Int J Earth Sci (Geol Rundsch) (2009) 98:665–676
DOI 10.1007/s00531-007-0263-2

ORIGINAL PAPER

Identifying low-temperature hydrothermal karst and palaeowaters using stable isotopes: a case study from an alpine cave, Entrische Kirche, Austria

Christoph Spötl · Yuri Dublyansky · Michael Meyer · Augusto Mangini

Received: 24 May 2007 / Accepted: 6 October 2007 / Published online: 30 October 2007

Abstract The area south of the prominent east–west trending Salzach Valley at the northern rim of the Central Alps of Austria has long been known to host anomalously warm springs emerging from a highly deformed calcite marble (Klammkalk). This unit also hosts cavities whose shapes suggest a hydrothermal karst origin and which are lined by calcite spar. We report here petrographic and isotopic evidence suggesting that dissolution by ascending low-temperature thermal waters also played an important role in the origin of a large cave in this region, Entrische Kirche. A paleo cave wall, preserved behind a thick flowstone in the interior of this cave, revealed a brownish bleaching zone which contrasts to the medium grey colour of the unaltered marble beneath. Across this zone the C and O isotope values gradually decrease by 3 and 11‰, respectively. These compositions are very different from those of the speleothem above but are similar to phreatic calcite spar from hydrothermal karst cavities in other outcrops in the area, where the absence of two-phase fluid inclusions suggests a low-temperature (less than ca. 50°C) hydrothermal origin. U/Th dating of the flowstone capping the alteration zone yielded a minimum age of the thermal water invasion in Entrische Kirche of ca. 240 kyr. There is no evidence in Entrische Kirche that these palaeowaters reached the point of calcite precipitation, but it is physically conceivable that higher and as yet unexplored parts of this deep (ca. 900 m) cave contain cavities lined by phreatic cave spar.

Keywords Hydrothermal karst · Stable isotopes · Cave · Water/rock interaction · Austria

C. Spötl (✉) · Y. Dublyansky · M. Meyer
Institut für Geologie und Paläontologie,
Universität Innsbruck, Innrain 52, 6020 Innsbruck, Austria
e-mail: christoph.spoetl@uibk.ac.at

A. Mangini
Forschungsstelle Radiometrie,
Heidelberger Akademie der Wissenschaften,
Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

Introduction

The term *hydrothermal karst* refers to processes of dissolution of cavities and mineral precipitation therein by thermal waters, i.e. waters whose temperature is appreciably (5°C or more) higher than the surrounding environment (Dublyansky 2005). Conventionally, the temperature of 20°C is considered to be the lower limit of the thermal environment (Hölting and Coldewey 2005). Most hydrothermal karst systems owe their existence to the role of carbon dioxide, whose origin—in contrast to normal karst—is not the soil zone, but are deep-seated CO_2 sources, e.g. decarbonation reactions during rock metamorphism. Thermal waters ascending from depth are commonly saturated with respect to CO_2, whose solubility depends both on temperature and pressure. Upon rising to shallower depth CO_2 must exsolve into the gaseous phase. Because the solubility of carbonate minerals is inversely related to temperature these rising and cooling thermal waters maintain their capacity to dissolve the surrounding carbonate rock even at decreasing CO_2 levels. Near the land surface (or the groundwater table), however, the solubility of calcite drops drastically (Dublyansky 1995). As a result, hydrothermal karst is commonly characterized by a deeper level of extensive carbonate rock dissolution topped by a zone of precipitation of carbonate minerals (mostly calcite).

Criteria to recognize (paleo)hydrothermal karst origin include (1) the lack of a genetic relationship between the caves' configuration and surface topography, (2) lack of fluvial sediments in the caves, (3) development of a three-dimensional maze form of equidimensional passages guided by major fracture systems, (4) bush-like upward-branching groups of spherical niches, and (5) coarsely crystalline calcite lining or entirely filling voids, locally accompanied by minerals such as barite, quartz or fluorite (Bakalowicz et al. 1987; Dublyansky 2000, 2005).

Well-known examples of hydrothermal speleogenesis are caves in the Hungarian karst (e.g., in the Buda Hills of the Transdanubian Range—Müller 1989; Dublyansky 1995) and in the Black Hills of South Dakota (USA—Bakalowicz et al. 1987). In the greater alpine realm evidence of thermal karst is rare, although thermal springs are known from several places (see Zötl and Goldbrunner 1993 for an overview). Here, we report on a cave in the interior of the Austrian Alps where new data suggest the presence of thermal palaeowaters. The purpose of this paper is to demonstrate that stable isotope data are a valuable geochemical tool to identify and quantify palaeowater–rock interactions in low-temperature hydrothermal karst systems (e.g. Bakalowicz et al. 1987; Bottrell et al. 2001; Plan et al. 2006).

Topographic and geologic setting

The Entrische Kirche cave (literally translated "weird church")—the name stems from the historical use of this cave as a shelter during the Counter Reformation—is located at the entrance of the Gastein Valley, a southern tributary of the main E–W trending Salzach Valley (Fig. 1). The cave opens beneath a waterfall at an elevation of 1,040 m, ca. 250 m above the valley bottom and comprises a lower subhorizontal gallery and an upper level which consists of a large, partially collapsed hall, narrow galleries and vertical shafts (Fig. 1). The total surveyed length of the cave is 1.6 km. Rock overburden above the presently explored cave network is ca. 900 m.

The cave developed in a calcite marble of Upper Jurassic age (Klammkalk) which crops out as a prominent unit immediately south of the Salzach Valley (Exner 1979; Peer and Zimmer 1980; Fig. 1). The tributaries of the Salzach River cut deeply into this rock and Entrische Kirche is situated high above one of these gorges (Gastein Gorge). The marble dips nearly vertically and shows penetrative deformation giving rise to a mylonitic fabric with a striking WSW–ENE lineation. This deformation is the

