1997) but

✉ corresponding author: Attila Demény
demeny.attila@csfk.hun-ren.hu

destroyed during quarry operations before the investigation of Győri et al. (2014) – show systematic rim-to-core zonation, which seems incompatible with speleothem formation. Instead this pattern more likely suggests calcite precipitation from hydrothermal fluids. The new techniques developed for investigating speleothem calcite formations in Hungary, such as oxygen isotope analysis of inclusion-hosted water (Demény et al. 2016) and clumped isotope analysis (Demény et al. 2021, 2024a), have provided fresh momentum for determining the formation conditions and genesis of red calcites. In this study, we examined red calcite occurrences at three locations in Hungary: the Sümeg–Sintérlap quarry, the Tatabánya–Keselő-hegy quarry, and the Piliscsaba–Jászfalu quarry (Fig. 1). A combination of stable isotope and clumped isotope analyses was employed to determine formation temperatures, fluid compositions, and to identify paleohydrological differences among the occurrences.

Samples and methods

In the Tatabánya and the Piliscsaba sites large (50–100 cm) debris blocks derived from the walls of the operating quarries were sampled, whereas in the Sümeg location a red calcite vein was sampled in situ. At the Sümeg site samples were taken from pale and dark red calcite bands (SÜ-1 and SÜ-2) and dark red massive calcite (SÜ-3). The contact between the host limestone and the vein was also sampled (SÜ-4). In the Tatabánya quarry two blocks were sampled comprising dark red (VK-1 and VK-6) and pale red calcite (VK-2 and VK-4). The block sampled in the Piliscsaba quarry comprised dark red (PCS-1) and lighter red, sparry calcite (PCS-2 and PCS-3). The collected samples were divided into subsamples to detect internal heterogeneities. A detailed description of samples along with information on fluid inclusion petrography and the analytical methods of stable and clumped isotope measurements, is provided in Demény et al. (2024b).

Stable hydrogen and oxygen isotope compositions of the inclusion-hosted water were determined at the Institute for Geological and Geochemical Research in Budapest, following Demény et al. (2016). Sample chips (2–5 mm pieces) of about

Fig. 1. Sampling locations in Hungary.

1–2 g were crushed under vacuum in 10 mm (outer diameter) stainless steel tubes, and the released H_2O was introduced into a LWIA-24d liquid water isotope analyzer (Los Gatos Research Ltd.). The isotope compositions are reported in ‰, relative to V-SMOW. Based on measurements of carbonate-hosted inclusion waters with known isotopic compositions, the estimated analytical accuracies are about ±0.5 and ±2 ‰ for $\delta^{18}O_{fi}$ and δ^2H_{fi} values, respectively (see Demény et al. 2021). Clumped, as well as stable carbon and oxygen isotope analyses of carbonates were carried out at the Isotope Climatology and Environmental Research Centre (ICER), HUN-REN Institute for Nuclear Research (ATOMKI) in Debrecen, Hungary. Carbonate sample analysis was performed on a Thermo Scientific™ 253 Plus 10 kV Isotope Ratio Mass Spectrometer (IRMS), after phosphoric acid digestion at 70 °C, using a Thermo Scientific Kiel IV automatic carbonate device. The raw measurement data are provided in the Supplementary Tables of Demény et al. (2024b). Stable carbon and oxygen isotope compositions of high-resolution (~0.1 mm) drilling of a selected sample from Sümeg (SÜ-4) were determined at the Institute for Geological and Geochemical Research in Budapest. The isotope compositions are expressed as $\delta^{13}C$ and $\delta^{18}O$ values in ‰ relative to V-PDB ($\delta^{13}C$, $\delta^{18}O$) and V-SMOW ($\delta^{18}O$), their uncertainty is about 0.1 ‰. We note here that since no radioactive isotope compositions were measured or discussed in this paper, the adjective "stable" will not be used in the following text. Oxygen isotope compositions for calcites, fluid inclusion-hosted water and calculated water compositions are denoted as $\delta^{18}O_{cc}$, $\delta^{18}O_{fi}$, $\delta^{18}O_w$, respectively.

Clumped isotope temperatures were calculated using the calibration of Anderson et al. (2021) and the D47crunch algorithm of Daëron (2021), the results are listed in Table 1. Oxygen isotope compositions of waters in equilibrium with the red calcites were calculated using the clumped isotope temperatures, the calcite $\delta^{18}O$ values, and the equations of Chacko & Deines (2008) and Däeron et al. (2019). Different calibrations of the temperature dependence of calcite-water oxygen isotope fractionation yield different water compositions at a given temperature and calcite $\delta^{18}O$ value. The Chacko & Deines (2008) and Däeron et al. (2019) equations yield the highest and the lowest water $\delta^{18}O$ values, respectively, among the available relationships (Demény et al. 2024a). Since the calibration whose measurement conditions would best fit the formation conditions of red calcites is not known, the two extreme equations are used, the average water composition is calculated including the uncertainty of equation selection (Demény et al. 2024a).

