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Review: Thermal water resources in carbonate rock aquifers

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Abstract The current knowledge on thermal water resources in carbonate rock aquifers is presented in this review, which also discusses geochemical processes that create reservoir porosity and different types of utilisations of these resources such as thermal baths, geothermal energy and carbon dioxide (CO_2) sequestration. Carbonate aquifers probably constitute the most important thermal water resources outside of volcanic areas. Several processes contribute to the creation of porosity, summarised under the term hypogenic (or hypogene) speleogenesis, including retrograde calcite solubility, mixing corrosion induced by cross-formational flow, and dissolution by geogenic acids from deep sources. Thermal and mineral waters from karst aquifers supply spas all over the world such as the famous bath in Budapest, Hungary. Geothermal installations use these resources for electricity production, district heating or other purposes, with low CO_2 emissions and land consumption, e.g. Germany's largest geothermal power plant at Unterhaching near Munich. Regional fault and fracture zones are often the most productive zones, but are sometimes difficult to locate, resulting in a relatively high exploration uncertainty. Geothermal installations in deep carbonate rocks could also be used for CO_2 sequestration (carbonate dissolution would partly neutralise this gas and increase reservoir porosity). The use of geothermal installations to this end should be further investigated.

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Introduction

Deep carbonate rock aquifers, most of which are to some degree karstified, are probably the most important thermal water resources outside of volcanic areas. Although there is no detailed and reliable global assessment of thermal water resources, the following examples illustrate the importance of karst aquifers for both thermal baths and geothermal installations.

Europe's largest naturally flowing thermal water system, the hot spring and wells that supply the baths of Budapest, Hungary, is discharging from Triassic carbonate rocks (Fig. 1). Many caves and related phenomena can be observed in the "Buda Karst" (Dublyansky 1995; Erőss et al. 2008b). Europe's second-largest occurrence of mineral and thermal springs, in Stuttgart, Germany, is also associated with a karst aquifer (Ufrecht 2006a), as are many other thermal springs and spas in Germany (Käss and Käss 2008), Switzerland (Muralt et al. 1997), France (Levet et al. 2002), Italy (Minissale et al. 2002), the UK (Brassington 2007; Gallois 2007), Turkey (Gemici and Filiz 2001), Jordan (Bajjali et al. 1997), Tunisia (Inoubli et al. 2006), Algeria (Djidi et al. 2008), Canada (Allen et al. 2006; Van Everdingen 1991), China (Ma et al. 2009; Zhou et al. 2008) and many other regions of the world.

Germany's largest geothermal power station, located at Unterhaching, near Munich, exploits thermal water from Upper Jurassic (Malm) limestone below the Molasse basin, the northern foreland basin of the Alps (Berge and Veal 2005; Keller 1991). This deep karst aquifer is considered to be the largest thermal water resource in Central Europe, but unlike the aquifers in Budapest or Stuttgart, it is mainly accessible via drilled wells. The production well at

Fig. 1 The “Rudas Thermal Bath” in Budapest, Hungary, supplied by thermal water from the karst aquifer that crops out behind the bath, situated near the Danube River representing the regional base level (photo: N. Goldscheider)

Unterhaching is 3,346 m deep and produces ca. 150 L/s of 123°C hot water, used for heating and electric power generation. Several other geothermal installations and baths in Switzerland, south Germany and Austria also use thermal water from the same regional aquifer.

Carbon dioxide (CO_2) plays a key role in the evolution of karst aquifers, including deep and thermal aquifers (Dreybrodt 1990; Klimchouk 2007). In turn, geothermal installations in deep karst aquifers offer promising possibilities for CO_2 sequestration, which would at the same time increase the transmissivity of these aquifers and, thus, the economic efficiency of geothermal installations, although not without drawbacks such as possible subsidence.

While many publications deal with freshwater and drinking-water resources from karst aquifers, there is no readily available study systematically investigating the role of carbonate rock aquifers as thermal water resources and the possible use of these aquifers for geothermal energy production and CO_2 sequestration. Therefore, the goals of this review are to:

1. Outline thermal water resources in carbonate rock aquifers as parts of deep regional groundwater flow systems and thermal springs as their discharge features.
2. Evaluate dissolution processes in deep carbonate rock aquifers, which are crucial for the creation of porosity and permeability (“hypogenic speleogenesis”).
3. Compile examples of thermal baths and geothermal power stations using thermal water from carbonate rock aquifers, with a focus on Central Europe.
4. Discuss the use of geothermal installations in carbonate aquifers for CO_2 sequestration.

Basic terms and concepts

Thermal water and hot springs

Springs are among the most characteristic features of karst areas (Ford and Williams 2007). Karst areas where springs with elevated temperatures occur can be termed thermal karst. There is no widely accepted definition for thermal water or thermal springs and for the related terms of cold, warm and hot springs, but two thresholds are often considered: the average local air temperature and the human body temperature (Pentecost et al. 2003). Springs whose temperature is more than 5°C above the mean annual air temperature can be defined as thermal (White 1957). An obvious drawback of this definition is that in cold regions, a spring with 5°C would be considered thermal (e.g. Grasby et al. 2000), while a 20°C warm spring in the tropics would not. The advantage is, however, that relative temperature differences point to hydrogeologically relevant heat anomalies. Relative temperatures are also of practical relevance: 20°C warm water is economically valuable in cold regions but not in a warm climate. The human body temperature of 37°C is an unambiguous threshold to differentiate warm and hot springs (Meinzer 1923; Pentecost et al. 2003). Cold springs can be defined either by relative or absolute temperatures, but are less relevant here.

Thermal water within the framework of hierarchical flow systems

Groundwater circulation at different scales can be understood within a conceptual framework of hierarchical flow systems, consisting of local, intermediate, and regional flow systems (Tóth 1962, 1963, 1999). Thermal water resources in continental carbonate rock aquifers outside volcanic zones are related to deep, regional flow systems, characterised by cross-formational hydraulic continuity (Fig. 2; Tóth 1995; Frumkin and Gvirtzman 2006; Klimchouk 2007). Springs draining these systems are often situated close to the regional base level (Worthington and Ford 1995; Gunn et al. 2006). Water circulation in thermal karst systems is generally gravity-driven, caused by topographic gradients (Tóth 2009). Temperature-induced density gradients act simultaneously and facilitate the upward flow of hot water toward springs; reduced viscosities further accelerate thermal water circulation. Fractures and faults are major controls on groundwater flow. Faults can form conduits or barriers, but their hydraulic function depends on several factors and is often difficult to predict (Caine et al. 1996; Underschultz et al. 2005). High-permeability faults are crucial for the development of thermal systems (Forster and Smith 1988a, b; Lopez and Smith 1995, 1996). The fault dip influences the circulation depth and, thus, the resulting water temperature; so thermal springs are also often aligned along faults (Grasby and Hutcheon 2001; Li et al. 2007).

The basic genetic settings of caves (Palmer 1991) can also be used to classify karst aquifer systems and speleogenetic processes: (1) coastal and oceanic, (2) deep-seated, confined, predominantly hypogenic speleogenesis, and (3) unconfined, predominantly epigenic speleogenesis (Klimchouk et al. 2000). Epigenic karst systems are directly influenced by the infiltration of meteoric water and CO_2 from the atmosphere and soil ("epi" means above or outermost, like epidermis) and are often associated with local–to–intermediate flow systems. Hypogenic systems are influenced by deep energy and gas sources (hypo means below or deep) and are associated with regional flow systems (Klimchouk 2007). Processes of hypogenic speleogenesis are crucial for the creation of certain types of porosity and permeability.

Sources of water and heat

Klimchouk (2007) stresses the dominantly meteoric origin of waters in hypogenic karst-aquifer systems, but also mentions that connate and magmatic waters are sometimes involved. Deming (2002) classified underground waters as oceanic, meteoric and evolved waters. Evolved water can originate from the ocean or atmosphere but its initial composition has changed by physical–chemical processes. The term juvenile is discarded because it is known from plate tectonics that water emitted at volcanoes is recycled oceanic water; also connate water is generally derived from the afore-mentioned sources. Thermal water can consequently be considered as evolved water. The main focus has to be on the understanding of its evolution in the context of the geologic development and structure of the karst system, together with the flow regime and boundary conditions in a hydraulic and geochemical sense. High topographic gradients between elevated meteoric recharge areas and low-lying dis-

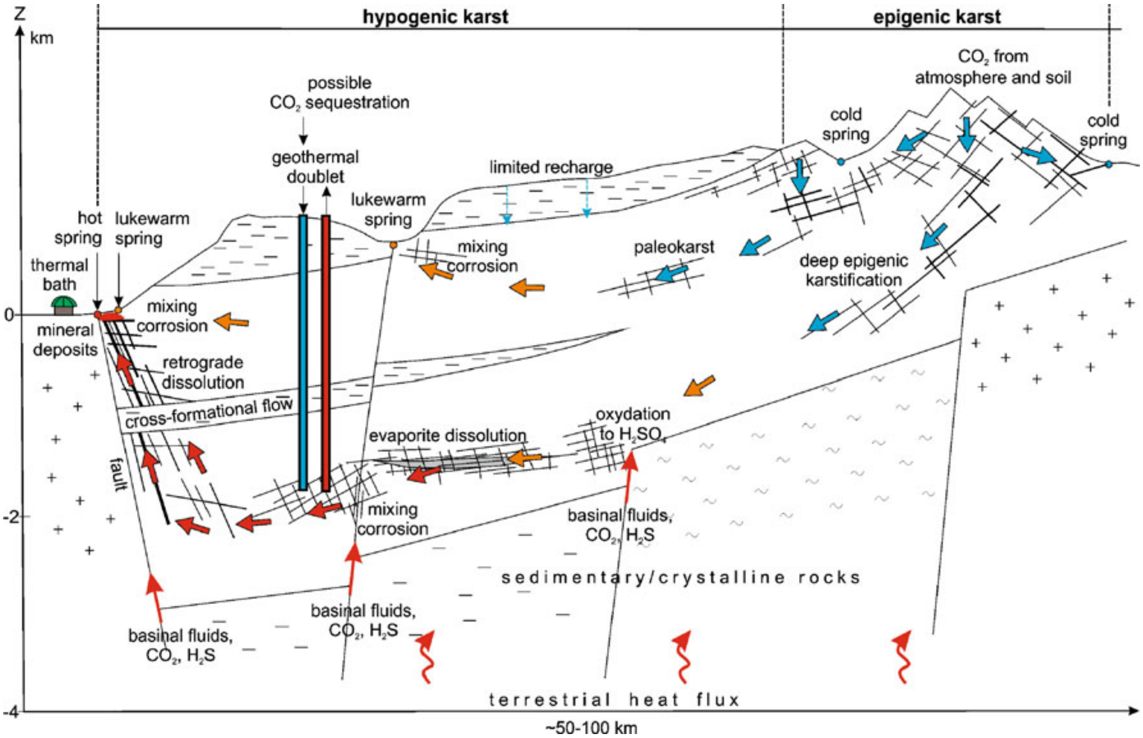

Fig. 2 Schematic illustration of groundwater flow and karstification processes in a deep and mostly hypogenic inland–carbonate–rock system. Potential position of a geothermal doublet that could also be used for CO_2 sequestration is also displayed. *Arrows* indicate flow direction, and *blue to red* colours indicate cold to hot water temperatures. The flow system is primarily gravity-driven, caused by topographic gradients between the recharge area and the thermal springs; sedimentary compaction, tectonic compression and density differences act as additional driving forces; thermal convection can occur near discharge zones

charge zones result in high hydraulic gradients, which generally act as the principal driving force, but other phenomena such as sediment compaction, tectonic compression and density gradients can also contribute (Bjorlykke 1993; Klimchouk 2007).