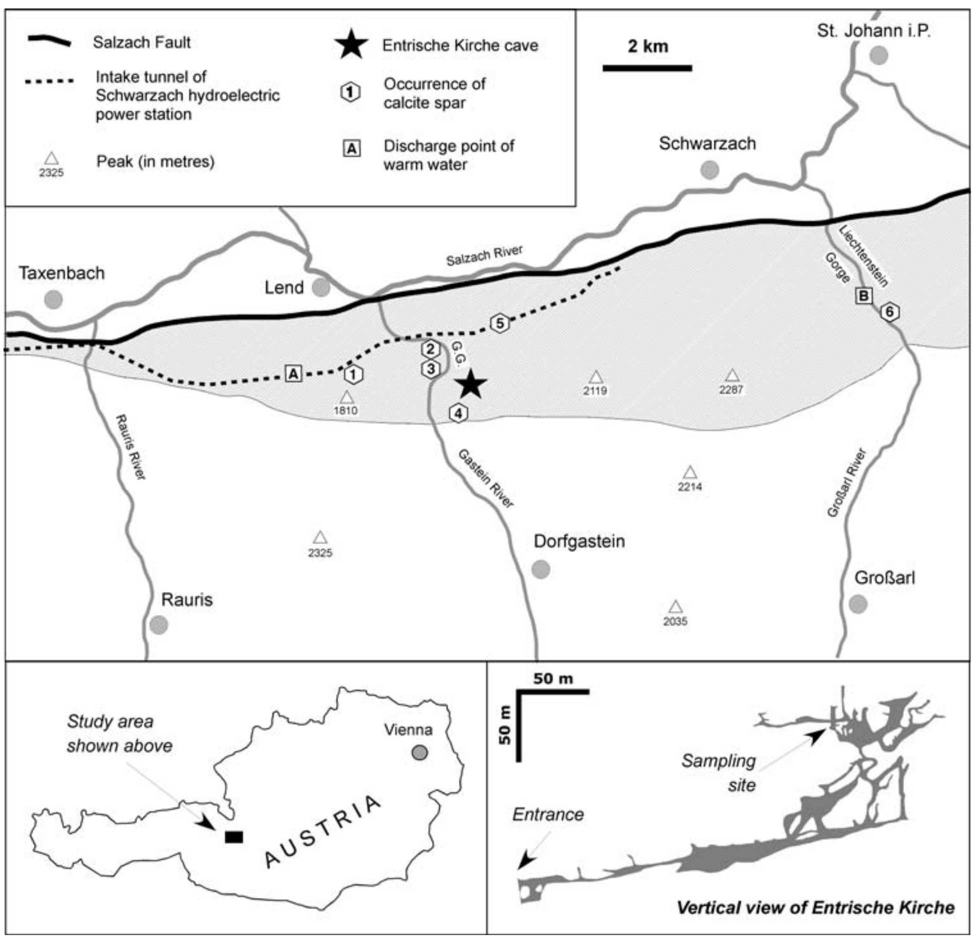

Fig. 1 Sketch map of the central Salzach Valley in the Province of Salzburg showing the location of the Entrische Kirche cave within the Klammkalk unit immediately south of the Salzach Fault (grey pattern; after Braunstingl 2005). Also shown are occurrences of warm waters (**a** in the intake tunnel near Lend, **b** in the southern part of the Liechtenstein Gorge of the Großarl River) and of calcite spar in presumably hydrothermal karst cavities (*1* Kristallgraben south of Lend, *2* and *3* Klammstein tunnel, *4* Klammstein quarry, *5* cave in intake tunnel, *6* Stegbachgraben). The location of the studied flowstone section (at the base of the Teufelskrallen pit) is indicated in the vertical section of Entrische Kirche cave. *G.G.* Gastein Gorge

result of sinistral strike-slip movement along the Salzach Fault during the Neogene (Wang and Neubauer 1998; Fig. 1).

The cave's galleries show evidence of a phreatic origin (e.g., near-circular cross sections), but most of passages were subsequently modified by vadose waters and collapse. The shafts are clearly of vadose origin and dissolution by seepage waters continues today as shown by water chemical analyses (Spötl, unpublished data). The cave hosts both siliciclastic sediments (gravel, sand, silt and loam), emplaced probably during cold climate periods, and speleothems (flowstones, stalagmites and stalactites) whose U-series dates indicate deposition during warm, interglacial periods, including the Holocene (Spötl, Meyer and Mangini, unpublished data).

There is no evidence of hydrothermal activity in Entrische Kirche today, nor is there in any of the few other smaller caves nearby (Klappacher 1992). Interior cave air and water temperature is close to 6°C, which corresponds to the mean annual air temperature outside the cave and the partial pressure of carbon dioxide in the cave air is only slightly higher than that of the outside air.

Modern and paleo-hydrothermal activity in the study area

While modern Entrische Kirche cave lacks evidence of hydrothermal waters, anomalously warm springs (up to 19°C) have long been known to emerge from the Klammkalk at the bottom of the gorge of the Großarl River 8.8 km east of Entrische Kirche (southern part of the Liechtenstein Gorge; Russegger 1836; Cudrigh 2002—symbol B in Fig. 1). Still warmer waters were encountered in the Klammkalk near Lend in the 1950s during construction of a 16 km-long intake tunnel for the Schwarzach hydroelectric power station (Horninger 1959a; Stini 1959). In one location, 3.7 km west of Entrische Kirche, water reached a temperature of up to 31°C, and discharge into the tunnel was initially very high (ca. 600 l/s) but decreased to 80–120 l/s after a period of a few weeks (Horninger 1959a—symbol A in Fig. 1). The tunnel also penetrated a cavern, 15–20 m high and up to 3 m wide. The Klammkalk showed a marked alteration zone up to half a meter in thickness (Horninger 1956). Chemical analyses revealed that this warm water had almost no free (aggressive) carbon dioxide (Horninger 1959b; analyses compiled by Cudrigh 2002). The same tunnel penetrated also a second cavern east of the Gastein Gorge, only 1.4 km northeast of Entrische Kirche (no. 5 in Fig. 1). The Klammkalk of this ca. 30 m-wide chamber was again bleached down to a depth of a few tens of centimetres and the walls were lined with calcite, both flowstone-like and euhedral scalenohedral and rhombohedral crystals. The crystals were up to 15 cm in size and showed prominent zoning patterns (Horninger 1958; Fig. 2). The calcite deposit reached a thickness of up to half a meter. The cave chamber was subsequently filled by yellowish brown, laminated loam. No hydrological activity was observed in this second chamber and temperature measurements showed no evidence of abnormal warmth (Horninger 1958).

During construction of the railway tunnel through the Gastein Gorge (ca. 1 km northeast of Entrische Kirche) a small cave was encountered in the Klammkalk (no. 2 in Fig. 1). Little is known about this cave, but it is reported that its walls were lined by scalenohedral calcite crystals 6–10 cm in length and grey clay-rich loam filled part of the cavity (Becke 1902). There are also surface outcrops, which suggest palaeohydrothermal activity in the Klammkalk. In the area west of the Gastein Gorge, karst pipes and veins were reportedly lined by euhedral calcite reaching several centimetres in length (Heissel 1955; Cudrigh 2002—no. 1 in Fig. 1). In a quarry 600 m SW of Entrische Kirche a cavern was encountered a few years ago whose walls were covered with yellowish scalenohedral calcite (J. Ratgeb, Rauris, oral comm. 2006—no. 4 in Fig. 1). Finally, a zone of extensive hydrothermal karst and calcite precipitation is exposed on the northern flank of Stegbachgraben, a steep gully 9.7 km east of Entrische Kirche (no. 6 in Fig. 1). Large cavities in the Klammkalk there are lined or entirely filled by a meter-thick calcite deposit, comprising multiple layers of palisade calcite aggregates. Calcite at this location was mined, reportedly in search for optical Iceland Spar, between 1945 and 1950 (H. Schwarz, Großarl, written comm., 2006). The marble adjacent to this calcite is commonly stained brownish.

Hydrothermal karst features were not known from the Entrische Kirche prior to our study. Although the cave

Fig. 2 Euhedral, yellow-stained scalenohedral calcite crystals from a palaeohydrothermal karst cavity intersected by the intake tunnel near Lend (no. 5 in Fig. 1; photo courtesy J. Reiterer). The specimen weighs about 10 kg

hosts calcite dating back to at least the marine isotope stage 7 (see below), none of this material is related to hydrothermal activity as shown by its morphology (mostly flowstones), crystal habit (no euhedral crystals), crystal fabric (mostly columnar crystals characteristic of speleothems—e.g., Kendall and Broughton 1978; Frisia et al. 2000), and stable isotopic composition (as discussed below). In this study, we not only focus on the evidence of past hydrothermal karst in Entrische Kirche cave but also provide preliminary results on some of the other occurrences in the Klammkalk unit in order to place the cave and its origin into a wider regional context.

Methods

An inactive flowstone in the interior upper part of the cave (base of the Teufelskrallen pit; Fig. 1) was drilled and two parallel cores taken ca. 1 m apart that reached the host rock beneath the speleothem (labelled TKS I and II) were examined both macroscopically and using thin sections. The transition from the host rock to the speleothem was continuously microsampled (cf. Spötl and Mattey 2006) and analyzed for its stable isotope composition using a carbonate preparation line interfaced with an isotope ratio mass spectrometer. For analytical details the reader is referred to Spötl and Vennemann (2003). U/Th disequilibrium dates were obtained from the lower part of this flowstone using thermal ionization mass spectrometry (for analytical details see Frank et al. 2000).

Samples of coarsely crystalline phreatic calcite from presumably hydrothermal karst cavities in the surrounding area were also analyzed for their stable isotopic composition, as well as for their fluid inclusions, which were examined using a Linkam TMHG 600 heating-cooling stage.

We also sampled water from springs in the Liechtenstein Gorge, currently the only occurrence of hydrothermal (actually lukewarm) water in the study area. Temperature, electrical conductivity, pH and alkalinity were determined in the field, cations and anions were analyzed using standard techniques (atomic absorption spectrometry and ion chromatography, respectively) and the stable isotopic composition of H and O was determined using continuous-flow isotope ratio mass spectrometry. Tritium was analyzed by Hydroisotop GmbH.