Results

Carbon and oxygen isotope compositions of calcites, hydrogen and oxygen isotope values of inclusion-hosted waters, using clumped isotope temperature calculations, and the corresponding water isotope compositions are detailed in Table 1. The three locations have distinct differences with the Sümeg
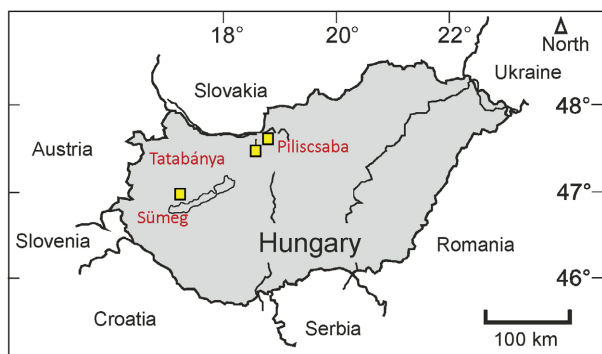
location's red calcites more enriched in ^2H and ^{13}C (δ^2H and $\delta^{13}C$ averages: -29 ± 7 ‰ and -4.8 ± 0.9 ‰, respectively) than the other two occurrences (Tatabánya: $\delta^2H_{fi}=-53\pm8$ ‰, $\delta^{13}C=-6.5\pm0.5$ ‰; Piliscsaba: $\delta^2H_{fi}=-53\pm5$ ‰, $\delta^{13}C=-10.2\pm1.2$ ‰), while the oxygen isotope compositions are quite similar to each other (Sümeg: 25.8 ± 0.2 ‰; Tatabánya: 26.2 ± 0.2 ‰; Piliscsaba: 24.3 ± 0.3 ‰). The $\delta^{18}O_{fi}$ values behave similarly to the δ^2H_{fi} data, i.e., the Sümeg location showing ^{18}O enrichment (-4.2 ± 0.6 ‰) compared to the other two locations (Tatabánya: -6.6 ± 1.8 ‰; Piliscsaba: -7.1 ± 1.9 ‰). The clumped isotope temperatures are overlapping at the studied locations with averages of 26.2 ± 9.4 °C for Sümeg, 35.5 ± 7.3 °C for Tatabánya, and 29.2 ± 4.3 °C for Piliscsaba.

Discussion

Formation conditions

The first issue to address is whether the current sampling is representative and if the samples from this study are comparable to those analysed by Demény et al. (1997) and Győri et al. (2014). Figure 2 displays the $\delta^{13}C$ and $\delta^{18}O$ values obtained in this study alongside the isotopic compositions from earlier investigations. Most of the new data align with the fields of

published compositions, although the low-$\delta^{13}C$ values of the Tatabánya site are not replicated here. These observations suggest that the current sample set is comparable to those from the earlier studies (Demény et al. 1997; Győri et al. 2014), allowing for a general interpretation of the results concerning fracture and cavity-filling red calcite in the studied area.

The next question is whether the calcite veins are associated with an alteration halo in the host limestone. Hydrothermal fluid movements in a fissure-cavity network may cause alteration in the host limestone. The shape and magnitude of the stable isotopic front from the vein to the limestone depends on the porosity and permeability of the limestone, the temperature, and the isotope composition of the infiltrating fluid (Spötl et al. 2021). Elevated temperature and high permeability would result in enhanced isotope change and sigmoidal-shaped isotope profile, whereas low temperature and dense host rock fabric leads to a 'stepped' isotopic profile (Spötl et al. 2021). The studied red calcite vein at Sümeg shows a visually sharp contact with limestone (Fig. 3). To identify the possible alteration zone, samples for stable isotope analysis were drilled along a high-resolution (~0.1 mm) transect across the red calcite-to-limestone contact (Fig. 3). The C and O isotope values show a sharp change from the limestone to the red calcite ($\delta^{13}C$: from 0 ‰ to -5 ‰, $\delta^{18}O_{cc}$: from -3.5 ‰ to -5 ‰) within 0.5 mm. The three transitional data points with intermediate values are artifacts resulting from inadvertent mixing of limestone and red calcite materials during the drilling process. This observation does not support the interaction of limestone with high-temperature hydrothermal fluids, as suggested by Demény et al. (1997). Instead, it indicates low-temperature calcite precipitation in the fractures of limestone, similar to the formation of speleothems (Spötl et al. 2021).