A variety of heat sources and transport mechanisms contribute to the formation and functioning of thermal karst systems (Drogue 1985). Heat comes from two sources: the residual heat of the Earth and radioactive decay. The average thermal gradient in continental areas is 30°C/km resulting in an average heat flow of 65 mW/m^2, but gradients of 100–200°C/km or more can be observed in volcanic zones (Economides and Ungemach 1987). Heat can be transported by conduction, convection and radiation; convective heat transport by flowing groundwater is the most efficient process (Sass 2007). Upward flow of thermal groundwater in discharge zones increases near-surface geothermal gradients and heat flows (Bredehoeft and Papadopulos 1965).

Thermal springs and other features in discharge zones of regional flow systems

At discharge areas, in addition to positive thermal anomalies, high levels of total dissolved solids and reducing conditions in the spring water, accumulation of transported material in the form of mineral deposits, and phreatophytic vegetation can be observed (Tóth 1971, 1999). Degassing of CO_2-rich thermal waters causes precipitation of carbonates such as the travertine terraces of Pamukkale, Turkey (Altunel and Hancock 1993; Dilsiz 2006), the widespread travertine deposits in central Italy (Minissale 2004) or the rich speleothems in the Buda Karst (Erőss et al. 2008b). Mixing of reducing water from deep flow systems, including dissolved Fe^{2+} and Mn^{2+} with oxygen-rich water from shallower flow systems, can cause precipitation of iron and manganese oxides and hydroxides in discharge zones. These mineral deposits accumulate ^{226}Ra, the mother isotope of ^{222}Rn, which can often be found at high levels in spring waters where mixing processes take place (Gainon et al. 2007). Microbial mats are often involved in such precipitation and accumulation processes, as shown for the Misasa hot springs in Japan (e.g. Fujisawa and Tazaki 2003) or for hydrothermal springs in the Massif Central, France (Casanova et al. 1999).

High sulphate concentrations frequently occur in thermal springs that discharge from carbonate aquifers. A direct relationship was found between sulphate and temperature, and an inverse relationship with discharge (Worthington and Ford 1995). Sulphate originates from the oxidation of sulphide minerals such as pyrite (Langmuir 1971) and/or from the dissolution of gypsum and anhydrite (Bretz 1949). Deep fluids containing hydrogen sulphide that transforms into sulphuric acid when it comes in contact with oxygen-rich water also contribute to the sulphate content of thermal springs (Egemeier 1981; Hill 1987).

Cold, warm and hot springs often discharge next to each other but originate from different flow systems. The discharge, chemical composition and temperature of thermal springs from regional flow systems are more stable compared to cold springs from local flow systems.

Karstification processes in deep carbonate rock aquifers

Basic geochemical process and hydrogeologic relevance

Most well-studied karst and cave systems are found in relatively shallow, unconfined geologic settings. Karstification and speleogenesis in such epigenic systems is driven by the infiltration and circulation of meteoric water including CO_2 from the atmosphere and soil. The basic chemical equation describing calcite dissolution is as follows (Dreybrodt 2000):

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2\,HCO_3^- \qquad (1)$$

It is often supposed that solution of carbonate rocks is not important at depth. However, according to Klimchouk (2007), hypogenic speleogenesis, i.e. the formation of solutional conduits in deep, confined aquifers, is widespread but often underestimated due to the limited accessibility of these systems. Many hypogenic caves have later been reshaped by meteoric waters and are thus difficult to recognise (Palmer 1991; Audra et al. 2007). Field observations and theoretical considerations confirm dissolution phenomena in deep aquifers, which is relevant for both hot springs and geothermal installations:

- Karst conduits allow rapid transfer of hot water from great depths toward springs, while diffuse flow favours cooling of the thermal fluids and mixing with cold groundwater.
- The presence of enlarged fractures and conduits increases the porosity and permeability of the thermal reservoir and, thus, the efficiency of geothermal installations.

Hypogenic speleogenesis enhances vertical hydraulic conductivity and cross-formational flow. Hence, there is a positive feedback between conduit development and the expression of thermal anomalies. In other words, hypogenic speleogenesis moves high-gradient thermal zones into relatively shallow positions and eventually allows transfer of hot water to springs (Klimchouk 2007). The following sections review different processes causing deep, hypogenic karstification. Figure 2 shows the typical location of these processes in a regional flow system; Fig. 3 illustrates the most relevant processes in a simplified way.

Paleokarst

Many deep carbonate rocks were exposed to epigenic karstification in earlier geologic times such as the Malm

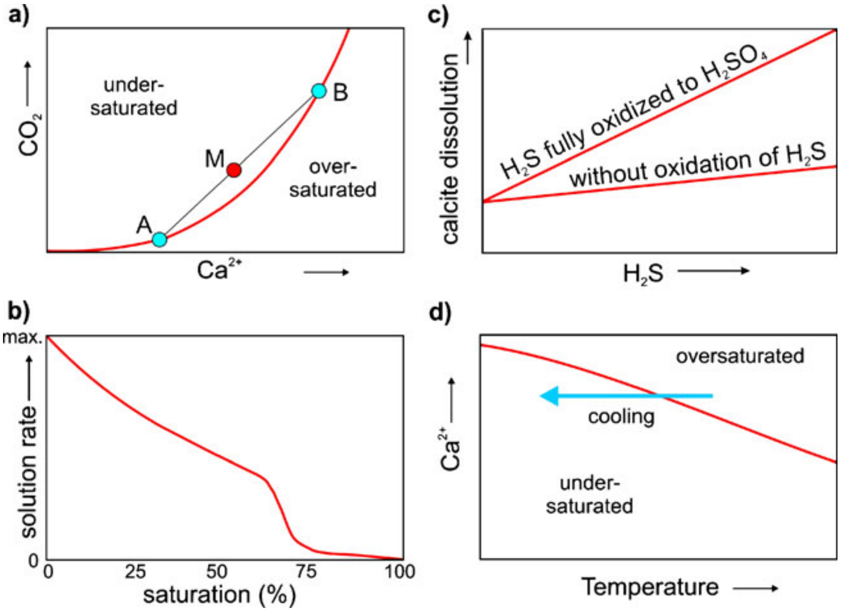

Fig. 3 Schematic diagrams illustrating geochemical processes contributing to hypogenic speleogenesis: **a** mixing corrosion—mixing of two waters (*A*, *B*) saturated with respect to calcite results in a mixture (*M*) that is undersaturated (Bögli 1964); **b** dissolution kinetics—when calcite-saturation exceeds 75%, dissolution rate drops to very low levels, thus allowing undersaturated waters to penetrate great depth (Plummer et al. 1978; Dreybrodt 1990); **c** other acids—oxidation of H_2S to H_2SO_4 boosts karstification (Palmer 1991); **d** retrograde solubility—in a closed system, calcite solubility increases with decreasing temperature, allowing for karstification by cooling of upward flowing fluids (Andre and Rajaram 2005)

aquifer below the Molasse Basin in the Alpine Foreland mentioned in the introduction, which was exposed during the Cretaceous and Palaeocene, and subsequently buried by sediment in the Oligocene and Miocene (Keller 1991). Paleokarst refers to fossilised karst features that are out of adjustment with the present geomorphic setting (Bosak et al. 1989). Nevertheless, paleokarst can contribute to aquifer porosity (Smosna et al. 2005) and is often reactivated by modern karstification (Ford 1995), including epigenic and hypogenic processes. According to Klimchouk (2007), karst phenomena encountered in deep thermal drillings are often erroneously classified as paleokarst, due to a lack of understanding of active hypogenic karst processes.

Mixing corrosion

When two different calcite-saturated waters mix, the resulting mixture is undersaturated with respect to calcite and thus aggressive (Fig. 3a). Bögli (1964) considered “mixing corrosion” the key process for karstification, but Gabrovsek and Dreybrodt (2000) showed that epigenic karst networks can evolve without this process, although mixing corrosion accelerates karstification. However, mixing corrosion is highly relevant for hypogenic systems, where waters of contrasting hydrochemical composition frequently mix by cross-formational flow, at stratigraphic contacts or along faults (Klimchouk 2007). In this way, the aggressiveness of previously saturated waters can be rejuvenated (Palmer 1991). Mixing is highly effective where water rises from depth and encounters near-surface meteoric water (Fig. 2). Flank margin caves that form in the mixing zone of freshwater and seawater represent a special case of mixing corrosion but are not further discussed here (Mylroie and Mylroie 2007).

Importance of calcite dissolution kinetics for deep karstification

In earlier times, deep karst phenomena were mostly explained as buried epigenic karst or due to the action of CO_2, H_2S or H_2SO_4 from deep sources. Otherwise, speleogenesis at great depth was considered impossible, because infiltrating meteoric waters containing CO_2 were supposed to become saturated with respect to calcite after short flow distances. However, experimental studies have shown that the dissolution rate gets extremely slow when calcite saturation exceeds approximately 75% (Fig. 3b; Plummer and Wigley 1976; Plummer et al. 1978). As a consequence, slightly undersaturated water can penetrate deep into fractures and cause initial karstification along the entire pathway, thus allowing for the formation of deep (but epigenic) conduit systems (Dreybrodt 1990; Rauch and White 1977). Worthington (2001) evaluated the depth of (epigenic) conduits in carbonate aquifers and found that conduit development and karst water flow can occur deep below the water table. High flow-path lengths and steeply dipping strata favour deep karstification.