Results

In both cores the top few centimetres of the Klammkalk—hereafter referred to as alteration zone—are stained brown which contrasts to the medium to dark grey colour of the unaltered marble beneath. Visually, this conspicuous layer shows considerable differences between the two adjacent cores. While TKS I shows a ca. 45 mm-thick band that is homogeneous light brown near the contact with the flowstone and grey–brown below, core TKS II reveals a ca. 50 mm thick, inclined band of irregularly laminated brown and grey layers (Fig. 3). In both cores, this alteration zone is overlain by flowstone. Thin-section petrography failed to show evidence of recrystallization or dissolution in the stained layer. In both cores the C and O isotope values reveal pronounced changes across the alteration zone (Figs. 4, 5). The unaltered marble shows δ^{13}C and δ^{18}O values from 1.0 to 1.3‰ and −3.5 to −3.0‰ VPDB, respectively (Fig. 6), which fall within the range of values measured in other marble samples from Entrische Kirche. Both isotope values then gradually decrease across the stained zone and reach minimum δ^{13}C and δ^{18}O values of −1.8 and −13.5‰ (−14.3‰ in TKS II), respectively. In contrast, the basal speleothem calcite above this most altered marble shows distinctly different compositions: δ^{13}C and δ^{18}O values range from −5.5 to −4.6‰ and −9.4 to −8.7‰, respectively (Figs. 4–6). Similar values were obtained in a detailed isotopic study of the remaining flowstone succession (Meyer 2006).

In order to constrain the age of speleothem deposition five U/Th dates were obtained from the lower part of this flowstone (i.e., the onset of vadose speleothem deposition). The basal flowstone calcite in core TKS I indicates an age of ca. 240 kyr, while a layer close to the base of the flowstone in the parallel core TKS II yielded a slightly younger age of ca. 220 kyr (Table 1). U/Th dates in stratigraphically higher layers of the flowstone show consistently younger ages (Meyer 2006).

In addition, we also examined samples of coarsely crystalline calcite from surface outcrops, which suggest palaeohydrothermal activity in the Klammkalk (Stegbachgraben, Klammstein quarry, Klammstein tunnel, intake tunnel Lend; Fig. 6). One location (Stegbachgraben) also showed macroscopic evidence of alteration (bleaching) of the uppermost part of the Klammkalk. The δ^{13}C values of coarsely crystalline calcite are slightly higher than those of the altered marble in Entrische Kirche, but similar to that of the altered marble from Stegbachgraben and unaltered marble from Entrische Kirche. The δ^{18}O values of the thick palisade calcite crusts from the Stegbachgraben deposit overlap with those of the most altered marble (from both this site and from Entrische Kirche), while δ^{18}O values measured on scalenohedral calcite crystals from the tunnels at Lend and Klammstein, as well as from the Klammstein quarry just south of Entrische Kirche extend to values as low as −23.0‰ (Fig. 6).

Calcite crystals from three of the locations discussed above were examined for the presence of fluid inclusions.

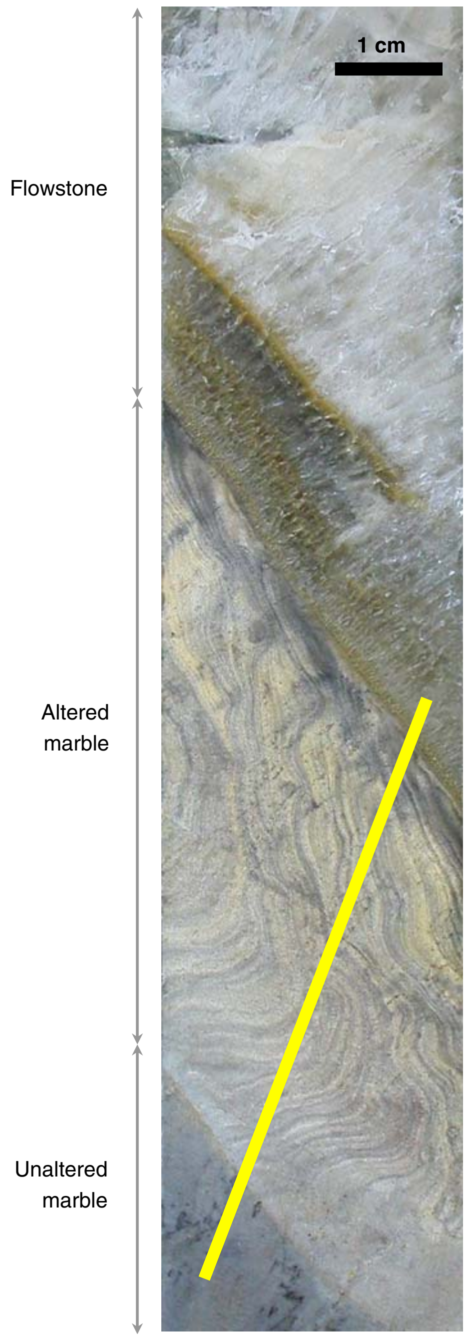

Fig. 3 Polished slab of TKS II drill core showing the top of the Klammkalk marble partly stained brown and overlain by coarsely crystalline flowstone (dated to the marine isotope stage 7). Note that the hydrothermal alteration emphasizes the deformation of the marble not well seen in the pristine marble beneath. The stable isotope traverse (*thick bright line* see Fig. 5) starts in the unaltered, grey marble, crosses the alteration zone and ends in the speleothem calcite

The two-phase inclusions, indicating elevated depositional temperatures, were observed in scalenohedral calcite from Klammstein tunnel and Klammstein quarry. Homogenization temperatures measured in calcite from Klammstein tunnel indicate minimum temperatures of the mineral-depositing water of 70–75°C (Fig. 7). Calcite from Stegbachgraben contained only single-phase aqueous inclusions, so that the temperatures of palaeowaters remain indeterminate.

We attempted to date the youngest generation of translucent rhombohedral calcite in the Stegbachgraben deposit using the U/Th-disequilibrium method. Unfortunately, the extremely low U content (0.92 ppb) precluded an age determination.

Analyses of lukewarm spring waters emerging at the bottom of the Liechtenstein Gorge (symbol B in Fig. 1) yielded $\delta^{18}O$ values between −13.1 and −12.7‰, δD values between −93.5 and −90.0 ‰ and a tritium content of 8 TU (Table 2).

Discussion

Geochemical evidence of palaeowater–rock interaction in Entrische Kirche cave

Both drill cores penetrated a distinct alteration zone preserved beneath a flowstone, whose thickness reaches about 1 m. High-resolution stable isotope transects demonstrate that the composition of the marble near the contact with the flowstone was changed considerably. While the only macroscopic difference to the pristine marble beneath is its brown stain, C and O isotopes reveal the presence of a reaction front (cf. Frimmel 1992), well expressed by the sigmoidal shape of the isotope value versus depth graphs (Figs. 4, 5). This shift toward lower $\delta^{13}C$ and $\delta^{18}O$ values in altered carbonate bedrock has been reported from caves influenced by thermal waters (e.g., Bakalowicz et al. 1987; Bottrell et al. 2001) and ^{18}O-depletion is a common feature of wall-rock alteration in hydrothermal conduits in general (e.g., Hoefs 2004).

The C isotope data suggest that the palaeowaters entrained dissolved inorganic carbon (DIC) whose isotopic signature was lower than that of the host marble by ca. 3‰ (ignoring the small fractionation between dissolved bicarbonate and calcite—Romanek et al. 1992), but still was much higher than that of speleothems. In other words, the DIC of the palaeowaters responsible for marble alteration most likely was not derived from the soil zone above Entrische Kirche; it probably represents a mixture of alkalinity (1) released during hydrothermal karst dissolution and (2) derived from a variety of reactions occurring at greater depth (e.g., thermal degradation of organic matter and/or decarbonation of limestone during greenschist metamorphism). A small contribution of soil-derived carbon cannot be excluded, however.

