

## Hypogene karst: speleogenetic mechanisms and geochemical methods of diagnostics

Yuri Dublyansky

Innsbruck University, Innrain 52, Innsbruck 6020, Austria, juri.dublyansky@uibk.ac.at

Two features define *hypogene speleogenesis*: (1) recharge of soluble formation from below, independent of recharge from overlying or immediately adjacent surface; and (2) predominance of the deep-seated sources of aggressiveness of karst water, independent of the environment at the overlying or immediately adjacent surface. Many “exotic” types of karst, such as hydrothermal karst or sulfuric acid speleogenesis are varieties of the hypogene speleogenesis.

Two principal types of speleogenetic mechanisms can be distinguished. *Geochemical mechanisms* are those responsible for creation (renewal) of aggressiveness of karst water. *Hydrogeological mechanisms* are those ensuring recharge of soluble formation by aggressive water and eventual removal of matter from the site of karstification.

Specific mechanisms depend on the zone in the Earth’s crust where hypogene karst develops. It is convenient to distinguish the following three categories (zones): endokarst, deep-seated hypogene karst, and shallow hypogene karst.

*Endokarst zone* occurs at depths exceeding 4–5 km, where the total pressure exceeds the strength of the rock, and the pressure of fluid approaches lithostatic values. Solutional porosity of carbonate rocks in endokarstic zone may reach 18–28%, and the porosity of aluminosilicate rocks – 35–30%. Pores and cavities may exist only if they are filled with fluid, which prevents them from failure. Although this type of karst apparently does not produce traversable caves (the size of endokarstic cavities does not normally exceed several centimeters), it may play a significant role in creation of deep-seated reservoirs for hydrocarbons.

*Deep-seated (low-gradient) hypogene karst zone* covers a range of depths (approximately 0.3 to 4.0 km) where the (geo)thermal gradients are relatively small, pressure is close to hydrostatic, and the influence of the temperature changes at the Earth’s surface is practically absent. The water aggressiveness may develop in response to the change in physicochemical parameters of fluids moving toward the surface, such as the decrease in temperature and pressure, due the mixing of different waters, and due to the change in bedrock chemistry/lithology.

*Shallow (high-gradient) hypogene karst zone* defines the area near the free surface of the hypogene water – both below and above it. In this zone the pressure is relatively low (down to atmospheric) and temperature may range from boiling to ambient. The temperature gradients may be significant, which lead to the appearance of some specific and powerful processes, like thermal convection and condensation corrosion. Also, in this zone upwelling hypogene waters meet oxidized meteoric waters, resulting in strong redox gradients. This may induce specific reactions and processes like H<sub>2</sub>S oxidation, mixing corrosion, and cooling corrosion.

Most of the hypogene caves in carbonate rocks are associated with either the CO<sub>2</sub>–bearing waters or with waters containing H<sub>2</sub>S.

### CO<sub>2</sub>-RICH WATER

Waters rising from significant depth are commonly thermal and are saturated with CO<sub>2</sub>, which may originate from metamorphism of carbonate rocks, igneous activity, or from degradation and oxidation of organic matter. Solubility of CO<sub>2</sub> in water depends on both temperature and pressure. Water saturated with respect to CO<sub>2</sub> at deep crustal levels (e. g., 2–4 km) becomes supersaturated as it moves toward the surface. Hence, CO<sub>2</sub> must exsolve in the gaseous phase and leave the system. Rising carbonic thermal waters also cool down. Due to inverse relationships between carbonate solubility and temperature, they may acquire and maintain aggressiveness – even at decreasing CO<sub>2</sub> levels. The solubility of CaCO<sub>3</sub> increases evenly along the ascending fluid path, but near the land surface (water table) it drops drastically. Such nonlinear behavior leads to the appearance of two geochemical zones: a zone of carbonate dissolution at depth and a zone of carbonate precipitation closer to the surface.

## OXIDATION OF H<sub>2</sub>S

In contrast to carbon dioxide-rich water, aggressiveness of the hydrogen sulphide-rich water is generally limited in the deep-seated settings, but increases dramatically when such water mixes with oxygenated water or contacts with the atmosphere, which results in rapid oxidation of H<sub>2</sub>S to H<sub>2</sub>SO<sub>4</sub>. The effect is attenuated when CO<sub>2</sub> generated by the H<sub>2</sub>SO<sub>4</sub>-CaCO<sub>3</sub> reaction is degassed. Such speleogenetic mechanism, known as Sulfuric Acid Speleogenesis (SAS) tends to occur at shallow levels, both below and above the water table. The second, subaerial setting is characterized by a specific speleogenetic mechanism, involving dissolution and subsequent replacement of calcite by gypsum and its consequent removal (*replacement corrosion*).