Geogenic carbon dioxide

CO_2 from other sources than the soil and atmosphere can also cause karstification. There are three principal origins of geogenic carbon dioxide: transformation of organic matter during oil, gas and coal formation; metamorphism of carbonatic rocks in the crust; or degassing of the Earth's mantle, often associated with volcanic activities (Palmer 1995; Bissig et al. 2006).

Aggressive fluids that evolved during organic diagenesis in subsiding basins are often charged with CO_2 and also with organic acids and H_2S (Mazzullo and Harris 1992; Palmer 1995). Such fluids can cause deep karstification, as demonstrated for several carbonate-hosted hydrocarbon reservoirs such as the Permian Basin in the USA (Mazzullo and Harris 1991). The karst system of Stuttgart mentioned in the introduction is characterised by high levels of CO_2 from the mantle, as demonstrated by isotopic studies (Ufrecht 2006b) and discussed further in the following. In central Italy, mixing of meteoric waters with ascending geothermal fluids of magmatic and metamorphic origin in Mesozoic limestones results in aggressive waters including high levels of both CO_2 and H_2S, which enhances limestone dissolution (Minissale 2004). Other outstanding examples of speleogenesis caused by geogenic CO_2 are the "Sistema Zacatón" in Mexico, the deepest underwater pit in the world (−325 m), caused by volcanogenic CO_2 (Gary and Sharp 2006), and deep sinkholes (Obruks) in Central Anatolia, Turkey, where CO_2 from the Earth's mantle has been identified as the source of aggressiveness (Bayari et al. 2009).

Hydrogen sulphide, sulphuric acid and the role of microorganisms

Other geogenic acids also cause karstification such as hydrogen sulphide (H_2S) and sulphuric acid (H_2SO_4) from different sources. H_2S is generated by microbial or thermal reduction of sulphates in contact with organic carbon (Hill 1987, 1990; Palmer 1995). Calcite dissolution by H_2S can be described as follows:

$$H_2S + CaCO_3 = Ca^{2+} + HS^- + HCO_3^- \tag{2}$$

However, the generation of H_2S is generally accompanied by supersaturation with respect to calcite or dolomite. Therefore, carbonate rock dissolution by H_2S is most effective if it escapes as a gas and is reabsorbed in freshwater, or if the H_2S-bearing water mixes with another water, thus combining conventional mixing corrosion and "rejuvenation" of H_2S aggressiveness (see the following; Palmer 2007). When H_2S comes into contact with oxygen-rich water, it forms sulphuric acid, either via the intermediate step of native sulphur or directly:

$$H_2S + 2O_2 = H_2SO_4 \tag{3}$$

The reaction of calcite with sulphuric acid or other strong acids (e.g. HCl) produces CO_2 that is either removed by degassing from an open system (Eq. 4) or can cause additional dissolution in a closed system (Eq. 5):

$$H_2SO_4 + CaCO_3 = Ca^{2+} + SO_4^{2-} + H_2O + CO_2 \uparrow \tag{4}$$

$$H_2SO_4 + 2\,CaCO_3 = 2\,Ca^{2+} + SO_4^{2-} + 2\,HCO_3^- \tag{5}$$

Equations 3 and 5 can be combined and explain the burst of solutional capacity when groundwater containing H_2S comes in contact with oxygen, as also shown in Fig. 3c:

$$H_2S + 2\,O_2 + 2\,CaCO_3 = 2Ca^{2+} + SO_4^{2-} + 2HCO_3^- \tag{6}$$

The oxygen requirement limits the depth to which this process can take place (Palmer 1991). Oxidation of pyrite (FeS_2) or other sulphide minerals can also dissolve calcite:

$$\begin{aligned} &FeS_2 + 2.5\,H_2O + 3.75\,O_2 + 4\,CaCO_3 \\ &\quad = FeOOH + 2\,SO_4^{2-} + 4\,HCO_3^- + 4\,Ca^{2+} \end{aligned} \tag{7}$$

Taking into account the molecular weights and densities, this equation means that 1 cm^3 of pyrite can dissolve 6.18 cm^3 of calcite. However, according to Palmer (1991), pyrite is generally too dispersed to create more than local porosity. Lauritzen and Bottrell (1994) studied thermal karst springs in Spitsbergen (Norwegian island in the Arctic Ocean) and found that H_2S from microbial sulphate reduction accelerates karstification. Hose et al. (2000) investigated a sulphur-rich cave in Mexico and observed oxidation of H_2S to H_2SO_4 and the influence of these acids on karst development. Yoshimura et al. (2001) studied a karst aquifer system in Taiwan and observed that CO_2 from deep sources and H_2SO_4 from pyrite oxidation cause karstification.

Microorganisms are involved in nearly all hydrogeochemical processes in aquifers (Goldscheider et al. 2006) and also contribute to speleogenesis (Boston et al. 2009). Sulphuric acid speleogenesis and limestone dissolution are directly affected by chemolithoautotrophic microorganisms through intimate cycling of carbon and sulphur. These bacteria drive subaqueous sulphuric acid speleogenesis by attachment to carbonate surfaces and by generating sulphuric acid, which focuses local carbonate undersaturation and dissolution in the phreatic environment (Bennett and Engel 2005). The simple oxidation of organic acids by chemoorganoheterotrophic bacteria generates CO_2 that can create initial karstification in deep fractures (Gabrovsek et al. 2000).

Rejuvenated aggressiveness due to evaporate dissolution

Dissolution by deep meteoric waters can be enhanced by the interaction between gypsum, dolomite and calcite even in the absence of an acid source (Bischoff et al 1994;

Palmer 2000). The incongruent dissolution of dolomite in which dissolution of gypsum allows dolomite to dissolve while forcing calcite to precipitate is an important but hardly studied karstification process (Plummer and Back 1980; Bischoff et al 1994; Palmer 2007). Carbonate rocks are often associated with highly soluble evaporitic rocks such as anhydrite and gypsum. Gunn et al. (2006) have studied a karst system consisting of a 2,000-m thick limestone sequence, draining toward several cold springs and thermal springs. Isotopic and hydrochemical data showed that the thermal springs include high sulphate concentrations from evaporite dissolution below the limestone sequence. Gunn et al. conclude that evaporite dissolution can be a significant process in deep carbonate rock massifs at regional scales, as it creates pathways for calcite-undersaturated groundwater, thus accelerating karstification (Fig. 2).

Retrograde solubility

Andre and Rajaram (2005) proposed a numerical model for the simulation of limestone dissolution along fractures by cooling of upward flowing thermal waters. The key process is “retrograde solubility” of calcite: In a closed system, the solubility of calcite increases with decreasing temperature (Fig. 3d). This effect increases with increasing CO_2 partial pressure. As a result, previously saturated thermal water can cause karstification during upward flow and cooling (Bakalowicz et al. 1987; Dublyansky 2000). The most favourable areas are at the downstream end of deep carbonate basins where water rises along faults or where thermal convection is induced by deep igneous sources (Fig. 2). Such settings are also favourable sites for mixing with shallow oxygen-rich water and rising hydrogen sulphide. These processes appear to be more significant than cooling alone (Palmer 2000). At shallower depths, in an open system, the escape of CO_2 by pressure release can cause calcite precipitation, leading to a typical succession of cave formation and subsequent calcite precipitation in karst systems that experience uplift such as in the Hungarian Buda Karst (Dublyansky 1995).

Thermal baths supplied from karst aquifer systems

Introduction to thermal baths

Archaeological evidence indicates that at least 5,000 years ago thermal waters were already being used for bathing (e.g. Käss and Käss 2008). More than a hundred public baths (*thermae*) were found in the former area of the Roman Empire. The Turkish also built famous baths in the Middle Ages, which served for cleaning and religious purifying. Balneology nowadays means a therapeutic use of mineral and thermal waters for the cure of diseases or simply for relaxing. The use of thermal water for bathing depends on its temperature, which has to be warm but not above the human body temperature, resulting in a favourable range of 20–37°C. Otherwise, the water has to be heated or cooled before use.

Most historic baths use thermal water from springs discharging from naturally flowing systems, while modern baths are often additionally or entirely supplied by wells. Many important thermal baths are related to karst aquifers. The following sections present three examples from Hungary, Germany and the UK. Deep karst systems discharging to thermal springs, often used for bathing, also occur in other regions of the world such as the examples from Europe, America, Africa, the Middle East and East Asia cited in the introduction.

The Buda Karst, Hungary

Budapest is the capital of spas and Europe’s largest naturally flowing thermal system (Fig. 4). There are more than 120 thermal springs (up to 65°C warm) and about 80 wells (up to 77°C warm) with a discharge of ca. 580 L/s (Papp 1940) and a total exploited flow rate of ca. 250 L/s (in 2002). The Buda Thermal Karst forms the NE part of the Transdanubian Central Range, consisting of several thousand metres of Mesozoic carbonates, mainly Triassic dolomites (Haas 1988). The Triassic rocks are separated from the overlying Eocene formations by a Late Cretaceous to Eocene hiatus. Continuous marine sedimentation from late Eocene to early Miocene resulted in the deposition of 700 m of limestone, marl and clay (Báldi 1983; Nagymarosy et al. 1986). Post-volcanic fluids penetrated the Triassic-Eocene carbonates via fractures and faults and precipitated barite, calcite and silica (Müller 1989; Nádor 1994; Dublyansky 1995). Gradual uplift of the area started in the Neogene, causing erosion of the clay cover and exposure of the Triassic-Eocene carbonate rocks. Related to this uplift, a regional groundwater flow system developed in the Transdanubian Central Range. There are three main discharge zones in Budapest, whose elevation represents the base level of erosion of the Buda Thermal Karst (Alföldi 1982). The thermal water rises up along faults toward the springs (Fig. 5). The ^{14}C age of the hot spring water (40–60°C) is 5,000–16,000 years (Deák 1978). Lukewarm springs (20–28°C) from intermediate flow systems discharge next to the hot springs, particularly in the central zone (discharge area b in Fig. 4).

The hot spring waters are rich in total dissolved solids (1,200–1,700 mg/L) and CO_2 (200–400 mg/L) and characterised by a $Ca–Na–Cl–SO_4–HCO_3$ hydrogeochemical facies. Extensive cave systems have developed below the water table, due to mixing of ascending thermal waters from the deep regional flow system and shallower water of meteoric origin from local flow systems (Takács-Bolner and Kraus 1989; Leél-Őssy and Surányi 2003; Erőss et al. 2008a).