Table 1: Stable isotope compositions (in ‰) of calcite ("cc") and fluid inclusion water ("fi"), as well as clumped isotope temperatures (T(Δ_{47}), in °C) calculated using the D47crunch algorithm (Daëron 2021). The data are from Demény et al. (2024b). δ^2H_{fi}, $\delta^{18}O_{fi}$ and $\delta^{18}O_{cc}$ values are relative to V-SMOW, $\delta^{13}C$ values are relative to V-PDB. $\delta^{18}O_w$ is water composition (in ‰ relative to V-SMOW) calculated in this study using and $\delta^{18}O_{cc}$ values and D47crunch temperatures.

|	δ^2H_{fi}	$\delta^{18}O_{fi}$	$\delta^{13}C$	$\delta^{18}O_{cc}$	T(Δ_{47})	$\delta^{18}O_w$	1σ
Sümeg							
SÜ-1a	-23.4	-4.4	-5.3	25.7	37.6	-1.2	3.3
SÜ-2	-22.1	-3.4	-4.6	25.5	17.4	-5.1	3.3
SÜ-3 sparic	-32.2	-5.1	-3.8	25.9	29.2	-2.5	3.7
SÜ-3 dark	-39.0	-4.3	-4.4	26.0	15.6	-5.1	3.7
SÜ-4	-27.3	-4.0	-6.1	25.9	31.1	-2.3	3.8
Tatabánya							
VK-1	-45.3	-5.0	-5.9	26.3	29.8	-2.1	2.5
VK-2	-47.8	-6.3	-7.0	26.2	29.8	0.5	2.4
VK-4	-63.0	-9.2	-6.1	26.0	45.2	-4.3	2.5
VK-6	-56.0	-5.9	-6.9	26.2	37.1	-0.4	2.4
Piliscsaba							
PCS-1-1	-59.7	-8.3	-10.1	24.0			
PCS-1-2	-57.6	-7.3	-9.2	24.2	29.2	-4.1	2.4
PCS-1-3	-56.7	-9.8	-8.8	24.1	32.5	-3.6	2.3
PCS-1-4	-47.4	-6.5	-11.5	24.4	27.5	-4.3	2.3
PCS-1-5	-49.4	-5.2	-10.3	24.0	26.2	-5.0	2.3
PCS-2-1	-60.2	-9.1	-7.7	24.1	30.1	-4.0	2.0
PCS-2-2	-49.1	-3.7	-11.3	24.0	22.7	-5.5	2.0
PCS-2-3	-53.5	-7.1	-11.3	24.4	34.8	-2.9	2.0
PCS-3-1	-47.4	-5.5	-10.6	24.7	35.1	-2.4	2.0
PCS-3-2	-46.9	-8.1	-10.8	24.7	24.8	-4.6	2.0
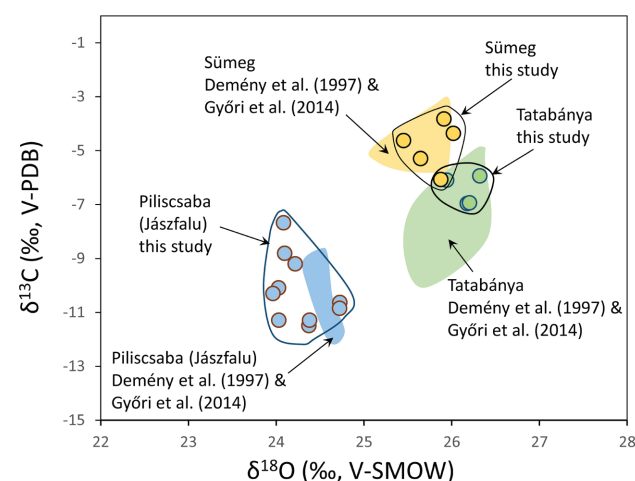
Fig. 2. Carbon and oxygen isotope compositions of red calcites. Color shaded fields show compositions obtained by earlier studies. Sümeg: n=4 from Demény et al. (1997), n=1 from Győri et al. (2014); Tatabánya: n=4 from Demény et al. (1997), n=3 from Győri et al. (2014); Piliscsaba: n=2 from Demény et al. (1997), n=1 from Győri et al. (2014).
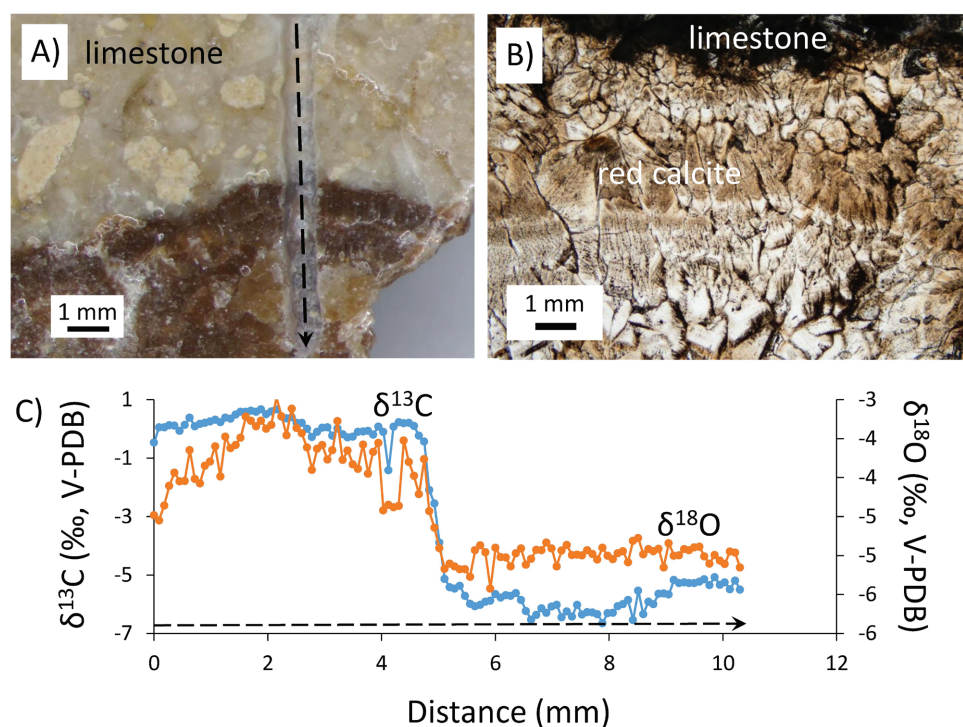
Fig. 3. A — Polished surface of sample SÜ-4 showing the contact between limestone and red calcite. Dashed arrow indicates drilling direction (see also C). **B** — Optical microscopic image (1N) of the limestone to red calcite contact. **C** — Carbon and oxygen isotope compositions obtained in the drilling trench shown in A.

