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Freshwater biodissolution rates of limestone in the temperate climate of the Dinaric karst in Slovenia

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ABSTRACT

Dissolution rates in two freshwater karst systems were determined by using tablets of dense micrite–biopelmicrite Cretaceous limestone. Submerged limestone tablets in riverbeds were subjected to a natural gradient from complete darkness to direct sunlight. Higher light rates significantly ($p < 0.05$) increased the epilithic biomass of phototrophs and the overall dissolution rates, which were highest at the Unica spring ($-49.2\ \mu m\ a^{-1}$), but the exact portion of light-dependent dissolution remains elusive. In the karst river Unica, with its big fluctuations in environmental parameters (e.g., discharge), light rates can be used in estimating the dissolution rates enhanced by phototrophs. Natural biofilms in aquatic systems have important implications for landform evolution, and the impact on limestone dissolution rates is comparable with rates of debris falling from steep slopes.

1. Introduction

Karst rocks interact with other components of the physical environment in three main systems: rocks covered with soil/sediment, rocks submerged under water and rocks exposed to the atmosphere. In nature combinations of such interactions are frequent, for example, limestone in tidal zones (Read and Grover, 1977). The impact of organisms on carbonate dissolution is complex (Garcia-Pichel, 2006). Biofilm structure does not depend solely on substratum but also on species dominance and depth distribution inside the biofilm (Roldán and Hernández-Mariné, 2009). In soil systems, microbial and plant CO_2 production plays a key role in the solubility of carbonate rocks (Kuzyakov, 2006). Biofilms are important for protecting and/or destroying rocks (Jones, 2010) that are submerged under water or exposed to the atmosphere. Any submerged surface is subjected to spontaneous absorption of organic molecules, which within a few hours is rapidly followed by adhesion of bacteria. Phototrophs, principally diatoms, colonize this new substrate in sunlit environments in a day to several weeks (Callow et al., 1986; Rosowski et al., 1986).

Different terms are used in the literature to describe the biological processes that alter rock surfaces: biological dissolution/biodissolution, biodeterioration, biological weathering/bioweathering (Jones, 1965; Viles, 1995; McIlroy de la Rosa et al., 2012), biodegradation (McIlroy de la Rosa et al., 2012), bioerosion (Naylor et al., 2012), biocorrosion (Perica and Marjanac, 2009), and biopitting (McIlroy de la Rosa et al., 2012). When other rock destructive processes overlap with biological dissolution, the term denudation is applied to describe the overall rock loss. Biologically driven processes of dissolution and/or deposition prevail in some places, and such features are named biokarst (Schneider and Torunski, 1983; Viles, 1984; Ford and Williams, 2007); phytokarst, if they are related predominantly to plant activities (Bull and Laverty, 1982); or even phytokarren, which are characterized by small dissolution features (Viles, 2009). Although they are not strictly related to biodissolution at some places but the sole inorganic processes (e.g., abrasion, mixing corrosion), among the most remarkable biokarst features are the marine notches that can be found in a variety of environments, from the cold shores of Newfoundland and Patagonia to the tropics, for example in Aldabra Atoll and Ha Long Bay (Ford and Williams, 2007). Abundance of marine notches and other biologically induced coastal karren in the (sub)tropics indicates the relative importance of biodissolution rates that presumably decrease with latitude (Lundberg, 2009; De Waele and Furlani, 2013).

Biodeterioration leads to microbial uptake of elements/nutrients from the rock, oxidation, and alteration of minerals, which results in increased porosity and permeability of rocky substrata (Warscheid and Braams, 2000). One of the most frequently investigated enzymes that promote limestone dissolution in undersatured water is carbonic anhydrase (CA), which catalyzes CO_2 hydration (Golubić and Schneider, 1979; Liu and Dreybrodt, 1997). When CO_2 starts to outgas from water, the reaction is reversed, and CA can promote calcite precipitation (Liu and Dreybrodt, 1997).

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The highest biologically induced denudation rates were measured at sea coasts, which can be spatially very variable and accompanied by mechanical processes, ranging maximally from −90 to −3800 μm a^{-1}; Lundberg, 2009) but generally between −0.1 and −1.1 μm a^{-1} (Schneider and Torunski, 1983; Table 1). Increased denudation after 2 years of exposure (when biological colonization of the freshly exposed limestone slab was finished), strongest denudation during the summer–autumn months, absence of wedging from crystallization, and abrasion at the measurement site at the Adriatic coast (Furlani and Cucchi, 2013) all suggest that the majority of denudation in the intertidal zone (up to −260 μm a^{-1}) is of biogenic origin. Lower rates (from −5 to −25 μm a^{-1}) are reported from terrestrial environments in semiarid climates (Danin, 1983; Danin and Caneva, 1990). Pentecost (1992) reported denudation rates of −30 μm a^{-1} (Yorkshire, UK), but the main denudation process seems to be related to dislodging as a result of dehydration and rehydration in sheath-pigmented cyanobacteria, i.e., Tintenstriche. Biodenudation is not solely limited to limestone: studies done mainly on volcanic rocks showed that lichens can enhance terrestrial denudation rates by 16 times (Brady et al., 1999) or up to 18 times (Stretch and Viles, 2002), and can increase Ca^{2+} concentration in water runoff by ~3.5 times (Zambell et al., 2012). Some authors have drawn attention to the dual role of biofilm because it can also protect bare rock against dissolution (Lüttge and Conrad, 2004). A similar phenomenon was observed under the thalli of lichens (McIlroy de la Rosa et al., 2012). Biological dissolution in a freshwater environment is frequently reported (Golubić and Schneider, 1979; Schneider and Le Campion-Alsumard, 1999; Komárek and Anagnostidis, 2000) but quantitatively overlooked. Dissolution rates in stream caves, where light is absent, of the NW Dinaric karst in Slovenia were generally lower by a magnitude or two in comparison with sites exposed to sun light (Prelovšek, 2009). Using slightly different methodology where upper (lighted) and lower (shaded) side of limestone tablets were exposed to denudation (Prelovšek, 2009, 2012); pitting as evidence of biological dissolution (Viles, 2009) was observed only in lighted sides of limestone surfaces submerged under water but not at all lighted measurement places (Prelovšek, 2009).

