GEOLOGICA CARPATHICA, 55, 5, BRATISLAVA, OCTOBER 2004
421–429

FLUID INCLUSION AND STABLE ISOTOPIC EVIDENCE FOR EARLY HYDROTHERMAL KARSTIFICATION IN VADOSE CAVES OF THE NÍZKE TATRY MOUNTAINS (WESTERN CARPATHIANS)

MONIKA ORVOŠOVÁ[1], VRATISLAV HURAI[2], KLAUS SIMON[3] and VIERA WIEGEROVÁ[4]

[1]Slovak Museum of Nature Protection and Speleology, Školská 4, 031 01 Liptovský Mikuláš, Slovak Republic; orvosova@smopaj.sk
[2]Department of Mineralogy and Petrology, Faculty of Natural Sciences, Comenius University, 842 15 Bratislava, Slovak Republic
[3]Geochemistry Institute, Georg-August University, 37077 Göttingen, Germany
[4]Geological Survey of Slovak Republic, Mlynská dolina 1, 841 07 Bratislava, Slovak Republic

(Manuscript received January 8, 2003; accepted in revised form December 16, 2003)

Abstract: Hydrothermal paleokarst cavities with calcite crystals up to 20 cm in diameter were found in two caves of the Nízke Tatry Mountains developed in Triassic limestone and dolomite of the Guttenstein type. In both caves, older zones of tectonic and hydrothermal activity have been overprinted by vadose speleogenesis. According to fluid inclusion microthermometry data, prismatic-scalenohedral calcite from the Silvošova Diera Cave has precipitated at temperatures between ~60 and 101 °C from low salinity aqueous solutions (≤ 0.7 wt. % NaCl eq.). Carbon and oxygen isotope profiling revealed significant $\delta^{13}C$ decrease accompanied by slight $\delta^{18}O$ increase during growth of calcite crystals. The negatively correlated carbon and oxygen isotope data cannot be interpreted in terms of any geologically reasonable models based on equilibrium isotopic fractionation. Fluid inclusion water exhibits minor decrease of δD values from crystal core (–31 ‰ SMOW) to rim (–41 ‰ SMOW). Scalenohedral calcite from the Nová Stanišovská Cave has precipitated at slightly higher temperatures (63–107 °C) from aqueous solutions with salinity ≤ 2.7 % NaCl eq. The positively correlated trend of $\delta^{13}C$ and $\delta^{18}O$ values is similar to common hydrothermal carbonates. The fluid inclusion water δD values differ significantly between the crystal core (–50 ‰ SMOW) and rim (–11 ‰ SMOW). The calcite crystals are interpreted as representing a product of an extinct hydrothermal system, which was gradually replaced by shallow circulation of meteoric water. Fossil hydrothermal fluids discharged along Alpine uplift-related NNW–SSE-trending faults in Paleogene–pre-Pliocene times. Increased deuterium concentration in the inclusion water compared to recent meteoric precipitation indicates a warmer climate during the calcite crystallization.

Key words: stable isotopes, fluid inclusions, hydrothermal karst, hydrothermal calcite.

Introduction

Products of hydrothermal karstification superimposed by younger meteoric speleogenesis have been described in many karst regions. Dublyanski & Lomaev (1980) found calcite veins and hydrothermal cavities lined by “Iceland spar” in at least two caves of the Mountainous Crimea, Ukraine (Khod Konem and Gvozdeckogo Caves). Cryptokarstic hydrothermal cavities modified by later vadose caves were described by Sgibnev (1986) from the Tchien Shan Mountains (Kazakhstan), by Bosák (1993) from the Tyuya-Muyun Ridge (Kyrghyzstan), and by Bac-Moszaszwili & Rudnicki (1991) from the Polish Tatra Mountains (Dziura Cave). Osborne (1999, 2000) and Osborne & Cooper (2001) studied sulphide-bearing hydrothermal paleokarsts invaded by meteoric speleogenesis from the Jenolan Caves (New South Wales) and Ida Bay (Tasmania). The most detailed study of Ford (2000) following his previous paper (Ford 1995) and completed later by Cordingley (2000), demonstrated a number of cases of the hydrothermal karst overprinted by younger vadose speleogenesis in the Castleton area (Derbyshire, UK). Typical hydrothermal karst also occurs in the Transdanubian and North Hungarian Ranges, where three settings have been defined according to fluid inclusion and stable isotope data (Dublyansky 1995, 1997; Dublyansky & Ford 1997). All authors emphasized the important role of the earlier hydrothermal paleokarst as a guide for infiltration of water incidental to the younger meteoric speleogenesis (Osborne 2000).

Hydrothermal karstification has not been described in the Western Carpathians until now. Recently, large calcite crystals have been reported from two caves located in northern slopes of the Nízke Tatry Mountains (Hochmuth & Holúbek 1996; Votoupal & Holúbek 1996; Orvošová 1999). The caves are developed in Triassic limestones and dolomites of the Guttenstein type belonging to the carbonate sequence of Choč Nappe thrusted over the crystalline basement and autochthonous Permian-Triassic cover of the Tatric Tectonic Unit (Fig. 1). Fluid inclusion and stable isotope studies were carried out with the aim of elucidating the origin of the calcite. Detailed measurements of carbon and oxygen isotope ratios across crystal growth zones, hydrogen isotope analyses of inclusion water, and microthermometry data from fluid inclusions were the principal analytical methods.

Sample location

The *Silvošova Diera Cave* situated at about 1500 meters above see level in the SE part of the Ohnište karst massif

