THE GENESIS OF MESOZOIC RED CALCITE DIKES OF THE TRANSDANUBIAN RANGE (HUNGARY): FLUID INCLUSION THERMOMETRY AND STABLE ISOTOPE COMPOSITIONS

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Abstract: Red calcite dikes with widths of 1–3 m were formed during the middle and upper Cretaceous within Mesozoic sedimentary carbonate rocks in the Transdanubian Range of Hungary. The dikes frequently develop a complex zonation with fine-grained dark red calcite at their margins and purer and more coarsely crystalline calcite toward their centres. The staining material responsible for their colour is amorphous Fe-oxide-hydroxide whose amount remains below 1 %. The fluid inclusions of carbonates contain rather dilute (<3.5 NaCl eq. wt. %) solutions and frequently show boiling phenomena. The evidence of boiling makes the use of T_h data (100–190 ^{o}C) as estimates of formation temperatures possible. The T_h-salinity plot of the microthermometric data reveals that boiling, cooling and dilution processes were operating during calcite precipitation. The stable carbon and oxygen isotope compositions of calcites and hydrogen isotope compositions of inclusion waters indicate that the formation of red calcite dikes was induced by the ascent of magmatic H_2O-CO_2 fluid which suffered degassing prior to and during dike formation and was contaminated by meteoric waters originating from the neighbouring rocks. The assumed movements of the magmatic fluids fit well into the results of earlier studies which have shown direct effects of magmatic fluids around lamprophyre dikes and influences of magmatic fluids in the formation of manganese oxide ores during the Cretaceous in the area of the Transdanubian Range.

Key words: Transdanubian Range, red calcite dikes, fluid inclusion microthermometry, stable isotope compositions, fluid evolution.

Introduction

Spectacular, reddish brown calcite dikes several metres wide cross-cut Mesozoic carbonate sequences in the Transdanubian Central Range. Fragments of the dike-filling material are popular among mineral collectors due to the intense, dark-red to brown colour, unusual for calcite. The dikes are mostly in Triassic carbonates, and have never been found in Tertiary rocks. Although Wein (1977) suggested a post-Cenomanian–pre-Senonian age for the dikes in the Buda Hills, there is only a single locality at Sümeg, where a middle to upper Cretaceous age of the dikes can be determined (Haas et al. 1985). Products of later hydrothermal activity are also widespread in the Transdanubian Central Range. The origin and timing of igneous dikes produced by Middle Miocene volcanism (Báldi & Nagymarosy 1976), and of speleothems in the thermal karst of the Buda hydrothermal zone (Alföldi 1979; Müller 1989; Juhász et al. 1995) are well known. The appearances of these formations are quite different from those of the red calcite dikes indicating different origins. On the basis of results of a preliminary stable isotope investigation, Demény & Kázmér (1994)

have presumed that movements of magmatic fluids played a major role in the formation of red calcite dikes, and — along with age evidence — this led them to suggest a genetic link with Cretaceous lamprophyre dikes of the same area. This suggestion has further implications, since if these very different formations are related, then the tectonic characteristics of the red calcite dikes might be used for paleogeographical reconstructions as has been done in the case of the lamprophyres (Kázmér & Szabó 1989a,b). In this study we present fluid inclusion and stable isotope data for the red calcite dikes, and using these results we provide a model of magmatic fluid movement and evolution by degassing and mixing with meteoric fluids and evolution.

Geological background and samples

There is a single locality at Sümeg, which provides a constraint on the biostratigraphic age of the red calcite dikes. The Sintérlap Quarry exposes the Tata Limestone Formation, cross-cut by a 3 m wide dike in the western part of the quarry. The

basal beds of the unconformably overlying Ugod Limestone contain pebbles both of the Tata Limestone and of the red calcite (Haas et al. 1985), proving that the hydrothermal activity responsible for the precipitation of the red calcite occurred between the deposition of the two formations. The Tata Limestone consists of crinoid ossicles and extraclasts mostly derived from Upper Jurassic–Lower Cretaceous limestone (Lelkes 1990). It is widespread in the Transdanubian Central Range reaching a thickness of up to 200 m. The Sümeg locality — where the upper part of the formation crops out — yielded the larger foraminiferal species *Orbitolina (Mesorbitolina) texana* (Roemer), which lived from Late Aptian (Gargasian) to Middle Albian (Görög 1996). Planktonic foraminifers from the same locality indicate the Globigerinelloides algerianus Zone (Sidó in Haas et al. 1985) of Late Aptian (Gargasian) age. Typical Clansayesian index fossils (e.g. *Ticinella bejauensis*) are missing even in the topmost beds. The locality Kálvária Hill at Tata (10 km NW from Tatabánya) exposes the lowermost beds of the Tata Limestone (Fülöp 1976). The condensed ammonite fauna from the basal beds contains Early Aptian to earliest Albian species (Szives 1996). We do not know, whether the deposition of the Tata Limestone was isochronous or heterochronous along its extent. However, the meagre data suggest, that any dike cross-cutting the Tata Limestone was certainly formed after the Middle Aptian (Gargasian), and possibly after the earliest Albian age.

The major unconformity between the Tata and Ugod Limestone Formations indicates the onset of the Senonian sedimentary cycle. The rudist-bearing Ugod Limestone unconformably covers the eroded surface of a tilted Tata Limestone block, which hosts the red calcite dike. The rudists suggest a Late Santonian to Early Campanian age for the deposition of the Ugod Limestone (Czabalay 1982; Bignot et al. 1984; Haas et al. 1985). Elsewhere the deposition of the Senonian complex started in the Santonian (Haas et al. 1985). The marine Senonian sediments are underlain by terrestrial bauxite and freshwater coal beds at nearby localities. Palynological data suggest Coniacian (and possibly latest Turonian) as the start of bauxite formation (Knauer & Siegl-Farkas 1992), i.e. the end of tectonic activity.