These observations align with the clumped isotope thermometry data from Demény et al. (2024b), which range from 16 to 45 °C. However, the dark red calcite samples (VK-1, VK-2, SÜ-1, SÜ-4, PCS-1), considered to be the earliest calcite precipitations during fluid influx into the fractures, exhibit a narrower temperature range of 30 to 37 °C (Demény et al. 2024b; Table 1). This temperature range is significantly higher than global cave temperatures, which typically do not exceed 27 °C, even in low-altitude tropical regions, such as South America and Borneo (e.g., Meckler et al. 2015; Voarintsoa et al. 2019; Mejía-Ortíz et al. 2020; Novello et al. 2021; Serrato Marks et al. 2021; Vieten et al. 2024). These temperatures suggest that hydrothermal fluid – characterized by temperatures exceeding the mean annual air temperature of the region – may have played a role in the genesis of the red calcites.

The hydrogen and oxygen isotope compositions of inclusion-hosted waters are presented in Table 1 and illustrated in Fig. 4A. Most data points plot on or near the Global Meteoric Water Line (GMWL, $\delta^2H = 8 \cdot \delta^{18}O + 10$; Craig 1961), indicating potential meteoric water movement. However, some data points are shifted toward more positive $\delta^{18}O$ values (to the right of the GMWL), suggesting that these solutions were influenced by water-rock interactions (Sheppard 1986; Dublyansky & Spötl 2010). Additionally, Demény et al. (2024b) noted that the temperatures calculated from the $\delta^{18}O$ of calcite ($\delta^{18}O_{cc}$) and the $\delta^{18}O$ of fluid inclusions ($\delta^{18}O_{fi}$) are too low compared with the clumped isotope data. The discrepancy