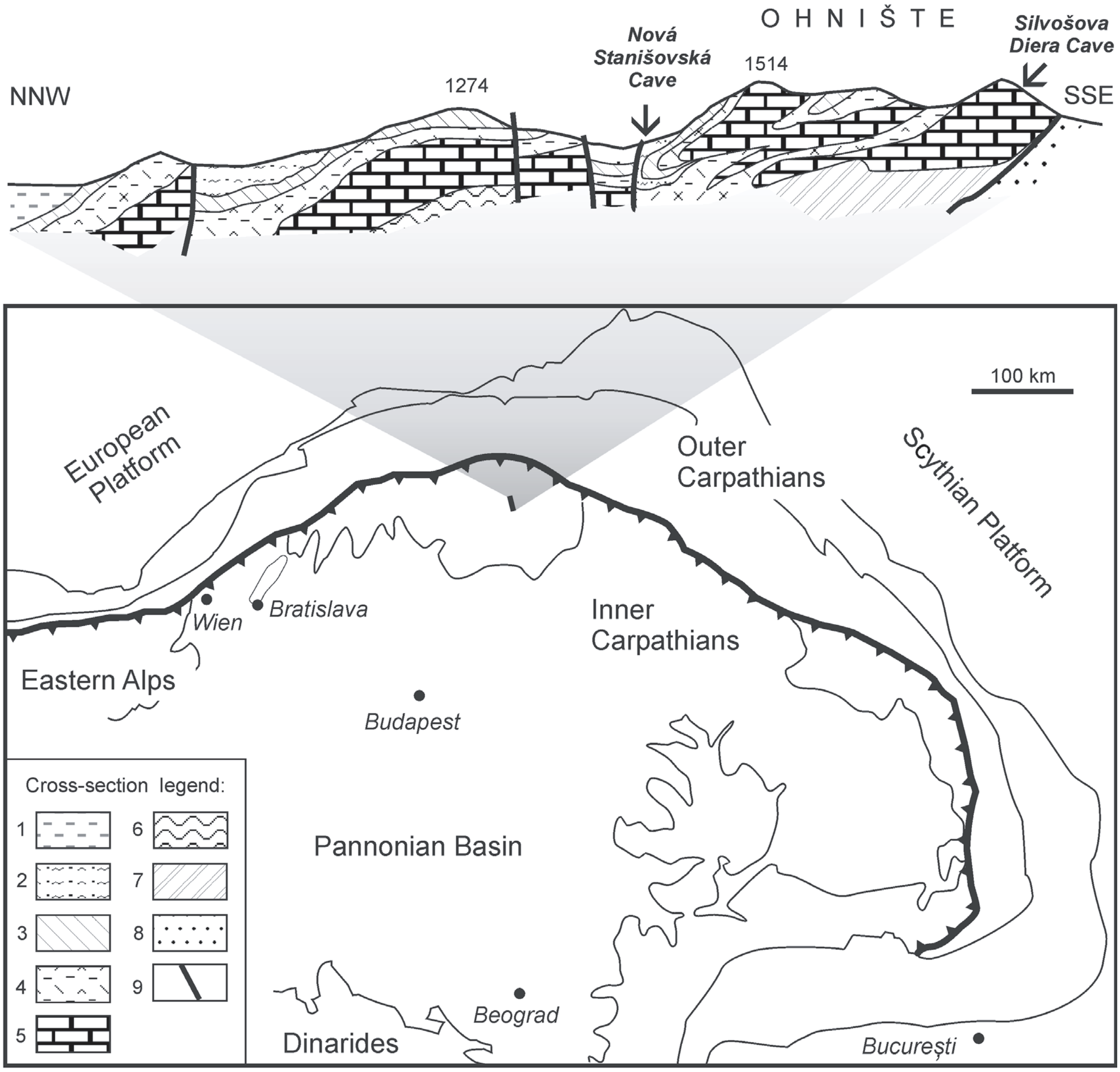

Fig. 1. Geological cross-section of the study area (modified after Maheľ 1986). **1** — Quaternary; **2–5** — Choč Nappe: 2 — Lunz Beds (Karnian), 3 — Reiflin Limestone (Upper Anisian–Ladinian), 4 — dolomite (Middle–Upper Triassic), 5 — Guttenstein Limestone (Anisian); **6–8** — Krížna Nappe: 6 — marly limestone (Titonian–Lower Cretaceous), 7 — dolomite (Middle to Upper Triassic), 8 — quartzite (Lower Triassic); **9** — fault.

(Fig. 1) is a fluvial cave with narrow corridors and small rooms. The cave represents a fragment of a fossil cave network developed in a ponor area along the contact of Variscan granitoids with karst rocks. Calcite crystals form linings of hydrothermally corroded nests in a NNW–SEE-trending tectonically disintegrated zone. Detached crystals were found together with rock debris in allochthonous clastic fill of a sump.

Smaller colourless, translucent crystals, up to 1 cm in size, display a rhombohedral habit, while larger ones have typical prismatic-scalenohedral shapes created by combination of dominant hexagonal prism $(10\bar{1}0)$ and a flat scalenohedron. The maximum length of the doubly terminated and partly translucent ochre-coloured crystals is 10 cm (Fig. 2). The prismatic facets of larger specimens exhibit etching figures. The interior of the crystals is oscillatory zoned.

The *Nová Stanišovská Cave* is located at about 700 m above see level at the junction of the Jánska and Stanišovská Valleys, delineating the Ohnište karst massif from north and west. The cave has developed on two horizontal levels, following a rhomboidal net of N–S (NNW–SSE)- and WNW–ESE-trending faults. Calcite crystals partly or completely fill small dissolution cavities, up to several decimeters in diameter (Fig. 3), following the NNW–SSE-trending fissures in the southernmost part of the system. Vadose speleothems have not been encountered in this part of the cave.

The calcite crystals are partly translucent, grey or yellow, 10–20 cm in size, and exhibit scalenohedral habit with dominant first-order $(21\bar{3}1)$ scalenohedron (Fig. 3). Larger crystals often display skeletal growth and etching figures. All the crystals consist of transparent core and rhythmically banded rim,

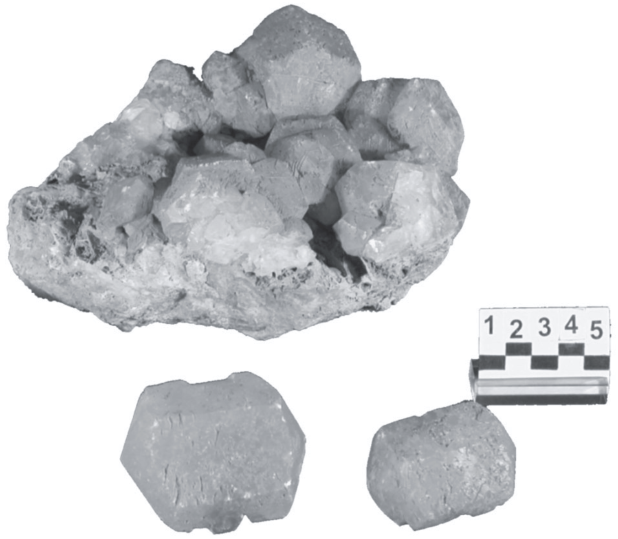

Fig. 2. Individual crystals and druses of prismatic-scalenohedral calcite recovered from sediments of the Silvošova Diera Cave.

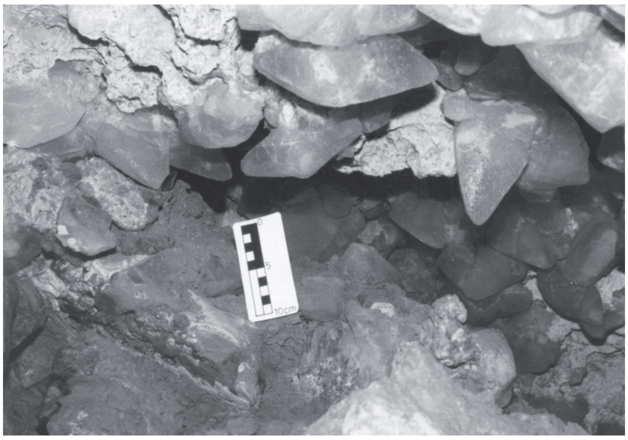

Fig. 3. Nest of giant scalenohedral calcite crystals lining dissolution vug in the Nová Stanišovská Cave.

1–2 cm thick, composed of recurrent dark-grey and transparent stripes. The grey colour of dark stripes results from a high density of small (several μm in diameter) clayey particles.

Both caves represent products of phreatic/vadose speleogenesis by cold water of deeply circulating meteoric waters. Typical speleothems (dripstones, flowstones, crusts, stalactites, stalagmites etc.) are connected with later vadose evolution of the caves. No other minerals are associated with the drusy calcite, belonging to the early hydrothermal stage of the cave development.