Summarizing the above considerations, we can conclude that dikes were opened and filled with red calcite not earlier than during the Late Aptian and possibly after the earliest Albian. Subaerial erosion of the red calcite and its host rock started not later than the Early Campanian, and took place in two stages (Early Albian and Turonian-Coniacian). Both the Tatabanya dike (Keselő Hill, uppermost level of the quarry) and the Piliscsaba-Jászfalu dike are hosted by Upper Triassic Dachstein Limestone. The thickness of both dikes is variable, up to several metres. There is no suitable sedimentary cover to constrain the age of dike emplacement at either localities.

The dike of Sümeg has been studied by fluid inclusion thermometry by Gatter (1984) who estimated the formation temperatures at about 135–155 °C. His cryoscopic measurements indicate that the fluids were rather diluted having 0–3 % NaCl equivalent salinity presumably in alkali bicarbonate and/or alkali earth chloride form. No free CO_2 was observed in the inclusion fluids by Gatter (1984), although it should be noted that water might contain up to 3.6 wt. % of dissolved CO_2 without developing a CO_2 hydrate on freezing. Tóth & Gecse (1981) studied "dedolomitized" zones in Triassic dolomites, whose appearance resemble that of the red calcite dikes studied in this paper. They attributed the "dedolomitization" to the influence of a magmatic body that supplied hydrothermal fluids. Dedolomitization is actually calcitization of dolomite, and can be produced by a variety of processes (diagenesis, metamorphism, alteration by hydrothermal fluids, weathering, etc.). Thus, the "dedolomitization" presumed by Tóth & Gecse (1981) does not provide a plausible explanation for the formation of the red calcite dikes.

A total of 5 dikes at three localities (Fig. 1) has been sampled for fluid inclusion thermometry and stable isotope analysis. As a common feature, the dikes show complex zonation proceeding from the neighbouring limestones toward dike centers: fine-grained dark-red calcite — dark-red sparic calcite — banded calcite with cm-scale concentric bands of white and red calcite — pale red sparic calcite (Figs. 1, 2). Electron microprobe measurements proved that the dike carbonate is calcite with negligible impurities. Since the marginal parts have the darkest red colour, the staining material has been determined in these samples by XRD measurements. It is amorphous Fe-oxide-hydroxide, whose amount is <1 %. Beside the Fe-oxide-hydroxide, in a dike at Tatabánya, xenomorphic zircon, a TiO_2 phase and monazite grains (<10 μm) have also been encountered. The sinuous contact between the dikes and the neighbouring limestones (see Fig. 1) indicates that the fluids responsible for calcite precipitation dissolved a significant amount of limestone and thus might have had an acidic pH. Colourless and white calcite veins formed at a later stage cut the red calcite dikes.
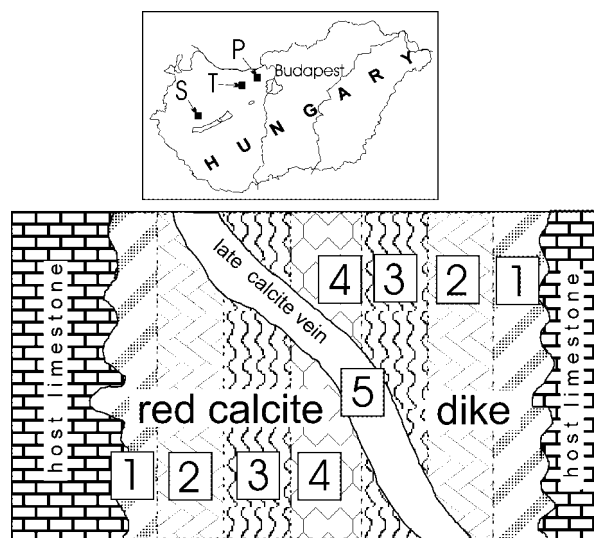

