

Dissolution of red sandstones exposed to siderophore-producing bacterium *Pseudomonas fluorescens*: Experimental bioweathering coupled to a geochemical model

Anna Potysz^{*}, Wojciech Bartz

University of Wrocław, Faculty of Earth Sciences and Environmental Management, Institute of Geological Sciences, Cybulskiego 30, 50-205 Wrocław, Poland

ARTICLE INFO

Keywords:

Red sandstone
Pseudomonas fluorescens
Siderophores
Bioweathering
Biodissolution

ABSTRACT

Petrological and geochemical approach was implemented to decipher red sandstone dissolution under biotic conditions with bacteria, *Pseudomonas fluorescens*. Bacteria accelerated dissolution by up to 3.4 times as compared to abiotic weathering rates. The degree of sandstone dissolution was calculated at 0.2–0.6% and 0.2–3.7% for Kopulak and Tumlin sandstones, respectively. Further, goethite was found to be more susceptible to bacterially mediated Fe releases as compared to hematite. Cement structure was also found to affect leaching potential, while abiotic weathering revealed dissolution not exceeding 0.5%. Study proves that bioweathering processes may affect durability of sandstones used as construction and building materials and cultural heritage objects.

1. Introduction

Stones used for building various monuments vary from one location to another and include sandstones, limestones, marble, granite, and volcanic rocks [1]. Sandstones hold great societal importance because these rocks have long been exploited and distributed throughout the world for cultural heritage applications [2]. Moreover, sandstone, among others, is the most widespread sedimentary rock used in architecture [3,4]. Thus, for a long period, sandstone-made monuments and ornaments have been exposed to a variety of weathering deteriorative factors [5–7]. The weathering conditions may vary depending on the region and season [6,8]. Therefore, the extent to which specific factors deteriorate sandstones has to be evaluated. However, an individual (bio) weathering factor influencing sandstone dissolution cannot be treated as a separate entity nor fully understood without considering the others [9]. Thus, experimental simulations, and long-term leaching experiments, in particular, are useful in understanding environmental processes and how specific sandstones may be weathered. In this context, a complete understanding of bioweathering processes can lead to the implementation of suitable strategies to prevent deterioration.

Chemical and biotic weathering are the sum of variables influencing the stability of solids. Long-term weathering of sandstones expose these stones to multiple decay factors acting at the same time [7,10].

However, the experimental research should be designed in a way evaluating the contribution of isolated weathering factor (individual agent) to the sandstone decay [11]. If many decay factors acting simultaneously are included in a one experiment, the interpretation can be limited to intensity of sandstone dissolution rather than to the interpretation on what factor plays prevailing role in the dissolution process [12]. On the other hand, some weathering factors play more of an important role when act together in comparison of their individual impacts [13]. Moreover, it has been demonstrated that even minor chemical, mineralogical and structural differences in the same stone type may be crucial for the weathering resulting in different dissolution rates and weathering signatures [7,14]. Obviously, moisture on sandstones may occur due to rainfall and changes in humidity [15]. Here, the moisture penetration of porous sandstone may affect its stability [15]. However, the extent to which moisture affects sandstones is a matter of contention. As reported by [16], changes in the compressive strength of sandstone may be observed after the wetting cycle. In contrast, [17] demonstrated that even if sandstones are somewhat disturbed by moisture, the effect is reversible during the drying period. As reported by [18] the moisture exposure periods were found to play relevant role in weathering. However, according to reports in the literature, the environmental behavior of sandstones that are exposed to wet-dry cycles is also dependent on the mineral composition and porosity, with the latter

^{*} Corresponding author.

E-mail addresses: anna.potysz@uwr.edu.pl (A. Potysz), wojciech.bartz@uwr.edu.pl (W. Bartz).

<https://doi.org/10.1016/j.conbuildmat.2023.130584>

Received 10 October 2022; Received in revised form 26 January 2023; Accepted 28 January 2023

Available online 8 February 2023

0950-0618/© 2023 Elsevier Ltd. All rights reserved.

increasing during weathering [19]. Other authors have also recognized that the moisture application amplitude is more of an important weathering factor than moisture content itself [20]. Furthermore, daily and seasonal temperature changes may cause temperature gradient within the stone may lead to breakdown because of a thermal expansion between the minerals [12,21,22]. Likewise, the grain contacts within the sandstone may also be crucial to weathering. It has been shown that sandstones having sandstones of concave–convex contacts are more resistant than those exhibiting straight grain contacts [19]. In addition, the importance of the temperature lies in its influence on other decay factors such as evaporation, wetting, drying and salt crystallization [12,23–25]. Significant differences in the physical and mechanical properties of sandstones may occur after stone exposure to cyclic freeze–thaw cycles [26]. For example, [25] demonstrated that the experimentally simulated freeze–thaw weathering cycles led to an increase of sandstone mass at the beginning of cycle and decrease at the end of cycle which was attributed to loss of particles and cement dissolution. As demonstrated by [14] fine-grained sandstone samples were more susceptible to weathering as compared to coarse-grained material as proven by an extensive debris release in the former stone and lower in the latter. The literature reports documented variety of sandstone degradation forms that included: granular disintegration, weight loss, deepening and widening of pre-existing pores and cracks, the occurrence of new cracks and micropores, decreased comprehensive strength [19,27,28]. In nature, some peculiar weathering forms, among others in sandstones, have been observed: large scale ruiniform systems, pinnacles; medium-sized arches, natural bridges, caves and small-scale pillars or half-pillars and small-scale tafone, including honeycombs [29,30]. Moreover, the small-scale weathering forms were also found for building stones; these included cracks, detachment, features induced by material loss (for example alveolization), deposits like crust etc., as well as forms caused by biological colonization [31,32]. Thus, it can be hypothesized that the intensity of weathering is governed by the individual dissolution factors (weathering agents) and depends on the chemical and mineralogical characteristic of the material being weathered.