Unlike 'pure carbonic acid' hypogene karst, which is a common phenomenon, the sulphuric acid karst is almost always a mixed process. Most natural H<sub>2</sub>S-rich groundwaters have also elevated contents of CO<sub>2</sub>; additional CO<sub>2</sub> is produced by dissolution of carbonate rocks by sulphuric acid. Under certain circumstances this additional CO<sub>2</sub> could significantly enhance carbonate dissolution.

## MIXING OF WATERS (CO<sub>2</sub> AND H<sub>2</sub>S)

When waters containing different amounts of dissolved CO<sub>2</sub> or H<sub>2</sub>S mix the aggressiveness of the resulting solution is greater than that of each of the initial solutions. Even when mixing waters are saturated with respect to carbonate, the resulting water can be aggressive. Because situations in which waters with varying chemistry mix are rather common in hydrogeology, this process – mixing corrosion – is an important speleogenetic mechanism.

## CONDENSATION

Sizable cavities with characteristic solutional morphology can develop above the (hypogene) water table by mechanism of condensation corrosion. Water which evaporates from surface of an underground thermal lake condenses on cooler bedrock. Dissolving CO<sub>2</sub> from the underground atmosphere, condensate becomes aggressive with respect to carbonate. Importantly, this speleogenetic mechanism – condensation corrosion – can operate above the underground lakes of non-karstic (e. g., tectonic) origin, containing non-aggressive or even supersaturated with respect to carbonate bedrock water.

## HYPOGENE SPELEOGENESIS IN NONCARBONATE ROCKS

The mechanisms described above pertain to the most common variety of hypogene karst developing in carbonate rocks. Besides, hypogene caves have been reported from silicate rocks (quartzite, scarn, jasperoid, quartz veins), sulfate rocks (gypsum, anhydrite), and rock salt.

## GYPSUM AND ANHYDRITE

Hypogene caves in gypsum and anhydrite are the second most-common lithologic type of hypogene karst. The solubility of gypsum in most natural water is roughly 10-20 times that of calcite. The solubility decreases with increasing temperature (retrograde solubility) and increases with increasing pressure. Several chemical and physical factors may considerably increase or renew gypsum solubility: (a) the presence of other salts in water (increasing ionic strength of solution increases gypsum solubility by up to a factor of 3); (b) anaerobic reduction of sulphates in the presence of organic matter; (c) de-dolomitization of dolomite bedrock; and (d) mechanical stress affecting the bedrock. The mechanism of gypsum dissolution by water enriched in CO<sub>2</sub> (which is common in deep-seated waters) is more complex and may involve additional dissolution of gypsum and deposition of calcite.

## DIAGNOSTICS OF HYPOGENE KARST

The presence in the cave of water with deep-seated characteristics is the surest indicator of the cave's hypogene origin. Obviously, this criterion applies only to active hypogene karst. Identification of the hypogene character of fossil or paleokarst relies on various indicators which must be applied in conjunction. The primary indicators are macro-, meso-, and micro-morphology of caves. Important

insights can be gained by reconstructing the position of the caves in the larger-scale hydrogeological structure.

In this presentation mineralogical and geochemical approaches are discussed. Besides helping to identify the involvement of the hypogene speleogenesis, these approaches help to decipher specific processes that operated during karstification and to reconstruct parameters of hypogene fluids (chemistry, temperature, isotopic composition, gas composition, etc.).

Minerals occurring in hypogene caves can be subdivided in two broad categories: (1) speleogenetic (i.e., whose deposition is directly related to karst process) and (2) non-speleogenetic (whose presence is due to processes other than karst).

Calcite is the most common speleogenetic mineral in carbonate hypogene caves developed in CO<sub>2</sub>-dominated systems, and gypsum is the main speleogenetic mineral in caves developed by SAS mechanism. Other speleogenetic minerals reported from SAS caves comprise alunite, natroalunite, dickite, tyuyamunite, metatyuyamunite, aluminite, and hydrobasaluminite. Hypogene caves in gypsum and anhydrite are typically poor in mineralization, represented by primarily by gypsum and calcite.

Non-speleogenetic quartz, barite, fluorite, and various sulfides are commonly reported from the deep-seated carbonate hypogene caves. The list of minerals in ore-related hypogene karst can be quite large.