The change in $\delta^{18}O$ across the reaction front is more pronounced than that of $\delta^{13}C$ (Figs. 4–6), which suggest

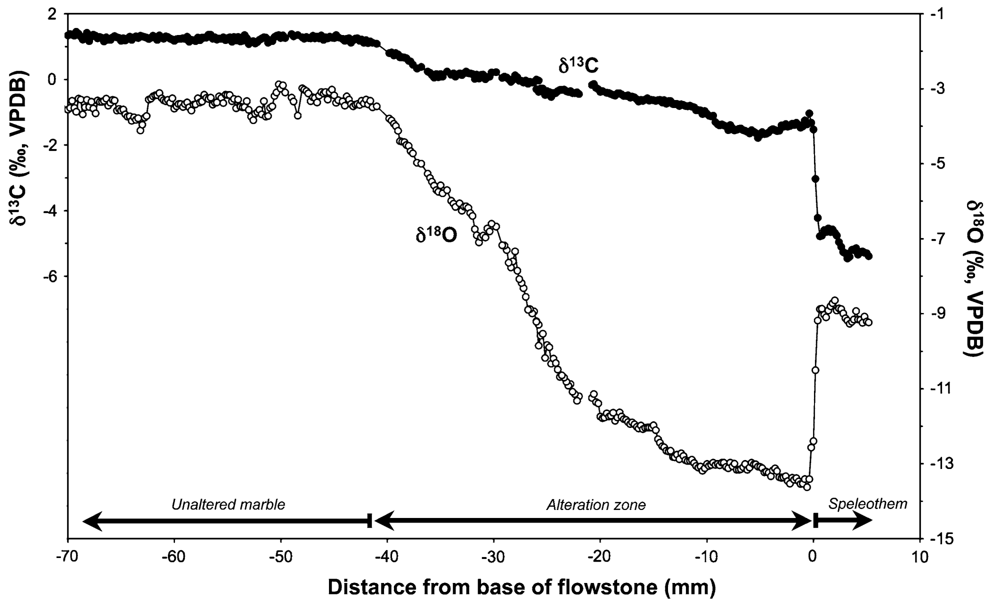

Fig. 4 Stable isotopic transect from the *grey*, unaltered marble across the alteration zone into the overlying flowstone, TKS I drill core

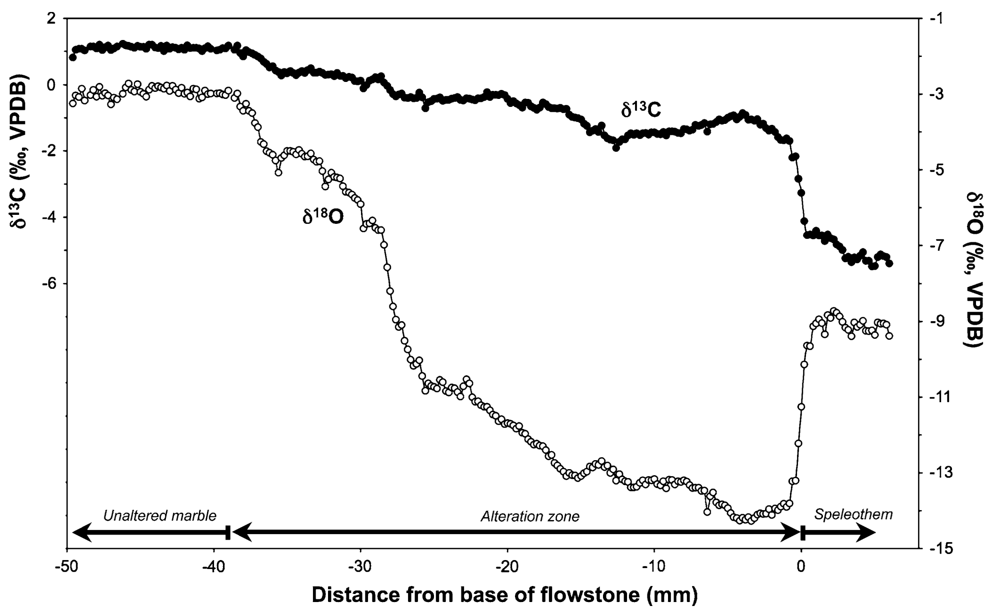

Fig. 5 Stable isotopic transect from the *grey*, unaltered marble across the alteration zone into the overlying flowstone, TKS II drill core. The apparently gradual transition into the speleothem is an artifact of the sampling procedure (micromilling across an oblique boundary)

the large extent of the palaeowaters-rock interaction. The O isotope data of the alteration zone allow placing some constraints on the origin and temperature of the palaeowaters. Qualitatively speaking, the δ^{18}O values of the altered marble are considerably lower than those of Quaternary speleothems (Fig. 6). This offset of ca. 5‰ is likely primarily a temperature effect. In order to constrain the temperature in the absence of direct measurements of the δ^{18}O value of these palaeowaters we use the present-day isotopic composition of seepage waters in Entrische Kirche (−13.5 to −12.1‰ VSMOW, mean −12.8‰; Spötl, unpublished data) as a starting point. These waters are derived from meteoric precipitation recharging the karst fissure aquifer at an elevation of ca. 1700–2000 m, consistent with precipitation data from meteorological stations nearby (Humer 1995). Using the range of modern cave water compositions (see above) as an approximation of the O isotopic composition of the palaeowaters, equilibrium isotope fractionation suggests temperatures of 16–22 and 19–26°C for the most depleted δ^{18}O values of the TKS I and II cores, respectively (Fig. 8). We note that these values are similar to the temperatures of thermal waters encountered near Lend and only slightly higher than the temperature of lukewarm springs that discharge into the Großarl river today (Fig. 8 and below).

It is unlikely, however, that the palaeowaters had precisely the same isotopic composition as modern cave waters and it is conceivable that their composition may also