Fig. 1. Localities of red calcite dikes studied in the Transdanubian Range (Hungary) and a schematic drawing of dike zonation. **P** — Piliscsaba (2 dikes), **T** — Tatabánya (2 dikes), **S** — Sümeg (1 dike); **1** — fine-grained dark-red calcite, **2** — dark-red sparic calcite, **3** — concentric bands of white and red calcites, **4** — pale red sparic calcite, **5** — later colourless calcite veins cross-cutting the red calcite dikes.
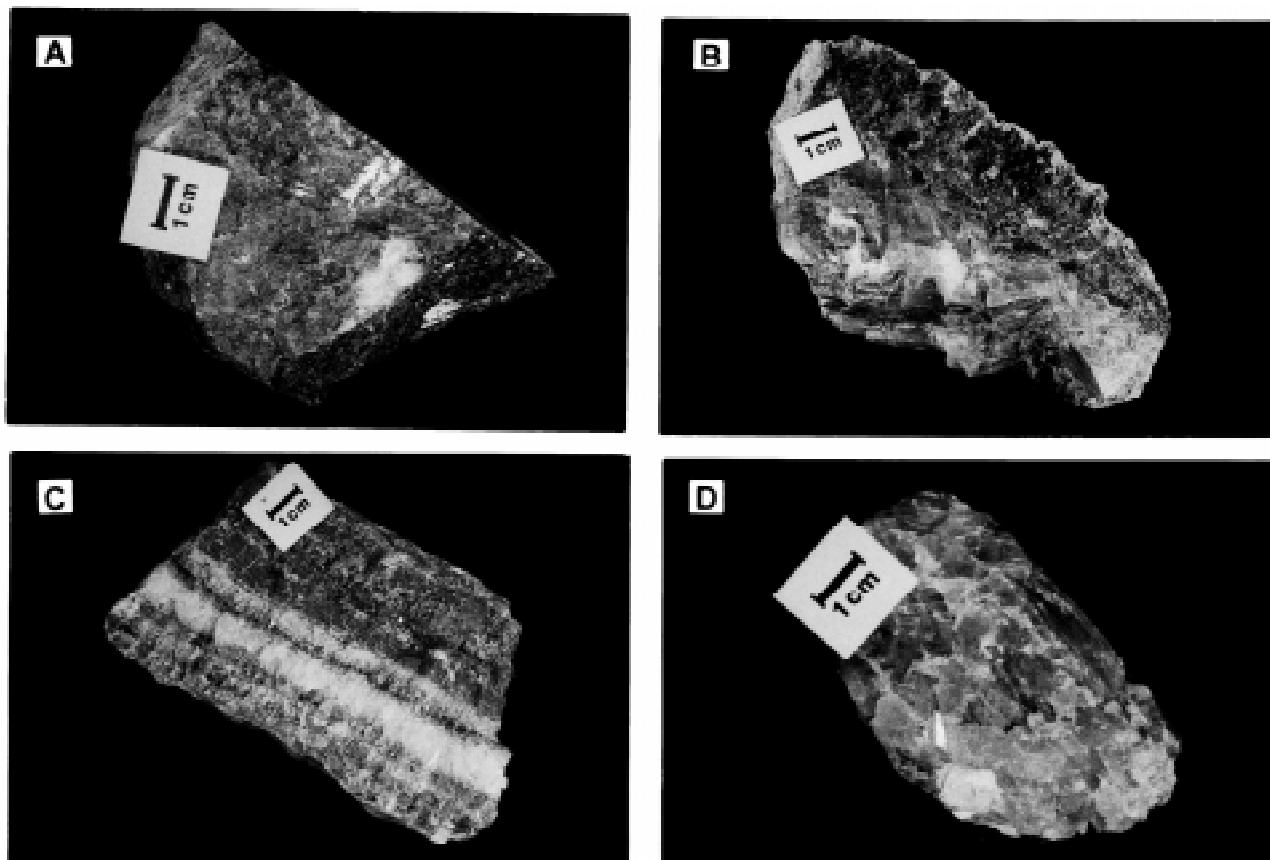
Fig. 2. Hand specimens of the main calcite types within the red calcite dikes of the Transdanubian Range. **A.** fine-grained dark red calcite, **B.** dark red sparic calcite, **C.** concentric bands of white and red calcites, **D.** pale red sparic calcite.

Analytical methods

Microthermometric measurements were carried out on a Chaixmeca stage (Poty et al. 1976) mounted on a Zeiss Amplival microscope using long working distance objectives (32× and 50×) at the Department of Mineralogy of the Eötvös Loránd University, Budapest. Fluid inclusion data were obtained from a total of ~20 double polished sections. The carbon and oxygen isotope composition of calcites were determined using the conventional phosphoric acid digestion method of McCrea (1950). Fluid inclusion waters were released by vacuum crushing and thermal decrepitation (in the case of calcites free of H-bearing impurities) after eliminating absorbed water by heating the samples at 150 °C for 2 hours under vacuum. Inclusion waters were converted to hydrogen gas by reaction with zinc alloy (obtained from Bloomington, USA) at 480 °C (Coleman et al. 1982) with special care for variations of hydrogen/zinc ratios (Demény 1995). $^{13}C/^{12}C$, $^{18}O/^{16}O$ and D/H ratios were determined using a Finnigan MAT delta S mass spectrometer at the Laboratory for Geochemical Research, Budapest. The isotopic compositions are expressed in the traditional δ notation in ‰ relative to V-PDB ($\delta^{13}C$) and V-SMOW ($\delta^{18}O$ and δD). Reproducibilities of $\delta^{13}C$ and $\delta^{18}O$ values are better than ±0.2 ‰. Within this analytical precision, theoretical data were obtained on the Har-

ding Iceland Spar standard ($\delta^{13}C$ = –4.80 ‰, $\delta^{18}O$ = 12.78 ‰, Landis 1983). The δD values are normalized to the V-SMOW–SLAP scale and reproducible to ±2 ‰.

Results and Discussions

Fluid inclusion studies

Inclusion petrography

The fluid inclusion groups were characterized by phase relations observed at room temperature. The genetic classification is based on Roedder (1984). According to an earlier study by Gatter (1984) and the present work, the fluid inclusion characteristics of the examined samples are as follows.

1. Solid inclusions. Calcites often contain euhedral carbonates a few tenths of μm in size. The red calcite samples contain rounded limonite blebs (~0.1 μm).

2. One-phase (liquid) inclusions. These inclusions have planar shapes and were formed along healed fractures. They are usually of secondary (S) type.

3. Vapour-rich inclusions. These inclusions are isometric, having often negative crystal shape with dark contours. A thin liquid film is sometimes visible.

