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Microbial effects on biofilm calcification, ambient water chemistry and stable isotope records in a highly supersaturated setting (Westerhöfer Bach, Germany)

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ABSTRACT

Cyanobacteria-dominated biofilms in a CO_2-degassing karst-water creek (Westerhöfer Bach, Germany) were investigated with regard to the effects of microbial activity on $CaCO_3$ precipitation, water chemistry of micro- and macroenvironments, stable isotopic records, and tufa fabric formation. *Ex situ* microelectrode measurements of pH, O_2, Ca^{2+} and CO_3^{2-} revealed that annually laminated calcified biofilms composed mainly of filamentous cyanobacteria (tufa stromatolites) strongly induced $CaCO_3$ precipitation by photosynthesis under illumination, but inhibited precipitation by respiration in the dark. In contrast, endolithic cyanobacterial biofilms and mosses did not cause photosynthesis-induced precipitation under experimental conditions. No spontaneous precipitation occurred on bare limestone substrates, despite high calcite supersaturation of the ambient water. Mass balance calculations suggest that biofilm photosynthesis was responsible for 10–20% of Ca^{2+} loss in the creek, while the remaining Ca^{2+} loss derived from physicochemical precipitation on branches, leaves and as fine-grained calcite particles. Neither analysis of bulk water chemistry nor oxygen nor carbon stable isotopic records of the tufa stromatolites confirmed photosynthetic effects, despite the evident photosynthesis-induced calcite precipitation. Oxygen stable isotopic values reflected seasonal changes in water temperature, and carbon stable isotope values probably recorded carbon isotopic composition of dissolved inorganic carbon in the creek water. Annual lamination and fabric formation of the tufa stromatolites is suggested to vary with photosynthesis-induced calcite precipitation rates that are affected by temperature dependency of diffusion coefficients. Photosynthesis-induced precipitation resulted in encrusted cyanobacterial sheaths, reflecting syntaxial overgrowth of microcrystalline cyanobacterial tubes by microspar, instead of microcrystalline sheath impregnation, which was previously suggested as an indicator of photosynthesis-induced precipitation. Therefore, sheath impregnation or encrustation by $CaCO_3$ cannot be used to distinguish photosynthesis-induced from physicochemically-induced $CaCO_3$ precipitation.

1. Introduction

Freshwater carbonates of karst-water creeks and lakes, commonly called “tufa” (Ford and Pedley, 1996), provide an important high-resolution archive of the Quaternary palaeoclimate (e.g., Andrews and Brasier, 2005; Andrews, 2006). Particularly, annually laminated porous tufa deposits (tufa stromatolites; Riding, 2000) in karst creeks provide accurate information on seasonal changes of water temperature, hydrochemistry, and rainfall events (Matsuoka et al., 2001; Ihlenfeld et al., 2003; Kano et al., 2004, 2007). In addition, tufa stromatolites are considered potential analogues of ancient marine stromatolites (Shiraishi et al., 2008; Bissett et al., in press) because they resemble many fossil marine stromatolites mainly formed by *in situ* precipitation, contrary to present-day marine stromatolites mainly forming by particle agglutination (Awramik, 1984). Therefore, tufa stromatolites also provide essential information on the mechanisms of microbial calcification, which may help to understand the palaeoenvironment and palaeoecology of the Phanerozoic and Precambrian earth (e.g., Riding, 1982, 2006; Grotzinger and Knoll, 1999; Arp et al., 2001a).

The depositional process of tufa is still a matter of controversy because physicochemical CO_2-degassing and photosynthesis, can both shift the carbonate equilibrium to cause calcite precipitation, occur simultaneously in tufa-forming creeks. Although it has been assumed for decades that both organic and inorganic mechanisms are involved in tufa precipitation (e.g., Golubic, 1973; Ford and Pedley, 1996), it has been difficult to evaluate the exact role of microorganisms because of technical limitations. Previous studies based on bulk water chemistry analysis demonstrated that calcite supersaturation of creek water is primarily attained by physiochemical CO_2-degassing (e.g., Jacobson and Usdowski, 1975), and microbial effect is negligible on tufa formation. In addition, it is thought that a significant effect of

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photosynthesis should result in diurnal cycles of pCO_2, pH, $\delta^{13}C$ and calcite saturation state, but such diurnal cycles have rarely been detected (Usdowski et al., 1979; Dandurand et al., 1982; Merz-Preiß and Riding, 1999). Moreover, there has been no clear signal of photosynthesis detected in carbon stable isotopic records of tufa stromatolites (Matsuoka et al., 2001). Therefore, many researchers are nowadays convinced that inorganic precipitation is the major process in fluvial tufa deposition, whereas microbial effects are thought to be restricted to low pCO_2 and/or slow flowing settings such as stagnant pools and lakes (Andrews et al., 1997; Merz-Preiß and Riding, 1999; Pedley, 2000; Arp et al., 2001b; Chen et al., 2004).

However, studies based on microelectrode measurements have recently revealed that photosynthesis induces $CaCO_3$ precipitation on the surface of tufa stromatolites under illumination, while respiration inhibits precipitation in the dark, even in a highly supersaturated fast-flowing environment (Shiraishi et al., 2008; Bissett et al., in press).

The aim of this work was to resolve these discrepancies and elucidate the process of tufa deposition by quantifying the effects of photosynthesis. Firstly, we evaluated the metabolic effects of several types of tufa biofilms by geomicrobiological methods including pH, O_2, Ca^{2+} and CO_3^{2-} microelectrode profiling and the detection of heterotrophic bacteria and EPS (extracellular polymeric substances) that potentially affect biofilm calcification. Secondly, analysis of bulk water chemistry, including 21 h-monitoring and stable isotope analysis of water and tufa deposits, was conducted to evaluate the microbial metabolic effects on bulk water chemistry and deposits.