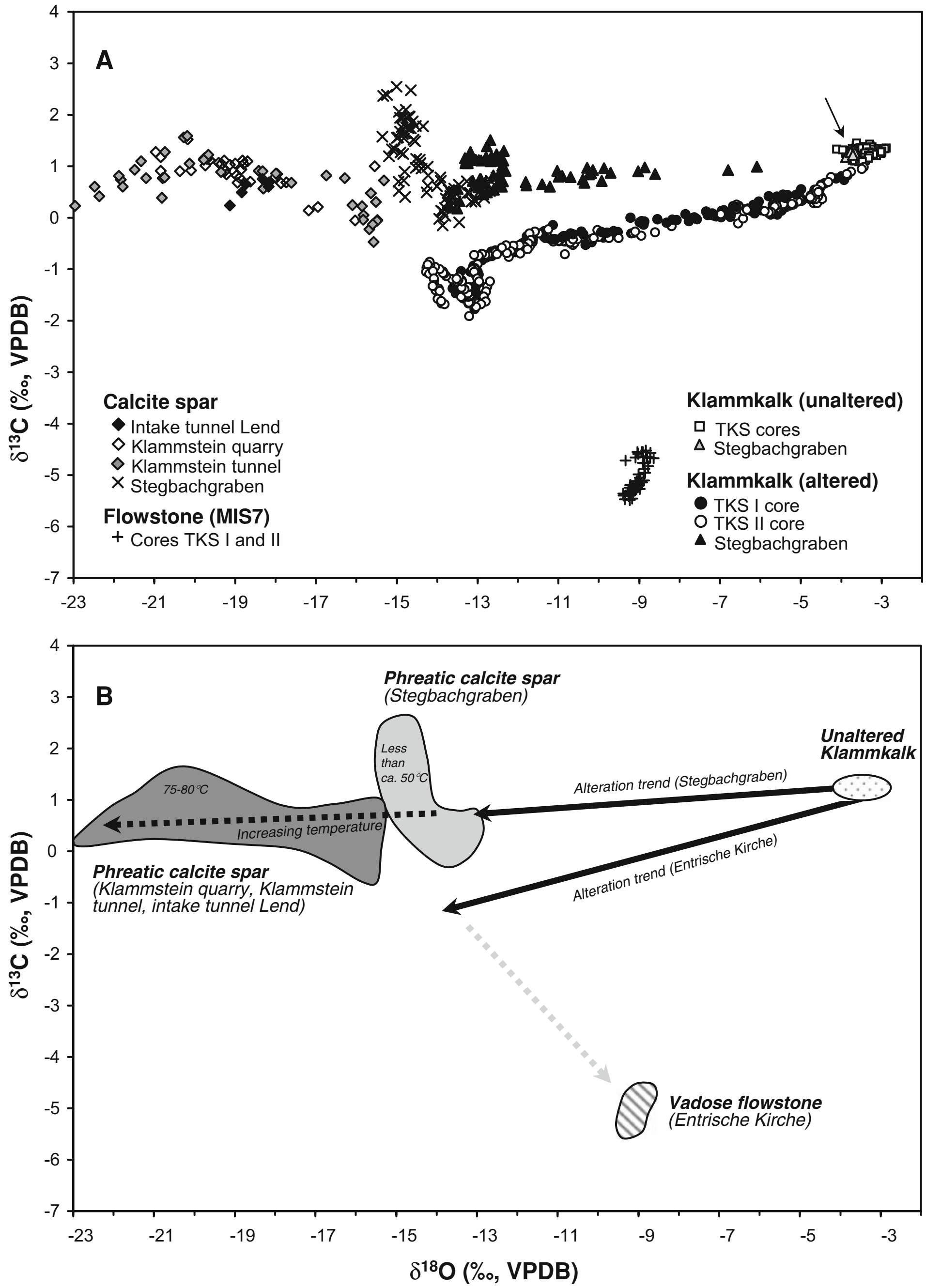

Fig. 6 Stable isotope compositions of unaltered and hydrothermally altered host marble (Klammkalk), meteoric-vadose speleothems, and presumably hydrothermal calcite spar from solutional cavities (see Fig. 1 for details). **a** Data; **b** interpretation. Note the near-linear bedrock alteration trend recorded across the brownish-stained alteration zone in the two drill cores from Entrische Kirche (TKS) and a similar trend in marble from the Stegbachgraben site. Note also the overlap in compositions of the most altered marble and calcite spar from the latter locality. The data of unaltered Klammkalk from Stegbachgraben plot within the narrow range of values from the Entrische Kirche cave (*arrow* in a)

have changed during time. We consider three factors which may have played a role in shifting the isotopic composition and hence the computed equilibrium temperatures. (1) Although the highly resolved isotope transects across the alteration zone show that the gradient decreases toward the base of the overlying speleothem in an asymptotic fashion we cannot exclude the possibility that some of this altered marble was removed (dissolved) prior to deposition of the flowstone. As a consequence the most altered calcite may have had still lower $\delta^{18}O$ values. The isotope profiles (Figs. 4 and 5) suggest, however, that this effect should not exceed 1–2‰, resulting in equilibrium temperatures ca. 5–10°C higher than those shown in Fig. 8. (2) Studies of modern geothermal systems have shown that the $\delta^{18}O$ values of these waters are commonly displaced from the global meteoric water line to the right (the so-called positive $\delta^{18}O$ shift; e.g. Truesdell and Hulston 1980; Criss and Taylor 1986). This enrichment in ^{18}O (δD remains nearly unaffected) reflects isotope exchange between the hot water and the (mostly volcanic) host rock. Isotopic modelling of carbonate aquifers has shown, however, that it is unlikely that the initial (meteoric) $\delta^{18}O$ value of the

Table 1 Th/U ages of the basal layers of flowstone overlying the alteration zone in Entrische Kirche cave

Lab #	Distance from base of flowstone (cm)	$\delta^{234}U$		Conc. ^{238}U		Conc. ^{232}Th		Conc. ^{230}Th		Age	
		(‰)	(±‰)	(μg/g)	± (μg/g)	(ng/g)	± (ng/g)	(pg/g)	± (pg/g)	(kyr)	± (kyr)
Core TKS I											
3707	9.2	178.2	5.1	0.05147	0.00010	1.0037	0.0062	0.890	0.014	217.9	10.8
3807	0.1	171.9	7.4	0.04637	0.00009	10.365	0.082	0.8192	0.0098	241.0	11.8
Core TKS II											
4151	11.1	181.2	6.9	0.04614	0.00009	1.4892	0.0046	0.7836	0.0074	205.3	6.6
4152	6.7	202.3	11.7	0.05634	0.00011	5.2924	0.0259	0.9825	0.0108	209.0	9.7
4312	0.5	171.6	6.4	0.05256	0.00011	13.0370	0.0660	0.9023	0.0090	219.6	8.0

Age uncertainties are given at the two-sigma level

water will be changed unless the water/rock ratio is very small (e.g., Banner and Hanson 1990). In a karstic aquifer such as the Klammkalk the situation is likely just the opposite, i.e. high permeability results in rather high flow rates and high water/rock ratios. We note that there is also no evidence of significant ^{18}O-enrichment in the famous thermal water district of Badgastein located ca. 12 km south of Entrische Kirche. There, waters as warm as ca. 46°C emerge at an altitude of ca. 950–1000 m a.s.l. and show clear evidence of interaction with the gneiss (e.g., high Na/Ca ratio, elevated Cl, sulphate, and Rn concentrations; Job and Zötl 1969; Zötl and Goldbrunner 1993). The $\delta^{18}O$ values (mostly −13.6 to −13.3‰; Zimmermann and Zötl 1971; Egle 1991), however, overlap with the range of modern seepage waters in Entrische Kirche (−13.5 to −12.1‰; see above), which is consistent with the observation that the mean altitude of both infiltration areas is similar (only slightly higher in the case of the Badgastein springs). (3) The changing climate, e.g. during the Quaternary, induced shifts in the O isotopic composition of meteoric precipitation, but it is unlikely that precipitation during previous interglacials differed by more than ca. 1‰ (annual mean) from today's values. Even during cold stages the effect would not have been dramatic. Previous studies of "old" groundwaters in the Alps have shown that the difference between modern groundwater and groundwater recharged during the Last Glacial Maximum—which is close to the maximum variability during the Quaternary—did not exceed 3‰ (Beyerle et al. 1998; review in Darling 2004). Preferential recharge during glacial periods (or during deglaciations) would actually result in *lower* equilibrium temperatures (cf. Fig. 8).

In the absence of direct information on the isotopic composition of the palaeowaters (e.g. by isotopic studies of water trapped in fluid inclusions), we regard the calculated equilibrium temperatures as minimum values, though it appears unlikely that the isotopic composition of Entrische

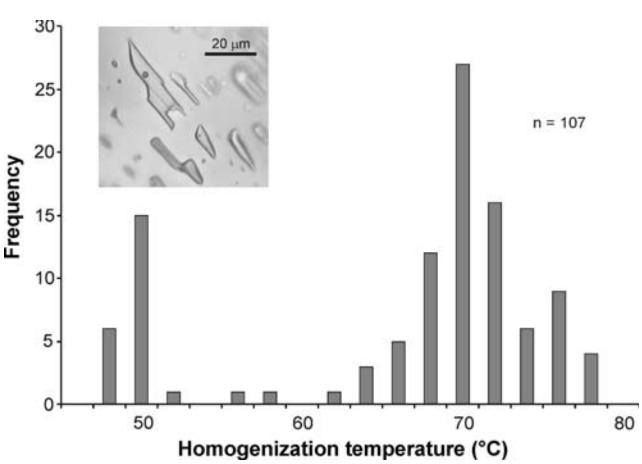

Fig. 7 Fluid-inclusion homogenization temperatures measured in calcite from Klammstein tunnel

Table 2 Chemical and isotopic composition of lukewarm springs discharging at the bottom of the Liechtenstein Gorge (min–max, $n = 4$)

