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Microbial bio-mineralization processes in hydrothermal travertine: the case study of two active travertine systems (Tuscany, Italy).

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Modern hydrothermal travertine deposits, occurring today at Bagni San Filippo (Radicofani Basin) and at Bagni di Saturnia (Albegna Valley) in Tuscany, Central Italy, have been investigated with the main purpose to improve the understanding of the processes that control calcium carbonate precipitation in hydrothermal-spring settings. Present-day thermal activity at Bagni di Saturnia is characterized by a 37.5°C thermal spring with a rate of about 800 l/s, with a pH of ca. 6.4. Thermal water discharges at Bagni San Filippo reach a rate of 20 litres per second at a maximum temperature of 50°C and a pH of ca. 7. The springs expel water enriched in H2S-CO_2-SO42- and HCO_3- and divalent cations (Ca and Mg). In the studied areas, travertine precipitation occurs in association with living microbial mats and biofilms, composed of a heterogeneous community of green algae, filamentous cyanobacteria and other types of prokaryotes, anoxygenic photosynthetic bacteria and heterotrophic heat-tolerant bacteria, with a variable amount of extracellular polymeric substances (EPS). Nine categories of fabric types, dominantly calcite and aragonite in composition, showing a wide range of macro- and micro-porosity, have been identified. High magnification analysis of dendritic and laminated boundstone, crystalline crust cementstone, raft boundstone, coated bubble boundstone, micrite mudstone and coated reed boundstone fabric types, suggests that precipitation occurs in association with organic matter. Diatoms, cyanobacteria filaments and other bacteria are then associated with the EPS and often appear totally or partially entombed (passively or actively) in it. Organic extracellular polymeric substances (EPS) and often the external surface of cyanobacterial sheaths are the location where the calcite minerals nucleate and grow. Precipitation begins with organomineral nano-globules consisting of nanometre-size, from sub-spherical to globular-like, raised structures (5 to 80 nm diameter). The nano-globules, that represent the first stage of precipitation, coalesce and organize in rods. The assemblage of these rods gives rise to triangular-like morphologies that, gradually, evolve to form well developed calcite crystals, substituting/replacing the organic matter. The presence of EPS, microbs, and calcite mineral phase suggest that biological activity and degradation of organic matter may play a fundamental role in the travertine formation. Acicular crystals of aragonite, nucleated also on organic compound and characterized by the lack of nano-globules, surround the calcite crystals aggregates. The precipitation of aragonite may suggest a change in micro-environmental conditions that involve a predominantly abiotic mechanism of precipitation. Gypsum crystals were mainly individuated in the upper zone of microbial mats and filamentous organic structures connected to the crystals have been observed. A biologically induced process is also claimed for the identified framboidal pyrite related to possible sulphate reducing bacteria. These observations suggest that biological activities are crucial in travertine precipitation. Travertine precipitation is not only related to abiotic parameters of calcium equilibrium, such us physicochemical carbon dioxid degassing and elevated temperature of the hydrothermal water. This study 1) demonstrates that organomineralization processes are not only exclusive of marine carbonate and tufa and 2) confirms the importance of micro- and nano-scale investigation to discriminate between biotic versus abiotic origin of the precipitates.