#### CHARACTER OF CAVE DEPOSITS

Large euhedral calcite crystals, palisade aggregates, thick crusts, and sediments reflecting stable hydrodynamic conditions are common in deep-seated hypogene caves. The size of individual crystals can be as large as 10-30 and even 100 cm. The crystal morphology is normally simple, dominated by scalenohedra (dogtooth spar). In contrast, the deposits of shallow karst caves commonly reflect a more dynamic environment. Euhedral crystals are rare, and the size of crystals in aggregates ranges from several millimeters to a few centimeters. The dominant crystal morphology is a combination of scalenohedra and prisms with the crystal tip blunted by flat rhombohedra (nailhead spar). Mineral surfaces might be contaminated by clay, which indicate that the paleo waters were dynamic enough to carry the particulate matter. In addition to subaqueous deposits, two more types of speleothems occur in shallow hypogene karst: waterline deposits (rafts, folia, cave cones), and subaerial deposits (e. g., cave popcorn). These two types are also common in cold karst.

#### GEOCHEMICAL STUDIES OF SECONDARY MINERALS

The presence of secondary minerals in hypogene caves is beneficial, because it opens various avenues for study of hypogene karst process. Fluid inclusions in minerals can be studied in order to determine temperature of mineral-forming waters, their salinity, isotopic composition, and composition of the dissolved gases. Calcite and gypsum can be studied isotopically ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{34}\text{S}$ ), providing further insights into the sources of dissolved matter and parameters of fluids. In some cases the minerals can be dated (U/<sup>230</sup>Th, U/Pb and <sup>40</sup>Ar/<sup>39</sup>Ar (alunite) methods). It is to be noted that any information obtained from studies of minerals is related to the specific stage of speleogenesis, at which the minerals were deposited.

#### ISOTOPIC STUDIES OF THE BEDROCK

Hypogene fluids circulating through carbonate bedrock can alter the isotopic composition ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) of the rock. The extent of alteration depends on a number of parameters, such as the diffusive permeability of the rock matrix, difference between isotopic composition of rock and water, temperature, and time. Alteration zones in the walls of the hypogene caves have been found at a number of hypogene karst sites and in some cases the data provided information on the parameters of fluids.

## HYDROGEOLOGICAL SETTINGS/MECHANISMS

Hydrogeological speleogenetic mechanisms of the hypogene karst characterize major driving forces which ensure that (a) water reaches the soluble formation and leaves it, carrying the dissolved load, and (b) water acquires or maintains aggressiveness, allowing enlargement of cavities. The flow of groundwater may occur in confined or unconfined regimes and may involve free (buoyant) convection, forced convection, gravity-driven flow, etc. Setting of stratified confined (artesian) aquifer is particularly conducive for the development of cross-formational flows, in the course of which waters with different mineralization mix and acquire additional aggressiveness.

### **Hydrogeology of the Buda Thermal Karst (Hungary) – new models for the discharge zone**

Anita Erőss, Judit Mádl-Szőnyi

Department of Physical and Applied Geology, Institute of Geography and Earth Sciences, Eötvös Loránd University, 1/c Pázmány Péter sétány, 1117 Budapest, Hungary, anita.eross@geology.elte.hu

Europe's largest naturally flowing thermal water system can be found in Budapest. The springs and wells that supply the famous spas of Budapest discharge from a regional Triassic carbonate rock aquifer system. As the result of the interaction of discharging waters, extensive cave systems has developed and still developing today. These caves belong to the group of hypogenic caves, and their special morphology and peculiar minerals make Budapest, beside the city of spas, also “the capital of caves”.

According to the recent developments in the speleogenetic theories (Klimchouk 2007, Goldscheider *et al.* 2010), hypogenic karsts and caves are viewed in the regional flow system concept of Tóth (1963), and can be considered as the manifestations of flowing groundwater (Tóth 1999, Tóth 2009, Mádl-Szőnyi & Erőss 2011). As a basic approach of this study, the virtual spring concept of Tóth (2009) was applied, which considers all discharge phenomena together as one single entity in the terminal area of a groundwater flow-system, and the investigation of which plays a crucial role in the understanding of the flow system itself.

In this study the discharge areas of the Buda Thermal Karst were investigated to determine how the discharging fluids and adjoining phenomena (e. g. caves, mineral precipitates) can be telltales of their parent fluid systems, the processes acting along the flow path and operating directly at the vicinity of the discharge zone.

Being a marginal area at the boundary of uplifted carbonates and a sedimentary basin, the Buda Thermal Karst serves as a discharge zone of the regional fluid flow. This implies that it may receive fluid components (karstic and basinal) from several sources resulting in a wide range of discharge features including springs, caves, and mineral precipitates. A comprehensive hydrogeological study was carried out for the investigation of these phenomena and for the characterization of processes acting today at the discharge zone of the Buda Thermal Karst. Methods included hydrogeochemical, mineralogical and microbiological investigations.