may be attributed to diagenetic alteration of the $\delta^{18}O_{fi}$ values or the presence of late-stage fluids in secondary inclusions that were mixed with the primary fluids during analyses. Considering these factors, the water oxygen isotope compositions in equilibrium with the red calcites at the clumped isotope temperatures were calculated. Although the uncertainties in the computed $\delta^{18}O_w$ data exceed ±2 ‰ due to the combined uncertainties from isotope analyses and variations in equations, Fig. 4B clearly demonstrates that most of the data are shifted from the GMWL toward more positive $\delta^{18}O$ values. The most straightforward interpretation of the positive $\delta^{18}O$ shift, combined with the elevated clumped isotope temperatures, is that the fluids entering the fractures were heated and interacted with ^{18}O-rich rocks (such as limestones) at the depth (Sheppard 1986) or were mixed with ^{18}O-rich hydrothermal solutions (Varsányi & Kovács 2009). This formation model does not exclude the possibility of flowstone-like carbonate precipitation from descending solutions as suggested by Győri et al. (2014). The red calcite-filled fractures may have been reactivated and tectonically opened (Kercsmár 2004), allowing for the infiltration of surficial fluids. However, the data suggest that the formation of red calcite veins was driven by the influx of low-temperature hydrothermal solutions originating from deep water circulation. The red color of the calcite veins is due to inclusions of hematite, which was transported from bauxite deposits, as noted by Győri et al. (2014). However, the precise transport mechanism of hematite
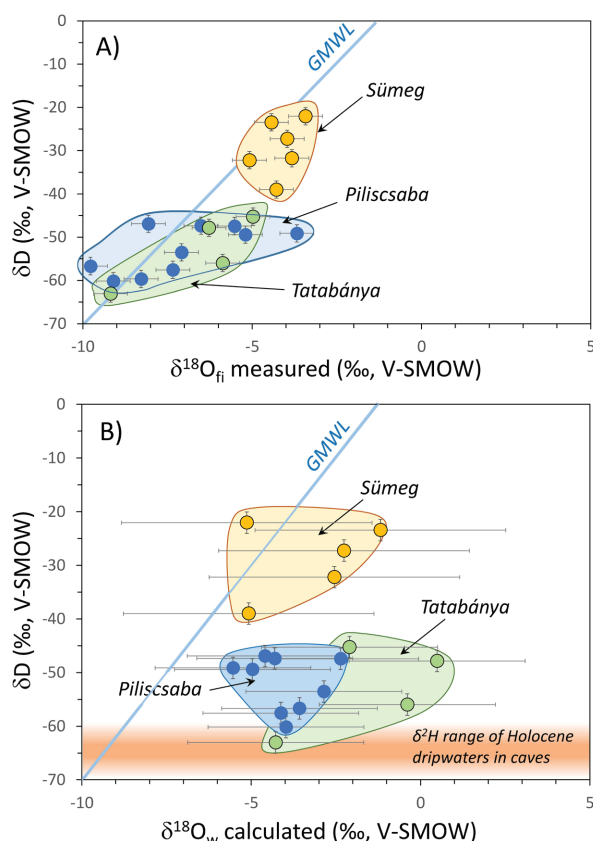
Fig. 4. Measured stable isotope values of inclusion-hosted waters of red calcites (**A**) and calculated stable isotope compositions of calcite-forming aqueous solutions (**B**). The range of hydrogen isotope compositions of Holocene dripwaters is provided by earlier studies (Demény et al. 2013, 2016, 2019, 2024c; Czuppon et al. 2018). GMWL: Global Meteoric Water Line (Craig 1961).

particles remains uncertain. Two potential routes have been proposed: (i) meteoric water could have carried the hematite particles to depths where the water interacted with hot rocks, or (ii) hydrothermal solutions may have mixed with descending meteoric water, which transported the bauxite-derived grains. The relatively homogeneous compositions and formation temperatures of the dark red calcites argue against the mixing of hot hydrothermal and cold surficial solutions. This supports model (i), where water infiltrated through bauxite, migrated downward, warmed at depth, and entered fractures, carrying a significant amount of iron-oxide particles.

Differences between the studied occurrences

Another notable phenomenon in Fig. 4B is the variation between the studied occurrences. The Sümeg occurrence has δ^2H_{fi} values that differ from those of the red calcites at the Tatabánya and the Piliscsaba locations. The high δ^2H_{fi} values (ranging from −40 to −20 ‰) align with the warm climate conditions assumed for the Cretaceous period, comparable to dripwater compositions above −40 ‰ observed in modern

