Morphological and textural variety of calcite-aragonite precipitations from Erma Reka geothermal reservoir

Морфоложко и текстурно разнообразие на калцит-арагонитови отложения от геотермалния резервоар Ерма река

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Travertines, freshwater tufa, and speleotherms are among the most important continental climate derived deposits (Ford, Pedley, 1996). Their formation is controlled by a number of factors including CO_2 degassing due to inorganic and organic processes. Travertines are carbonate deposits formed in hydrothermal water that contains a high concentration of dissolved Ca^{2+} and carbonate species. In addition to highly saturated water chemistry, rapid precipitation requires intensive water flow, which enhances the diffusion of Ca^{2+} and CO_3^{2-} to the substrate and activates CO_2 degassing. Thus, precipitation rates within a travertine system vary with hydrological conditions (Liu et al., 1995), often resulting in formation of various textures associated with microbial components (Chafetz, Folk, 1984).

In this work, we focus on the morphological and textural variety of carbonate precipitations from natural hot water of Erma Reka geothermal source as an unique combination with a polymetallic Pb-Zn mineralization that is located in the Rhodopes massif, South Bulgaria, close to the Greek border. The reservoir is cross bordered and is discharged in the Therme springs, North Greece.

Hydrogeological background

Numerous studies and complex exploration have been performed in the Erma Reka region (Andreev, 1995) in addition of about 60 drilled wells. They crossed huge cavities and caverns up to 400–1300 m without being able to reach their bottom. The thermal water is accumulated in karst and cavernous marble body, located at a depth of 450 m below the surface and embedded in a gneiss complex (Petrov, Andreev, 1973). The thermal water from Erma Reka reservoir discharges through several springs in the valley of Ilidza, Therme springs (Minissale et al., 1989). The TDS ranges from 0.6 to 1.3 g/l and correlates with the main species ratios HCO^{3-}/SO_4^{2-}, Ca^{2+}/Na^+, and with H_2SiO_3, which reaches up to 250 mg/l (Andreev, 1995). Hot water upwards through the faults and fractures in the gneisses to the piezometric surface of the absolute elevation +490 m. The faults have also favoured in depth conditions for cold waters penetration. A hydraulic link exists between cold and warmed fractured unconfined waters formed in gneisses and confined waters containing in the upper zone of the marble body. The rainfall influences on the variation of water level in the whole massif. When cold waters penetrate in depth the thermal water piezometric level becomes deeper as a result of cooling. The thermal water temperature (T) is from 30 to 90 °C and several factors control the deposition of oversaturated water with respect to corresponding mineral phases. It was found that the hot water becomes unsaturated at T below 50–60 °C in regard to calcite.

Morphological peculiarities

Various textures of carbonate precipitations from the Erma Reka underground mines as well as samples from the surfaces travertine depositions from Therme springs are studied.

Erma Reka. The carbonate precipitations from underground mines were observed as encrustations on wallrocks fragments or as incrustations in casing wells and others (Fig. 1a). The incrustations grow from the margins towards the channel axis of the casing well and represent concentric banded layers. Distinct lamination was observed in this travertine as the superposition of crystalline and porous layers. The XRD analyses are evidence that mineralogical composition of the crystalline section is pure calcite while porous masses are aragonite (~85%). The crystalline layer consists of laterally combined radial crystal fans ~2–3 mm in height. SEM images showed that these layers are built of fans of elongated and distorted calcite crystals. In

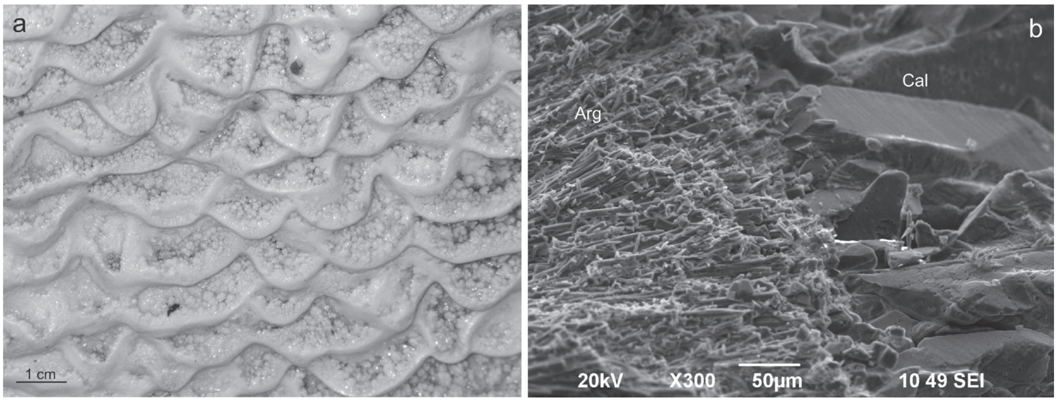

Fig. 1. Travertine terraces developed on the slope in front of the water flow on underground wall, Gyudyurska mine (*a*); boundary between distorted calcite crystals (Cal) and acicular fine aragonite crystals (Arg), Erma Reka, SEM (*b*)

contrast, the porous layer consists of spherical aggregations of acicular fine aragonite crystals Fig. 1b).

Therme springs. Precipitation from these spring waters has produced the calcite deposits with their spectacular arrays of terraces and rim stones pools. Microterrace pools developed on the proximal slope in front of spring water have been observed. The white slopes are covered mostly by crystalline dendritic calcite aggregates, whereas lime mud, pisoids, are common in the terrace pool. Paper thin rafts and biomorhic forms are characteristic from older parts of the travertine mound. Present day travertine formed around spring vents from Therme region show similar textural characteristics as the carbonate precipitations observed on underground wall of Gyudyurska mine.

Discussion and conclusions

Although calcite is the dominant mineral from both sites, aragonite is present in the concentric banded crystalline crust from underground Erma Reka casing wells. The aragonite and calcite found at Erma Reka were original precipitates with no evidence that the calcite has been formed by inversion of the aragonite (Perdikouri et al., 2011). In some deposits, aragonite precipitation has been attributed to periods of rapid CO_2 degassing and the consequent high levels of supersaturation (Jones, Renaut, 2010). Occasionally, aragonites needle aggregates may have microbial nuclei such as bacteria and pollen, on which they grew (Guo, Riding, 1992). The aragonite in the fine crystalline porous crust examined in this study is formed from needle aggregates that do not appear to include any microbial nucleus. Spherulitic aragonite growth, without microbial nucleus, has been ascribed to high disequilibrium conditions or inorganic processes that include rapid CO_2 degassing.

Travertines, derived from Erma Reka thermal waters are widespread and are still forming today in underground mine shafts and around the surface spring in the valley of Ilidza river, Therme area. Understanding the process of thermal water scaling is essential for the future use for a space heating and healing prevention purposes from Erma Reka geothermal reservoir. Very similar textural characteristics have also been described for the Pamukkale travertine (Özkul et al., 2013), designed as a UNESCO world heritage site.

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