Furthermore, until relatively recently, microbial influences on solid materials were underestimated, but now it is known that their real impact may, in fact, be more important than previously expected [33–35]. Further, the presence of microorganisms such as bacteria and fungi on sandstones is evident [36–39]. Bacteria may interact with geological materials by mechanisms such as redox reactions, acidolysis, and complexolysis [40]. The occurrence of heterotrophic bacteria on sandstones has already been evaluated and its seasonal variability reported [8]; therefore, an evaluation of specific bacterial strains is relevant to improve the current state of fundamental knowledge. However, an intensive debate is currently ongoing among researchers as to how microorganisms actually affect the stability of rocks [41,42]. On the one hand, biofilm is known to play a protective role, while on the other, the concentration of microbial metabolites increases beneath the biofilm [43]. Thus, the counterbalance between deteriorative and protective bacterial functions is an interesting subject in the context of stone materials. An interesting example of a bacterially produced agent is siderophore, which is a chelating agent with a high affinity towards Fe [44]. Here, it is important to note that iron is an essential element for the functioning of living organisms as it plays a variety of functions from DNA/RNA to metabolic syntheses [44]. Therefore, its acquisition has to be achieved by bacteria. In this context, an excretion of siderophores by bacteria is particularly promoted when there is Fe scarcity. More specifically, as recently demonstrated, more intense siderophore production by *Pseudomonas aeruginosa* occurred when bacteria were incubated in iron deficient conditions [45].

Based on the above discussion, it can be noted that sandstones vary in Fe composition [46]. Thus, it is hypothesized that siderophore-producing bacteria may have a different impact on sandstones incorporating different Fe-bearing minerals and, in turn, bacterial behavior in the presence of these two sandstones may also differ. In this regard,

evaluation studies need a completely interdisciplinary approach that links these two primary aspects. These aspects are not only fundamentally important for science but also the future preservation of cultural heritage.

Thus, this work was undertaken to unravel the impact of heterotrophic bacteria on the dissolution kinetics of red sandstones in the presence of *Pseudomonas fluorescens* bacteria. The fundamental aim of this study is to decipher whether Fe content in sandstone material determines the activity of microorganisms and associated (bio)weathering intensity. Since hematite and goethite are the main Fe-bearing cement minerals in studied rocks, it has been hypothesized that bacteria *Pseudomonas fluorescens* excreting iron chelating agents (siderophores) may contribute to weathering to different extent than abiotic weathering conditions. To this end, a combined approach applying petrological and geochemical methods was implemented to experimentally demonstrate the long-term (119 days) bioweathering processes and mechanisms involved. It is important to highlight that this study has both local and international implications, as there are many locations around the world where red sandstones occur naturally and are used in heritage structures [47–53].

2. Materials

Two general types of sandstones were used: Tumlin (Tu) and Kopulak (Ko). The red sandstones, occurring and exploited for building purposes as a dimension stone in the Holy Cross Mountains (SE Poland), are traditionally divided into the following types: I) Tumlin; II) Wąchock; and III) Suchedniów type, which has the Kopulak, Baranów, and Włochy varieties [54]. More specifically, Tumlin sandstone is from the Lower Triassic age and deposited in an aeolian environment [55], while Kopulak sandstone is from the Upper Triassic age and deposited in a fluvial environment [56]. The history of their exploitation generally dates back to the 12th century [54,57–60] and can be found in Romanesque and Gothic monuments [54] as well as Renaissance and Baroque architecture [61]. Additionally, red sandstones were mainly used to rebuild the capital city of Warsaw, which was almost completely razed to the ground during the Second World War. They were also used in the production of acid-resistant tubs and linings for metallurgical furnaces [54,62]. Thus, it is clear that these rocks are exposed to various biotic factors, which substantiates the need for experimental work. Sandstones were crushed to receive the grains of 0.5–2 mm size. In addition, cubes were prepared from the fresh (unweathered) rock using a laser guided stone cutting machine. Subsequently, each wall of the cube was precisely flattened on a lapping machine using 400-grid abrasive to achieve required dimensions. Such prepared materials have been subjected to further preparations for the weathering experiments.

3. Methods

3.1. Chemical and mineralogical characterization of sandstones

The chemical composition of sandstones (Table 1) was determined in a commercial laboratory (Bureau Veritas Analytical Laboratories, Vancouver, Canada). Samples were subjected to lithium borate/tetraborate fusion and digestion of the melting product with nitric acid. Inductively coupled plasma atomic mass spectrometry (ICP-MS) measurement allowed us to determine bulk elemental composition.

Next, mineral composition (modal analysis) was determined using an optical microscope (Zeiss Axiolab polarising microscope), differential scanning calorimetry-thermogravimetric analyses (DSC-TG), and powder X-ray diffraction (PXRD). Then, a scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM-EDS) analysis was carried out on the freshly exposed surfaces. The analysis was performed using a Jeol JSM IT-100 scanning microscope (JEOL, Akishima City, Tokyo, Japan) equipped with an Oxford EDX system in back-scattered

Table 1
Chemical and modal composition of the studied sandstones.

Chemical composition [wt. %]:	Sandstone Ko	Sandstone Tu
SiO ₂	94.82	96.86
Al ₂ O ₃	2.33	1.47
Fe ₂ O ₃	1.18	0.25
MgO	0.03	0.07
CaO	0.01	0.02
Na ₂ O	0.02	0.02
K ₂ O	0.09	0.38
Ti ₂ O	0.12	0.04
LOI	1.1	0.6
Minerals [vol. %]:		
Quartz	77.2	61.3
Feldspar	0.9	1.3
Lithic	7.8	17.4
Accessory minerals	0.4	0.7
Cement	13.7	19.3
Pores	12.4	19.1

electrons mode without any conductive coating and under low vacuum ($\sim 30 \pm 5$ Pa). The SEM was operated at 16 kV with a working distance of 10 mm.

Subsequently, DSC-TG and PXRD were used for a more complete characterization of the fine constituents of sandstones (i.e. matrix and cement). Fresh samples of Kopulak and Tumlin sandstones (c.a. 150 g each) were gently crushed in an agate mortar and then sieved (using a 63- μ m sieve) to separate framework grains (oversized fraction, screened off).

More specifically, the XRD analysis was carried out on unoriented mounts using a Bruker D8 Advance diffractometer (Bragg-Brentano geometry, CuK α radiation) in the range of 2θ 3–75 deg. The obtained results were compared with standard reference patterns using the ICDD PDF-2 [63] database. Meanwhile, the DSC-TG analysis was performed with a Perkin Elmer STA 6000 analyzer. Samples ($70 \text{ mg} \pm 5 \%$) were analyzed in a ceramic pan crucible at a temperature range of 40–1000 °C, heating rate of $15 \text{ }^\circ\text{C min}^{-1}$, and flowing dry nitrogen gas (a steady gas flow rate of 25 ml min^{-1}).