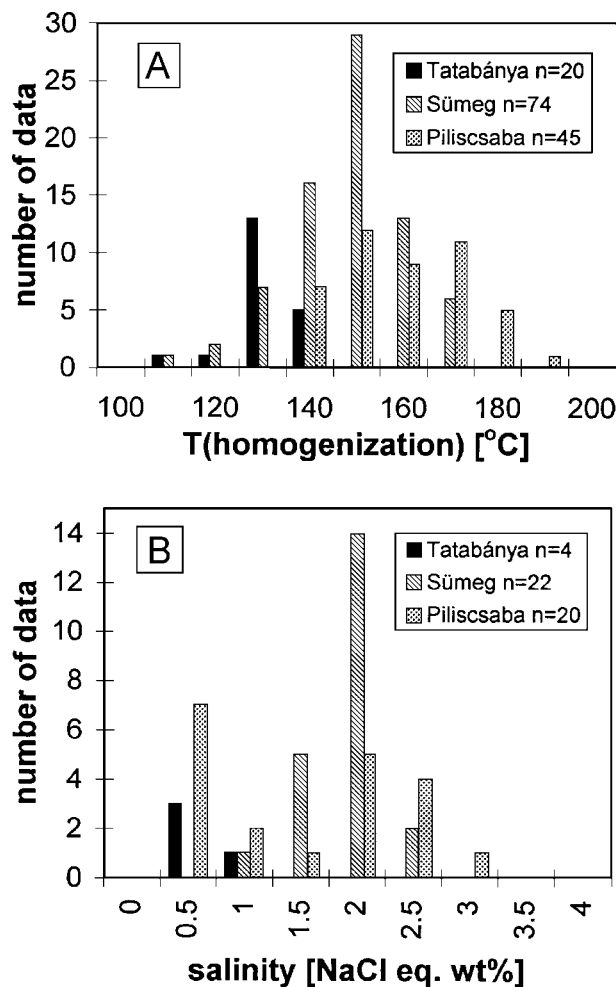**Table 1:** Statistical data of microthermometric measurements on fluid inclusions.

Homogenization temperatures [Th, ^{o}C]					
Samples	n	min	max	mean	std.
Gatter (1984)	45	106.7	168.3	146.1	11.8
VK-2	4	134.4	147.1	140.1	6
VK-3	4	129.5	156.9	144	11.2
VK-4	11	126.5	158.9	144.5	9.8
VK-5	10	115.2	149.6	132.4	9.5
VK-13 dark-red	13	122.4	138.3	129.6	5.4
VK-13 sparic	7	103.4	127	120.9	8.3
VK-19	10	156.8	176.3	162.6	5.9
VK-20 red	8	135.8	147	142.2	4.4
VK-20 white	10	134.4	147.1	141.1	4.5
VK-21	17	146.6	185.1	165.3	9.2
Temperatures of ice melting [T_m(ice), ^{o}C]					
Samples	n	min	max	mean	std.
Gatter (1984)	17	-1.3	-0.5	-0.9	0.2
VK-2	0				
VK-3	0				
VK-4	1	-0.8	-0.8		
VK-5	4	-1	-0.9	-1	0.1
VK-13 dark-red	4	-0.3	-0.1	-0.2	0.1
VK-13 sparic	0				
VK-19	3	-0.3	-0.2	-0.3	0.1
VK-20 red	3	-0.3	-0.2	-0.3	0.1
VK-20 white	6	-0.2	-0.1	-0.2	0.1
VK-21	7	-1.6	-1	-1.2	0.2
Salinities [NaCl eg. wt %]					
Samples	n	min	max	mean	std.
Gatter (1984)	17	0.9	2.2	1.6	0.4
VK-2	0				
VK-3	0				
VK-4	1	1.4	1.4		
VK-5	4	1.6	1.7	1.6	0.1
VK-13 dark-red	4	0.2	0.5	0.2	0.2
VK-13 sparic	0				
VK-19	3	0.4	0.5	0.5	0.1
VK-20 red	3	1.4	1.7	1.6	0.1
VK-20 white	6	0.2	0.4	0.3	0.1
VK-21	7	1.7	2.7	2	0.2

Fig. 3. Homogenization temperatures and salinities of fluid inclusions of the red calcite dikes of the Transdanubian Range (Hungary).

iv. Secondary (S type) inclusions with planar shapes and formed along healed fractures (50–100 μm).

5. Three-phase inclusions. The two-phase inclusions rarely contain carbonate crystallites, 2–3 μm in diameter.

Microthermometry

Summary of the measurement statistics is given in Table 1. The homogenization temperatures (T_h) of the two-phase inclusions range from 107 to 185 ^{o}C. In all cases the homogenization was observed in liquid phase. As shown in Fig. 3, there are some small differences between the localities studied.

Cryoscopic measurements showed fluid freezing between –45 and –35 ^{o}C. During gradual reheating of the inclusions to ambient temperature, slight, sometimes cloudy phase changes were detected in the –40 to –35, –25 to –20 and –12 to –8 ^{o}C intervals, indicating the presence of Na, Ca-chloride and alkali bicarbonate/sulphate in the solutions. No visible gas hydrates were observed.

The temperature of the last ice crystal disappearance ($T_{m/ice}$) was observed between –1.6 and –0.1 ^{o}C. The apparent salini-

4. Two-phase (liquid+vapour) inclusions. These inclusions appear in various forms:

i. isolated, large (up to 100–200 μm), elongated inclusions with negative rhombohedron or spindle shapes, arranged parallel to the rhombohedron's planes. These inclusions can be considered as primary (P type).

ii. elongated, or tooth-like cavities (10–50 μm) cutting the banded structure of the samples.

iii. isometric rounded inclusions or corroded rhombohedron forms (5–20 μm), usually confined to calcite growth zones. The latter two types are classified as pseudosecondary (PS).
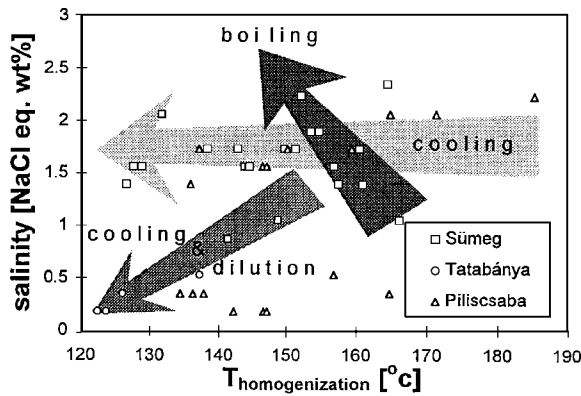
Fig. 4. Salinity vs. homogenization temperatures of fluid inclusions of the red calcite dikes of the Transdanubian Range (Hungary).

ties (expressed as NaCl eq. wt. %) range from 0 to 3.5 % (Fig. 3).