Analytical methods

Calcite crystals were cut perpendicular to the *c*-axis to obtain an elongated strip, 1 cm thick, 2 cm wide, with length corresponding to crystal diameter. The strip was further split into 10–11 consecutively numbered aliquots, each about 2–2.5 cm^3 in volume, representing individual growth zones of the crystal.

About 10 mg from each aliquot was taken for determination of carbon and oxygen isotopes. Common closed-reaction-vessel method of McCrea (1950) was used to convert the carbonate to CO_2. Carbon and oxygen isotope ratios of CO_2 were measured using a Finnigan MAT 250 mass spectrometer at the Geological Survey, Bratislava. The results are given in conventional δ-notation as ‰ deviation from the V-PDB and V-SMOW standards. Uncertainty for both the $\delta^{13}C$ and $\delta^{18}O$ values is ±0.1 ‰.

Remaining part of each aliquot was gently split into thin cleavage fragments and carefully inspected under polarizing microscope. Cleavage fragments containing fluid inclusions were selected for microthermometry and hydrogen isotope analysis of inclusion water.

Inclusion water was extracted from ~2 g of desiccated calcite fragments by vacuum milling at 60 °C (Simon 2001). The liberated water was converted to hydrogen by reduction with uranium at 750 °C. The hydrogen was adsorbed onto activated charcoal in a liquid nitrogen-cooled glass container and immediately analysed by mass spectrometry. The inclusion water extraction and hydrogen isotope measurements were carried out at the Institute of Geochemistry, Göttingen, using a Finnigan MAT 251 mass spectrometer. The δD values are expressed relative to the V-SMOW standard. The uncertainty limit is within ±1 ‰.

Cleavage fragments were used for microthermometry in order to avoid thermal and/or mechanical re-equilibration of fluid inclusions during sawing and polishing. Homogenization temperatures were measured first to eliminate errors due to expansion of ice and concomitant inclusion stretching on cooling. Only one heating–freezing cycle was applied to each cleavage fragment. The heating-freezing stage used was a Linkam THM-600 at the Geological Survey of the Slovak Republic, Bratislava, mounted on a Nikon Optiphot microscope with long-working distance objectives and a JVC CCD camera. The stage was calibrated using redistilled water, pure chemical substances and synthetic fluid inclusions. The uncertainty of the temperatures of phase transitions is about ±0.1 °C.

Fluid inclusions

Fluid inclusions are abundant in both calcite types. They can be classified as primary (Fig. 4a,b,d,e) and pseudosecondary (Fig. 4c,f) *sensu* Roedder (1984). True secondary inclusions with compositions and densities significantly differing from those in primary and pseudosecondary inclusions, or cross-cutting outer surface of calcite crystals, were not detected.

Extraordinarily large primary inclusions, with diameters up to 1000 μm, are typical of scalenohedral calcite from the Nová Stanišovská Cave (Fig. 4e). The inclusions are strongly elongated and often exhibit a saw-tooth shape. Other large inclusions have strongly irregular walls, but the smaller ones become equant, acquiring a normal negative-crystal shape of host crystal (Fig. 4a,b). Pseudosecondary inclusions are grouped into planes along healed fractures, which cross-cut