The objective of the study was to define biodissolution rates in a freshwater environment and to correlate rates with the light gradient. Despite relatively wide distribution of such systems in temperate karst areas, no relevant data for biological dissolution on a temporal scale are available. Interactions and community structure might have more pronounced geomorphological effects as previously believed. We hypothesize that, with increasing light, the level of primary production is elevated and that the impact of benthic biofilm on substrate and subsequently landscape evolution is more pronounced.

2. Study site description

Experiments were carried out at Malni spring (45° 49′ 10″ N., 14° 14′ 34″ E.) and at the Unica spring in front of Planina Cave (45° 49′ 20″ N., 14° 15′ 20″ E.) with the sunlight gradient (Fig. 1). These two karst features, which are 0.8 km apart, developed in lower Cretaceous limestones (Gospodarič, 1976) and share similar recharge areas with combined authigenic recharge from the Javorniki Mountains (Kogovšek, 2004) and allogenic recharge from the Cerknica Lake (Kogovšek, 2001). Unica spring gets a significant quantity of water from the Pivka River that sinks into the Postojna Cave system (Gabrovšek et al., 2010).

Measurements took place at the Malni spring at two sites: in the dark pumping reservoir that serves for the public water supply (Mal-1) and 50 m away in the naturally lit, diffuse spring (Mal-2). Five measurement sites were established in the riverbed of the Unica River, starting from complete darkness (Pla-1), to a twilight zone (Pla-2 and Pla-3) in the Planina Cave; followed by two sites, one in the shady zone (Pla-4) and another in the section that is exposed to direct sunlight in the Unica riverbed (Pla-5; Fig. 2; see Table 2 for illumination rates). Microlocations in the field were carefully selected on the following basis: permanent presence of running water at the site, minimum turbulence, and relative inaccessibility to animals and humans.

At Malni spring during the experimental period (451 days), discharge ranged from 0.98 to 9.29 m^3 s^{-1}, specific electrical conductivity from 334 to 424 μS cm^{-1}, and temperature from 5.0 to 17.7 °C. In the same period, Unica spring had a discharge between 0.16 and 58.03 m^3 s^{-1}, specific electrical conductivity from 287 to 478 μS cm^{-1}, and a temperature from 4.1 to 14.7 °C (data were gathered during a water tracing test in 2008; Gabrovšek et al., 2010). The water at Unica and Malni springs is close to saturation with regard to calcite ($SI_{Ca} \approx 0.27$) and enriched in dissolved CO_2 ($pCO_{2(eq)} \approx 3120$ ppm), owing to the important contribution of authigenic recharge through the forested catchment area.

3. Materials and methods

3.1. Experiment set-up

To define dissolution rates, to mimic the natural substratum for biofilm formation, and to observe a biodissolution pattern under an optical magnifier and subsequent identification of a periphyton community (Viles, 1987a), 5.5–6.5 mm thick micrite–biopelmicrite "standard" limestone tablets (after Gams, 1979), with a diameter of 41 mm and with a central hole for attachment to a prefabricated holder, were prepared and exposed to the natural conditions in riverbeds inundated year round (Fig. 3), similar to the previous studies (Prelovšek, 2009, 2012; Covington et al., 2013). Stone tablets were cut from a limestone slab with a honed surface from homogenous upper Cretaceous Lipica limestone composed mainly of $CaCO_3$ (97.7–98.7%), MgO (0.2%), <0.1% SiO_2, and <3% of other unanalyzed substances (Gams, 1985). Among many microscopic techniques proposed by Taylor and Viles (2000) to characterize the nature and impacts of colonizing organisms, optical microscopy under 10–63× magnification was used to provide a better insight into the etching pattern.

The limestone tablets were attached with stainless steel screws to avoid overestimation of dissolution caused by iron rusting on the limestone tablets (Prelovšek, 2012). Rubber tape and a felted washer were used to ensure a well-defined reaction surface and to avoid abrasion from the PVC foamboard (Fig. 3). Tight fixation prevented dissolution outside of the reaction surface, even in the case of measurement site Pla-3, which was partly broken during the experiment (Fig. 4A). Air dry (~40% of relative humidity) limestone tablets were weighed before and after

Table 1
Denudation rates measured in different environmental settings where biodissolution plays a significant or exclusive role.

Location	Lithology	Rate (μm a^{-1})	Reference
Marine, Southern Great Barrier Reef (Australia)	Young reef limestone	from −200 to −2900 (chitons home scars) from −200 to −700 (chitons grazing)	Trudgill (1983)
Marine, Grand Cayman Island (West Indies)	Pleistocene limestones	−2770^{a} (open coast), −450^{a} (reef-protected coast), −170^{a} (where bioconstruction dominates over bioerosion)	Spencer (1985)
Marine, northern Adriatic Sea	Cretaceous limestone	Up to −260	Furlani and Cucchi (2013)
Marine, western Australian coast	Calcareous sandstone	From −200 to −800^{a}	Abensperg-Traun et al. (1990)
Terrestrial, subaerial, Jerusalem	Limestone	From −2 to −25	Danin (1983); Danin and Caneva (1990)
Terrestrial, subaerial, North Yorkshire (UK)	Limestone	−30	Pentecost (1992)

[a] Without clear distinction between organic and inorganic dissolution.