



Trace element partitioning in fluvial tufa reveals variable portions of biologically influenced calcite precipitation

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Abstract

The formation of tufa is essentially influenced by biological processes and, in order to infer environmental information from tufa deposits, it has to be determined how the geochemistry of biologically influenced tufa deviates from equilibrium conditions between water and calcite precipitate. We investigated the evolution of the water and tufa geochemistry of consecutive tufa barrages in a small tufa-depositing creek in Southern Germany. High incorporation of divalent cations into tufa is ubiquitous, which is probably promoted by an influence of biofilms in the tufa element partitioning. The distribution coefficients for the incorporation of Mg, Sr and Ba into tufa at the Kaisinger creek $D(\text{Mg})$, $D(\text{Sr})$ and $D(\text{Ba})$ are 0.020–0.031, 0.13–0.18 and 0.26–0.43, respectively. This agrees with previous research suggesting that biofilm influenced tufa will be enriched in divalent cations over equilibrium values in the order of $\text{Mg} < \text{Sr} < \text{Ba}$. Furthermore, the incorporation of Mg, Sr and Ba into tufa of the Kaisinger creek decreases downstream, which can be attributed to changes of the relative portions of bio-influenced tufa formation with likely higher distribution coefficients and inorganically-driven tufa formation with likely lower distribution coefficients. Additionally, the distribution coefficients of metals in tufa of the Kaisinger creek $D(\text{Cd})$, $D(\text{Zn})$, $D(\text{Co})$ and $D(\text{Mn})$ show values of 11–22, 2.2–12, 0.7–4.9 and 30–57, respectively. These metals are highly enriched in upstream tufa deposits and their contents in tufa strongly decrease downstream. Such highly compatible elements could therefore be used to distinguish easily between different lateral sections in fluvial barrage-dam tufa depositional systems and could serve as a useful geochemical tool in studying ancient barrage-dam tufa depositional systems.

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1. INTRODUCTION

Tufas are freshwater carbonates, which are a common feature of limestone-karstic areas where they are formed by calcium carbonate precipitation under subaerial cool-

ambient temperature conditions (e.g. Capezuoli et al., 2014). Similar to speleothems, tufas have great potential as geochemical archives to inform on paleoclimate conditions (Andrews et al., 1994; Ihlenfeld et al., 2003; Lojen et al., 2004; Andrews and Brasier, 2005; Lojen et al., 2009; Dabkowski et al., 2012; Zavadlav et al., 2017). However, tufa formation is essentially linked to biological processes and biofilms play an important role in its formation (Emsis et al., 1987; Pedley, 1992; Merz-Preiß

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and Riding, 1999; Arp et al., 2001; Bissett et al., 2008; Shiraishi et al., 2008; Rogerson et al., 2008; Dupraz et al., 2009; Decho, 2010; Perri et al., 2012; Pedley, 2014; Rogerson et al., 2014; Saunders et al., 2014). To infer environmental information from tufa deposits, it is important to determine how biologically influenced calcite precipitation deviates from physico-chemical equilibrium of the water and calcite (Rogerson et al., 2014). Laboratory experiments with natural tufa biofilms showed that tufa precipitation rates, the calcite crystal morphologies and the geochemistry of tufa is strongly influenced by the presence of biofilms (Rogerson et al., 2008; Pedley et al., 2009; Saunders et al., 2014). However, biological influences on tufa geochemistry remain elusive with respect to its contribution to the spatial and temporal variance of the calcite composition of natural tufa depositional systems.

We conducted field experiments and monitoring to complement the laboratory experiments, with the aim to further contribute to a better understanding of the role of biofilms on the tufa geochemical composition. We present comprehensive data of water and tufa geochemistry in a barrage-dam tufa depositional system focusing on variable element partitioning into tufa. Furthermore, we discuss a pronounced and pervasive influence of biofilms on the tufa trace element geochemistry.

1.1. Review on geochemistry of fluvial tufa

A state of the art review concerning tufa and travertines is given by Capezzuoli et al. (2014). Tufa deposits are formed in lacustrine or riverine environments, where two end-member facies, barrage-dam tufa and braided-fluviatile tufa are recognized (Pedley, 1990). The latter is characterized by braided small channels of constantly calm flowing shallow water. Barrage-dam tufa depositional systems are found in creeks and rivers with focused water flow. Tufa formation tends to build up damming tufa barrages that reduce the water flow. Famous examples of barrage-dam systems are the Krka waterfalls in the Krka National Park (e.g. Lojen et al., 2004) and the Plitvice lakes national park in Croatia (e.g. Emeis et al., 1987).