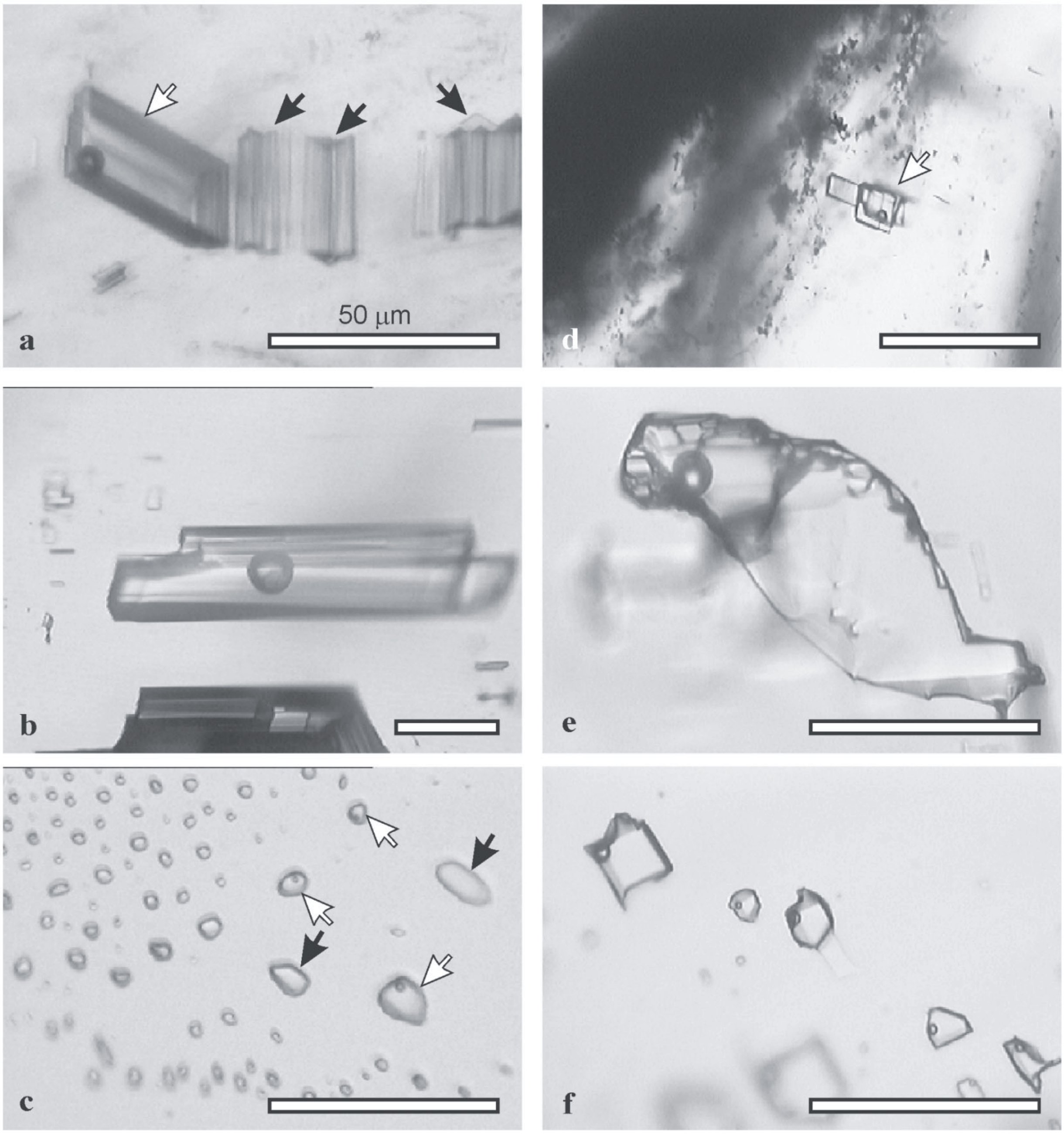

Fig. 4. Aqueous fluid inclusions trapped in prismatic-scalenohedral calcite (the Silvošova Diera Cave: a–c) and scalenohedral calcite (the Nová Stanišovská Cave: d–f). **a** — Group of primary, negative crystal-shaped inclusions. Two-phase inclusion consisting of vapour bubble and aqueous liquid is indicated by open arrow, while the remaining inclusions marked by solid arrows are filled only with aqueous liquid; **b** — Extremely large primary, negative crystal-shaped, two-phase inclusion; **c** — Group of fracture-bound, pseudosecondary inclusions, consisting of monophase (liquid, marked by solid arrows) and two phase (liquid+vapour, marked by open arrows) inclusions; **d** — Primary, two-phase aqueous inclusion (marked by open arrow) trapped in rhythmically banded rim of the crystal along dark growth zone with dense concentration of clay particles (upper left part of the photomicrograph); **e** — Primary, two-phase inclusion from the transparent core of the crystal; **f** — Group of pseudosecondary, two-phase inclusions with consistent liquid-to-vapour ratios. The absence of monophase aqueous inclusions is indicative of higher crystallization temperatures of the scalenohedral calcite compared to the prismatic-scalenohedral type. Scale bars in all photomicrographs represent 50 μm.

several growth zones, but terminate within the crystal interior (Fig. 4c,f).

Mono- and two-phase inclusions, both dominated by aqueous liquid, have been distinguished according to phase composition at room temperature. Two-phase inclusions contain small (1–5 vol. %) vapour bubbles (Fig. 4b,d,e,f). Monophase aqueous inclusions accompanying two-phase aqueous inclusions occur only in prismatic-scalenohedral calcite from the Silvošova Diera Cave (Fig. 4a,c). Consistent volumetric phase ratios in neighbouring inclusions in scalenohedral calcite from the Nová Stanišovská Cave are indicative of entrapment of a homogeneous fluid (Fig. 4f). Boiling-related, vapour-dominated inclusions have not been recognized. Air bubbles indicating a low-temperature vadose environment (e.g. Goldstein & Reynolds 1994) are also absent.

Homogenization temperatures (T_h) of two-phase inclusions in prismatic-scalenohedral calcite from the Silvošova Diera Cave are clustered mostly between 75 and 85 °C, with the total range between 58.6 and 100.5 °C. No significant changes in T_h values were recorded in various growth zones (Fig. 5). Temperatures of ice melting (0 to −0.4 °C) correspond to salinities between zero and 0.7 wt. % NaCl eq. (Bodnar 1993), with the majority of the determinations approaching the freshwater salinity. Eutectic temperatures could not be determined due to very low salt content and the small volume of the eutectic solution remaining after ice freezing.

The microthermometry data for scalenohedral calcite of the Nová Stanišovská Cave are slightly different (Fig. 6). Although the total range of the T_h values is similar (63.1–107.1 °C), significant differences exist between the crystal core and its rim. Most determinations from the core are grouped between 96 and 108 °C. Lower T_h values (80–94 °C) pertain either to pseudosecondary inclusions in the core or to primary inclusions in rhythmically banded rim. Temperatures of ice melting varied between 0 and −1.6 °C, thus corresponding to salinities between zero and 2.7 wt. % NaCl eq. No correlation between salinities and T_h values has been observed. Eutectic temperatures fall consistently between −21 and −22 °C, thus indicating either binary H_2O–NaCl mixture, or its combination with Na_2CO_3 and/or $NaHCO_3$ salts (Borisenko 1977).

Stable isotopes

The carbon and oxygen isotope ratios in both calcite types are remarkably different (Table 1). Prismatic-scalenohedral type shows lower $\delta^{18}O$ (9.8–12.6 ‰) and $\delta^{13}C$ (−3.2 to −11.7 ‰) values compared to the scalenohedral type ($\delta^{18}O$ = 11.1–17.8 ‰, $\delta^{13}C$ = −3.3 to −6.8 ‰). The $\delta^{18}O$ and $\delta^{13}C$ values of prismatic-scalenohedral type are negatively correlated, showing distinct changes along crystal growth direction (Fig. 5), where the large depletion in ^{13}C (Δ = −8 ‰) is accompanied by moderate enrichment in ^{18}O (Δ = +3 ‰). In contrast, except for the thin rims, a substantial portion of scalenohedral calcites is almost homogeneous in terms of isotopic composition, showing only weak concomitant increase in the $\delta^{18}O$ (Δ = +0.4 ‰) and the $\delta^{13}C$ (Δ = +1 ‰) values (Fig. 6). The rhythmically banded rim is characterized by strongly fluctuating and non-proportional changes in the $\delta^{18}O$ and $\delta^{13}C$ values indicative of a non-equilibrium precipitation.

The δD values of inclusion water differ in both caves. A decrease in δD values from −31 ‰ in core to −45 ‰ in the rim has been recorded in prismatic-scalenohedral calcite from the Silvošova Diera Cave. Inclusion water from homogeneous core of scalenohedral calcite from Nová Stanišovská Cave is somewhat lighter (−50 ‰), but rhythmically banded rim contains inclusion water with extraordinarily high δD value (−11 ‰).

Table 1: Isotope composition of calcite crystals (Nos. 1658, 1659, HO-1) from the Silvošova Diera, and a calcite crystal (No. 1819) from the Nová Stanišovská Caves.

Sample No.	Zone No.	$\delta^{18}O$ ‰ V-SMOW	$\delta^{13}C$ ‰ V-PDB	$\delta^{18}O$ ‰ V-PDB
1658	11 rim	12.6	−10.3	−17.7
	12	12.5	−11.0	−17.8
	13	12.3	−10.2	−18.0
	14	12.1	−8.8	−18.2
	15	11.0	−5.5	−19.3
	16 core	10.3	−3.2	−20.0
	17	10.7	−4.6	−19.6
	18	10.7	−5.4	−19.6
	19	12.1	−10.3	−18.2
	20 rim	12.4	−10.0	−17.9
1659	11 rim	12.2	−11.7	−18.1
	12	12.1	−11.0	−18.2
	13	12.1	−10.3	−18.2
	14	11.5	−8.1	−18.8
	15	10.2	−5.3	−20.0
	16 core	9.8	−3.8	−20.4
	17	9.8	−3.6	−20.4
	18	10.3	−4.8	−20.0
	19	11.5	−7.1	−18.8
	20	12.4	−9.9	−17.9
	21 rim	12.2	−10.3	−18.1
HO-1	core	11.2	−4.0	−19.1
	rim	12.5	−10.6	−17.8
1819	11 core	18.1	−3.3	−12.4
	12	17.9	−3.5	−12.6
	13	17.7	−3.6	−12.8
	14	17.7	−3.8	−12.8
	15	17.6	−4.0	−12.9
	16	17.8	−3.9	−12.6
	17	17.7	−4.3	−12.8
	18	13.2	−6.8	−17.1
	19	11.1	−3.7	−19.2
	20 rim	16.8	−5.2	−13.7

Discussion

Crystallization PT *conditions*

Consistent volumetric phase ratios and absence of vapour-dominated inclusions in both calcite types indicate a homogeneous trapping in a high-temperature phreatic zone (Goldstein & Reynolds 1994). The homogenization temperatures thus represent the minimum possible trapping temperature. The T_h values in scalenohedral calcite (63.1–107.1 °C) are somewhat higher than those in the prismatic-scalenohedral type (58.6–100.5 °C). Primary monophase aqueous inclusions, not resulting from necking-down process (e.g. Fig. 4a), indicate an episodic decrease in crystallization temperature of the prismatic-scalenohedral calcite below ~50 °C, corresponding to a low-temperature phreatic zone. However, absence of air-filled bubbles rules out crystallization in the vadose zone (Goldstein & Reynolds 1994).