Temp (°C)	13.8–14.9
El. cond. (μS/cm)	511–547
pH	7.31–7.39
Na (mg/l)	22.8–26.4
K (mg/l)	2.2–2.6
Ca (mg/l)	72.5–84.1
Mg (mg/l)	6.8–8.4
F (mg/l)	0.30–0.43
Cl (mg/l)	22.2–29.6
NO_3 (mg/l)	2.1–2.5
HCO_3 (mg/l)	235–240
SO_4 (mg/l)	34.2–43.5
SiO_2 (mg/l)	4.6–8.1
$\delta^{13}C$ (‰, VPDB)	−4.7 to −4.6
δD (‰, VSMOW)	−93.5 to −90.0
$\delta^{18}O$ (‰, VSMOW)	−13.1 to −12.7

The samples were collected during winter (20 February 2007), because the springs are mostly flooded by the Großarl River during the warm season

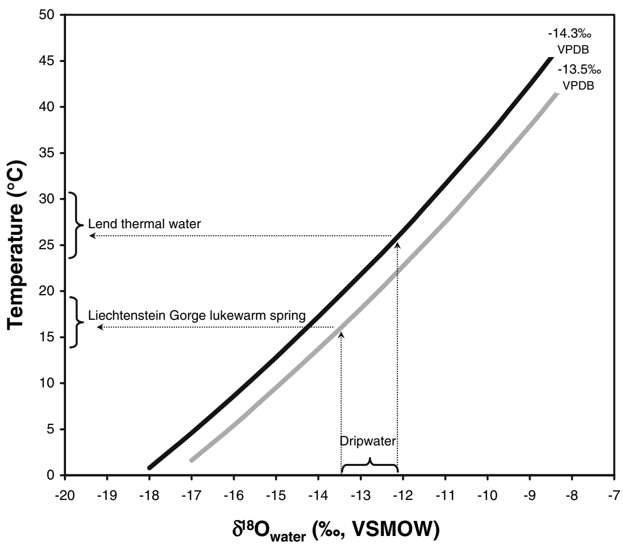

Fig. 8 Equilibrium isotope relationship between the most altered calcite in the alteration zone of the Klammkalk in the two drill cores from Entrische Kirche (*grey line* core TSK I, *black line* core TSK II) and possible combinations of the O isotopic composition of the palaeowaters and temperature (data of the most altered marble from Stegbachgraben would plot between the two lines). Using the range of isotopic compositions of modern drip water in Entrische Kirche, equilibrium temperatures between 16 and 26°C can be calculated (*dotted lines* fractionation equation of Friedman and O'Neil 1977). Temperatures of warm waters encountered in the intake tunnel near Lend and in the Liechtenstein Gorge (see Fig. 1 for the location of these sites) are shown for comparison. The temperature range for the latter springs includes data from earlier measurements (see text)

Kirche palaeowaters deviated drastically (i.e. by more than few tens of ‰) from the modern range of groundwaters in this area. This premise is corroborated by analyses of lukewarm spring waters from the Liechtenstein Gorge, whose stable isotope values are within the range of modern seepage waters in Entrische Kirche and on the Local Meteoric Water Line (as defined by Humer 1995).

Evidence from coarsely crystalline, phreatic calcite in the study area

Hydrothermal calcite deposits, which might carry a more direct record of the palaeowaters, are unknown from Entrische Kirche. Occurrences of euhedral calcite crystals as well as thick, coarsely crystalline palisade linings, however, are known from other locations in the vicinity of Entrische Kirche where they occur in cavities showing features of hydrothermal karst dissolution.

The δ^{18}O values suggest that the Stegbachgraben calcite deposit formed at temperatures similar to those characteristic of the alteration preserved in Entrische Kirche cave, whereas crystallization of the other three calcite occurrences (Klammstein quarry, Klammstein tunnel, intake tunnel at Lend; Fig. 6) probably took place at somewhat higher temperatures (up to ca. 80°C, assuming the same water compositions as in Fig. 8). These estimates are consistent with preliminary fluid inclusion data, whereby two-phase inclusions in scalenohedral calcite from Klammstein tunnel and Klammstein quarry homogenized at 70–75°C (Fig. 7) and calcite from Stegbachgraben contained only single-phase aqueous inclusions, indicative of depositional temperatures lower than ca. 50°C (Goldstein and Reynolds 1994).

Attempts to date rhombohedral calcite in the Stegbachgraben deposit using U/Th were unsuccessful. The very low U content of the calcite (0.9 ppb) might seem surprising given the much higher U contents of speleothem calcite in Entrische Kirche (typically 100–200 ppb), whose U is most likely also sourced from the Klammkalk unit. Preliminary cathodoluminescence observations suggest that this difference likely reflects low Eh values during formation of the hydrothermal calcite, which displays bright orange (Mn^{2+}-activated) cathodoluminescence (e.g., Budd et al. 2000), while speleothem calcite lacks such luminescence. The mobility of U in the reducing environment is limited (Langmuir 1978).

It is instructive to compare our isotope results to those of a study of Jewel Cave and Wind Cave (Black Hills, South Dakota, USA), two of the most famous hydrothermal caves hosting coarsely crystalline calcite. Both caves represent very large maze systems with a combined length of over 400 km (as of 2006). A stable isotope study of these calcite deposits, which average 15 cm in thickness, showed that their δ^{18}O values are significantly lower than those of stalagmites and stalactites formed subsequently from vadose meteoric drip water (Bakalowicz et al. 1987), consistent with our results (cf. Figs. 4, 5). Hydrothermal and meteoric-vadose calcites from Jewel und Wind Caves overlap in their C isotopic compositions, although speleothems show a trend toward lower δ^{13}C values (as also shown by the data from Entrische Kirche cave; Fig. 6). The authors concluded that the thermal palaeowaters, which created these caves and precipitated euhedral calcite at least 1.5 ma ago had a similar O isotopic composition as modern hot springs in the Black Hills region (Bakalowicz et al. 1987).

Hydrogeochemical considerations

It is also interesting to examine the major ionic composition of the warm waters from Lend and from the Liechtenstein Gorge to compare them to modern cave waters from Entrische Kirche. Only few analyses are available from Lend and there is some intersample

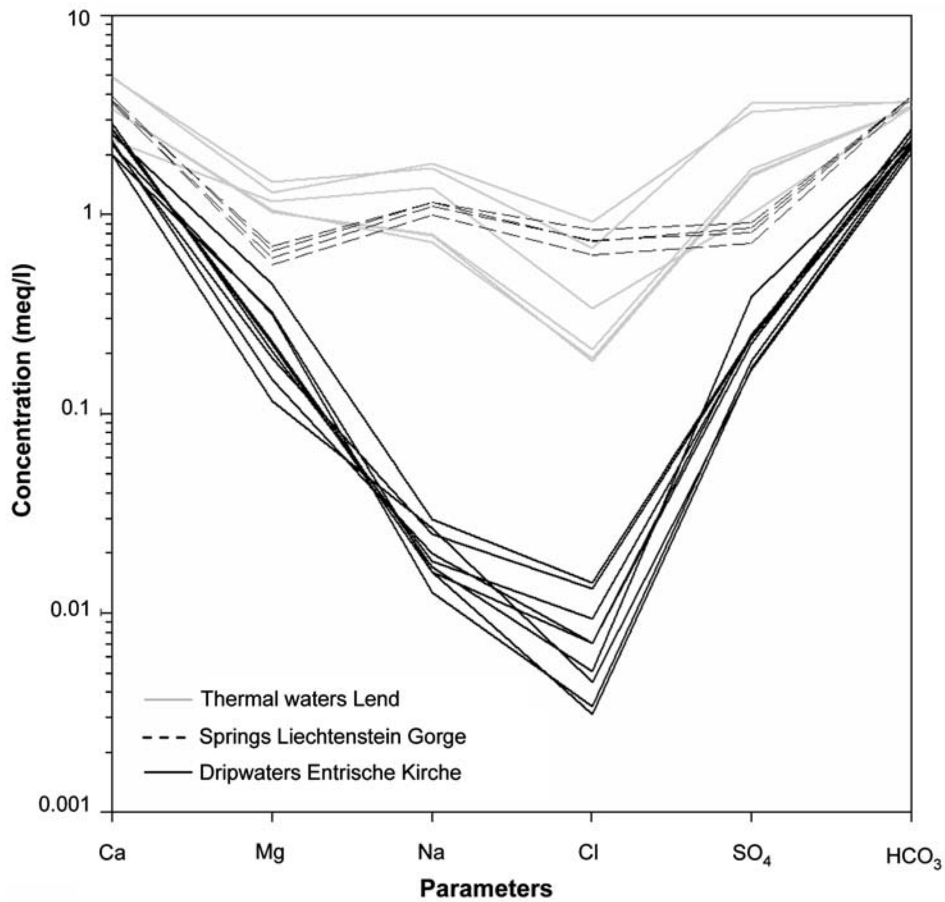

Fig. 9 Schoeller diagram showing the difference between the thermal waters encountered in the intake tunnel near Lend, the lukewarm waters discharging at the bottom of the Liechtenstein Gorge and the non-thermal seepage waters from Entrische Kirche cave. Each line represents an individual sample