The potential of fluvial tufa deposits as a valuable archive for paleoenvironment and paleoclimate reconstructions was investigated in several studies concerning the tufa oxygen and carbon isotopic records as well as geochemical proxies (Andrews et al., 1994; Ihlenfeld et al., 2003; Garnett et al., 2004; Lojen et al., 2004; Andrews and Brasier, 2005; Andrews, 2006; Lojen et al., 2009; Brasier et al., 2010; Dabkowski et al., 2012; Zavadlav et al., 2017). Ihlenfeld et al. (2003) showed that Mg/Ca in recent tufa deposits rather reflects hydrological conditions than equilibrium temperatures as the temperatures derived by Mg/Ca-thermometer strongly deviate from those of the measured temperatures and the ones derived from the oxygen isotope record. Such hydrological control on Mg/Ca was also found for tufa deposited during the marine isotope stage 11 (MIS 11) (Dabkowski et al., 2012).

Although early studies concluded that the formation of tufas is predominantly physicochemical in nature due to CO₂-degassing and subsequent calcite oversaturation (e.g.

Irion and Müller, 1968), the current consensus is that microbial communities or biofilms are fundamental for calcite precipitation in freshwater alkaline settings (Pedley et al., 2009). Emeis et al. (1987) investigated the chemical versus biological control of tufa formation and concluded that biofilms (biological activity and formation of mucus) are crucial for the initiation of calcite precipitation. Biofilms are ubiquitous in ambient-temperature tufa depositional systems and many studies describe the important role of biofilms in tufa formation (Merz-Preiß and Riding, 1999; Arp et al., 2001; Dittrich et al., 2003; Shiraishi et al., 2008; Pedley, 2014; Rogerson et al., 2014). An overview of the biological role for carbonate formation is provided by Dupraz et al. (2009). Biofilms mainly consist of extracellular polymeric substances (EPS), which have the capacity to bind divalent cations through several negatively charged functional groups that deprotonate with increasing pH (Dupraz et al., 2009; Decho, 2010; Dittrich and Sibling, 2010). Consequently, in this EPS environment an oversaturation of carbonate can be enhanced due to selective enrichment of Ca²⁺ favoring calcite precipitation even in environments which would otherwise be chemically stable (Rogerson et al., 2008). This is also supported by Bissett et al. (2008) who showed that the pH-values of interstitial waters in tufa biofilms remain constant regardless of changes in the macro-environment. Furthermore, the cyanobacteria within the biofilms impact on the carbonate chemistry by fixing CO₂ through photosynthesis. More precisely HCO₃⁻ is taken up and converted to CO₂ via intracellular carboxyases, and hence force calcite precipitation in the direct environment of biofilms (Cam et al., 2015). However, such biomineralization is not restricted to the exterior of the cells and the EPS-environment. Several species of cyanobacteria have been discovered to be capable of forming intracellular carbonate inclusions (Couradeau et al., 2012; Benzerara et al., 2014) and these inclusions are highly enriched with earth alkali elements (Cam et al., 2016). Couradeau et al. (2012) found that Sr/Ca and Ba/Ca in intracellular carbonates in *Candidatus Gloemargarita lithophora* were 86 and 1370 times higher than in the extracellular solution.

Rogerson et al. (2008) investigated the biological influence on the geochemistry of tufa deposits in laboratory flume experiments with biofilms extracted from a natural tufa-depositing site. They found that biofilms and EPS are capable of accumulating large inventories of Ca²⁺ and other divalent dissolved ions Ba²⁺, Sr²⁺ and Mg²⁺ via chelation processes. They further showed that this chelation process is chemoselective in favor of ions with low charge densities that favor the incorporation of ions in the order of Ca > Ba > Sr > Mg into tufa biofilms. As a consequence, the authors concluded that bio-influenced tufa deposits will enhance Ba/Ca in tufa carbonates over equilibrium values and on the other hand Mg/Ca ratios will be reduced. Saunders et al. (2014) subsequently investigated the relationship between temperature and Mg/Ca ratios in tufa environments in laboratory flume and flask experiments. They found no strong relationship between Mg/Ca ratios in tufa and temperature, but a pronounced kinetic control of Mg/Ca ratios in tufa. In experiments, where the calcite

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