Derbyshire thermal springs, UK

Derbyshire in England (UK) is known for its ten thermal springs with temperatures up to 27.5°C and the associated spas such as Buxton and Matlock. The springs discharge from a karstified limestone aquifer of Dinantian age along the boundary with the overlying strata related to the

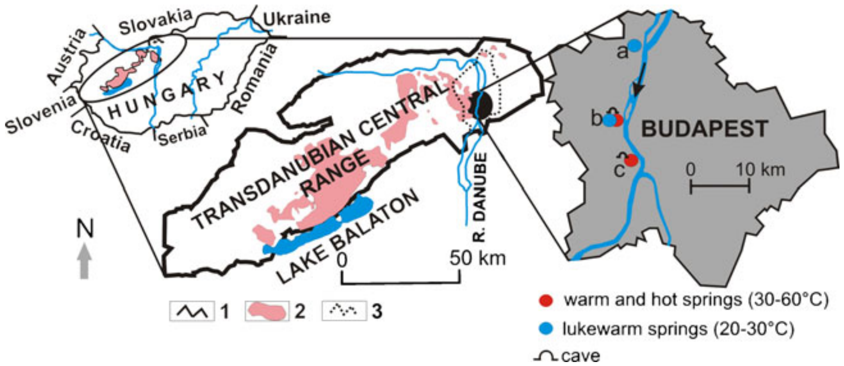

Fig. 4 Location of the Buda Thermal Karst in the Transdanubian Central Range and the natural discharge areas in Budapest. Legend: *1* Subsurface boundary of Mesozoic carbonates, *2* Uncovered Mesozoic carbonates, *3* Buda Thermal Karst, *a–c* northern, central and southern discharge areas (modified after Erőss et al. 2008b)

regional "Derbyshire dome" structure (Brassington 2007). The entire carbonate succession is included in the Peak Limestone Group with about 2,000 m total thickness. The water is heated by circulation down to 1 km in depth. The water of the warmest spring is 5,000 years old, determined by isotope methods. The confining layers were eroded during the Pliocene, thus exposing the formerly confined system to meteoric recharge. The location of individual springs was determined by valley deepening during the late Pleistocene. The thermal springs are situated close to the lowest outcrop point of the limestone and were found to have higher sulphate concentration than the cold springs (Edmunds 1971; Christopher et al. 1977). The cold karst waters gain sulphate from the oxidation of sulphide minerals, and inorganic carbon is depleted in ^{13}C. Thermal waters have higher Sr/Ca ratios and ^{13}C signatures, as a result of intense water–rock interaction and long residence time. The elevated sulphate concentration of the thermal waters is derived from interaction with buried evaporites during deep groundwater flow. Gypsum dissolution has produced significant porosity and permeability in the carbonate aquifer, which contributes to karst development (Worthington and Ford 1995; Gunn et al. 2006).

The medicinal springs and baths of Stuttgart, Germany

The baths of Stuttgart represent Europe's second largest mineral-water resource. The total discharge of 500 L/s is similar to that at Budapest, but water temperatures are lower. The springs are located near the Neckar River, i.e. at the regional base level, and issue from a karst aquifer formed by Middle Triassic Upper Muschelkalk Limestone (Ufrecht 2006a). Between the meteoric recharge area 20–30 km to the SW and the discharge zone, the aquifer is mostly confined by low permeability formations (Fig. 6). The mineral water includes high levels of CO_2 rising up

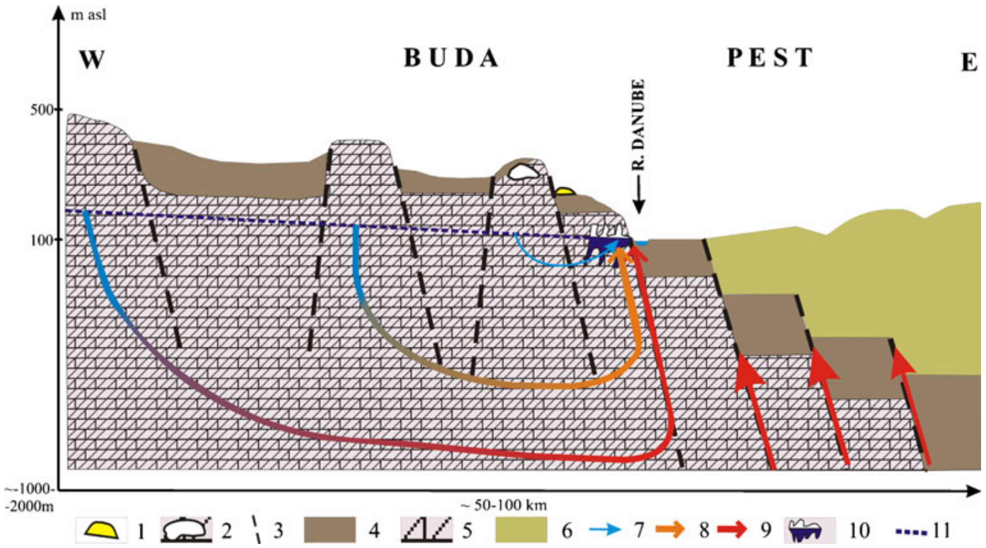

Fig. 5 Generalised model for the flow systems of the Buda Thermal Karst (Buda being the western part of Budapest city and Pest being the eastern part). Legend: *1* travertine; *2* inactive, dry cave; *3* fault; *4* marls and clays; *5* carbonate rocks; *6* Neogene sediments; *7* local flow system; *8* intermediate flow system; *9* upward regional flow from the basement; *10* active underwater cave; *11* karst water table (modified after Erőss et al. 2008b)

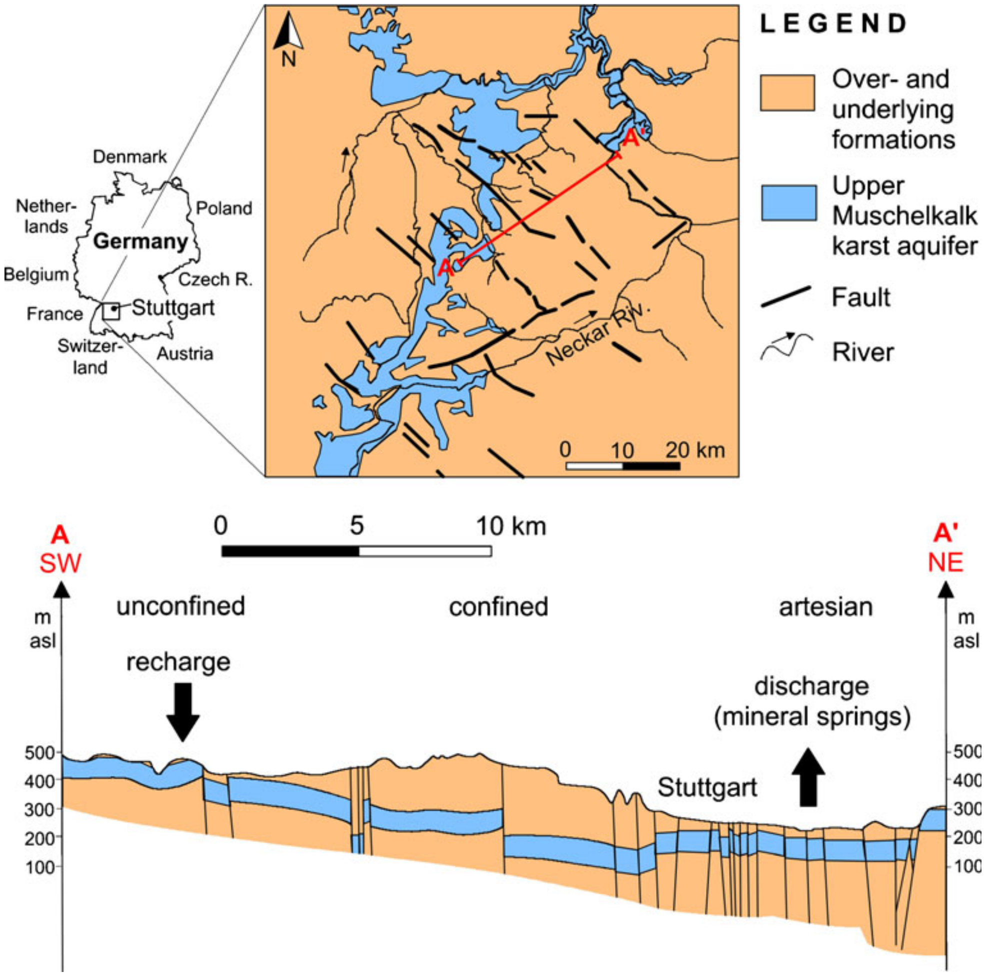

Fig. 6 Location, geologic map and hydrogeologic section of the hypogenic karst aquifer system of Stuttgart, from the recharge zone to the mineral springs (modified after Goldscheider et al. 2003)

from the Earth's mantle along faults (Ufrecht 2006b). The springs can be subdivided into two groups: Low mineralised springs in the northern sector with 0.5–1.6 g/L total dissolved solids (TDS), CO_2<250 mg/L and water temperatures of 12–17°C; and highly mineralised springs in the southern sector, used for cures and leisure baths, with 3–7 g/L TDS, 1.3–2.4 g/L CO_2 and water temperatures of 17–21°C.

Since 1984, chlorinated solvents at very low concentration levels have been detected in some of the springs. This was the starting point of a detailed hydrogeologic research program including two multitracer tests (Goldscheider et al. 2003). In the zone of highly mineralised springs, the tracer test revealed maximum flow velocities of up to 230 m/day (first tracer detection), dominant velocities of 36 m/day (peak concentration) and 29% recovery. The tracer was detected at eight highly mineralised springs, demonstrating that a single contamination event in the city area could impact most of the medicinal springs. The breakthrough curves displayed extremely long tails, some lasting up to 2 years, suggesting intermediate storage of tracer in large cavities and subsequent slow release into the active conduit network (Goldscheider 2008). The supposed caves are probably the result of hypogenic speleogenesis due to mixing, retrograde calcite dissolution and CO_2 from the mantle. Indeed, in areas where the Upper Muschelkalk limestone has been exposed by uplift and erosion such as in parts of Baden-Württemberg (SW Germany) or Luxemburg, maze caves are known that show typical features of hypogenic speleogenesis (Klimchouk 2007). Currently, the planned construction of a huge underground railway station ("Stuttgart 21") upgradient from the medicinal springs represents a potential threat to the integrity of this mineral water resource, although the excavations will be done in the formations overlying the karst aquifer.