The observed homogenization temperatures above 100 °C, slightly exceeding freshwater boiling point at atmospheric pressure, enable calculation of minimum trapping pressure. Considering *PT* conditions close to the liquid–vapour phase boundary for pure H_2O (e.g. Haas 1976), the T_h value of

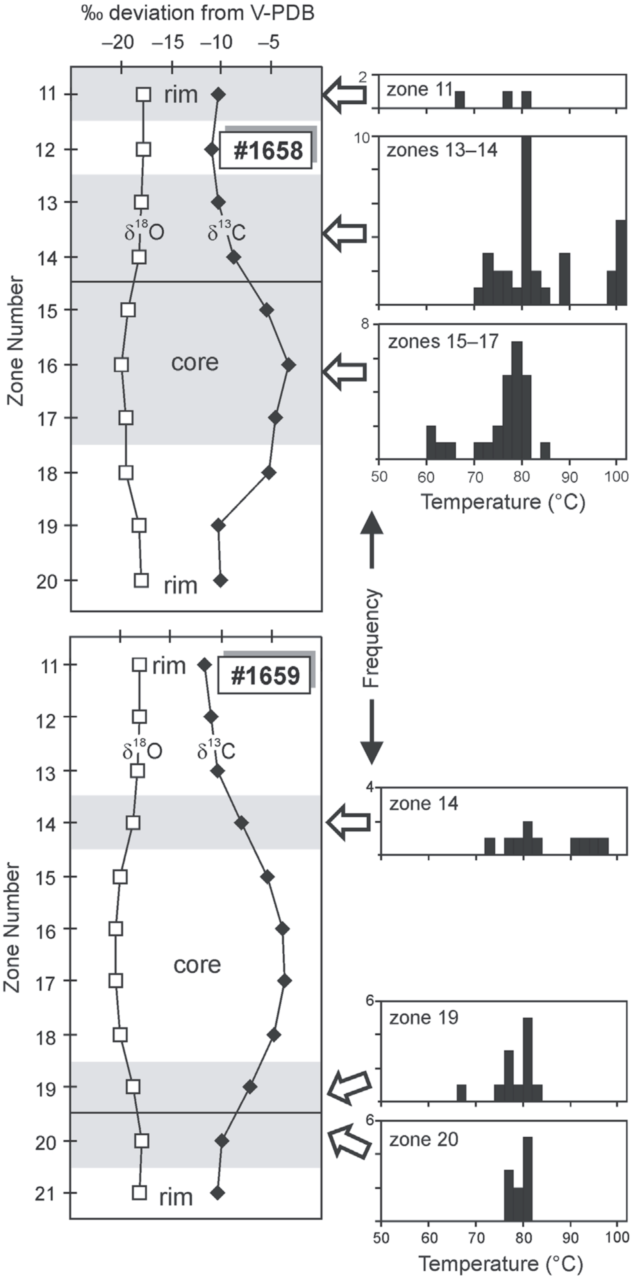

Fig. 5. Two isotopic profiles and fluid inclusion data for prismatic-scalenohedral calcite from Silvošova Diera Cave. The fluid inclusion homogenization temperatures are consistent in all the growth zones.

107.1 °C corresponds to a trapping pressure of 0.13 MPa. Assuming a hydrostatic regime with a fluid density of 967 kg.m^{-3} (average density of H_2O-liquid at 63.1–107.1 °C), the corresponding water column must have been higher than 3.2 m to prevent boiling at the bottom of the column. Calculation with 2.7 % NaCl-H_2O solution (maximum salinity determined in the scalenohedral calcite) does not substantially modify the estimated minimum height of the water column, because decreased saturation vapour pressure is counterbalanced by increased fluid density.

Isotopic composition of hydrothermal fluids

Prismatic-scalenohedral calcite

The δD values of inclusion water provide direct information on the isotope composition of the calcite-forming fluids, whilst the carbon and oxygen isotope ratios in the calcite must be recalculated using an appropriate model to obtain isotopic composition of the parental fluid.

An inverse correlation between the $\delta^{18}O$ and $\delta^{13}C$ values (Fig. 5), with large depletion in ^{13}C (~ −8 ‰) accompanied by a moderate enrichment in ^{18}O (~ +3 ‰) from core to rim is unique. A qualitatively similar isotopic trend has been hitherto recorded only in hydrothermal carbonate veins genetically linked with lamprophyres, where the isotopic trend resulted from extreme CO_2 devolatilization (Demény et al. 1994). DeVivo et al. (1987) have described a qualitatively similar trend in hydrothermal karst from western Sardinia, where scalenohedral calcite accompanied by quartz and barite in Cambrian carbonates shows an increase in $\delta^{18}O$ values from 13.8–16.3 ‰ in the core to 20.3–22.2 ‰ in the rim accompanied by $\delta^{13}C$ decrease from 0.1 ‰ in the core to −5.1 ‰ in the rim.

A negatively correlated C–O fractionation has recently been attributed to advanced CO_2 degassing of boiling aqueous solutions combined with progressive cooling (Zheng 1990; Demény et al. 1994). A simple cooling by ~ 70° proposed by DeVivo et al. (1987) for Sardinian calcites cannot be accepted in light of fractionation models applied to hydrothermal carbonates (Zheng 1990; Zheng & Hoefs 1993a), because the temperature decrease cannot lead to calcite precipitation due to increasing solubility of the carbonates in the aqueous solutions (Segnit et al. 1962). To precipitate the carbonate, the temperature decrease of the aqueous fluid must be accompanied by *p*H increase due to CO_2 outgassing and concomitant breakdown of HCO_3^- to H^+ and CO_3^{2-} (Rimstidt 1997).

The extensive CO_2-devolatilization cannot be accepted as a viable precipitation mechanism of hydrothermal calcites studied, because of negligible CO_2 concentrations potentially dissoluble at low temperature and pressure in the aqueous fluid. Furthermore, HCO_3^- should be the dominant dissolved carbonic species at temperatures around 100 °C and *p*H values corresponding to the stability of calcite. At this temperature, the carbon isotope composition of fluid does not change substantially, because the effect of CO_2 degassing is counterbalanced by carbonate precipitation owing to proportional fractionation factors (Ohmoto & Rye 1979). During CO_2 degassing at temperatures below 100 °C, the residual HCO_3^- rich fluid tends to be enriched in ^{13}C, which is inconsistent with the observed large depletion in the ^{13}C during growth of the prismatic-scalenohedral calcite.