Interpretation of fluid inclusion data

Boiling phenomena were observed in almost all the samples, thus the calcite precipitation took place along or close to the boiling curve of the liquid system, making pressure correction unnecessary (Potter 1978; Roedder & Bodnar 1980). It follows from this consideration that the T_h data provide the lower limit of formation temperature.

Using salinity and T_h data pairs measured on the same inclusions, the average fluid density is estimated at 0.90–0.95 g/cm^3 (Bodnar 1983). The dynamic features of the investigated fluids can be studied on the salinity–T_h plot (Fig. 4) introduced by Hedenquist & Henley (1985) and Shepherd et al. (1985). Two trends can be observed in Fig. 4. In the higher salinity field, both cooling+dilution and boiling effects appear, whereas in the lower salinity field only cooling+dilution processes can be observed. The presence of trace amounts of CO_2 might be indicated by salinity–T_h correlations. However, this feature would be concealed by the effect of coupled cooling and dilution. Thus, the influence of the CO_2 degasing cannot be assessed unequivocally.

Stable isotope compositions

The stable carbon and oxygen isotope compositions of calcites are listed in Table 2 and plotted in Fig. 5. Although the data show a large scatter, some systematic trends within the selected calcite types can be observed.

Based on the data from two sections of the dikes at Sümeg and Tatabánya, the carbon isotope compositions of the red calcite dikes display fluctuations (~4 ‰, see Fig. 6), as opposed to the $\delta^{18}O$ data which are almost constant. The dark-red calcite of the dike margins have $\delta^{13}C$ data of –5.5 ‰ (VK2) and –7.1 ‰ (VK13/2), then the $\delta^{13}C$ values decrease towards the dikes' centers (VK4: –7.5 ‰, VK13/3: –9.7 ‰), then increase again in the concentric banded calcite (VK5: –3.2 ‰, VK13/5: –6.8 ‰). The $\delta^{13}C$ variation is <1 ‰ in the Piliscsaba dike.

Table 2: Stable carbon, oxygen and hydrogen isotopic compositions [‰] and water contents [ppm] of calcite samples and fluid inclusions trapped in the calcites of the red calcite dikes of the Transdanubian Range.

Samples	Description	$\delta^{13}C$	$\delta^{18}O$	H_2O	δD
Sümeg					
VK1	limestone	0.2	26.7		
VK2	dark-red calcite	-5.5	25.5	400	-35
VK3	banded dark-red calcite	-5.2	25.2	450	-27
VK4	concentric banded calcite	-7.5	25.6	95	-49
VK5	pale red sparic calcite	-3.2	25.6	100	-63
VK6/1	limestone	0.1	27.9		
VK6/2	limestone	-0.3	27.9		
VK6/3	dark-red calcite	-5.5	25.9		
VK7/1	dark-red calcite	-5.3	25.8		
VK7/2	colourless drusy calcite	-5.7	25.9	100	-102
VK8	dark-red sparic calcite	-6.1	25.4	515	-30
Tatabánya					
VK10/1	limestone	2.3	29.6		
VK10/2	limestone	2.3	29.7		
VK10/3	dark-red calcite	-8.1	26.3		
VK11	dark-red calcite	-7.3	26.1	650	-47
VK12	colourless drusy calcite	-3.6	17.3	20	-113
VK13/1	pale red calcite	-5.8	22.9		
VK13/2	dark-red calcite	-7.1	25.7	1050	-36
VK13/3	dark-red sparic calcite	-9.7	25.7	450	-45
VK13/4	concentric banded calcite (red)	-8.8	26.1		
VK13/5	concentric banded calcite (white)	-6.8	26.0		
VK13/4+5				205	-64
VK13/4+5	Q	470	-69		
VK13/6	colourless drusy calcite	-5.2	21.4	180	-47
Piliscsaba					
VK18/1-1	limestone	0.2	26.2		
VK18/1	limestone	-5.1	27.2		
VK18/2	dark-red calcite	-9.1	24.5	1000	-48
VK19	dark-red calcite	-10.0	24.5	1060	-48
VK20	concentric banded calcite (red)	-9.0	24.3	760	-49
VK21/1	pale red sparic calcite	-10.1	23.7		
VK21/2	colourless drusy calcite	0.1	17.9		
VK22Q	white calcite vein	1.0	16.5	95	-108
VK24Q	white calcite vein	0.5	16.5	44	-111

The limestones usually preserved their original sedimentary isotopic compositions, but strong $\delta^{13}C$ and $\delta^{18}O$ shifts also occur (e.g. VK13/1) frequently associated with a colour change of the limestone to pale red.

