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## Geochemical insights into an active calcareous tufa depositing system in southern Germany

Simon M. Ritter<sup>1,a</sup>, Margot Isenbeck-Schröter<sup>a</sup>, Andrea Schröder-Ritzrau<sup>b</sup>, Christian Scholz<sup>a</sup> and Norbert Frank<sup>b</sup>

<sup>a</sup>*Institute of Earth Sciences, Heidelberg University*

<sup>b</sup>*Institute of Environmental Physics, Heidelberg University*

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### Abstract

Calcareous tufa deposition in bicarbonate-rich karstic spring waters is essentially linked to complex microbiological communities that alter the geochemistry of the deposited tufa and hydrochemistry of the creek water. A monthly monitoring of the creek water chemistry of a natural tufa depositing site in the Franconian Alb in southern Germany reflects the tufa formation well, which is expressed in a decrease of calcium and bicarbonate concentrations and  $SI_{\text{calcite}}$  oversaturation. The accompanying decrease of barium ions is most likely due to chemoselective chelation by Extracellular Polymeric Substances (EPS) of the tufa biofilms that favour divalent ions with low charge densities in the order of  $Ba > Sr > Mg$ . Tufa geochemistry is altered with respect to increasing Mg/Ca ratios downstream reflecting increasing Mg/Ca ratios downstream of the creek water due to continuing low-Mg-Calcite precipitation. Especially the decrease of barium holds the potential to monitor seasonal variabilities of the relative portion of biofilm influence on tufa formation, which is important regarding the use of calcareous tufa as an archive of paleoclimate information.

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### 1. Introduction

Calcareous tufa is formed by precipitation of calcium carbonate under subaerial cool-ambient temperature conditions in various depositional systems, where calcium and bicarbonate-rich waters are involved, such as creeks, springs or lakes in limestone karstic settings<sup>1</sup>. While the calcite precipitation in such settings is partially solely

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\* Corresponding author. Tel.: +49 6221 546004; fax: +49 6221 545503  
*E-mail address:* [simon.ritter@geow.uni-heidelberg.de](mailto:simon.ritter@geow.uni-heidelberg.de)

physical, due to CO<sub>2</sub>-degassing and subsequent oversaturation of calcium carbonate, tufa formation is yet essentially linked to complex microbiological communities<sup>2,3</sup>. Laboratory flume experiments revealed large inventories of Ca<sup>2+</sup> and other ions (Ba, Sr, Mg) in tufa biofilms chelated by extra cellular substances (EPS) and that this chelation process is chemoselective in favour of divalent ions with low charge densities in the order of Ba>Sr>Mg<sup>4</sup>. This may conflict with the use of fast growing tufa deposits as paleoclimate archive for temperature reconstructions with Mg/Ca-Thermometry<sup>3,5</sup> in regard to the alteration of Mg/Ca ratios of calcite in the presence of EPS<sup>4,6</sup>.

This study examines a natural calcareous tufa depositing site with the focus on quantifying the role of biofilms in tufa formation and its effects on the water and tufa geochemistry.

The investigated Kaisinger creek is located 2 km south-east of the municipal Greiding in the southern Franconian Alb, about 50 km south of the city Nürnberg in Germany. In the typical cuesta landscape, rapid draining of the limestone plateaus takes place in karstic cavern systems and so, many CO<sub>2</sub>-supersaturated karstic springs discharge along the valleys.

The Kaisinger creek is subdivided into an upstream section, where no tufa deposition occurs, a tufa depositing section with three distinguishing tufa morphologies and a downstream section with only minor tufa deposition (Fig. 1a, b). Tufa in the Kaisinger Brunnenbach is deposited in three main sedimentary facies<sup>7</sup>: (i) Tufa-barrages composed of irregularly voided phytoherm boundstones with a high content of organic remains that dam the water forming the typical terraces. (ii) Laminated Tufa-Stromatolites predominantly occurring in areas of fast water flow and (iii) Pool-Sediments composed of fragments of (i) and (ii), as well as calcite-encrusted organic remains that are accumulated in the numerous pools in between the damming Tufa-barrages.

## 2. Methods

Water samples for determination of dissolved main cation and anion contents were taken at 15 sampling locations along the creek stream course (Fig. 1). Samples for determination of main-cations were filtered (0.45 µm) and acidified to pH < 2, stored cool in PP centrifuge tubes for subsequent ICP-OES analysis. Samples for determination of anion contents were filtered and stored cool in PP centrifuge tubes for immediate (less than 1 day after sampling) subsequent Ion-chromatography and Total Carbon Analyzer analysis. On-site parameters temperature, pH and electrical conductivity were monitored. For determination of Mg/Ca, Sr/Ca and Ba/Ca ratios in tufa samples, 200 mg of powdered tufa were digested in 22 % nitric acid and subsequently analyzed by ICP-OES. Relative uncertainties of measurement (2σ) are 5 % for calcium, 1.3 % for magnesium, 2.5 % for strontium and 2.7 % for barium. Saturation indices and CO<sub>2</sub> partial pressures of the water samples were calculated with PhreeqC<sup>8</sup>.

## 3. Results

The water of the Kaisinger creek is a Ca-HCO<sub>3</sub>-type. Minor constituents are sulfate, nitrate, chloride, magnesium, sodium and potassium, which concentrations remain constant along the stream course, thus they behave chemically conservative referring to tufa formation in the Kaisinger creek.

The pH values rise along the stream course from around 7.1 at the spring to around 8.1 at the beginning of the tufa section and remain at values of around 8.1 throughout the tufa section (Fig. 1c). At the resurgence point, pH-values are lower, but increase again further downstream.

The tufa depositing section in the Kaisinger creek is well reflected by SI<sub>calcite</sub> > 0 (Fig. 1d). The P<sub>CO2</sub> decreases downstream due to CO<sub>2</sub>-degassing, leading to increasing SI<sub>calcite</sub> and thus an oversaturation and subsequent deposition of calcareous tufa (Fig. 1d). A slightly higher P<sub>CO2</sub> and calcite undersaturation is observed at the resurgence point of the creek. Further downstream, P<sub>CO2</sub> declines again and calcite saturation increases leading to another, yet smaller, tufa deposition.

Calcium concentrations strongly decrease in the tufa forming section of the creek while the main decrease occurs in section Tufa-2 and Tufa-3 (Fig. 1e). Barium concentrations show a similar, though weaker, decline in the tufa forming sections. The decreases of calcium and barium can be expressed as the relative difference of the maximum value (mean of samples of the upstream section + Tufa 1) and the minimum value (mean of the two lowest values of samples in the tufa section Tufa-1 – Tufa-3). The relative decreases are ΔCa<sub>max-min</sub> = 14.6 ± 1.5 % and ΔBa<sub>max-min</sub> = 6.4 ± 1.3 %, whereas the uncertainties are calculated from the mean deviations and the relative uncertainty of measurement of each element. Magnesium and strontium concentrations remain constant along the stream course,

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