tropical caves; e.g., Griffiths et al. 2010; Lases-Hernandez et al. 2019). As shown in Fig. 4B, the Sümeg samples with the lowest δ^2H_{fi} values (−32 and −39 ‰) appear to shift toward the compositions of the Piliscsaba vein, suggesting they may be related to the influx of late-stage fluids and the mixing of primary and secondary fluid inclusions during the isotope analyses of bulk samples (Demény et al. 2024b). The highest δ^2H_{fi} values (−27 to −22 ‰) clearly indicate that the meteoric water, which infiltrated and warmed at depth, originated during a warm climate. The red calcites from Tatabánya and Piliscsaba yielded δ^2H_{fi} values ranging between −63 and −45 ‰, which are transitional between the values observed at the Sümeg location and the δ^2H values of recent and Holocene drip waters (Fig. 4B), as inferred from cave monitoring and speleothem analyses (Demény et al. 2013, 2016, 2019, 2024c; Czuppon et al. 2018). Since the δ^2H values of infiltrating meteoric waters can reflect the surface climate conditions (Demény et al. 2021), the δ^2H_{fi} value around −50 ‰ suggests a climate colder than that of the Cretaceous but warmer than Holocene cave temperatures. This interpretation is in agreement with the pre-Oligocene age proposed by Győri et al. (2014). However, the difference in δ^2H_{fi} values, along with the variations in $\delta^{13}C$ and $\delta^{18}O$ shown in Fig. 2 suggest that the formation of red calcites at these locations may have been influenced by fluid movements of significantly different ages and origins. The lower $\delta^{13}C$ values of the Piliscsaba occurrence, compared to other locations, indicate that organic-rich layers were present along the migration route of the hydrothermal fluids. We suggest that interaction with the Middle to Upper Norian Feketehegy Formation consisting of dolomite and limestone abundant in organic matter (Haas et al. 2010), may have contributed to the measured values.

A potential extension of this research could involve investigating similar calcite veins in the Alpine and Carpathian regions to better understand the hydrothermal and diagenetic evolution of these systems. However, during the Cretaceous and Paleogene, the carbonate rocks in the Transdanubian Range that host the red calcite veins were located several hundred kilometers to the west (Kázmér & Kovács 1985). Therefore, the paleogeographic position must be considered when studying hydrothermal or diagenetic calcite formations and comparing them with the findings of the current paper.

Conclusions

Three locations of red calcite veins in the Transdanubian Range, western Hungary – Sümeg, Tatabánya and Piliscsaba – were investigated using stable isotope analyses of calcites and inclusion-hosted waters, as well as clumped isotope measurements. The main goal was to determine the formation temperatures and to ascertain whether the precipitation of red calcites was induced by high-temperature hydrothermal fluids, as suggested by Demény et al. (1997), or by low-temperature meteoric waters, as proposed by Győri et al. (2014). The clumped isotope analyses indicated a temperature range

of 30 to 37 °C for the earliest dark red calcite samples, which is significantly higher than current tropical cave temperatures. Water oxygen isotope compositions were calculated from the calcite compositions and clumped isotope temperatures using published calcite-water oxygen isotope fractionation equations (Chacko & Deines 2008; Däeron et al. 2019). The calculated $\delta^{18}O_w$ data are shifted in positive direction (indicating ^{18}O-enrichment) compared to the measured fluid inclusion water values ($\delta^{18}O_{fi}$), suggesting diagenetic alterations in the inclusion water and a hydrothermal origin for the infiltrating solutions. The hydrogen isotope data of inclusion-hosted waters, along with the carbon and oxygen isotope values of calcites, suggest fluid movements that exhibit significant differences in age, origin, or both. The hydrogen isotope compositions of the Sümeg occurrence align with a warm Mesozoic climate, while the red calcite from the Tatabánya and the Piliscsaba quarries may have formed in the cooler climate of the early Cenozoic. Therefore, the formation of red calcite veins in in the Transdanubian Range cannot be attributed to a single event. Instead, it appears to result from independent instances of hydrothermal fluid migration, with the common feature that these solutions infiltrated through bauxite deposits before entering the fractures.

References

Anderson N.T., Kelson J.R., Kele S., Daëron M., Bonifacie M., Horita J., Mackey T.J., John C.M., Kluge T., Petschnig P., Jost A.B., Huntington K.W., Bernasconi S.M. & Bergmann K.D. 2021: A Unified Clumped Isotope Thermometer Calibration (0.5–1,100 °C) Using Carbonate-Based Standardization. *Geophysical Research Letters* 48, 1–11. https://doi.org/10.1029/2020GL092069

Chacko T. & Deines P. 2008: Theoretical Calculation of Oxygen Isotopic Fractionation Factors In Carbonate Systems. *Geochimica et Cosmochimica Acta* 72, 3642–3660. https://doi.org/10.1016/j.gca.2008.06.001

Craig H. 1961: Isotopic variations in meteoric waters. *Science* 133, 1702–1703. https://doi.org/10.1126/science.133.3465.1

Czuppon Gy., Demény A., Leél-Őssy Sz., Óvári M., Molnár M., Stieber J., Kiss K., Kármán K., Surányi G. & Haszpra L. 2018: Cave monitoring in the Béke and Baradla caves (Northeastern Hungary): implications for the conditions for the formation cave carbonates. *International Journal of Speleology* 47, 13–28. https://doi.org/10.5038/1827-806X.47.1.2110

Daëron M. 2021: Full propagation of analytical uncertainties in Δ_{47} measurements. *Geochemistry, Geophysics, Geosystems* 22, E2020GC009592. https://doi.org/10.1029/2020GC009592

Daëron M., Drysdale R.N., Peral M., Huyghe D., Blamart D., Coplen T.B., Lartaud F. & Zanchetta G. 2019: Most earth-surface calcites precipitate out of isotopic equilibrium. *Nature Communications* 10, 429. https://doi.org/10.1038/s41467-019-08336-5

Demény A., Gatter I. & Kázmér M. 1997: The genesis of Mesozoic red calcite dikes of the Transdanubian Range (Hungary): fluid inclusion thermometry and stable isotope compositions. *Geologica Carpathica* 48, 1–9.