The isotopic compositions of the colourless calcite veins and white calcite dikes are very different from those described above with $\delta^{13}C$ data resembling those of limestones, and $\delta^{18}O$ data shifted to more negative values (see Fig. 5), thus their formation might be related to a later fluid movement independent of the formation of the red calcite dikes.
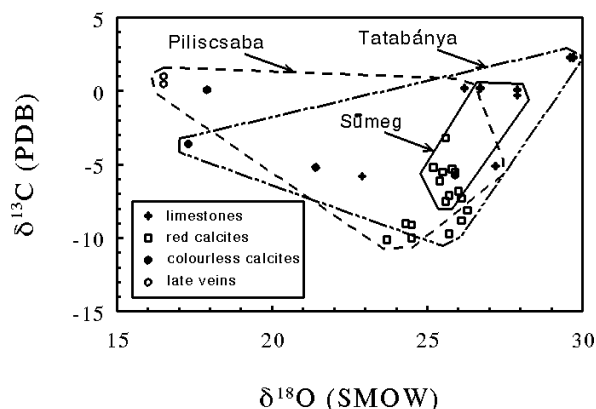
Fig. 5. Stable carbon and oxygen isotope compositions (in ‰) in red calcite dikes and associated rocks in the Transdanubian Range (Hungary).
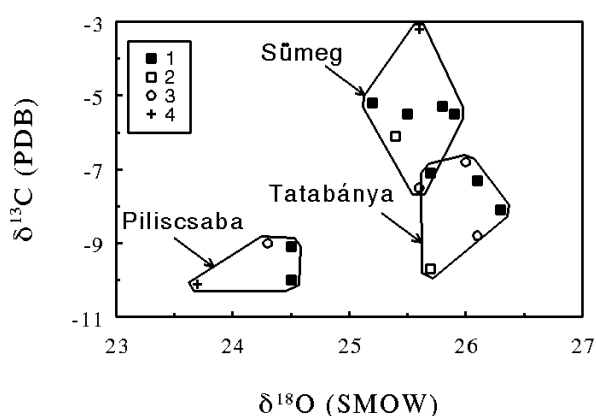

Fig. 6. Internal variations of stable carbon and oxygen isotope compositions (in ‰) in red calcite dikes of the Transdanubian Range (Hungary). **1** — dark-red calcite at dike margin, **2** — dark-red sparic calcite zone, **3** — concentric banded calcite zone, **4** — pale red sparic calcite zone.
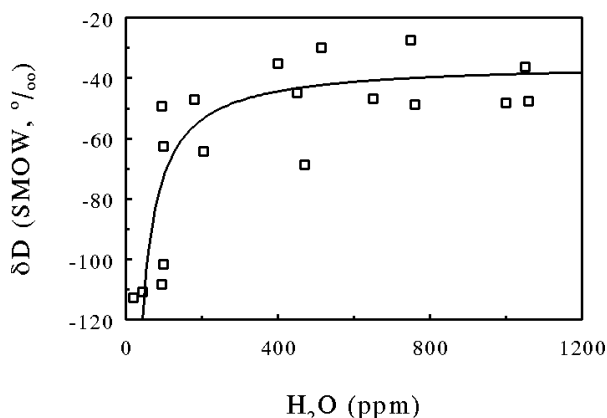

Fig. 7. Stable hydrogen isotope compositions of inclusion fluids vs. water contents of the red calcite dikes of the Transdanubian Range (Hungary).

The stable hydrogen isotope compositions of fluid inclusion waters are listed in Table 2 together with the water contents of calcite samples. The δD values scatter in a very wide range from –113 ‰ to –27 ‰, showing correlation with the water content (Fig. 7). The distribution of data points fits to a

curve of mixing of two components with δD values of –120 ‰ and –35 ‰. The δD variation is also correlated with the dike zonation. The highest δD values are found in the dark-red calcite at dike margins, whereas progressively more negative δD values appear toward the centres. The most deuterium-depleted fluids were detected in the late calcite veins that cross-cut the red calcite dikes. These late veins have sedimentary $\delta^{13}C$ compositions, thus their formation might be related to movements of meteoric water carrying dissolved sedimentary carbonate. Beside the observed shifts within individual dikes, the C and H isotope compositions of the dark-red calcite of dike margins — which represents the beginning of dike formation — display variations between different localities (Fig. 8).

Interpretation of the isotopic compositions

Since inclusions sample the dike-forming fluids and the carbonate is precipitated from the dissolved C, stable carbon and hydrogen isotope compositions of calcites and inclusion waters provide constraints on fluid origin, whereas the $\delta^{18}O$ data of calcites largely depend on both fluid composition (related to the origin) and precipitation temperature. Thus, using formation temperature estimations and oxygen isotope compositions of the carbonates, the $\delta^{18}O$ compositions of the fluids can be assessed, provided that the temperature dependence of the carbonate-water oxygen isotope fractionation is well established. Fig. 9 shows the hydrogen and oxygen isotope compositions of fluids measured and calculated using the relationship of O'Neil et al. (1969) recalculated by Friedman & O'Neil (1977), respectively. The isotopic compositions of the main water types (after Sheppard 1986) are also shown for comparison. The data points fall into the overlap area of several water types, however the tendency of shifting to more negative δD and $\delta^{18}O$ with dike evolution appears in the figure.

The observed $\delta^{13}C$, $\delta^{18}O$ and δD changes during dike evolution raise two questions. What is the origin of the fluid whose movement gave rise to the formation of the red calcite dikes? What kind of processes are responsible for the variations in the isotopic compositions?