Next, JMicroVision software [64] and a set of stitched microphotographs were used for modal analysis and to measure grain dimensions. Quantitative mineralogical data was determined by means of point-counting method, and 1000 randomly generated points were counted for each sample. The Feret max (the longest Feret diameter) for 500 grains located along the traversing lines (1 mm grid) was found, and the resultant data were processed using GRADISTAT software [65]. This allowed us to determine the grain-size distribution of the framework grains presented as bar-diagrams as well as parameters such as geometric mean, sorting, skewness, and kurtosis [66]. The grain degree of roundness [67] and sphericity [68] was studied for 50 grains per thin section, which were selected by randomly traversing along a straight line.

Mercury porosimetry measurements were done using a Micropore Autopore II 9220, on eight $50 \times 50 \times 50$ mm cubes per each rock variety. Mercury was injected starting at the pressure of 0.5 psi (0.003 MPa) up to 6×10^4 psi (413.4 MPa), which allows penetration to pores of size bigger than 3 nm. The obtained results were evaluated using Washburn's equation. The following parameters were calculated: 1. the total pore volume, 2. the surface area of the pore space, 3. the average pore diameter, 4. the bulk density of rock, and 5. the permeability hysteresis [69,70].

3.2. Bacterial strain used for experimental weathering

The gram-negative bacterial strain of *Pseudomonas fluorescens* (strain DSM 50091) used in the biotic experiments was taken from the Deutsche Sammlung von Mikroorganismen und Zellkulturen; Braunschweig, Germany. Bacteria were cultivated according to the provider's

recommendation and grown in the Luria-Bertani medium for 24 h. Afterwards, the cells were harvested and cleaned three times with sterile 5 % NaCl and resuspended in a growth medium composed of 4 g of succinic acid (C₄H₆O₄), 1 g of ammonium sulphate ((NH₄)₂SO₄), 0.2 g of disodium hydrogen phosphate (Na₂HPO₄), and 6 g of Tris buffer (C₄H₁₁NO₃). Later, the initial pH of the growth medium was adjusted to of 7.0 ± 0.1 using 5 M NaOH. The growth medium was deliberately devoid of iron to create Fe-deficient conditions and promote the production of siderophore. Thereafter, cells were introduced to the experimental reactors (described below, section 2.3). The conductivity of the initial solutions was 0.02 mS/cm for H₂O and 5.59 mS/cm for GM and GMB.

3.3. Experimental set-ups

Two types of (bio)weathering experiments were performed: i) a semi-open pass flow-through experiment including 0.5–2 mm sandstones in perforated tubes; and ii) a batch experiment including 1 cm³ cubes of sandstones. The differentiation of experimental setups was done to investigate how sandstone behavior varies depending on the bioweathering conditions. More specifically, the first experiment mentioned above was characterized by dynamic conditions—solution renewal aimed to check sandstones behaviors under far from equilibrium conditions where bacterial regeneration occurs periodically. Meanwhile, the second experiment with polished cubic-shaped sandstones aimed to demonstrate how sandstone dissolution and bacterial activity change over time without solution renewal and how flat the weathered surface is as compared to the surface in the semi-open experiment. These experiments lasted 119 days.

Sandstone samples with a particle size of 0.5–2 mm, all glassware and polypropylene materials were sterilized at 121 °C for 20 min prior to the experiments. Next, 1 g of each sample was placed in perforated polypropylene tubes and immersed in the following weathering solutions: i) demineralized water (H₂O) simulating non-aggressive weathering conditions (pH 6.0); ii) a sterile growth medium (GM) simulating abiotic weathering conditions (pH 7.0); and iii) a growth medium inoculated with the bacteria (pH 7.0), *Pseudomonas fluorescens* (GMB) simulating biotic weathering. Reactors were kept on an orbital shaker set at 100 rpm. Periodically, the tubes were transferred to the fresh corresponding medium, whereas solution from the previous period was filtered using 0.22- μ m filters. Here, one portion of this solution was acidified using HNO₃ for element concentration measurement, while another was immediately used for ion analysis. Parameters such as pH and siderophore production were also measured. Bioweathering experiments were carried out in Erlenmeyer flasks shut with cotton plugs that enabled the passage of air to maintain aerobic conditions. All biotic experiments were inoculated with bacteria from the same pre-growth flask in order to start the bioweathering tests with bacteria of identical age and initial nutritional status.

3.4. Analysis of microbial activity and siderophore detection

For all sampling times, the bacterial growth rate was monitored by measurements of optical density (OD₆₀₀) using UV spectrophotometry (HACH DR9300). The spectrophotometric measurements were done in the wavelength range 330–480 nm for siderophore detection [45]. The occurrence of two specific shoulder peaks was the basis for determination of siderophore concentration. Here, it should be noted that according to the Beer-Lambert law [71], siderophore concentration can be estimated based on absorbance measured at 405 nm and the co-efficient of free pyoverdine.

3.5. Composition of the weathering solution

The concentrations of elements in the weathering solutions were analyzed by a certified laboratory using ICP-MS (Nexion 300D Perkin

Elmer) with internal standards. Moreover, quality control included systematic analysis of certified reference materials. Sulfate, phosphate, and nitrate concentrations in the solutions were measured by the colorimetric method using Permachem reagents (HACH), while the carbonate content was determined by back titration with HCl.

3.6. Geochemical modelling

The geochemical simulation using Visual Minteq modeling software (version 3.1) was performed to calculate saturation indices and predict the formation of precipitates in the studied (bio)weathering systems. The chemical composition of the leaching solutions (i.e., ion content) and pH values were used as input data. The temperature fixed in a simulation (geochemical model) was 30 °C and atmospheric pressure conditions.

3.7. Scanning electron microscope observations

At the end of the experiments, sandstone grains and polished cubic-shaped sandstones were gently washed with ultrapure water and kept for drying at room temperature. Then, the fresh sandstones (unweathered) and samples after experimental bioweathering were observed in terms of the surface changes using a scanning electron microscope (JEOL JSM-IT100) at 16 kV and low vacuum working mode. For each mineral, at least 100 EDS spectra were acquired and data revealing chemical composition were treated statistically.