A mixing of two fluids might represent an alternative model, which could account for the unusual $\delta^{13}C$–$\delta^{18}O$ data array in the prismatic-scalenohedral calcite. The model illustrated in Fig. 7 assumes mixing of hot (120 °C) H_2O-H_2CO_3 fluid *A* with cool (20 °C) fluid *B* with H_2O-HCO_3^- composition. The fluid *A* may represent a deeply circulating meteoric water dissolving CO_2 obtained by acid leaching of fresh limestone ($\delta^{13}C_{lim.}$ = ~ 0 ‰) during initial stages of the Rayleigh frac-

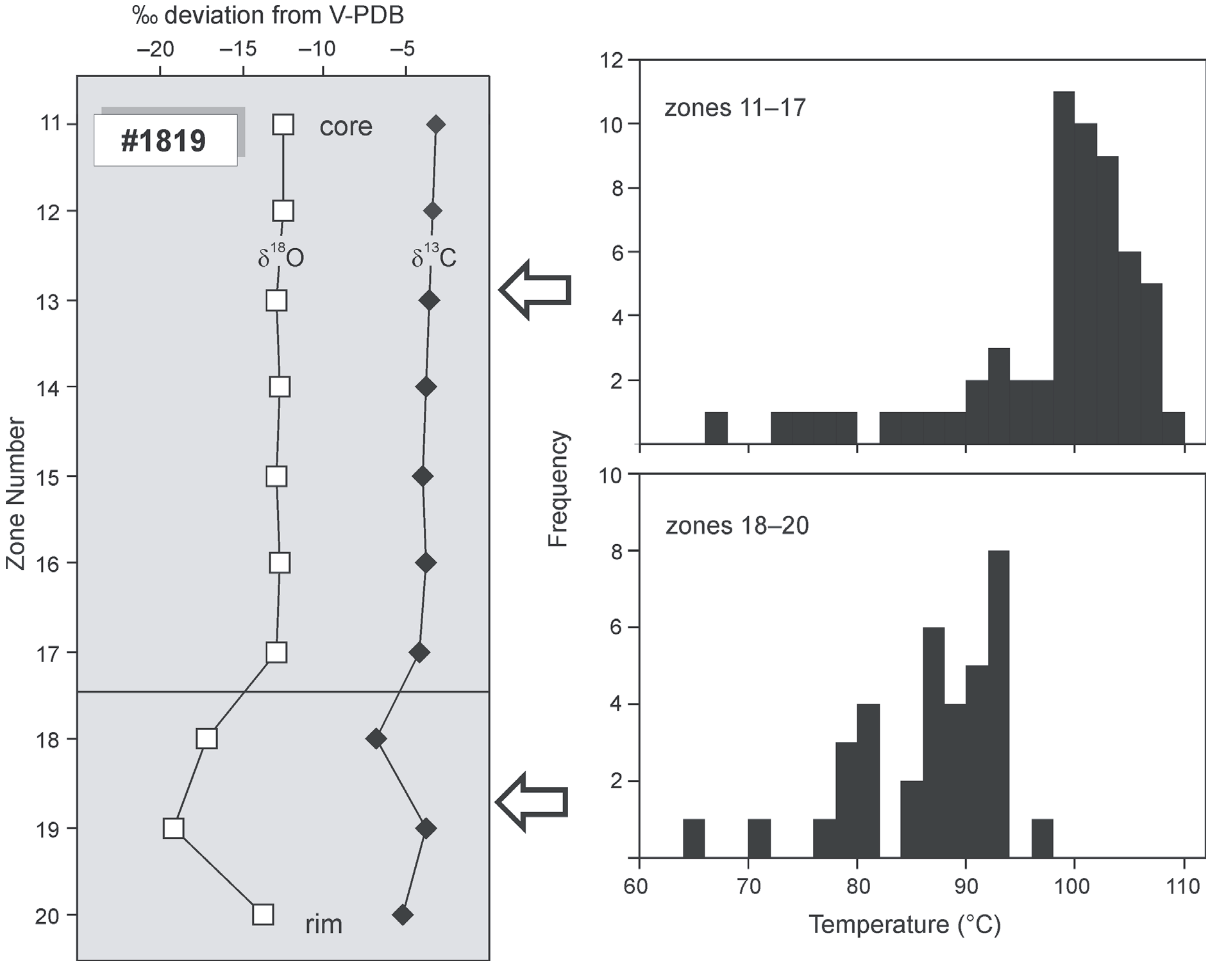

Fig. 6. Isotopic profile and fluid inclusion data for scalenohedral calcite from the Nová Stanišovská Cave. The fluid inclusion homogenization temperatures in the rim are lower than those in the core.

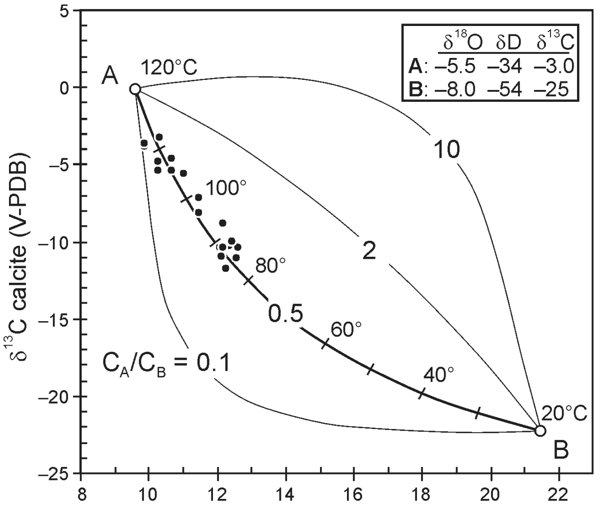

Fig. 7. Mixing model (Zheng & Hoefs 1993a) applied to C- and O-isotope composition of the prismatic-scalenohedral calcite. Isotope compositions of two mixing fluids *A* and *B* are given in the insert. C_A/C_B ratios denote relative carbon concentration in two mixing fluids.

tionation. The fluid *B* could correspond to shallowly circulating meteoric water saturated with CO_2 of pedogenic origin ($\delta^{13}C_{CO_2}$ = −25 ‰) produced by rainforest plants (e.g. Cerling 1984). The δD and $\delta^{18}O$ values for the mixing fluids *A* and *B* (−34 and −5.5 ‰, −54 ‰ and −8 ‰, respectively) are roughly identical with the recent meteoric water line (Craig 1961). The δD values of the inclusion water (−35 and −41 ‰ in the core and rim, respectively) correspond to 10 and 35 % admixture of the fluid *B* in the fluid *A*. It is interesting to note that input of ^{18}O-depleted fluid *B* into the fluid *A* results in precipitation of a ^{18}O-enriched calcite. Thus, at temperatures below 100 °C, the mixing mechanism can produce inversely correlated δD_{fluid}–$\delta^{18}O_{cc}$ and $\delta^{13}C_{cc}$–$\delta^{18}O_{cc}$ data arrays.