The carbon isotope compositions of dissolved sedimentary carbonate (0 ± 2 ‰), magmatic CO_2 (–8 to –4 ‰) and CO_2 derived from oxidation of organic matter (–30 to –20 ‰) differ significantly from each other (Hoefs 1980). Thus, the origin of the dissolved C derived from these sources can be assessed by $\delta^{13}C$ measurements, although intermediate values can be produced by mixing of fluids of different origins. The $\delta^{13}C$ data of the dark-red calcite of dike margins (–10 ‰ to –5.5 ‰) might indicate influence of magmatic CO_2 or a fluid derived from mixing of CO_2 originated from oxidation of organic matter and dissolved sedimentary carbonate. The interpretation of the trend in $\delta^{13}C$-δD correlation in the dark-red calcites (see Fig. 8) needs further considerations. Oxidation of organic matter yields only a small amount of water, although it is significantly depleted in deuterium (see Fig. 9). The $\delta^{13}C$ data indicate that — assuming that the fluid is derived from a sedimentary sequence — the amount of organic-derived CO_2 in the total dissolved carbon would not have exceeded 50 %. Since the fluids were dominated by H_2O, the addition of proportional amounts of organic water (Sheppard

& Charef 1986) to the fluid would not shift its δD value by more than 1–2 ‰. On the contrary, a δD difference of about 20 ‰ is observed in the dark-red calcites (Fig. 8).

Another possibility for explaining the variations is the ascent and evolution of magmatic fluids. The isotopic compositions of the dark-red calcite of the Sümeg dike are consistent with a magmatic H_2O-CO_2 fluid (see discussion above and Fig. 9). Open system degassing of this fluid is suggested by the ubiquitous appearance of boiling phenomena in fluid inclusions, and — since the dark-red calcites were formed at the beginning of dike formation — this degassing might have started at deeper levels. The T_h data give the minimum temperature of calcite precipitation, thus, any preceding process might have occurred at higher temperatures. The dark-red calcites forming the dike margins have high δD values up to –27 ‰. In complience with their $\delta^{13}C$ data which indicate magmatic fluids, such high δD values are frequent in magmatic fluids derived from magma degassing at convergent plate margins (Giggenbach 1992; D'Amore & Bolognesi 1994). These data suggest that the fluids responsible for the formation of the red calcite dikes originated from degassing of a deep-seated magmatic source. This assumption is in accord with the low salinities of the fluid inclusions, since fluids derived from degassing would not contain high amounts of dissolved material.

The other question to be discussed is the cause of isotopic variations related to dike zonations. On the basis of the above considerations, the isotope changes might be attributed to the evolution of extinquishing magmatic fluids, undergoing degassing and having been contaminated by a steady influx of formation water of meteoric origin from the surrounding sedimentary rocks. In order to test this hypothesis, a model has been established using the following input data and assumptions:

— starting compositions of the magmatic fluid are $\delta^{13}C$ = –5.5 ‰, δD = –27 ‰.
— the water content of the calcites precipitated from magmatic and meteoric fluids (1000 ppm and 50 ppm, respectively) are used to estimate the ratio of the fluid components.
— the contaminating meteoric water has a δD value of –120 ‰ and carried a dissolved CO_2 with $\delta^{13}C$ = 0 ‰. This solution is assumed to have supplied about 1 % of the total C content of the mixed meteoric-magmatic fluid at the beginning of red calcite precipitation. The significance of the sedimentary C component increases with the degree of CO_2 degassing from the magmatic fluids.
— the CO_2 degassing might have occurred at or above the calcite precipitation temperatures (>150–200 °C). In the case of an H_2CO_3-dominated system, the CO_2-fluid carbon isotope fractionation is 0 to ~1 ‰ (Deines et al. 1974; Robinson 1975), whereas the CO_2-HCO_3^- fractionation is about 2 ‰ at 150–200 °C, tending to increase with temperature (see Friedman & O'Neil 1977, and references therein). The apparent dissolution of the neighbouring limestone at the dike margins indicates low-pH, H_2CO_3-dominated fluids. However, admixing of solutions originating from the surrounding carbonate rocks might have affected the pH conditions. Since we have no exact data on the actual temperature of the CO_2 degassing and the H_2CO_3-HCO_3^- speciation, an arbitrary $\delta^{13}C(CO_2$-fluid) fractionation value of 2 ‰ was chosen.
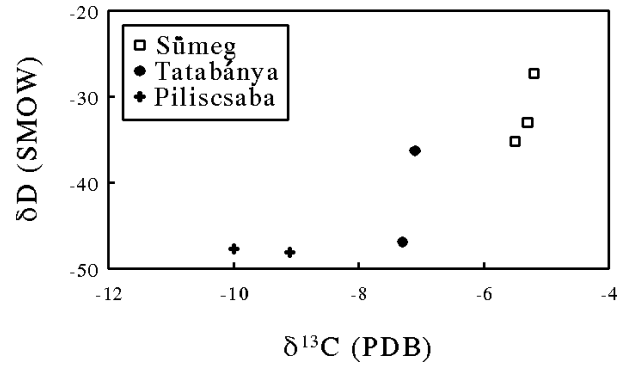

Fig. 8. Variations in stable hydrogen and carbon isotope compositions (in ‰) of dark-red calcites of dike margins in different red calcite dike localities.
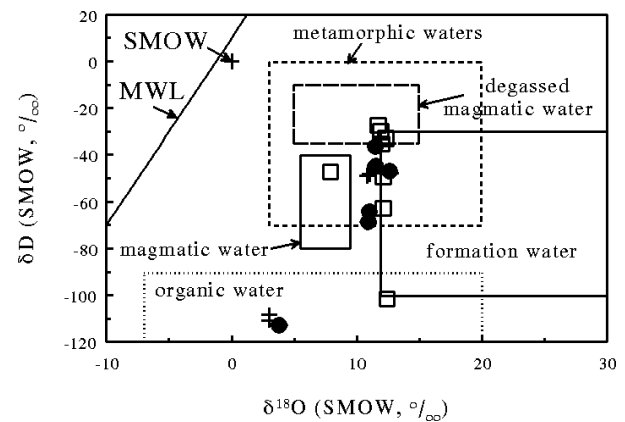