3.8. Sandstone properties

Cubes of identical size and shape resulting from bioweathering experiments with bacteria, growth medium and water were checked for hardness properties with respect to unweathered samples. Equotip-540 hardness tester, recommended for rocks having a thin weathering layer [72,73] was employed to measure difference in sandstones hardness. The 10 impacts with standard impact D probe were randomly made in each side of the cube, avoiding measuring on the same spot. The instrument has been placed to different spots moving the each measurement point vertically and horizontally. After each measurement equipment made a spot signature on the cube and the following measurement was checked for placement in another position. Total of 60 measurements were made overall for each cube, far exceeding the minimum 30 measurements recommended by [74] or 45 readings by [75].

Due to low weight of the samples measurements were performed on a stable granite worktop covered with coupling paste as recommended by equipment supplier in order to eliminate vibrations.

4. Results

4.1. Chemical and mineralogical characterization of fresh sandstones

The Kopulak sandstone (Fig. 1) is classified as quartz arenite [76], for which none or very weakly proffered orientation is visible. Quartz (61.3 %, Fig. 2, spectrum 1) and polycrystalline quartz (14.3 %) are the main constituents and prevail over very sparse, untwined, and altered feldspar grains (1.3 %). Lithoclasts (3.1 %) of fine-grained clastic sedimentary

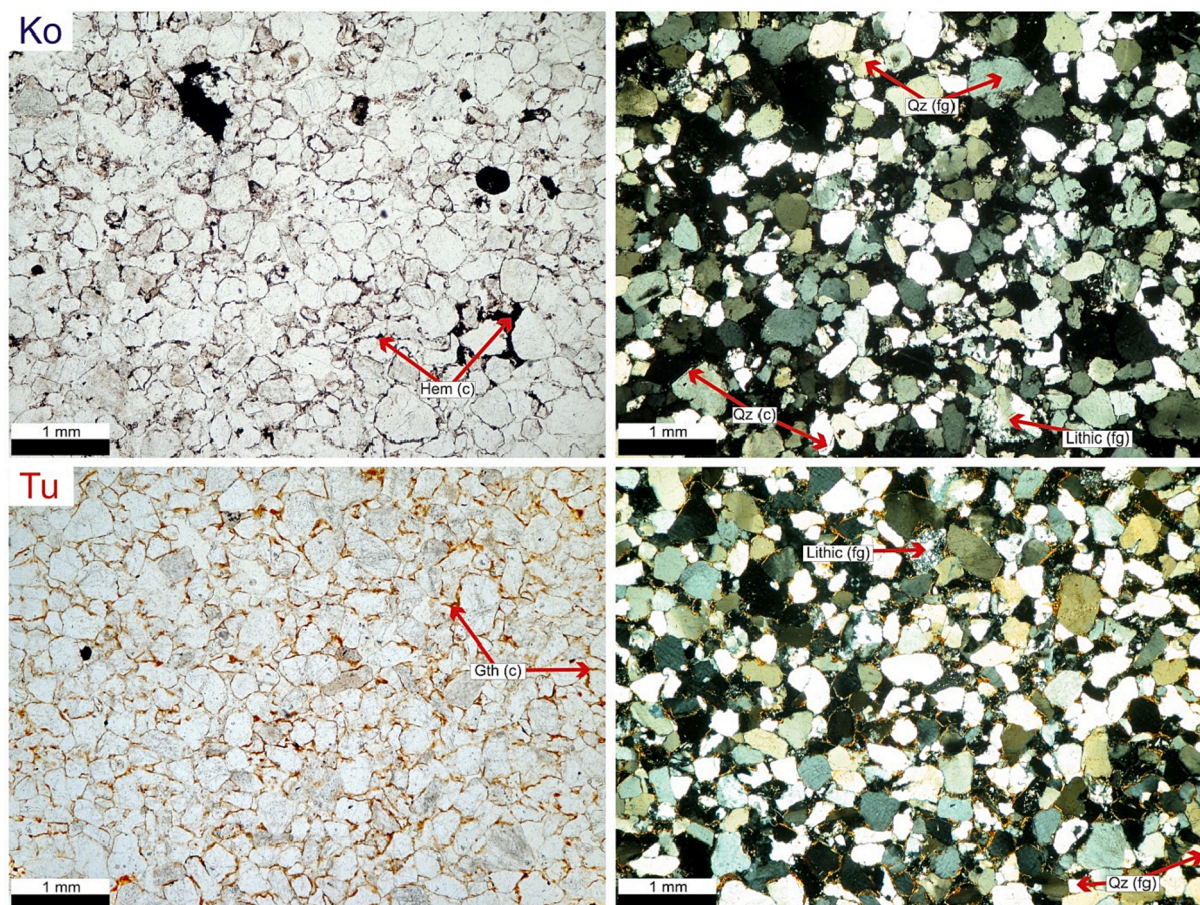


Fig. 1. Microphotographs of the studied sandstones taken in plane-polarized light (left column) and cross-polarized light (right column). Abbreviations used: cement (c), framework grain (fg), quartz (qz), hematite (hem), goethite (gth), fragment of rock (lithic).