variability. The original analysis (Komma and Scheminzky 1954, reported by Zötl and Goldbrunner 1993) showed a significantly lower electric conductivity (385 µS/cm) than analyses taken four decades later (476–727 µS/cm; Pfleger 1994, reported by Cudrigh 2002), but their chemical compositions are broadly similar (Fig. 9). Our analyses of lukewarm spring waters emerging at the bottom of the Liechtenstein Gorge, collected during winter, yielded conductivity values of 511–547 µS/cm (Table 2). In comparison, modern cave waters from Entrische Kirche are characterized by consistently lower conductivity values, mostly between 220 and 270 µS/cm. Thermal waters from Lend and Liechtenstein Gorge differ from those of modern Entrische Kirche by higher concentrations of alkalies and chloride and higher sulphate versus bicarbonate (as seen in the Schoeller plot; Fig. 9). These differences can be readily explained by the higher extent of water-rock interaction that took place along the flow path of these thermal waters. The waters of Lend and modern cave waters are slightly to moderately supersaturated with respect to calcite (Lend: +0.1 to +0.5; Entrische Kirche: +0.3 to +0.7, expressed as the thermodynamic saturation index calculated using PHREEQC – Parkhurst and Appelo 1999), whereas the lukewarm water from the Liechtenstein Gorge is in equilibrium with calcite (−0.1 to 0.0). The fact that the latter are similar in ionic composition to the slightly warmer waters encountered in the intake tunnel near Lend but different from modern seepage waters of Entrische Kirche cave is also illustrated by the Piper plot (Fig. 10). Despite the fact that the compositional data of the lukewarm water from the Liechtenstein Gorge suggest significant water-rock interaction, this water is young (less then 50 years), as shown by its tritium content (8 ± 0.7 TU) which is within the current (2007) tritium level of precipitation in Austria.

Implications for speleogenesis

The tunnel near Lend encountered cavities inside the Klammkalk whose walls showed an alteration zone up to 50 cm wide (Horninger 1956). No detailed studies are available yet on the Stegbachgraben calcite deposit, but our preliminary results suggest that the wall rock was also altered to a depth of a few tens of centimetres and the stable isotope data reflect this pronouncedly (Fig. 6). Although the thickness of the alteration zone in Entrische Kirche is only a fraction of that at Lend and Stegbachgraben and small in comparison to the 1–3 m thick

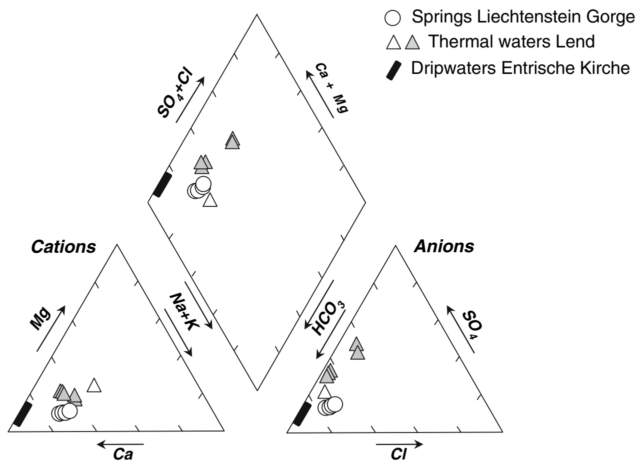

Fig. 10 Piper plot of major ions in lukewarm springs from the Liechtenstein Gorge, thermal waters from Lend and seepage waters from Entrische Kirche cave. The *open triangle* represents the original analysis of thermal water from Lend from 1954 (by Komma and Scheminzky in Zötl and Goldbrunner 1993), while the *grey triangle* symbols are analyses of samples taken in 1994 (by Pfleger, reported in Cudrigh 2002). One anomalous sample from Lend was omitted

alteration zones reported from hydrothermal karst in the Buda Hills of Hungary (where fluid-inclusion data indicate temperatures up to 95°C—Dublyansky 1995) it is a significant new finding which sheds light on the origin of Entrische Kirche. The thickness of the alteration zone (4 to 5 cm) should be regarded as a minimum value, because the amount of possible subsequent dissolution by normal vadose karst waters is unknown (see above). It is important to remember that this alteration zone represents the surface of a paleo-cave wall, presently hidden behind a flowstone, in the deep interior of the cave system. This type of alteration and the proximity to modern occurrences of anomalously warm groundwater in the same geotectonic unit strongly suggest that waters similar to those encountered in the intake tunnel near Lend were once present in the interior of what is known as Entrische Kirche today. Although we have no direct age control, U/Th dates from the flowstone above provide a minimum age for this episode of water–rock interaction (ca. 240 kyr). Other segments of this palaeohydrothermal system were encountered in a tunnel east of the Gastein Gorge (no. 5 in Fig. 1) and are exposed by erosion at Stegbachgraben, demonstrating the spatial and temporal evolution of this warm-water flow system.

Our results therefore suggest that part of what constitutes today's Entrische Kirche cave was once invaded by thermal waters causing geochemical alteration of the cave walls. Subsequent studies may find further evidence of this alteration in the cave, although chances are probably not high. The walls of cave chambers and pits in Entrische Kirche are typically fresh in the sense that dark-grey marble is exposed, whose surface shows sharp features diagnostic of vadose dissolution, in particular near vertical shafts. In other parts of the cave breakdown material and/or loam partly cover the walls. The question of how important these thermal palaeowaters were in terms of speleogenesis of Entrische Kirche therefore remains enigmatic. The fact that the cave is surprisingly deep-seated (rock overburden ca. 900 m), however, hints toward a hypogenic origin of the "proto-cave" upon which the Entrische Kirche cave was superimposed. Subsequent non-thermal karstification likely modified this "proto-cave" profoundly, including its sedimentary inventory. If our model is correct that the early history of this cave was indeed related to thermal groundwater, higher and as yet unexplored parts of Entrische Kirche may preserve remnants of hydrothermal calcite deposits similar to those at Stegbachgraben and as predicted by physical models (Dubylansky 2005). It is equally possible, however, that this branch of the deep-seated groundwater convection-flow system never reached the point of calcite precipitation.

Acknowledgments The Amt der Salzburger Landesregierung, Abteilung Naturschutz granted permission to study and sample speleothems for Entrische Kirche. We are grateful to R. Erlmoser and E. Frank for their help in the cave, to J. Reiterer, J. Kaml and J. Ratgeb for kindly providing samples, to W. Gadermayr for discussion and useful hints, to M. Wimmer for preparing the samples for isotopic analysis, to R. Bakker for his help with the fluid-inclusion analyses, to editor W.-C. Dullo and an anonymous referee for comments on an earlier version of the manuscript and to the FWF for financial support (grants Y122-GEO and P18207-N10).