Geothermal energy from deep carbonate rock aquifers

Advantages and challenges of geothermal resources in carbonate rock aquifers

Deep carbonate rock aquifers are predestined for both direct thermal-water use for district heating and electric power generation, generally by means of doublet systems consisting of an injection and production well (Fig. 2). The dominant parameters determining the type and use of geothermal resources are wellhead temperature and flow rate (Dickson and Fanelli 2003; Gupta and Roy 2007). The temperature depends on the local geothermal gradient and drilling depth. The flow rate is a function of the pumping energy and the natural or enhanced transmissivity of the aquifer, which depends on its mean permeability and thickness. Geothermal installations are only economically viable if the produced energy is significantly higher than the energy required for pumping and other purposes, which applies both for heating and electricity production. The higher the transmissivity, the lower the pumping energy required to obtain a specific flow rate. Consequently, the efficiency of geothermal power plants directly depends on reservoir permeability and transmissivity (DiPippo 2008). Deep carbonate rocks often have higher permeabilities than other reservoirs, as illustrated by the three following representative examples from fractured, porous and karst aquifers:

The well-known Enhanced Geothermal System (EGS) project at Soultz-sous-Forêts (France) is an example of a fractured crystalline rock (granite) reservoir. A mean permeability of $3\times10^{-14}\,\mathrm{m}^2$ was found in the most fractured zones, inferred from temperature models (Kohl et al. 2000). This is in agreement with maximum hydraulic conductivities of 2.3×10^{-6} m/s determined from tracer tests (Aquilina et al. 2004).

A typical geothermal aquifer with predominantly intergranular porosity is present at Neustadt-Glewe (Germany), where a doublet system produces thermal water from porous Middle Raethian Sandstone with a mean permeability of $7\times10^{-13}\,\mathrm{m}^2$ (Menzel et al. 2000).

The power plant at Riehen (Switzerland) exploits the Upper Muschelkalk Limestone aquifer. A permeability of $2\times10^{-12}\,\mathrm{m}^2$ was measured at the injection well, i.e. substantially higher than the values for porous and fractured reservoirs in the examples in the preceding. Thermal water with a temperature of 66°C and a flow rate of 18 L/s is obtained at the production well and used for district heating (Dickson and Fanelli 2003). Both wells are located at a highly fractured zone near the main boundary fault of the Upper Rhine Graben (Boissavy and Hauber 1994).

Heterogeneity is a major challenge in the exploitation of geothermal resources in carbonate rock aquifers. Geothermal installations in these aquifers are not only characterised by a high efficiency if the drillings encounter highly fractured and/or karstified zones (hypogenic speleogenesis) such as in the case of Riehen and other successful examples discussed in the following, but also by a high exploration risk if these high-permeability zones are missed (Paschen et al. 2003). Therefore, detailed geological, geophysical and hydrogeological prospection is indispensible for the reservoir assessment, as well as a better understanding of hypogenic speleogenesis.

Geothermal resources and operating systems in carbonate aquifers in Central Europe

The best examples of geothermal power plants in deep carbonate rocks can be found in Central Europe, particularly in the Upper Malm of the Northern Alpine Molasse Basin, the Upper Malm and Dogger of the Paris Basin, and the Upper Muschelkalk in the Upper Rhine Graben. Currently operating geothermal systems using hot water from these reservoirs are summarised in Table 1.

The Middle Triassic Upper Muschelkalk Limestone represents an important geothermal reservoir in Central Europe, particularly in the region of the Upper Rhine Graben between Germany, France and northern Switzerland (Paschen et al. 2003). Stober and Jodocy (2009) evaluated different geothermal reservoirs in this region and found ca. 10-times higher mean-transmissivity-thickness ratios in the Muschelkalk Limestone (2.0×10^{-6} m/s) than in the Lower Triassic Bunter Sandstone (2.4×10^{-7} m/s). This finding suggests at least some degree of karstification of the Muschelkalk Limestone. According to Fischer et al. (1971) and a report published by Nagra (1990), fracturing and karstification of this limestone formation have caused hydraulic conductivities ranging from 7×10^{-7} m/s to 3×10^{-6} m/s at fault zones. The example of Riehen has already been discussed in the preceding and is summarised in Table 1.

The Paris Basin in France includes four main aquifers, among which the carbonate rocks of the Dogger are most relevant for geothermics (Ungemach et al. 2005). The Bathonian includes three productive levels, known as Comblanchian, Oolitic and Cyclical units. The oolitic limestones have high matrix porosity and are most productive. This formation and one of the Comblanchian units have preserved their original porosity, whereas the void porosity of the Cyclical units has been reduced by diagenesis. Fracturing and dissolution may have contributed to an enhancement of porosity, but this has not been studied in detail. The Dogger occurs at depths between 1,500 and 2,000 m with reservoir temperatures between 50 and 85°C. The most productive horizon in the Upper Malm of the Paris Basin is the Lusitanian Limestone. There are currently 31 operating doublet systems used for district heating, with flow rates of 40–170 L/s and a total thermal energy production of 12,500 MWh (Vathaire et al. 2006).

At the moment, Germany's largest geothermal power plant is located at Unterhaching near Munich (Fig. 7) and uses hot water from the Upper Malm Limestone aquifer that is present at the base of the Molasse Basin in the northern foreland of the Alps in Switzerland, Germany and Austria (Paschen et al. 2003; Table 1). The production well at Unterhaching is 3,346 m deep and produces 150 L/s of 123°C hot water, used for heating and electric power generation. Wolfgramm et al. (2007) estimated a mean permeability of 1.3 to $2.0\times10^{-12}\,\mathrm{m}^2$ at this well, assuming an aquifer thickness of 350 m; however, two thirds of the inflow comes from a 100-m thick zone. The power plant is located at a major NNW–SSE striking fault zone. The injection well was drilled through a fault with a vertical displacement of

Table 1 Summary of geothermal installations currently producing geothermal energy for district heating and electric power generation from selected karst aquifers in Central Europe (compiled from different sources)

Location	Production/ injection *T* (°C)	Flow rates (L/s) pump/no pump	Well depth (m) production/injection	Aquifer	Thermal power (MW)
Altheim (Austria)	106/65	ca. 50/46	2,300/2,165	Upper Malm	11.5
Bad Blumau (Austria)	110/50	ca. 80/30	2,843/2,583	Upper Malm	7.6
Bad Waltersdorf (Austria)	63/55	NA/17	1,400/1,061	Upper Malm	2.3
Geinberg (Austria)	105/35	ND/25	2,225/NA	Upper Malm	7.8
Simbach Braunau (Austria)	81/ND	74/30	2,200/1,848	Upper Malm	9.3
Paris Basin (France) 31 operating doublets	50–85/ca. 45	40–170/ND	1,400–2,000/900–2,000	Dogger	NA
Riehen (Switzerland)	66.4/52.2	18/ND	1,547/1,247	Upper Muschelkalk	3.6
Erding (Germany)	65/ND	55/ND	2,350/2,060	Upper Malm	8
Pullach (Germany)	107/ND	50/ND	3,443/3,370	Upper Malm	6
Riem (Germany)	93/ca. 50	75/ND	2,746/3,020	Upper Malm	9
Unterföhring (Germany)	86/ND	50/ND	2,512/2,120	Upper Malm	ND
Unterhaching (Germany)	123/ND	150/ND	3,346/3,590	Upper Malm	40
Unterschleissheim (Germany)	81/ND	90/ND	1,960/2,000	Upper Malm	13

Legend: *NA* not applicable (e.g. injection data for single-well systems); *ND* no data available

238 m. This example illustrates again the high heterogeneity of carbonate rock aquifers and the important role of fault zones.

The geothermal installation in the village of Altheim (Austria) also uses hot water from the Malm aquifer (Table 1) and provides an example of a cascade system (Fig. 8), allowing the multiple use of geothermal resources. A temperature of 90°C is required for the district heating system, while 65°C suffices for the swimming pool and for heating the school. This allows a parallel circuit for district heating and electric power production and a serial circuit for electric power production and heating of the swimming pool and school. The geothermal brine reaches 106°C at the wellhead. The output temperature at the first heat exchanger is 90°C, which is reduced by the heating system to about 70°C. The heat exchanger of the power plant also provides hot water at 70°C, which then supplies the third heat exchanger for the swimming pool and the school. The doublet system of Bad Blumau (Austria) combines electric power generation with spa utilisation. Up to 80 L/s of 110°C hot thermal water are pumped from the Malm Limestone aquifer.

CO_2 sequestration at geothermal installations in carbonate rock aquifers

The equation describing calcite dissolution (Eq. 1) illustrates that karst processes are natural sinks for CO_2. Based on this observation, Rau et al. (2007) proposed using water and waste fines from crushed limestone production to capture CO_2 from fossil energy combustion and release the dissolved compounds into the ocean; unlike direct CO_2 release into the ocean or atmosphere, this would not cause acidification. CO_2 can also be sequestered in different types of geologic reservoirs (Bachu 2002; Bickle 2009). The major concerns and problems of this approach

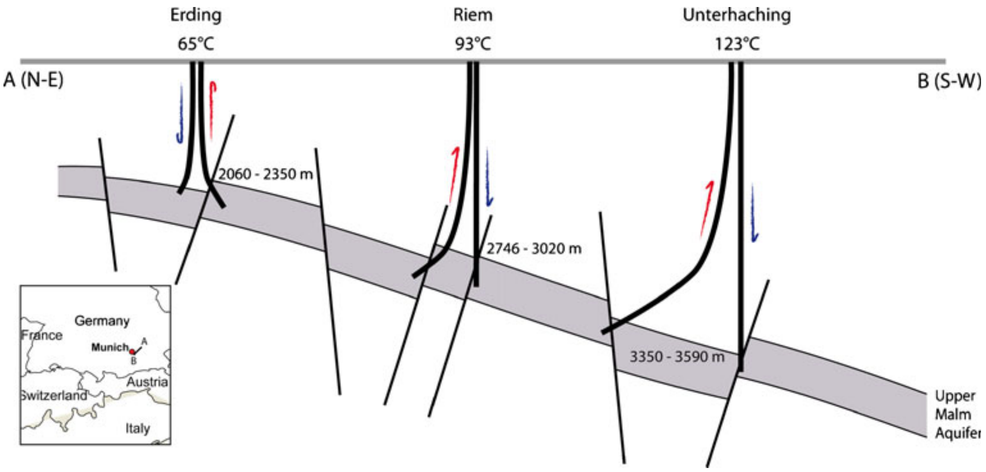

Fig. 7 Schematic NE–SW profile illustrating geothermal resources in the Upper Malm Limestone aquifer below the northern foreland of the Alps (Bavaria, Germany), with increasing depth and temperature towards the Alps (SW). Three examples of geothermal installations are shown (technical details in Table 1), which exploit the fault-bound thermal water reservoirs in this aquifer