Fig. 9. Measured and calculated hydrogen and oxygen isotope compositions, respectively, of waters in equilibrium with red calcite dikes and associated later colourless calcite veins of the Transdanubian Range (Hungary). $\delta^{18}O$ data were calculated using the calcite-water fractionation of O'Neil et al. (1967) re-calculated by Friedman and O'Neil (1977) and equilibrium temperatures estimated from fluid inclusion microthermometry data (see text). Fields of main water types are from Sheppard (1986). *Squares* — Sümeg, *solid circles* — Tatabánya, *crosses* — Piliscsaba.
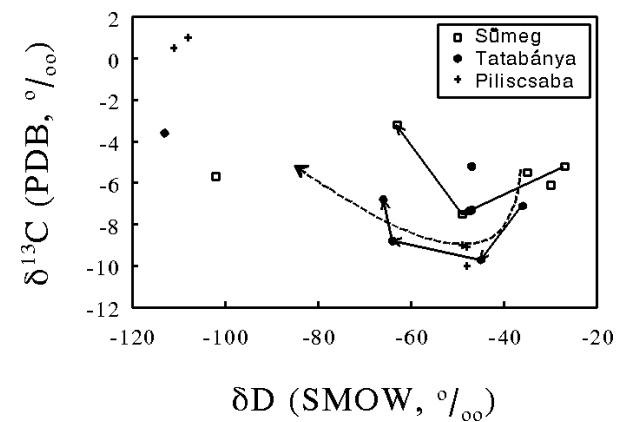

Fig. 10. $\delta^{13}C$ vs. δD plot of red calcite dikes and associated colourless calcite veins of the Transdanubian Range (Hungary). Dashed line is based on calculations for influences of fluid mixing and degassing (see text). Arrows show trends from dike margins to centres.

— we assume that the depletion in the magmatic H_2O is equal to the degree of CO_2 degassing. These parameters have similar meanings (i.e. rate of change) and quantities, thus this assumption is used for the sake of simplicity. A comparable approach was made by Zheng (1990) concerning CO_2 degassing and rate of calcite crystallization from an H_2O-CO_2 fluid.

— the CO_2 degassing took place in an open system, thus the Rayleigh fractionation relationship is used.

The resulting model curve is shown in Fig. 10 together with the measured isotopic compositions. The curve shows similar $\delta^{13}C$ and δD changes as those observed in the red calcite dikes. This observation indicates that — although we have made assumptions that might not be entirely valid — the scenario of magmatic fluid evolution describes the actual processes operating during the formation of the red calcite dikes.

Correlations with other studies and further implications

Direct and indirect evidence of magmatic fluid influences during the Cretaceous has been investigated by Demény (1992), Demény et al. (1994) and Pantó et al. (1996). Direct effects of the magmatic fluids appear in the formation of ubiquitous carbonate veins around upper Cretaceous lamprophyre bodies which intruded into Mesozoic sedimentary carbonate sequences of the Transdanubian Range. The lamprophyre series has carbonatitic affinities as proved by the appearance of carbonate ocelli of magmatic origin in these rocks. Local enrichment resulted in ~50% carbonate, leading Horváth et al. (1983) to classify these rocks as beforsite (dolomite-carbonatite). The isotopic compositions of the accompanying carbonate veins indicate the presence of magmatic H_2O-CO_2 fluids (Demény 1992; Demény et al. 1994).

Indirect evidence for the involvement of magmatic fluid has been described in the Transdanubian Range by Pantó et al. (1996) who have shown that secondary oxidation of manganese carbonates and formation of Sr- and Ba-rich manganese oxides (with up to 1 % Sr and 0.5 % Ba) in the Úrkút Mn-deposit can be attributed to movements of magmatic fluids during the middle Cretaceous.

These studies together with the results of the present work indicate that a significant magmatic activity took place during the Cretaceous within and underneath the Mesozoic complex of the Transdanubian Range. During the Cretaceous, this sedimentary complex was situated in an intermediate position between the units that now comprise the Mesozoic nappes of the Southern Alps and the Northern Calcareous Alps several hundred km from the Transdanubian Range to the west, thus belonging to the Alpine edifice. Kázmér & Szabó (1989a,b) have suggested, that these magmatic activities were related to orogenic processes acting in the hinterland of the Alpine deformation front.

Conclusions

On the basis of fluid inclusion microthermometry, the formation of Cretaceous red calcite dikes of the Transdanubian

Range was induced by movements of rather dilute (<3.5 NaCl eq. wt. %) H_2O-rich fluids at 100–190 °C. The dikes were formed in Mesozoic sedimentary carbonate rocks and generally show complex zonation with fine-grained dark red calcite at their margins stained by <1% Fe-oxide-hydroxide and more pure and coarser grained calcite at their centres. They are cut by colourless calcite veins. The stable C, H and O isotope compositions of carbonates and their inclusion fluids are most consistent with a magmatic origin. The isotopic compositions correlate well with dike zonation which is attributed to the coupled effects of CO_2 degassing and increasing contamination by meteoric waters during crack propagation. The formation of the late stage calcite veins can be assigned to movements of meteoric solutions carrying dissolved sedimentary carbonate.

The presumed movements of magmatic fluids are consistent with the results of earlier studies of Cretaceous lamprophyre dikes and manganese oxide ores of the Transdanubian Range whose formation provides evidence for direct and indirect magmatic influences in the area.

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