2. Study area and environmental settings

The investigated tufa-forming karst-water creek, the Westerhöfer Bach, is located west of the Harz Mountains, Central Germany (51°45′N, 10°5′E; Fig. 1A). The creek water recharges from the limestone-dominated upper Muschelkalk Group (Anisian–Ladinian), which is underlain by the middle Muschelkalk Group (Anisian), which is composed of dolomite with gypsum lenses (Jacobson and Usdowski, 1975). The initial 330 m section of the creek, where active tufa formation occurs, was selected for this study. Here, the width of the creek is 1–2 m and water flows ESE (Fig. 1B). There is one main spring, and lateral seepage influx is negligible except for one recognizable subspring that enters the creek 288 m downstream from the main spring. At the spring site, water flows gently over limestone gravels colonized by non-calcifying biofilms (Fig. 2A), mainly composed of endolithic cyanobacteria. Continuous tufa deposition starts approximately 150 m downstream from the spring where water flow becomes turbulent (Figs. 1B, C and 2B). Tufa stromatolites usually develop in the center of the flow path. Their biofilm communities are mainly composed of filamentous cyanobacteria accompanied by diatoms, green algae and a number of heterotrophic bacteria (Shiraishi et al., 2008). At both sides of the main flow path and in stagnant pools of the middle and lower creek section, conspicuous amounts of calcified particles and fragments, such as branches, leaves, and fine-grained calcite sands accumulate, and sometimes oncoids are recognized (Fig. 2C, D). Mosses mostly colonize the low flowing middle to lower creek and inactive tufa deposits, although some occur in the fast-flowing reaches. In the lower section, the creek branches off and rejoins at several locations. A tufa cascade about 2 m in height developed 250 m downstream (Fig. 2E) of the spring. After this cascade, water flows through a narrow channel (Fig. 2F) and then over widely developing tufa stromatolites in the lowermost part of the creek (Fig. 2G, H). Typically, tufa stromatolites exhibit a green colour during summer (Fig. 2G), while brownish biofilms develop in the marginal part of the flow path during autumn (Fig. 2H).

Five sampling sites (WB1.0–WB5.0; Fig. 1B) were chosen for main investigations, and some complementary sites along the creek were also

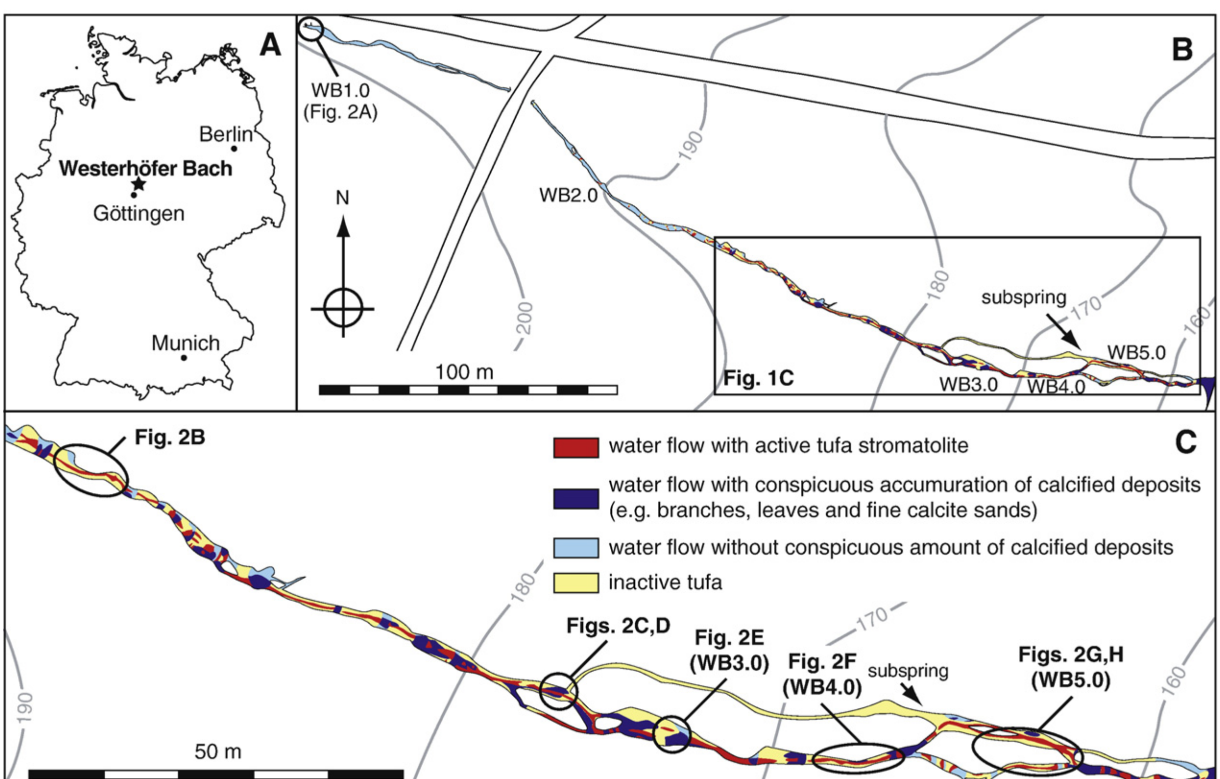

Fig. 1. (A) Location of the Westerhöfer Bach. (B) Map of the Westerhöfer Bach. (C) Detail of (B) showing the distribution of active tufa stromatolites, inactive tufa, calcified deposits, and areas without conspicuous amounts of calcified particles in the middle and lower creek section.