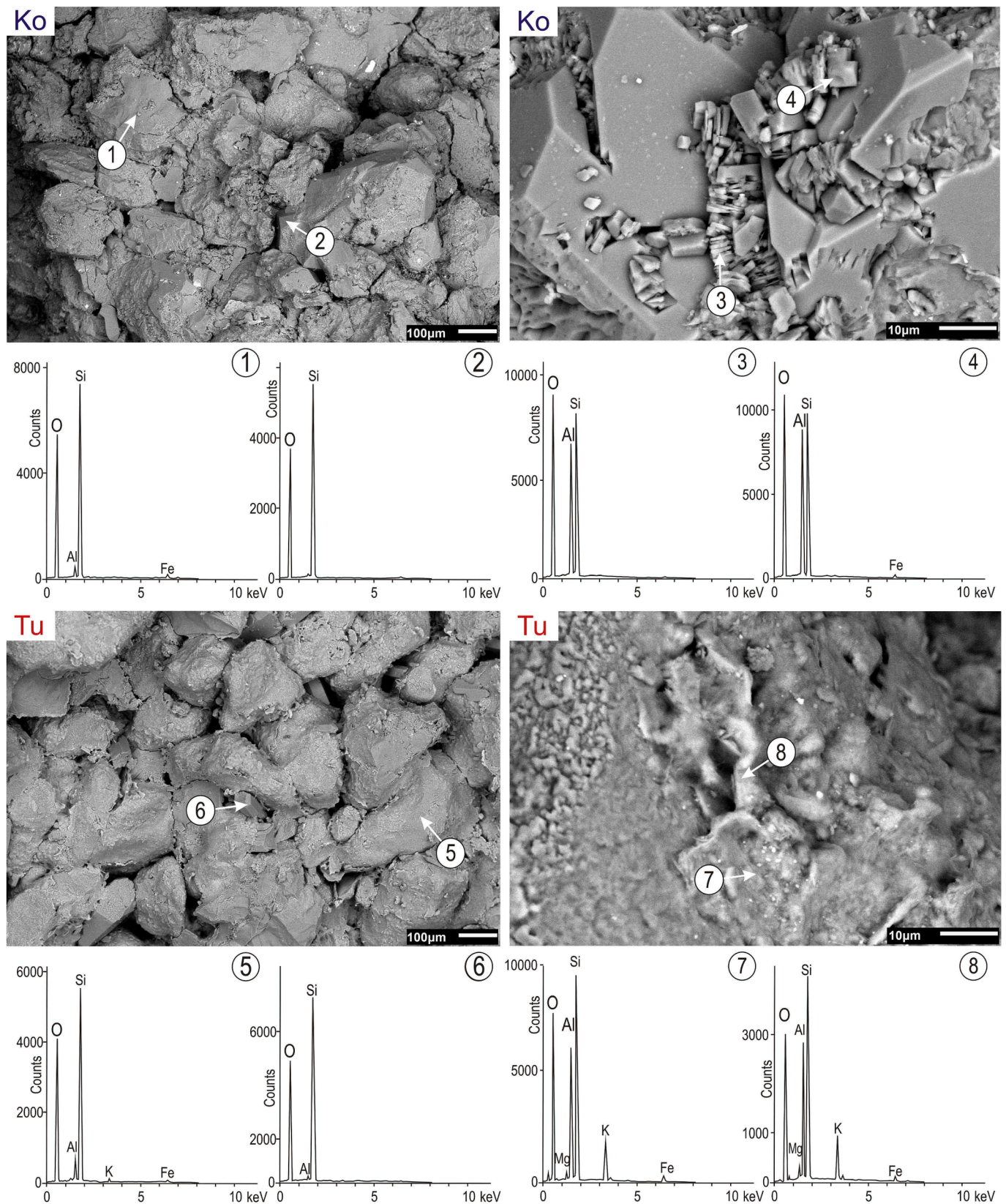


Fig. 2. SEM images of the investigated sandstones and representative EDS-spectra.

rocks (mudstone-like) are sparse. Zircon, tourmaline, and rutile (0.7 %) are accessory minerals. The framework grains are generally sub-angular to sub-rounded; very equant grains to less common subequant grains dominate over very sparse subelongated and elongated grains (Fig. 1). A

concave-convex and long contact between framework grains are most common, while point contact or suture contact are subordinate (Fig. 1).

In this context, quartz syntaxial overgrowth is one of the cement types, precipitating around the detrital grain, visible in a polarized

microscope as tiny fringes separated from it by a film of opaque minerals (Fig. 1), and giving them partly euhedral shapes (Fig. 2, spectrum 2, and the upper-right photo). However, in terms of volume, the pore-filling clay-ferruginous cement prevails. Moreover, the XRD pattern of the sieved fraction revealed strong peaks assigned to quartz (ICDD 01–083–2465; Fig. 3). Here, it can be concluded that the finest framework grains had to pass through the 63- μm sieve. A large amount of quartz in the sample is reflected in the strong thermal effect at 570 °C (Fig. 3)

associated with the transformation of low-temperature quartz into a high-temperature modification [77]. Despite the occurrence of quartz, hematite (ICDD 01–079–0007; peaks at 2.69 Å, 2.51 Å, 1.69 Å) is the main constituent of the sieved fraction. Its presence confirms the thermal effect associated with hematite polymorphic ($\alpha \rightarrow \beta$) transition at c. 670 °C [77]. This cement precipitates directly in the intergranular pore space or less common line on the grain surfaces (Fig. 1).