Among the results of the study, several processes were identified which can be responsible for cave development and formation of minerals, among them mixing corrosion and microbially mediated sulphuric acid speleogenesis have crucial role. Furthermore, the role of the adjacent sedimentary basin was reevaluated. Based on the results of this study, new, differentiated conceptual flow and process models were developed for the study areas.

These results bring a new insight into the processes acting at a regional discharge zone which could be responsible for hypogenic cave development. It was demonstrated that several processes can be simultaneously active in karst development. These processes are connected to the regional discharge zone as the manifestation of flowing groundwater.

**Keywords:** hypogenic karst, flow systems, regional discharge area, Buda Thermal Karst

### References

- Goldscheider, N., Mádl-Szőnyi, J., Erőss, A., Schill, E., 2010, Review: Thermal water resources in carbonate rock aquifers. *Hydrogeology Journal*, 18: 1303–1318.
- Klimchouk, A. B., 2007, Hypogene Speleogenesis: Hydrogeological and Morphogenetic Perspective Special Paper no.1, National Cave and Karst Research Institute, Carlsbad, NM, 106 p.
- Mádl-Szőnyi, J., Erőss, A., 2011, Hypogenic karstification processes and products in flow system framework. In: Bertrand, C., Carry, N., Mudry, J., Pronk, M., Zwahlen F. (eds.) *Proc. H2Karst, 9th Conference on Limestone Hydrogeology, Besançon (France)* ISBN:978-2-7466-3694-1, pp. 315–318.
- Tóth, J., 1963, A theoretical analysis of groundwater flow in small drainage basins. *Journal of Geophysical Research*, 68(16): 4795–4812.
- Tóth, J., 1999, Groundwater as a geologic agent: An overview of the causes, processes, and manifestations. *Hydrogeology Journal*, 7(1): 1–14.
- Tóth, J., 2009, Springs seen and interpreted in the context of groundwater flow-systems, GSA Annual Meeting 2009 (18–21 October 2009) Portland, Geological Society of America Abstracts with Programs, 41(7) p. 173.

### Hypogene vs epigene caves: the S and O isotope fingerprint

Bogdan P. Onac

University of South Florida, Department of Geology, Tampa, FL, USA, bonac@usf.edu

The classical epigene speleogenetic model in which CO<sub>2</sub> is considered the main source of acidity has been challenged over the last three decades by observations that revealed cave passages unrelated to groundwater drainage routes and surface topography. Most of these passages show unusual morphologies, such as condensation cupolas, floor feeders (i.e., inlets for deep-seated fluids), huge irregular-shaped rooms that terminate abruptly, and without exceptions, contain abundant gypsum deposits, and often a rich and diverse mineral association (sulfate-dominated). This evidence prompted scientists to suggest a new theory (i.e., sulfuric acid speleogenesis, SAS) of cave development. In the hypogenic SAS model, the source of acidity is the sulfuric acid produced by oxidation of H<sub>2</sub>S (originating from sulfate reduction or petroleum reservoirs) near or at the water table, where it dissolves the limestone bedrock and precipitates extensive gypsum deposits. SAS is now thoroughly documented from numerous caves around the world, with the best examples coming from the Guadalupe Mountains (NM), Frasassi caves (Italy), selected caves in France, Cueva de Villa Luz (Mexico), and Cerna Valley (SW Romania).

To date, discrimination between epigene and hypogene speleogenetic pathways is made using cave morphology criteria, exotic mineral assemblages, and the predominantly negative δ<sup>34</sup>S values for the cave sulfates. This presentation highlights the role sulfur and oxygen stable isotope analyses have in discriminating between epigene and hypogene caves.

Based on a number of case studies in caves of the Cerna Valley (Romania) we found that relatively S-depleted isotopic composition of cave minerals alone does not provide enough information to clearly distinguish SAS from other complex speleogenetic pathways. In fact, δ<sup>34</sup>S values of SAS by-products depend not only on the source of the S, but also on the completeness of S redox reactions. Therefore, similar studies to this are needed to precisely diagnose SAS and to provide information on the S cycle in a given karst system.

Integrating cave mineralogy, passage morphology, and geochemical studies may shed light on the interpretation of polygenetic caves, offering clues to processes, mechanisms, and parameters involved in their genesis.

**Keywords:** sulfur isotopes, mineralogy, geochemistry, hypogene speleogenesis