The proposed mixing model is, however, inconsistent with the microthermometry data, because the calculated cooling trajectory from 110 to 85 °C does not match the observed nearly isothermal precipitation at ~80±20 °C (Fig. 5). Moreover, the essentially CO_2-dominated, acidic mixture should dissolve calcite, rather than precipitate it. In summary, the distinctive inversely correlated stable isotopic record in the prismatic-scalenohedral calcite cannot be interpreted in terms of a geologically reasonable mixing model, assuming equilibrium isotopic fractionation. The isotopic signature of the calcite is inconsistent with most features of the hydrothermal karst environments as defined by Dublyansky & Ford (1997).

Scalenohedral calcite

The positively correlated $\delta^{13}C$ and $\delta^{18}O$ values in the core of the scalenohedral calcite are qualitatively similar to trends observed in typical hydrothermal carbonates (e.g. Zheng & Hoefs 1993b), although the small extent of fractionation (Δ = 0.4 ‰ for $\delta^{18}O$, 1 ‰ for $\delta^{13}C$) could also be explained in terms of intracrystalline differences in natural carbonates (e.g. Dickson 1997) without invoking isotopic, compositional and/or temperature changes of the parental fluid. Alternatively, the positively correlated $\delta^{13}C$ and $\delta^{18}O$ values can be interpreted using optional precipitation–devolatilization, mixing, or fluid-rock interaction models (Zheng & Hoefs 1993a).

The $\delta^{13}C$ value of the fluid parental to the scalenohedral calcite can vary only in relatively narrow interval within −5 ± 1 ‰, what corresponds to carbonates from most hydrothermal deposits fluxed with CO_2 from the Earth's mantle or magmatic intrusions (e.g. Hoefs 1997). However, CO_2 with a similar isotopic ratio can also be generated by acid leaching of fresh limestone with $\delta^{13}C \sim 0$ ‰ at around 100 °C, or hydrothermally altered limestone with $\delta^{13}C << 0$ ‰ at proportionally higher temperatures (e.g. Ohmoto & Rye 1979). Alternatively, the $\delta^{13}C_{fluid}$ value of −5 ‰ can be obtained by mixing of ^{13}C-enriched CO_2 from dissolved unaltered carbonate with organic matter-derived CO_2.

Assuming oxygen isotope fractionation in the calcite–water system (O'Neil 1969) and temperatures obtained from fluid inclusions, an aqueous fluid with $\delta^{18}O$ between 0 and 5 ‰ must have been present during growth of the core of the scalenohedral calcite. Such an isotopic signature can be attributed to magmatic, formation, metamorphic, or meteoric water and their mixtures equilibrated by interaction with dissolving limestone at low fluid/rock ratio. Neither of the alternatives, however, is unequivocally supported by the fluid inclusion data. The measured salinity (0–2.7 wt. % NaCl eq.) is considerably lower than the value of ~20 wt. % commonly attributed to a typical formation water (e.g. DeVivo et al. 1987).

Abrupt enrichment in deuterium of the inclusion water to as much as −11 ‰ in the rhythmically banded rim of the scalenohedral calcite probably results from contamination from clay particles, which could liberate water at grinding. The other δD values for prismatic-scalenohedral (from −31 to −45 ‰) and scalenohedral calcites (−50 ‰) are significantly higher than the average of recent meteoric waters (−70 ‰) in the studied area. Thus, the calcite crystals are interpreted as having formed in a warmer climatic period, during which the meteoric waters with higher D/H isotope ratios circulated. Except for the low $\delta^{18}O$ and $\delta^{13}C$ values, fluid inclusion and isotope characteristics of the scalenohedral calcite overlap nearly all essential features postulated by Dublyansky & Ford (1997) for a deep-seated hydrothermal karst.

The age of hydrothermal karstification

The structure of the studied area is complicated due to overturned folds, local digitations and recurrent bedding sequences caused by normal faulting. The complicated setting is influenced mostly by neo-Alpine deformations. The formation of joint and fault systems in the sedimentary cover is only poorly constrained due to inhomogeneity and strong rotation. However, the sedimentary cover and crystalline basement are interconnected with the N–S and WNW–ESE-trending fault systems, along which vadose caves originated. The N–S to NNW–SSE-trending faults in the Silvošova Diera and the Nová Stanišovská Caves are probably coeval with the uplift-related shear fractures of strike-slip origin in the southern part of a Paleogene basin located north of the study area (Marko 1995). The WNW–ESE-trending faults have been linked with post-Paleogene down-slip faults limiting horst structure along the northern margin of the Nízke Tatry Mts (Maheľ 1986). Transversal NW–SE tectonics were connected with uplift at 40–52 Ma constrained by apatite fission-track dating (Kráľ 1977). Intense block movements and rejuvenation of older fault systems also occurred during the Neogene (Nemčok 1989) and Middle Pleistocene (Droppa 1964). The fossilization of the caves in an extremely high altitude position results from Pliocene processes, as indicated by the magneto-stratigraphic interpretation of the cave fills (Kadlec et al. 2002). Hydrothermal karstification in the Nízke Tatry Mountains can therefore be placed in pre-Pliocene times, most likely in the Paleogene.

Conclusions

1. Vadose caves uncovered an earlier hydrothermal paleokarst system in the northern slopes of the Nízke Tatry Mountains.

2. Two morphological types of hydrothermal calcite with distinctive isotopic signatures have been distinguished.

3. Hydrothermal fluids with temperatures between 50 and 107 °C were discharged along regional N–S-trending fault systems, which were reactivated during Paleogene–pre-Pliocene times.

4. The isotopic characteristics of the calcite differ in many aspects from those typical of hydrothermal caves in Hungary.

Acknowledgments: The manuscript has benefited from perceptive reviews by V. Suchý, A. Demény, and J. Zachariáš. We acknowledge K. Žák (Czech Geological Survey, Prague) for many valuable comments, O. Lintnerová (Comenius University, Bratislava) for critical review of the manuscript, and P. Bosák (Academy of Sciences CR, Prague) for assistance during preparation of the manuscript.

References

Bac-Moszaszwilli M. & Rudnicki J. 1991: Dziura Cave. Example of hydrothermal karst in Tatras. *Tatry* 1, 10–12 (in Polish).

Bodnar R.J. 1993: Revised equation and table for determining the freezing point depression of H_2O-NaCl solutions. *Geochim. Cosmochim. Acta* 57, 683–684.

Borisenko A.S. 1977: The study of salt composition of fluid inclusions in minerals using the cryometric technique. *Geol. i Geofiz.* 8, 16–27 (in Russian).

Bosák P. 1993: Evolution of karst on Tyuya-Muyun deposit in Khyrgyzstan. *Knih. Čes. Speleol. Spol.* 21, 61–68 (in Czech).

Cerling T.E. 1984: The stable isotopic composition of modern soil carbonate and its relationship to climate. *Earth Planet. Sci. Lett.* 71, 229–240.

Cordingley J. 2000: Vein cavities in the Castleton caves: further information. *Cave Karst Sci*. 27, 85–88.

Craig H. 1961: Isotopic variations in meteoric waters. *Science* 133, 1702–1703.