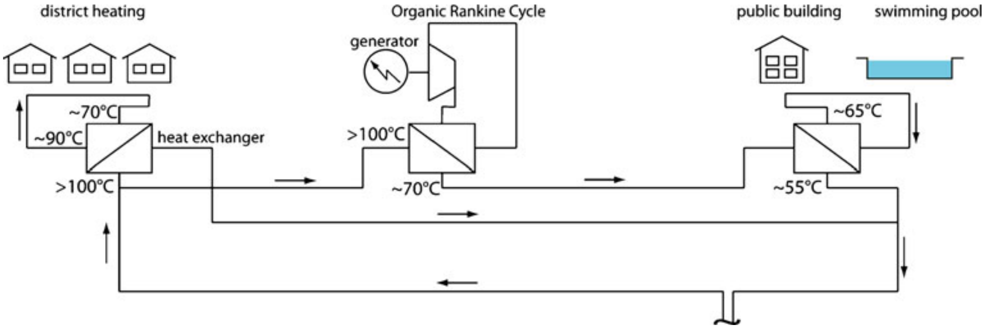

Fig. 8 Scheme of heat and power production for a typical cascade utilisation with priority of district heating and additional electric power generation in an *Organic Rankine Cycle* process, as well as utilisation of rest heat for a public building and swimming pool (example from Altheim, Austria; generalised)

are the long-term safety (concentrated CO_2 escaping from the reservoir could potentially kill people) and the energy consumption for pumping the gas underground. Rosenbauer et al. (2004) studied the interactions of CO_2 with different types of host aquifers and report that increasing porosity due to limestone dissolution results in higher permeability and, thus, alleviates formation-plugging problems near injection zones (Fig. 2). Pruess (2008) evaluated the use of CO_2 as a working fluid for enhanced geothermal systems and found that it is superior to water in its ability to mine heat from hot fractured crystalline rock.

Several of these approaches could be combined by using geothermal installations in deep carbonate rock aquifers for CO_2 sequestration, which appears to be a promising approach:

- Operating injection wells and pumps could be used for sequestration, thus minimising additional infrastructure and energy demand.
- CO_2 partly reacts with limestone to form soluble and harmless calcium and bicarbonate ions, so there would be less safety concerns.
- This process would at the same time increase reservoir porosity and transmissivity, which also means higher production rates and better efficiency of the geothermal installation.

The following example, based on rough estimations and simplified assumptions, illustrates the approach. The pumping rate of large geothermal installations can reach 150 L/s (Table 1). Natural carbogaseous waters often include several g/L of CO_2 (Bissig et al. 2006; Ufrecht 2006b). On this basis, it is estimated that, for the purpose of sequestration, 1–10 g/L of CO_2 could be mixed with the water and pumped into the aquifer via the injection well, although feasible CO_2 concentrations critically depend on pressure–temperature conditions and technical aspects, which would require further investigation. These values correspond to a CO_2 sequestration rate of 150–1,500 g/s or 4.7×10^3 to 4.7×10^4 tons/year, for one geothermal installation. Under the simplified assumption that all CO_2 reacts with the limestone, this quantity would dissolve 1.1×10^4 to 1.1×10^5 tons of calcite, corresponding to 4.0×10^3 to $4.0\times10^4 m^3$/year. For an assumed carbonate rock reservoir of 1 km × 1 km × 100 m (10^8 m^3), this means an additional porosity of 0.004–0.04% per year, resulting in 0.12–1.2% total additional reservoir porosity for an assumed lifetime of 30 years.

Due to the dissolution kinetics of limestone (Dreybrodt 1990), porosity would not only be created around the injection well but increase fracture apertures in a wider network and, thus, increase aquifer transmissivity and the efficiency of the geothermal installation. Due to the favourable mechanical properties of limestones, cavities are generally stable, so that the risk of collapse or subsidence would be low. However, as ill-conceived interventions into the geologic environment can cause avoidable damage (e.g. Goldscheider and Bechtel 2009), the feasibility of this technique should be carefully evaluated prior to implementation.

Conclusions and outlook

Most previous hydrogeologic karst and cave research has focused on relatively shallow and accessible cave systems and cold-water karst aquifers, so-called epigenic karst systems, which are crucial for drinking-water supply (Ford and Williams 2007; Goldscheider and Drew 2007). Only relatively recently, have geoscientists become aware of other types of cave and karst systems, which are generally deeply confined and, thus, inaccessible, often without any discernible surface karst landforms. These hypogenic karst systems are related to deep regional groundwater circulation systems and are probably much more widespread than previously suspected. Groundwater is a geologic agent (Tóth 1999) and also the main driver for the creation of porosity in deep carbonate rock aquifers. These processes can be summarised under the term hypogenic speleogenesis (Palmer 1991; Klimchouk 2007). Many different hydrogeochemical reactions are involved such as mixing corrosion, retrograde calcite solubility, dissolution due to geogenic acids from deep sources, and other processes.

From a practical point of view, thermal and mineral water resources in deep carbonate-rock aquifers are important for humanity. Many thermal baths around the world are supplied by hot springs issuing from karst aquifers or by pumping wells drilled into these aquifers.

The world-famous baths of Budapest are probably the best example. Thermal water from deep carbonate aquifers is increasingly used by geothermal installations, usually doublet systems, for electricity production, district heating and other purposes. The main advantages of geothermal energy are the low CO_2 emissions (unlike fossil energy) and the low land consumption (unlike so-called "bio-fuels"), while the comparatively high costs currently still represent a limitation. The most productive zones in deep carbonate-rock aquifers are often associated with fault and fracture zones, where high permeabilities and, thus, high flow rates of hot water can be encountered, resulting in a high efficiency of the geothermal installation. Zones affected by hypogenic speleogenesis would also be promising targets for geothermal drillings. However, due to the heterogeneity of carbonate rock aquifers, the exploration risk (or exploration uncertainty) of geothermal drillings in such aquifers is relatively high, i.e. the drillings might miss the high-permeability zones. Further progress in understanding of hypogenic speleogenesis could reduce this risk. The sequestration of CO_2 in geologic reservoirs is increasingly discussed (e.g. Bickle 2009). Sequestration into deep carbonate-rock aquifers via geothermal injection wells is a promising approach, both economically and in terms of safety, although not without drawbacks such as possible land subsidence.

The vulnerability of freshwater resources in karst aquifers to contamination is common knowledge. Thermal aquifers, due to their often deep and confined setting, might be considered as naturally well protected, renewable and quasi-infinite resources. However, contamination of thermal and mineral water supplying spas does occur, although it is rarely reported (e.g. Goldscheider et al. 2003). The increased use of geothermal energy and possible future large-scale CO_2 sequestration in geologic reservoirs also represent potential conflicts of interests and threats to the natural quantity and quality of thermal water. Consequently, this review also aims at drawing the attention of hydrogeologists to the challenges and problems associated with the sustainable use of thermal water resources from carbonate rock aquifers. A systematic assessment, evaluation and mapping of these resources, both at national scales and globally, would be an ambitious project but would provide a useful basis for the management of thermal water from deep carbonate-rock aquifers.

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References

Alföldi L (1982) A layered thermal-water twin flow system. J Hydrol 56:99–105

Allen DM, Grasby SE, Voormeij DA (2006) Determining the circulation depth of thermal springs in the southern Rocky Mountain Trench, south-eastern British Columbia, Canada using geothermometry and borehole temperature logs. Hydrogeol J 14(1–2):159–172

Altunel E, Hancock PL (1993) Morphology and structural setting of Quaternary travertines at Pamukkale, Turkey. Geol J 28(3–4):335–346

Andre BJ, Rajaram H (2005) Dissolution of limestone fractures by cooling waters: early development of hypogene karst systems. Water Resour Res 41:W01015

Aquilina L, De Dreuzy JR, Bour O, Davy P (2004) Porosity and fluid velocities in the upper continental crust (2 to 4km) inferred from injection tests at the Soultz-sous-Forêts geothermal site. Geochim Cosmochim Acta 68(11):2405–2415

Audra P, Bini A, Gabrovsek F, Hauselmann P, Hoblea F, Jeannin PY, Kunaver J, Monbaron M, Sustersic F, Tognini P, Trimmel H, Wildberger A (2007) Cave and karst evolution in the Alps and their relation to paleoclimate and paleotopography. Acta Carsol 36:53–67

Bachu S (2002) Sequestration of CO_2 in geological media in response to climate change: road map for site selection using the transform of the geological space into the CO_2 phase space. Energy Convers Manage 43:87–102

Bajjali W, Clark ID, Fritz P (1997) The artesian thermal groundwaters of northern Jordan: insights into their recharge history and age. J Hydrol 192(1–4):355–382

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

Báldi T (1983) Magyarországi oligocén és alsómiocén formációk [Oligocene and Lower Miocene Formations in Hungary] Akadémiai Kiadó, Budapest, 293 pp

Bayari S, Ozyurt N, Pekkans E (2009) Giant collapse structures formed by hypogenic karstification: the Obruks of the Central Anatolia, Turkey. In: Klimchouk A, Ford D (eds) Hypogene speleogenesis and karst hydrogeology of artesian basins. Special Paper 1, Ukrainian Institute of Speleology and Karstology, Simferopol, Ukraine, pp 83–90

Bennett PC, Engel AS (2005) Microbial contributions to karstification. In Gadd GM, Semple KT, Lappin-Scott HM (eds) Micro-organisms and Earth Systems. Advances in Geomicrobiology, Society for General Microbiology (SGM) Symposium 65, Cambridge University Press, Cambridge, pp 345–363

Berge TB, Veal SL (2005) Structure of the Alpine foreland. Tectonics 24:TC5011

Bickle MJ (2009) Geological carbon storage. Nature Geosci 2 (12):815–818

Bischoff JL, Julia R, Shanks WC, Rosenbauer RJ (1994) Karstification without carbonic acid; bedrock dissolution by gypsum-driven dedolomitization. Geology 22:995–998

Bissig P, Goldscheider N, Mayoraz J, Surbeck H, Vuataz FD (2006) Carbogaseous spring waters, coldwater geysers and dry CO_2 exhalations in the tectonic window of the Lower Engadine Valley, Switzerland. Eclogae Geol Helv 99:143–155

Bjorlykke K (1993) Fluid-flow in sedimentary basins. Sed Geol 86 (1–2):137–158

Bögli A (1964) Mischungskorrosion: ein Beitrag zum Verkarstungsproblem [Mixing corrosion: a contribution to understand karst phemomena]. Erdkunde 18:83–92

Boissavy C, Hauber L (1994) Results of the geothermal boreholes Riehen 1 and Riehen 2 (Basel, Switzerland). Doc. Int. Symp. Geothermics 94 in Europe, Doc. BRGM 230, BRGM, Orléans, pp 453–460