Demény A., Czuppon Gy., Siklósy Z., Leél-Őssy Sz., Lin K., Shen Ch.-Ch. & Gulyás K. 2013: Mid-Holocene climate conditions and moisture source variations based on stable H, C and O isotope compositions of speleothems in Hungary. *Quaternary International* 293, 150–156. https://doi.org/10.1016/j.quaint.2012.05.035

Demény A., Czuppon Gy., Kern Z., Leél-Őssy Sz., Németh A., Szabó M., Tóth M., Wu Ch.-Ch., Shen Ch.-Ch., Molnár M., Németh T., Németh P. & Óvári M. 2016: Recrystallization-induced oxygen isotope changes in inclusion-hosted water of speleothems – Paleoclimatological implications. *Quaternary International* 415, 25–32. https://doi.org/10.1016/j.quaint.2015.11.137

Demény A., Kern Z., Czuppon Gy., Németh A., Schöll-Barna G., Siklósy Z., Leél-Őssy Sz., Cook G., Serlegi G., Bajnóczi B., Sümegi P., Király Á., Kiss V., Kulcsár G. & Bondár M. 2019: Middle Bronze Age humidity and temperature variations, and societal changes in East-Central Europe. Quaternary International 504, 80–95. https://doi.org/10.1016/j.quaint.2017.11.023

Demény A., Rinyu L., Kern Z., Hatvani I.G., Czuppon Gy., Surányi G., Leél-Őssy Sz., Shen Ch.-Ch. & Koltai G. 2021: Paleotemperature reconstructions using speleothem fluid inclusion analyses from Hungary. *Chemical Geology* 563, 120051. https://doi.org/10.1016/j.chemgeo.2020.120051

Demény A., Berentés A., Rinyu L., Kovács I., Surányi G. & Virág M. 2024a: Subaqueous carbonate speleothems as paleotemperature archives – clumped isotope thermometry and stable isotope compositions of inclusion-hosted water. *International Journal of Speleology* 53, 25–37. https://doi.org/10.5038/1827-806X.53.1.2480

Demény A., Rinyu L. & Dublyansky Y. 2024b: Preservation, alteration: comparison of inclusion-based calcite-water oxygen isotope and clumped isotope temperature signals in calcite veins. *Scientific Reports* (submitted).

Demény A., Czuppon G., Kern Z., Hatvani I., Topál D., Karlik M., Surányi G., Molnár M., Kiss G.I., Szabó M., Shen C.-C., Hu H.-M. & May Z. 2024c: A speleothem record of seasonality and moisture transport around the 8.2 ka event in Central Europe (Vacska Cave, Hungary). *Quaternary Research* 118, 195–210. https://doi.org/10.1017/qua.2023.33

Dublyansky Y. & Spötl C. 2010: Evidence for a hypogene paleohydrogeological event at the prospective nuclear waste disposal site Yucca Mountain, Nevada, USA, revealed by the isotope composition of fluid-inclusion water. *Earth and Planetary Science Letters* 289, 583–594. https://doi.org/10.1016/j.epsl.2009.11.061

Gatter I. 1984: Investigation of embedded fluids in vein fillings and in crusts precipitated from thermal waters on the walls of caves in carbonate rocks (in Hungarian). *Karszt és Barlang* 1, 9–18.

Griffiths M.L., Drysdale R.N., Vonhof H.B., Gagan M.K., Zhao J.X., Ayliffe L.K., Hantoro W.S., Hellstrom J.C., Cartwright I., Frisia S. & Suwargadi B.W. 2010: Younger Dryas-Holocene temperature and rainfall history of Southern Indonesia from $\delta^{18}O$ in speleothem calcite and fluid inclusions. *Earth and Planetary Science Letters* 295, 30–36. https://doi.org/10.1016/j.epsl.2010.03.018

Győri O., Orbán R., Mindszenty A., Fodor L., Poros Zs., Erőss A., Benkó Zs. & Molnár F. 2014: Red calcite: an indicator of paleokarst systems associated with bauxitic unconformities. *Geofluids* 14, 459–480. https://doi.org/10.1111/gfl.12088

Haas J., Jocha-Edelényi E., Gidai L., Kaiser M., Kretzoi M. & Oravecz J. 1985: Geology of the Sümeg area. *Geologica Hungarica Series Geologica* 20, 365.