Demény A., Forisz I. & Molnár F. 1994: Stable isotope and chemical compositions of carbonate ocelli and veins in Mesozoic lamprophyres of Hungary. *Eur. J. Mineral.* 6, 679–690.

DeVivo B., Maiorani A., Perna G. & Turi B. 1987: Fluid inclusion and stable isotope studies of calcite, quartz and barite from karstic caves in the Masua Mine, Southwestern Sardinia, Italy. *Chem. d. Erde* 46, 259–273.

Dickson J.A.D. 1997: Synchronous intracrystalline $\delta^{13}C$ and $\delta^{18}O$ differences in natural calcite crystals. *Mineral. Mag*. 61, 243–248.

Droppa A. 1964: Paralellisation of river terraces and horizontal caves. *Geol. Práce, Spr.* 64, 93–96 (in Slovak).

Dublyanski V.N. & Lomaev A.A. 1980: Karst caves of Ukraine. *Naukova Dumka*, Kiev, 1–180 (in Russian).

Dublyansky Y.V. 1995: Speleogenetic history of the Hungarian hydrothermal karst. *Environmental Geol.* 25, 24–35.

Dublyansky Y. 1997: Transition between hydrothermal and cold-water karst. In: Jeannin J.Y. (Ed.): Proceedings of the 12th Intl. Congress of Speleology, La Chaux de Fonds, Switzerland, August 10–17, 1997. *Swiss Speleol. Soc.,* 267–270.

Dublyansky Y. & Ford D. 1997: Paleoenvironment in hydrothermal karst: evidence from fluid inclusions and isotopes of carbon and oxygen. In: Boiron M.C. & Pironon J. (Eds.): XIVth European Current Research on Fluid Inclusions, Nancy, France, July 1–4, 1997. *Abstracts* 92–93.

Ford T.D. 1995: Some thoughts on hydrothermal karst. *Cave Karst Sci*. 22, 107–118.

Ford T.D. 2000: Vein cavities: an early stage in the evolution of the Castleton Caves, Derbyshire, UK. *Cave Karst Sci*. 27, 5–14.

Friedman I. & O'Neil J.R. 1977: Compilation of stable isotope fractionation factors of geochemical interest. *U.S. Geol. Surv. Profess. Paper* 440-KK.

Goldstein R.H. & Reynolds T.J. 1994: Systematics of fluid inclusions in diagenetic minerals. *SEPM Short Course* 31, 1–212.

Haas J.L. Jr. 1976: Physical properties of the coexisting phases and the thermochemical properties of the H_2O component in boiling NaCl solutions. *U.S. Geol. Surv. Bull.* 1421-A, 1–73.

Hoefs J. 1997: Stable isotope geochemistry. *Springer,* Berlin, Heidelberg, New York, 1–201.

Hochmuth Z. & Holúbek P. 1996: Survey and investigation of the Nová Stanišovská Cave. *Spravodaj SSS* 1, 19–23 (in Slovak).

Kadlec J., Pruner P., Chadima M. & Bosák P. 2002: Magnetostratigraphy and mineral magnetic properties of cave deposits preserved in cave systems located in the Nízke Tatry Mts. (Slovakia) — preliminary results (abs.). — *8th Castle Meeting: Paleo, Rock and Environmental Magnetism*: 1p. Geophys. Inst. AS CR and Geophys. Inst. SAS, Praha–Bratislava.

Kráľ J. 1977: Fission track ages of apatites from some granitoid rocks in Western Carpathians. *Geol. Zbor. Geol. Carpath.* 28, 269–276.

Maheľ M. 1986: Geological structure of the Czechoslovakian Carpathians. I. Paleoalpine units. *VEDA,* Bratislava, 1–510 (in Slovak).

Marko F. 1995: Dynamic analysis of fault distortion of the Central Carpathian Paleogene basin on the basis of structural observations from the northwestern and southern periphery of the Levočské Vrchy Mountains. Open File Report. *GÚ SAV,* Bratislava, 1–24 (in Slovak).

McCrea J.M. 1950: On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.* 18, 849–857.

Nemčok M. 1989: Structural tectonics of the Dead Bats Cave. *Open File Report SMOPaJ,* Liptovský Mikuláš, 1–40 (in Slovak).

Ohmoto H. & Rye R.O. 1979: Isotopes of sulphur and carbon. In: Barnes H.L. (Ed.): Geochemistry of hydrothermal deposits. *John Wiley and Sons, Inc.,* New York, 509–563.

Orvošová M. 1999: Allochthonous sediments in caves of the Nízke Tatry Mts. *Open File Report SMOPaJ,* Liptovský Mikuláš, 1–32 (in Slovak).

Osborne R.A.L. 1999: The origin of Jenolan Caves: Elements of a new synthesis and framework chronology. *Proc. Linn. Soc. N.S.W.* 121, 1–27.

Osborne R.A.L. 2000: Paleokarst and its significance for speleogenesis. In: Klimchouk A.B., Ford D.C., Palmer A.N. & Dreybrodt W. (Eds.): Speleogenesis. Evolution of karst aquifers. *Natl. Speleol. Soc*., Huntsville, 113–123.

Osborne R.A.L. & Cooper I.B. 2001: Sulfide-bearing palaeokarst deposits at Lune River Quarry, Ida Bay, Tasmania. *Aust. J. Earth Sci*. 48, 409–416.

Rimstidt J.D. 1997: Gangue mineral transport and deposition. In: Barnes H.L. (Ed.): Geochemistry of hydrothermal deposits. *John Wiley and Sons, Inc.,* New York, 487–515.

Roedder E. 1984: Fluid inclusions. *Mineral. Soc. Amer*., *Rev. Mineral.* 12, 1–644.

Segnit E.R., Holland H.D. & Biscardi C.J. 1962: The solubility of calcite in aqueous solutions — I. The solubility of calcite in water between 75° and 200 °C and CO_2 pressures up to 60 atm. *Geochim. Cosmochim. Acta* 26, 1301–1331.

Sgibnev V.V. 1989: Tectonic boundaries and stages of karstification in Tien-Shan. *Proc. 10th Int. Congr. Speleol. Budapest*, Vol. 1, 186–187.

Simon K. 2001: Does δD from fluid inclusion in quartz reflect the original hydrothermal fluid? *Chem. Geol.* 177, 483–495.

Votoupal S. & Holúbek P. 1996: A new speleological locality at the Ohnište — the Silvošova Diera cave. *Spravodaj SSS* 1, 39–41 (in Slovak).

Zheng Y.F. 1990: Carbon-oxygen isotopic covariation in hydrothermal calcite during degassing of CO_2. *Mineral. Deposita* 25, 246–250.

Zheng Y.F. & Hoefs J. 1993a: Carbon and oxygen isotopic covariations in hydrothermal calcites. Theoretical modeling on mixing processes and application to Pb-Zn deposits in the Harz Mountains, Germany. *Mineral. Deposita* 28, 79–89.

Zheng Y.F. & Hoefs J. 1993b: Stable isotope geochemistry of hydrothermal mineralizations in the Harz Mountains: I. Carbon and oxygen isotopes of carbonates and implications for the origin of hydrothermal fluids. *Monogr. Ser. Mineral. Deposita* 30, 169–187.