Meanwhile, tiny plates of aluminosilicates (Fig. 2, spectra 3, 4) are

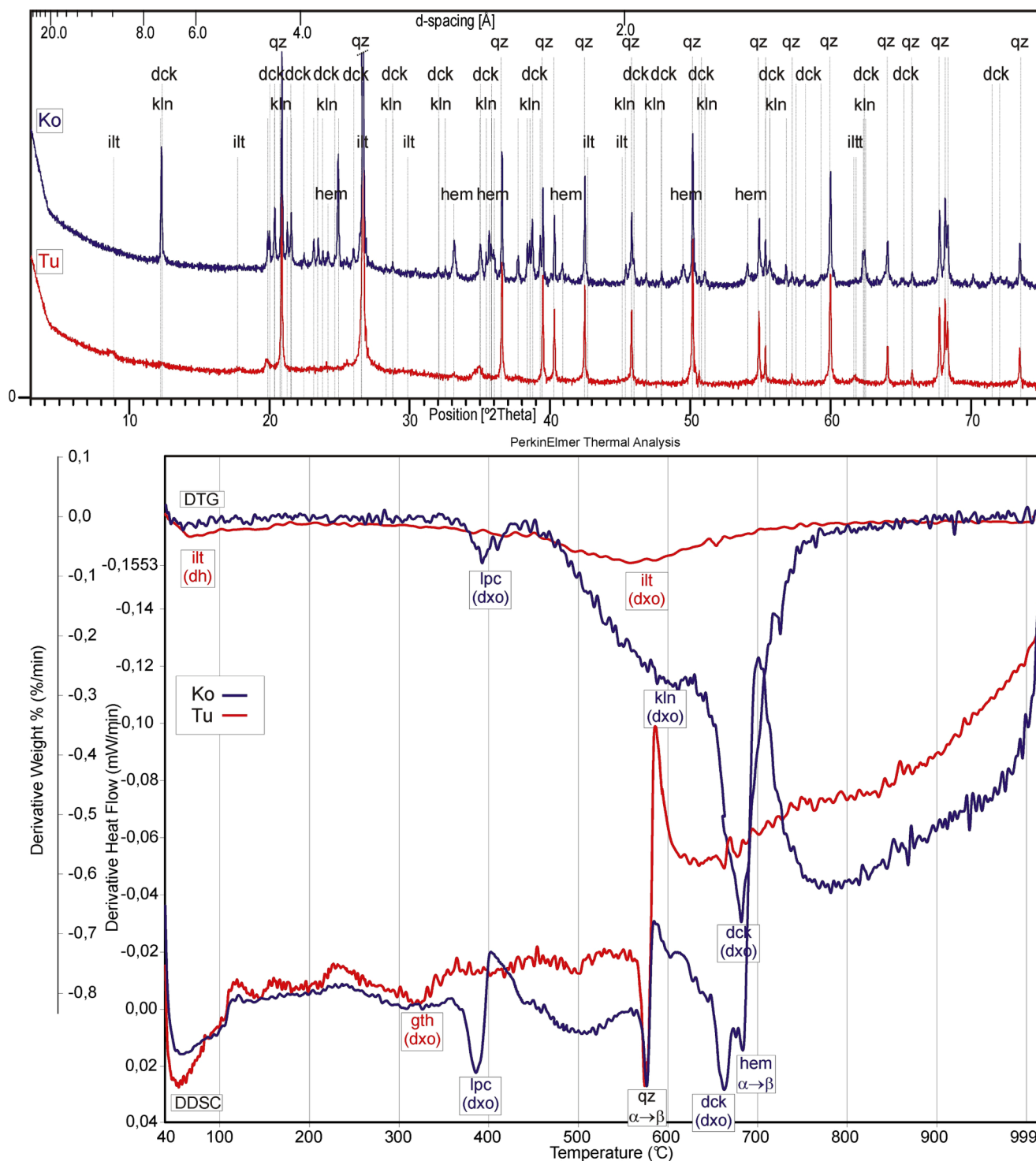


Fig. 3. DSC-TG results for the separated fraction < 63 mm (A) and PXRD diffractograms of the separated fraction < 63 mm (B) and XRD data. Abbreviations are based on [78]: dickite (dck), kaolinite (kln), illite (ilt), hematite (hem), lepidocrocite (lpc), goethite (gth), and quartz (qz); dehydration (dh), dehydroxylation (dxo), α , β – polymorphic transition.

the second most important constituent. They take the form of pore-filling mineral mass, sometimes developed in the form of concertina-like aggregates, and have the chemical composition (Fig. 2, spectra 3, 4) and structure of kaolinite (ICDD 01–080–0886) and dickite (ICDD 01–072–1163; Fig. 3). They share many peaks at the same or similar d-spacing (e.g., 7.14–7.15 Å, $I = 100$, 3.57 Å). However, peaks at 4.46 Å and 4.44 Å should be considered diagnostic for kaolinite and dickite, respectively. Moreover, the results of the DSC-TG analysis showed double-step weight loss (Fig. 3) with maxima at 580 °C and 670 °C, which correspond to the dehydroxylation of kaolinite and dickite, respectively [77]. Additionally, these results prove the presence of iron oxide-hydroxide (Fig. 3) in the form of lepidocrocite, which undergoes dehydroxylation at 370 °C [77]. This phase, not detected by the XRD method, occurs in small quantities and presumably should be considered as a secondary phase—i.e., the weathering product of primordial hematite cement. The total amount of cement is significant (19.3 %), but the pore volume is also large (19.1 %). The pore radius [70] ranges from 1.11 to 2.57 µm (1.64 µm on average).

Meanwhile, Tumlin sandstone (Fig. 1) has a quartz arenitic composition [76] and moderate to weakly preferred orientation. Quartz (Fig. 1, Fig. 2, spectrum 5) is the most ubiquitous constituent (77.2 %), sometimes showing undulatory extinction, with a small percentage of feldspar grains (0.9 %) and rock fragments (7.8 %). The feldspars are untwinned and partly altered, sometimes weakly tartan-twinned and resembling microcline. The rock fragments comprise very sparse polycrystalline quartz and are mostly made up of typical lithic grains composed of quartz and feldspars, representing a kind of leucocratic crystalline rock (of granite-like composition). Additionally, micas were also found, but are very uncommon. Accessory minerals (0.4 %), such as rutile, zircon, and ilmenite, are rounded or well rounded. Moreover, despite their occurrence, the sandstone comprises subangular and subrounded to less-common rounded grains as well as predominantly very equant grains over those that are equant and subequant, while elongate to very elongate grains are subordinate. The grain contacts are point or long, while a concave-convex type of contact or suture is present but very uncommon (Fig. 1).

Furthermore, the SEM-EDS analysis revealed extremely sparse, well-developed, and euhedral quartz crystals formed as syntaxial cement occurs locally (Fig. 2, spectrum 6). However, ferruginous cement appears dominant (13.7 %). Most of the detrital grains have been “stained” by thin and yellowish-orange limonitic fringes that are very visible in polarized light (Fig. 1). This type of a pore-lining cement contributes to the relatively significant porosity of the rock (12.4 %). The pore radius [70] varies from 0.32 to 1.25 µm (0.78 µm on average). Additionally, the SEM-EDS analysis revealed that the fringes consist of potassium aluminosilicates with a minor amount of magnesium and iron (Fig. 2, spectrum 7, 8). Further, the combined results of the XRD and DSC-TG analysis showed the presence of clay minerals and iron oxide-hydroxides. Quartz (ICDD 01–083–2465; Fig. 3) was also detected, but we consider it to be a framework component. Illite (ICDD 00–002–0050) was recognized based on the X-ray diffraction peaks at 10.00 Å, 19.89 Å, 2.56 Å and thermal dehydration in the temperature range 80–110 °C (Fig. 3), followed by dehydroxylation in the range 450–650 °C [77]. Moreover, the endothermic effect at 330 °C can be interpreted as the thermal dissociation of goethite (α -FeOOH) [77]. The goethite occurs in small quantities (below the detection limit of the diffractometer for a polycrystalline sample) and/or is weakly crystallized and therefore was not detected by the XRD analysis.