References

Bakalowicz MJ, Ford DC, Miller TE, Palmer AN, Palmer MV (1987) Thermal genesis of dissolution caves in the Black Hills, South Dakota. Geol Soc Am Bull 99:729–738

Banner JL, Hanson GN (1990) Calculation of simultaneous isotopic and trace element variations during water–rock interaction with applications to carbonate diagenesis. Geochim Cosmochim Acta 54:3123–3137

Becke F (1902) Calcit vom oberen Klammtunnel an der Strecke Schwarzach-St.Veit–Gastein der Tauernbahn. Tschermaks Min Petrogr Mitt 21:460

Beyerle U, Purtschert R, Aeschbach-Hertig W, Imboden DM, Loosli HH, Wieler R, Kipfer R (1998) Climate and groundwater recharge during the Last Glaciation in an ice-covered region. Science 282:731–734

Bottrell SH, Crowley S, Self C (2001) Invasion of a karst aquifer by hydrothermal fluids: evidence from stable isotopic compositions of cave mineralization. Geofluids 1:1103–1121

Braunstingl R (2005) Geologische Karte von Salzburg 1:200000. Geologische Bundesanstalt, Vienna

Budd DA, Hammes U, Ward WB (2000) Cathodoluminescence in calcite cements: new insights on Pb and Zn sensitizing, Mn activation, and Fe quenching at low trace-element concentrations. J Sed Res 70:217–226

Criss RE, Taylor HP (1986) Meteoric-hydrothermal systems. In: Valley JW, Taylor HP, O'Neil JR (eds) Stable isotopes in high temperature geological processes. Rev. Mineral., vol 16. Am. Mineral. Soc., Blacksburg, pp 373–424

Cudrigh SF (2002) Die Wasserwegigkeit des Gasteiner Thermalwassersystems unter Berücksichtigung der Strukturgeologie und im Vergleich zum Thermalsystem Lend. Unpubl. Master thesis, Univ. Salzburg, p 76

Darling WG (2004) Hydrological factors in the interpretation of stable isotopic proxy data present and past: a European perspective. Quat Sci Rev 23:743–770

Dublyansky YV (1995) Speleogenetic history of the Hungarian hydrothermal karst. Environ Geol 25:24–35

Dublyansky YV (2000) Hydrothermal speleogenesis—its settings and peculiar features. In: Klimchouk AB, Ford DC, Palmer AN, Dreybrodt W (eds) Speleogenesis. Evolution of karst aquifers. National Speleol. Soc, Huntsville, pp 292–297

Dublyansky YV (2005) Hydrothermal caves. In: Culver DC, White WB (eds) Encyclopedia of caves. Elsevier, Amsterdam, pp 300–304

Egle S (1991) Geochemische und isotopengeochemische Untersuchungen des Gasteiner Thermalwassers unter besonderer Berücksichtigung der Wechselwirkung mit dem Zentralgneis. Unpubl. MS thesis, Univ. Vienna, p 119

Exner C (1979) Geologie des Salzachtales zwischen Taxenbach und Lend. Jahrb Geol Bundesanstalt 122:1–73

Frank N, Braum M, Hambach U, Mangini A, Wagner G (2000) Warm period growth of travertine during the Last Interglaciation in southern Germany. Quat Res 54:38–48

Friedman I, O'Neil, JR (1977) Compilation of stable isotope fractionation factors of geochemical interest. In: Fleischer M (ed) Data of geochemistry, 6th edn. U. S. Geol. Survey Prof. Paper, 440-KK, pp 1–12

Frimmel HE (1992) Isotopic fronts in hydrothermally mineralized carbonate rocks. Mineral Deposita 27:257–267

Frisia S, Borsato A, Fairchild IJ, McDermott F (2000) Calcite fabrics, growth mechanisms, and environments of formation in speleothems from the Italian Alps and southwestern Ireland. J Sed Res 70:1183–1196

Goldstein RH, Reynolds TJ (1994) Systematics of fluid inclusions in diagenetic minerals. SEPM Short Course 31. SEPM, Tulsa, 199p

Heissel W (1955) Aufnahmsbericht 1954 Kartenblätter 124-Saalfelden und 125-Bischofshofen. Verh Geol Bundesanstalt 1955:36–37

Hoefs J (2004) Stable isotope geochemistry, 5th edn. Springer, Berlin, pp 244

Hölting B, Coldewey WG (2005) Hydrogeologie. Einführung in die Allgemeine und Angewandte Hydrogeologie, 6th edn. Spektrum, Munich, pp 326

Horninger G (1956) Geologische Ergebnisse bei einigen Kraftwerksbauten. Verh Geol Bundesanstalt 1956:114–118

Horninger G (1958) Geologische Ergebnisse bei einigen Kraftwerksbauten. Verh Geol Bundesanstalt 1958:282–286

Horninger G (1959a) Baugeologisches vom Salzach-Kraftwerk Schwarzach. Österr Z Elektrizitätswirtschaft 12:48–50

Horninger G (1959b) Geologische Ergebnisse bei einigen Kraftwerksbauten in Österreich. Verh Geol Bundesanstalt 1959:A112–A115

Humer G (1995) Niederschlagsisotopennetz Österreich Teil 2: Daten. Umweltbundesamt Berichte 33:1–110

Job C, Zőtl J (1969) Zur Frage der Herkunft des gasteiner Thermalwassers. Steir Beitr Hydrogeol 21:51–115

Kendall AC, Broughton PL (1978) Origin of fabrics in speleothems composed of columnar calcite crystals. J Sed Petrol 48:519–538

Klappacher W (1992) Salzburger Höhlenbuch Band 5. Salzburger Mittelgebirge und Zentralalpen. Landesverein für Höhlenkunde in Salzburg, Salzburg, p 625

Langmuir D (1978) Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochim Cosmochim Acta 42:547–569

Meyer M (2006) Laminated speleothems as high-resolution archives of alpine paleoclimate. Unpubl. Ph.D. thesis, Univ. Innsbruck, 120p

Müller P (1989) Hydrothermal paleokarst of Hungary. In: Bosak P (Ed) Paleo-Karst: a systematical and regional review. Academia, Prague, pp 155–163

Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC (Version 2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water-Resources Investigations Report 99–4259, 312p

Peer H, Zimmer W (1980) Geologie der Nordrahmenzone der Hohen Tauern (Gasteiner Ache bis Saukarkopf-Großarltal). Jahrb Geol Bundesanstalt 123:411–466

Plan L, Pavuza R, Seemann R (2006) Das Nasse Schacht bei Mannersdorf am Leithagebirge, NÖ (2911/21) – eine thermal beeinflusste Höhle am Ostrand des Wiener Beckens. Die Höhle 57:30–46

Romanek CS, Grossman EL, Morse JW (1992) Carbon isotopic fractionation in synthetic aragonite and calcite: effects of temperature and precipitation rate. Geochim Cosmochim Acta 56:419–430

Russegger J (1836) Ueber die warmen Quellen des Arlbaches am Ausgange des Groß-Arl-Thales im Salzburgischen. Steiermärkische Zeitschrift N F 3:100–114

Spötl C, Vennemann T (2003) Continuous-flow IRMS analysis of carbonate minerals. Rapid Comm Mass Spectrom 17:1004–1006

Spötl C, Mattey D (2006) Stable isotope microsampling of speleothems: a comparison of drill, micromill and laser ablation techniques. Chem Geol 235:48–58

Stini J (1959) Gastein und der Warmwassereinbruch in den Lender Druckstollen. Geol Bauwesen 23:258–265

Truesdell AH, Hulston JR (1980) Isotopic evidence on environments of geothermal systems. In: Fritz P, Fontes J (eds.) Handbook of environmental isotope geochemistry, vol 1. Elsevier, New York, 179–226

Wang X, Neubauer F (1998) Orogen-parallel strike-slip faults bordering metamorphic core complexes: the Salzach-Enns fault zone in the Eastern Alps, Austria. J Struct Geol 20:799–818

Zimmermann U, Zötl J (1971) Deuterium- und Sauerstoff-18-Gehalt von Gasteiner Thermal- und Kaltwässern. Steirische Beiträge Hydrogeol 23:127–132

Zötl J, Goldbrunner JE (1993) Die Mineral- und Heilwässer Österreichs. Geologische Grundlagen und Spurenelemente. Springer, Vienna, p 324