Bosak P, Ford D, Glazek J, Horacek I (eds) (1989) Paleokarst: a systematic and regional review. Elsevier, New York, 725 pp

Boston PJ, Spilde MN, Northup DE, Curry MD, Melim LA, Rosales-Lagarde L (2009) Microorganisms as speleogenetic agents: geochemical diversity but geomicrobial unity. In: Klimchouk A, Ford D (eds) Hypogene speleogenesis and karst hydrogeology of artesian basins. Special Paper 1, Ukrainian Institute of Speleology and Karstology, Simferopol, Ukraine, pp 51–58

Bredehoeft JD, Papadopulos IS (1965) Rates of vertical groundwater movement estimated from the earth's thermal profile. Water Resour Res 1:325–328

Brassington FC (2007) A proposed conceptual model for the genesis of the Derbyshire thermal springs. Q J Eng Geol Hydrogeol 40:35–46

Bretz JH (1949) Carlsbad Caverns and other caves of the Guadalupe block, New Mexico. J Geol 57:447–463

Caine JS, Evans JP, Forster CB (1996) Fault zone architecture and permeability structure. Geology 24(11):1025–1028

Casanova J, Bodénan F, Négrel Ph, Azaroual M (1999) Microbial control on the precipitation of modern ferrihydrite and carbonate deposits from the Cézallier hydrothermal springs (Massif Central, France). Sed Geol 126:125–145

Christopher NSJ, Beck JS, Mellors PT (1977) Hydrology: water in limestone. In: Ford TD (ed) Limestone and caves of the Peak District. Geo Abstracts, Norwich, pp 185–230

Deák J (1978) Environmental isotopes and water chemical studies for groundwater research in Hungary. Isotope Hydrology, IAEA-SM-228/13, IAEA, Vienna, pp 221–249

Deming D (2002) Introduction to hydrogeology. McGraw-Hill, New York, 468 pp

Dickson MH, Fanelli M (eds) (2003) Geothermal energy, utilization and technology. UNESCO, New York, 205 pp

Dilsiz C (2006) Conceptual hydrodynamic model of the Pamukkale hydrothermal field, southwestern Turkey, based on hydrochemical and isotopic data. Hydrogeol J 14(4):562–572

DiPippo R (2008) Geothermal power plants: principles, applications, case studies and environmental impacts, 2nd edn. Elsevier, Amsterdam, 493 pp

Djidi K, Bakalowicz M, Benali AM (2008) Mixed, classical and hydrothermal karstification in a carbonate aquifer: hydrogeological consequences—the case of the Saida aquifer system, Algeria. C R Geosci 340(7):462–473

Dreybrodt W (1990) The role of dissolution kinetics in the development of karstification in limestone: a model simulation of karst evolution. J Geol 98:639–655

Dreybrodt W (2000) Equilibrium chemistry of karst waters in limestone terranes. In: Klimchouk A, Ford DC, Palmer AN, Dreybrodt W (eds) Speleogenesis, evolution of karst aquifers, National Speleological Society, Huntsville, AL, pp 126–135

Drogue C (1985) Geothermal gradients and groundwater circulation in fissured and karstic rocks: the role played by the structure of the permeable network. J Geodyn 4(1–4):219–231

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 Speleological Society, Huntsville, Alabama, pp 298–303

Economides M, Ungemach P (1987) Applied geothermics. Wiley, Chichester, UK, 238 pp

Edmunds WM (1971) Hydrogeochemistry of groundwaters in the Derbyeshire Dome with special reference to trace constituents. Inst Geol Sci Rep 71/7, BGS, Keyworth, UK, 52 pp

Egemeier SJ (1981) Cavern development by thermal waters. Nat Speleol Soc Bull 43:31–51

Erőss A, Csoma ÉA, Mádl-Szőnyi J (2008a) The effects of mixed hydrothermal and meteoric fluids on karst reservoir development, Buda Thermal Karst, Hungary. In: Sasowsky ID, Feazel CT, Mylorie JE, Palmer AN, Palmer MV (eds) Karst from recent to reservoirs, Karst Waters Institute, Spec Publ 14, Leesburg, VA, pp 57–63

Erőss A, Mádl-Szőnyi J, Csoma A (2008b) Characteristics of discharge at Rose and Gellért Hills, Budapest, Hungary. Central Euro Geol 51(3):267–281

Fischer H, Hauber L, Wittmann O (1971) Erläuterungen zum Blatt 1047 Basel. Geologischer Atlas der Schweiz 1:25000 [Geologic Atlas of Switzerland 1:25000, explanatory note for map sheet 1047 Basel]. Federal Office of Topography, Wabern, Switzerland, pp 1–55

Ford DC (1995) Paleokarst as a target for modern karstification. Paleokarst Field Conference on Macroscopic Dissolution Features in the Rock Record, San Salvador Island, Bahamas, February 1995, pp 138–147

Ford D, Williams P (2007) Karst hydrogeology and geomorphology. Wiley, Chichester, UK, 576 pp

Forster C, Smith L (1988a) Groundwater flow systems in mountainous terrain 1: numerical modelling technique. Water Resour Res 24:999–1010

Forster C, Smith L (1988b) Groundwater flow systems in mountainous terrain 2: controlling factors. Water Resour Res 24:1011–1023

Frumkin A, Gvirtzman H (2006) Cross-formational rising groundwater at an artesian karstic basin: the Ayalon Saline Anomaly, Israel. J Hydrol 318:316–333

Fujisawa A, Tazaki K (2003) The radioactive microbial mats: in case of Misasa hot springs in Tottori Prefecture. In: Kamata N (ed) Proceedings: International Symposium of the Kanazawa University 21st-Century COE Program vol 1. Kanazawa University, Kanazawa, Japan, pp 328–331

Gabrovsek F, Dreybrodt W (2000) Role of mixing corrosion in calcite-aggressive H_2O–CO_2–$CaCO_3$ solutions in the early evolution of karst aquifers in limestone. Water Resour Res 36:1179–1188

Gabrovsek F, Menne B, Dreybrodt W (2000) A model of early evolution of karst conduits affected by subterranean CO_2 sources. Environ Geol 39(6):531–543

Gainon F, Goldscheider N, Surbeck H (2007) Conceptual model for the origin of high radon levels in spring waters: the example of the St. Placidus spring, Grisons, Swiss Alps. Swiss J Geosci 100 (2):251–262

Gallois R (2007) The formation of the hot springs at Bath Spa, UK. Geol Mag 144:741–747

Gary M, Sharp JM (2006) Volcanogenic karstification of Sistema Zacatón, Mexico. Geol Soc Am Spec Pap 404:79–89

Gemici U, Filiz S (2001) Hydrochemistry of the Cesme geothermal area in western Turkey. J Volcanol Geoth Res 110:171–187

Goldscheider N (2008) A new quantitative interpretation of the long-tail and plateau-like breakthrough curves from tracer tests in the artesian karst aquifer of Stuttgart, Germany. Hydrogeol J 16(7):1311–1317

Goldscheider N, Bechtel TD (2009) Editors' message: the housing crisis from underground—damage to a historic town by geothermal drillings through anhydrite, Staufen, Germany. Hydrogeol J 17(3):491–493

Goldscheider N, Drew D (2007) Methods in karst hydrogeology. International Contributions to Hydrogeology 26. Taylor & Francis, London, 264 pp

Goldscheider N, Hötzl H, Käss W, Ufrecht W (2003) Combined tracer tests in the karst aquifer of the artesian mineral springs of Stuttgart, Germany. Environ Geol 43(8):922–929

Goldscheider N, Hunkeler D, Rossi P (2006) Review: microbial biocenoses in pristine aquifers and an assessment of investigative methods. Hydrogeol J 14(6):926–941

Grasby SE, Hutcheon I (2001) Controls on the distribution of thermal springs in the southern Canadian Cordillera. Can J Earth Sci 38:427–440

Grasby SE, Hutcheon I, Krouse HR (2000) The influence of water–rock interaction on the chemistry of thermal springs in western Canada. Appl Geochem 15:439–454

Gunn J, Bottrell SH, Lowe DJ, Worthington SRH (2006) Deep groundwater flow and geochemical processes in limestone aquifers: evidence from thermal waters in Derbyshire, England, UK. Hydrogeol J 14:868–881

Gupta H, Roy S (2007) Geothermal Energy, an alternative resource for the 21st Century. Elsevier, Amsterdam, 279 pp

Haas J (1988) Upper Triassic carbonate platform evolution in the Transdanubian Mid-Mountains. Acta Geol Hung 31(3–4):299–312

Hill CA (1987) Geology of Carlsbad Cavern and other caves in the Guadalupe Mountains, New Mexico and Texas. Bulletin 117, New Mexico Bureau of Mines and Mineral Resources, Sante Fe, NM, 150 pp

Hill CA (1990) Sulfuric acid speleogenesis of Carlsbad Cavern and its relationship to hydrocarbons, Delaware Basin, New Mexico and Texas. AAPG Bull 74(11):1685–1694

Hose LD, Palmer AN, Palmer MV, Northup DE, Boston PJ, DuChene HR (2000) Microbiology and geochemistry in a hydrogen-sulphide-rich karst environment. Chem Geol 169:399–423

Inoubli N, Gouasmia M, Gasmi M, Mharndi A, Ben Dhia H (2006) Integration of geological, hydrochemical and geophysical methods for prospecting thermal water resources: the case of the Hmeima region (central-western Tunisia). J Afr Earth Sci 46 (3):180–186

Käss W, Käss H (2008) Deutsches Bäderbuch, 2. Aufl. [German Spa Book, 2nd edn]. Schweizerbart, Stuttgart, Germany

Keller B (1991) Hydrology of the Swiss Molasse Basin: a review of current knowledge and considerations for the future. Eclogae Geol Helv 85(3):611–652

Klimchouk AB (2007) Hypogene speleogenesis: hydrogeological and morphogenetic perspective. Special Paper no. 1, National Cave and Karst Research Institute, Carlsbad, NM

Klimchouk AB, Ford DC (2000) Types of karst and evolution of hydrogeologic setting. In: Klimchouk A, Ford DC, Palmer AN, Dreybrodt W (eds) Speleogenesis, evolution of karst aquifers. National Speleological Society, Huntsville, AL, pp 45–53

Klimchouk A, Ford DC, Palmer AN, Dreybrodt W (eds) (2000) Speleogenesis, evolution of karst aquifers. National Speleological Society, Huntsville, AL, 527 pp

Kohl T, Bächler D, Rybach L (2000) Steps towards a comprehensive thermo-hydraulic analysis of the HDR test site Soultz-sous-Forêts. Proc. of the World Geothermal Congress 2000, Tohoku, Japan, 28 May–10 June 2000, pp 2671–2676