4.2. Leaching rates achieved during biotic and abiotic dynamic experimental weathering

The results from the dynamic leaching experiments were expressed as leaching rates in order to clearly show how the release of individual elements changed over time. The cumulative release of analyzed elements was presented in column/bar graphs for the final sampling point

on day 119 of the experiment.

The leaching rates observed at the beginning of the experiment (14 days) were noticeably higher for Si and Al under biotic compared to abiotic conditions, whereas Fe leaching rates were less intensively accelerated (Fig. 4). At this early stage (14 days) of the experiment, the differences between the amount of Si released under biotic (GMB) and abiotic conditions (GM) were observed for both sandstones. The Si leaching rates from sandstones at the beginning of the experiment (14 days) were similar and reached 4.6–5.0 µg g⁻¹ day⁻¹ for GMB < 0.22 µm, while only 2.5–2.8 µg g⁻¹ day⁻¹ were released in the abiotic GM (Fig. 4). The total release of Si considering the total GMB was rather irrelevant throughout the experiment, with an exception observed for Ko (14 days) and Tu (28–42 days) sandstones. Meanwhile, the leaching rates observed for abiotic and biotic conditions (GMB < 0.22 µm) were higher for Si toward the end of the experiment. Overall, the Si leaching rates under biotic conditions (GMB < 0.22 µm) oscillated between 3.5 and 7.1 µg g⁻¹ day⁻¹ and 3.4–6.4 µg g⁻¹ day⁻¹ for Ko and Tu sandstones, respectively. In contrast, the Si leaching rates under abiotic conditions (GM) did not exceed 2.9 µg g⁻¹ day⁻¹ for both sandstones.

The release of Al was notably higher in the total GMB than in the GMB < 0.22 reaching 1.2 µg g⁻¹ day⁻¹ versus 0.5 µg g⁻¹ day⁻¹ for Ko. Whereas, in the case of Tu, the Al associated with the total GMB became notable at the end of the experiment (day 119) reaching 1.8 (total GMB) versus 0.8 (GMB < 0.22 µm). The leaching rates observed for abiotic and biotic conditions were higher for Al toward the end of the experiment, particularly with Tu sandstone. The overall rates achieved under biotic conditions (GMB < 0.22 µm) were 0.2–0.5 µg g⁻¹ day⁻¹ and 0.5–2.2 for Ko and Tu sandstones, respectively.

The maximal Fe leaching rates achieved throughout the 119 days of experiments were 0.4 µg g⁻¹ day⁻¹ for Ko sandstone and 1.3 µg g⁻¹ day⁻¹ for Tu sandstone in terms of total GMB. The rate of Fe release was higher under biotic than abiotic conditions throughout the entire experiment. For Ko sandstone, Fe leaching rates were 0.1–0.2 µg g⁻¹ day⁻¹ under biotic conditions (GMB < 0.22 µm) and 0.04–0.15 µg g⁻¹ day⁻¹ under abiotic conditions (GM). In the case of Tu sandstone, Fe leaching rates were 0.02–0.5 µg g⁻¹ day⁻¹ under biotic (GMB < 0.22 µm) and only up to 0.15 µg g⁻¹ day⁻¹ under abiotic conditions (GM).

Meanwhile, the release of elements from Tu sandstone exposed to H₂O conditions oscillated between 0.8 and 3.4 µg g⁻¹ day⁻¹ (Si), 0.2–0.4 µg g⁻¹ day⁻¹ (Al), and up to 0.1 µg g⁻¹ day⁻¹ (Fe), whereas leaching rates achieved for Ko sandstone exposed to the same conditions were 0.8–1.4 µg g⁻¹ day⁻¹ (Si), 0.1–0.2 µg g⁻¹ day⁻¹ (Al), and up to 0.2 µg g⁻¹ day⁻¹ (Fe).

4.3. Leaching rates achieved during biotic and abiotic continuous experimental weathering

The element leaching rates achieved throughout the 119-day continuous leaching experiments were generally higher in biotic experiments (GMB < 0.22 µm) as compared to abiotic experiments (GM). The Si release was accelerated by bacteria and reached 0.3–2.9 µg g⁻¹ day⁻¹ (GMB < 0.22) and slightly lower values of 0.3–2.5 µg g⁻¹ day⁻¹ (GM) for Ko sandstone. Likewise, Si leaching rates from Tu sandstone were higher in the biotic medium and reached 1.0–3.0 µg g⁻¹ day⁻¹ (GMB < 0.22), whereas rates achieved in GM did not exceed 1.9 µg g⁻¹ day⁻¹ (Fig. 5).

Furthermore, Al leaching rates were also accelerated, reaching up to 0.4 in GMB < 0.22 and 0.2 in GM for Ko sandstone and up to 0.8 µg g⁻¹ day⁻¹ in GMB < 0.22 and 0.3 µg g⁻¹ day⁻¹ in GM for Tu sandstone. The Fe leaching rates in GMB < 0.22 oscillated between 0.03 and 0.15 µg g⁻¹ day⁻¹ for both sandstones, whereas leaching in GM oscillated up to 0.4 µg g⁻¹ day⁻¹ (Fig. 5).