Haas J., Budai T., Piros O., Szeitz P. & Görög Á. 2010: Late Triassic platform, slope and basin deposits in the Pilis Mountains, Transdanubian Range, Hungary. *Central European Geology* 53, 233–259. https://doi.org/10.1556/CEuGeol.53.2010.2–3.7

Kázmér M. & Kovács S. 1985: Permian–Palaeogene paleogeography along the eastern part of the Insubric–Periadriatic Lineament system: evidence for continental escape of the Bakony–Drauzug Block. *Acta Geologica Hungarica* 28, 71–84.

Kercsmár Zs. 2004: Structural analysis of red calcite veins on Keselő Hill, Tatabánya Basin. *Annual Report of the Geological Institute of Hungary* 2002, 163–74.

Lases-Hernandez F., Medina-Elizalde M., Burns S. & DeCesare M. 2019: Long-term monitoring of drip water and groundwater stable isotopic variability in the Yucatán Peninsula: Implications for recharge and speleothem rainfall reconstruction. *Geochimica et Cosmochimica Acta* 246, 41–59. https://doi.org/10.1016/j.gca.2018.11.028

Meckler A.N., Affolter S., Dublyansky Y.V., Krüger Y., Vogel N., Bernasconi S.M., Frenz M., Kipfer R., Leuenberger M., Spötl C., Carolin S., Cobb K.M., Moerman J., Adkins J.F. & Fleitmann D. 2015: Glacial–interglacial temperature change in the tropical West Pacific: A comparison of stalagmite-based paleo-thermometers. *Quaternary Science Reviews* 127, 90–116. https://doi.org/10.1016/j.quascirev.2015.06.015

Mejía-Ortíz L., Christman M.C., Pipan T. & Culver D.C. 2020: What's the temperature in tropical caves? *PLoS ONE* 15, e0237051. https://doi.org/10.1371/journal.pone.0237051

Novello V.F., William da Cruz F., Vuille M., Pereira Silveira Campos J.L., Stríkis N.M., Apa´estegui J., Moquet J.S., Azevedo V., Ampuero A., Utida G., Wang X., Paula-Santos G.M., Jaqueto P., Ruiz Pessenda L.C., Breecker D.O. & Karmann I. 2021: Investigating $\delta^{13}C$ values in stalagmites from tropical South America for the last two millennia. *Quaternary Science Reviews* 255, 106822. https://doi.org/10.1016/j.quascirev.2021.106822

Serrato Marks G., Medina-Elizalde M., Burns S., Weldeab S., Lases-Hernandez F., Cazares G. & McGee D. 2021: Evidence for decreased precipitation variability in the Yucatán Peninsula during the mid-Holocene. *Paleoceanography and Paleoclimatology* 36, e2021PA004219. https://doi.org/10.1029/2021PA004219

Sheppard S.M.F. 1986: Characterization and isotopic variations in natural waters. In: Valley J.W., Taylor H.P., Jr., O'Neil J.R., Jr. (Eds.): Stable Isotopes in High Temperature Geological Processes. *Reviews in Mineralogy* 16, 165–184.

Spötl C., Dublyansky Y., Koltai G., Honiat C., Plan L. & Angerer T. 2021: Stable isotope imprint of hypogene speleogenesis: Lessons from Austrian caves. *Chemical Geology* 572, 120279. https://doi.org/10.1016/j.chemgeo.2021.120209

Varsányi I. & Kovács L.Ó. 2009: Origin, chemical and isotopic evolution of formation water in geopressured zones in the Pannonian Basin, Hungary. *Chemical Geology* 264, 187–196. https://doi.org/10.1016/j.chemgeo.2009.03.006

Vieten R., Warken S.F., Winter A., Scholz D., Zanchettin D., Black D. & Lachniet M. 2024: A sequence of abrupt climatic fluctuations in the north-eastern Caribbean related to the 8.2 ka event. *Holocene* 34, 325–337. https://doi.org/10.1177/09596836231211874

Voarintsoa N.R.G., Matero I.S.O., Railsback L.B., Gregoire L.J., Tindall J., Sime L., Cheng H., Edwards R.L., Brook G.A., Kathayat G., Li X., Michel Rakotondrazafy A.F. & Madison Razanatseheno M.O. 2019: Investigating the 8.2 ka event in northwestern Madagascar: Insight from data–model comparisons. *Quaternary Science Reviews* 204, 172–186. https://doi.org/10.1016/j.quascirev.2018.11.030