Langmuir D (1971) The geochemistry of carbonate ground waters in central Pennsylvania. Geochim Cosmochim Acta 35:1023–1045

Lauritzen SE, Bottrell S (1994) Microbiological activity in thermoglacial karst springs, south Spitsbergen. Geomicrobiol J 12:161–173

Leél-Őssy Sz, Surányi G (2003) Peculiar hydrothermal caves in Budapest, Hungary. Acta Geol Hung 46(4):407–436

Levet S, Toutain JP, Munoz M, Berger G, Negrel P, Jendrzejewski N, Agrinier P, Sortino F (2002) Geochemistry of the Bagneres-de-Bigorre thermal waters from the North Pyrenean Zone (France). Geofluids 2(1):25–40

Li M, Li GM, Yang L, Dang XY, Zhao CH, Hou GC, Zhang MS (2007) Numerical modeling of geothermal groundwater flow in karst aquifer system in eastern Weibei, Shaanxi Province, China. Sci China Series D: Earth Sci 50:36–41

Lopez DL, Smith L (1995) Fluid flow in fault zones: analysis of the interplay of convective circulation and topographically driven groundwater flow. Water Resour Res 31:1489–1503

Lopez DL, Smith L (1996) Fluid flow in fault zones: influence of hydraulic anisotropy and heterogeneity on the fluid flow and heat transfer regime. Water Resour Res 32:3227–3235

Ma T, Wang YX, Guo QH, Yan CM, Ma R, Huang Z (2009) Hydrochemical and isotopic evidence of origin of thermal karst water at Taiyuan, northern China. J Earth Sci 20(5):879–889

Mazzullo SJ, Harris PM (1991) An overview of dissolution porosity development in the deep-burial environment, with examples from carbonate reservoirs in the Permian Basin. West Texas Geological Society, Midland, TX, pp 91–89, 125–138

Mazzullo SJ, Harris PM (1992) Mesogenetic dissolution: its role in porosity development in carbonate reservoirs. AAPG Bull 76 (5):607–620

Meinzer OE (1923) Outline of ground-water hydrology, with definitions. US Geol Surv Water Suppl Pap 494, 71 pp

Menzel H, Seibt P, Kellner T (2000) Five years of experience in the operation of the Neustadt-Glewe geothermal project. Proc. of the World Geothermal Congress 2000, Tohoku, Japan, 28 May–10 June 2000, pp 2671–2676

Minissale A (2004) Origin, transport and discharge of CO_2 in central Italy. Earth Sci Rev 66(1–2):89–141

Minissale A, Vaselli O, Tassi F, Magro G, Grechi GP (2002) Fluid mixing in carbonate aquifers near Rapolano (central Italy): chemical and isotopic constraints. Appl Geochem 17:1329–1342

Muralt R, Vuataz FD, Schonborn G, Sommaruga A, Jenny J (1997) Integration of hydrochemical, geological and geophysical methods for the exploration of a new thermal water resource: case of Yverdon-les-Bains, foot of the Jura range. Eclogae Geol Helv 90:179–197

Müller P (1989) Hydrothermal paleokarst of Hungary. In: Bosák P, Ford DC, Glazek J, Horacek I (eds) Paleokarst: a systematic and regional review. Elsevier and Academia, Amsterdam and Praha, pp 155–163

Mylroie JR, Mylroie JE (2007) Development of the carbonate island karst model. J Caves Karst Stud 69:59–75

Nagra (National Cooperative for the Disposal of Radioactive Waste) (1990) Sondierbohrung Riniken [Exploration drilling Riniken]. Nagra Technischer Bericht, NTB 88-09, Baden, Germany

Nagymarosy A, Báldi T, Horváth M (1986) The Eocene-Oligocene boundary in Hungary. In: Pomerol C et al (eds) Terminal Eocene events. Elsevier, Amsterdam, pp 113–116

Nádor A (1994) Paleokarstic features in Triassic-Eocene carbonates: multiple unconformities of a 200 million year karst evolution, Buda Mountain, Hungary. Zbl Geol Paläont Teil I 1992(11/12):1317–1329

Palmer AN (1991) Origin and morphology of limestone caves. Geol Soc Am Bull 103:1–21

Palmer AN (1995) Geochemical models for the origin of macroscopic solution porosity in carbonate rocks. In: Budd AD, Saller AH, Harris PM (eds) Unconformities and porosity in carbonate strata. AAPG Memoir 63:77–101

Palmer AN (2000) Hydrogeologic control of cave patterns. In: Klimchouk A, Ford DC, Palmer AN, Dreybrodt W (eds) Speleogenesis, evolution of karst aquifers, National Speleological Society, Huntsville, AL, pp 77–90

Palmer AN (2007) Cave geology. Cave Books, Dayton, OH, 454 pp

Papp F (1940) Budapest gyógyvizei [Mineral waters of Budapest]. Hidrol Közlöny 20:68–80

Pentecost A, Jones B, Renaut RW (2003) What is a hot spring? Can J Earth Sci 40:1443–1446

Paschen H, Oertel D, Grünwald R (2003) Möglichkeiten geothermischer Stromerzeugung in Deutschland [Potential of geothermal electricity generation in Germany]. TAB Report no. 4, 124pp, TAB, Berlin

Pruess K (2008) On production behavior of enhanced geothermal systems with CO_2 as working fluid. Energy Convers Manage 49:1446–1454

Plummer LN, Back W (1980) The mass balance approach: application to interpreting the chemical evolution of hydrologic systems. Am J Sci 280:130–142

Plummer LN, Wigley TML (1976) Dissolution of calcite in CO_2-saturated solutions at 25°C and 1 atmosphere total pressure. Geochim Cosmochim Acta 40(2):191–202

Plummer LN, Wigley TML, Parkhurst DL (1978) Kinetics of calcite dissolution in CO_2-water systems at 5°C to 60°C and 0.0 to 1.0atm CO_2. Am J Sci 278(2):179–216

Rau GH, Knauss KG, Langer WH, Caldeira K (2007) Reducing energy-related CO_2 emissions using accelerated weathering of limestone. Energy 32:1471–1477

Rauch HW, White WB (1977) Dissolution kinetics of carbonate rocks. 1. Effects of lithology on dissolution rate. Water Resour Res 13:381–394

Rosenbauer RJ, Koksalan T, Palandri JL (2004) Experimental investigation of CO_2-brine-rock interactions at elevated temperature and pressure: implications for CO_2 sequestration in deep-saline aquifers. Symposium on Carbon Dioxide Capture and Sequestration held at the 227th National Meeting of the American-Chemical-Society, Anaheim, CA, 27 March–1 April 2004, pp 1581–1597

Sass I (2007) Geothermie und Grundwasser [Geothermics and groundwater]. Grundwasser 12(2):93

Smosna R, Bruner KR, Riley RA (2005) Paleokarst and reservoir porosity in the Ordovician Beekmantown Dolomite of the central Appalachian basin. Carbonates Evaporites 20:50–63

Stober I, Jodocy M (2009) Characteristics of geothermal reservoirs in the Upper Rhine Graben of Baden-Württemberg and France. Grundwasser 14:127–137

Takács-Bolner K, Kraus S (1989) The results of research into caves of thermal water origin. Karszt és Barlang Special Issue 31–38, Hungarian Speleological Society, Budapest

Tóth J (1962) A theory of groundwater motion in small drainage basins in central Alberta, Canada. J Geophys Res 67(11):4375–4387

Tóth J (1963) A theoretical analysis of groundwater flow in small drainage basins. J Geophys Res 68:4795–4812

Tóth J (1971) Groundwater discharge: a common generator of diverse geologic and morphologic phenomena. IASH Bull 16(1–3):7–24

Tóth J (1995) Hydraulic continuity in large sedimentary basins. Hydrogeol J 3(4):4–16

Tóth J (2009) Springs seen and interpreted in the context of groundwater flow-systems. GSA Annual Meeting, Portland, OR, 18–21 October 2009

Tóth J (1999) Groundwater as a geologic agent: an overview of the causes, processes, and manifestations. Hydrogeol J 7:1–14

Ufrecht (2006a) Hydrogeologie des Stuttgarter Mineralwassersystems [Hydrogeology of the mineral water system of Stuttgart]. Schrift Amters Umweltschutz 2006 (3):1–151

Ufrecht W (2006b) Zusammensetzung und Herkunft der Gase in den Säuerlingen von Stuttgart-Bad Canstatt und -Berg [Origin and composition of the gas in the carbogaseous springs of Stuttgart Bad Canstatt and Berg]. Schriftenreihe des Amters für Umweltschutz 2006(3):103–114

Underschultz JR, Otto CJ, Bartlett R (2005) Formation fluids in faulted aquifers: examples from the foothills of Western Canada and the North West Shelf of Australia. In: Boult P, Kaldi J (eds) Evaluating fault and cap rock seals. AAPG Hedberg Series no. 2, AAPG, Tulsa, OK, pp 247–260

Ungemach P, Antics M, Papachristou M (2005) Sustainable geothermal reservoir management. Paper 0517, World Geothermal Congress, Antalya, Turkey, 15–19 April 2005

Van Everdingen RO (1991) Physical, chemical, and distributional aspects of Canadian springs. Mem Entomol Soc Can (155): 7–28

Vathaire J, Boissavy C, Gérard A (2006) Géothermie: aquifères et eaux souterraines en France [Geothermics: aquifers and groundwater in France]. BRGM, Orleans, France

White DE (1957) Thermal waters of volcanic origin. Bull Geol Soc Am 68:1637–1658

Wolfgramm M, Bartels J, Hoffmann F, Kittl G, Lenz G, Seibt P, Schulz R, Thomas R, Unger HJ (2007) Unterhaching geothermal well doublet: structural and hydrodynamic reservoir characteristic; Bavaria (Germany). European Geothermal Congress 2007, Unterhaching, Germany, 30 May–1 June 2007

Worthington SRH (2001) Depth of conduit flow in unconfined carbonate aquifers. Geology 29:335–338

Worthington SRH, Ford DC (1995) High sulfate concentrations in limestone springs: an important factor in conduit initiation? Environ Geol 25:9–15

Yoshimura K, Nakao S, Noto M, Inokura Y, Urata K, Chen M, Lin PW (2001) Geochemical and stable isotope studies on natural water in the Taroko Gorge karst area, Taiwan: chemical weathering of carbonate rocks by deep source CO_2 and sulfuric acid. Chem Geol 177:415–430

Zhou HY, Zhou X, Chai R, Yu L, Liu CH, Li LP (2008) Occurrence and evolution of the Xiaotangshan hot spring in Beijing, China. Environ Geol 53(7):1483–1489