4.4. Characterization of experimentally weathered sandstones

Mineralogical characterization of experimentally weathered

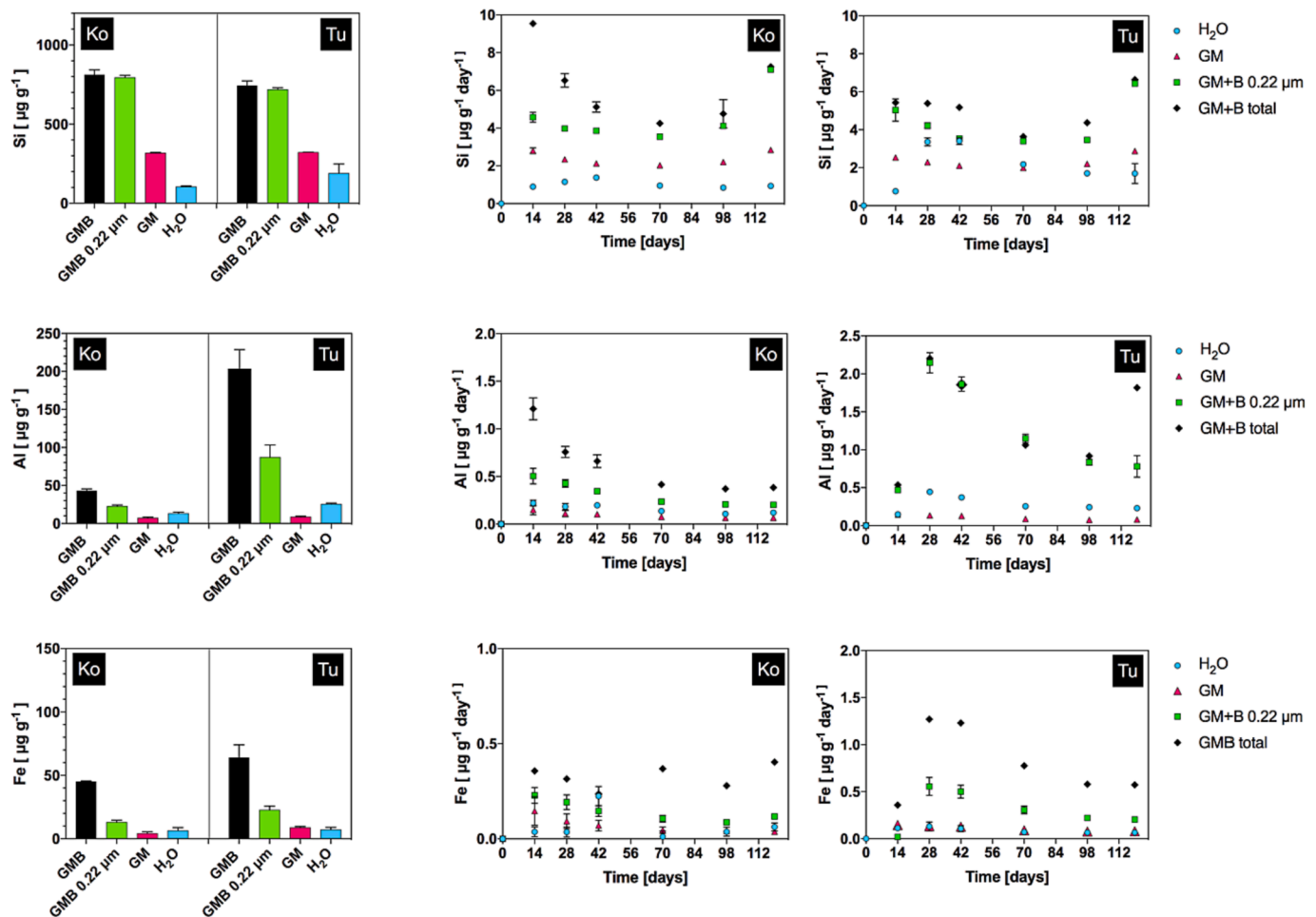


Fig. 4. Total release of elements achieved after 119 days of the experiment (bars) and evolution of leaching rates throughout the entire experiment (points) calculated based on the concentration of elements in the leachates (GMB total: growth medium with bacteria digested; GMB: growth medium with bacteria filtered at $< 0.22 \mu\text{m}$; GM: sterile growth medium; H₂O: sterile water). Error bars present standard deviation of the replicate values.

sandstones revealed some differences in the composition of individual components. Tables 2 and 3 summarize the results of the cement elemental composition. Here, Tu and Ko sandstone samples treated with water (H₂O), A growth medium (GM), and a medium and bacteria (GMB) were analyzed and expressed as weight percentages (wt.%). All statistical data were calculated considering 100 ± 5 analytical points per treated sample. This study also evaluated durability of studied sandstones tracking dissolution of these materials as well as measuring the rebound values after the treatments (Fig. 6). It is shown that after weathering, both sandstones (Ko and Tu) revealed slightly lower durability (median value) than that of unweathered sandstones. Furthermore, result for cubes treated with growth medium and medium and bacteria shows much larger range for first and third quartile, comparing to unweathered samples. The same trend but much higher spread of minimum and maximum (whiskers) characterize samples GM and GMB versus control samples. These results indicated that exposure to biotic and abiotic weathering changed initial properties of these materials (Fig. 6). Therefore, application of Equotip tester is considered here as qualitative measurement to support data obtained from the leaching experiments. In other words, results of this measurement cannot serve as sole source of unequivocal information about studied samples durability, but it rather summarizes the various contributions of different weathering treatments.

Since clay minerals (kaolinite group) and hematite are distributed heterogeneously in the Ko sandstone, only single and well-developed crystals of the former were analyzed. For this reason, the contents of

Si and Al were taken into account. The obtained results showed that the average Si content, the median, and the 1st and 3rd quartiles reached the highest values for the sample resulting from the H₂O experiment (Tab. 2). The lowest values of these parameters were observed for the bio-weathered sample (GMB), while the sample weathered with GM showed intermediate values. Moreover, the H₂O and GM samples were characterized by the lowest standard deviation for the silicon content, while the highest was observed for the GMB sample (Tab. 2). The content of Al in the cement showed the complete opposite relationship (Tab. 2), as compared to the Si content. The statistical parameters (including the standard deviation) describing the aluminum content reached the highest values in the GMB sample, while the lowest was observed for the H₂O sample (Tab. 2). Here, aluminum and silicon exhibit a strong negative correlation, and the Pearson correlation coefficient (PCC) ranged from -0.99 to -0.93 (for the H₂O and GMB samples, respectively).

In contrast to the Ko sandstone, the relatively homogeneous cement fringes in the Tu sandstone allowed for the analysis of the content of silicon and aluminum as well as potassium and iron (Tab. 3). The highest content of silicon and aluminum (median, 1st and 3rd quartiles) characterized the H₂O sample. It decreased in the GM sample, reaching the lowermost content in the GMB sample. A completely opposite trend was observed for iron and potassium contents. The lowermost content characterized the GMB sample, while the highest was typical for the H₂O sample, with the GM sample as the intermediate (Tab. 3).

The highest standard deviation value was observed consistently for

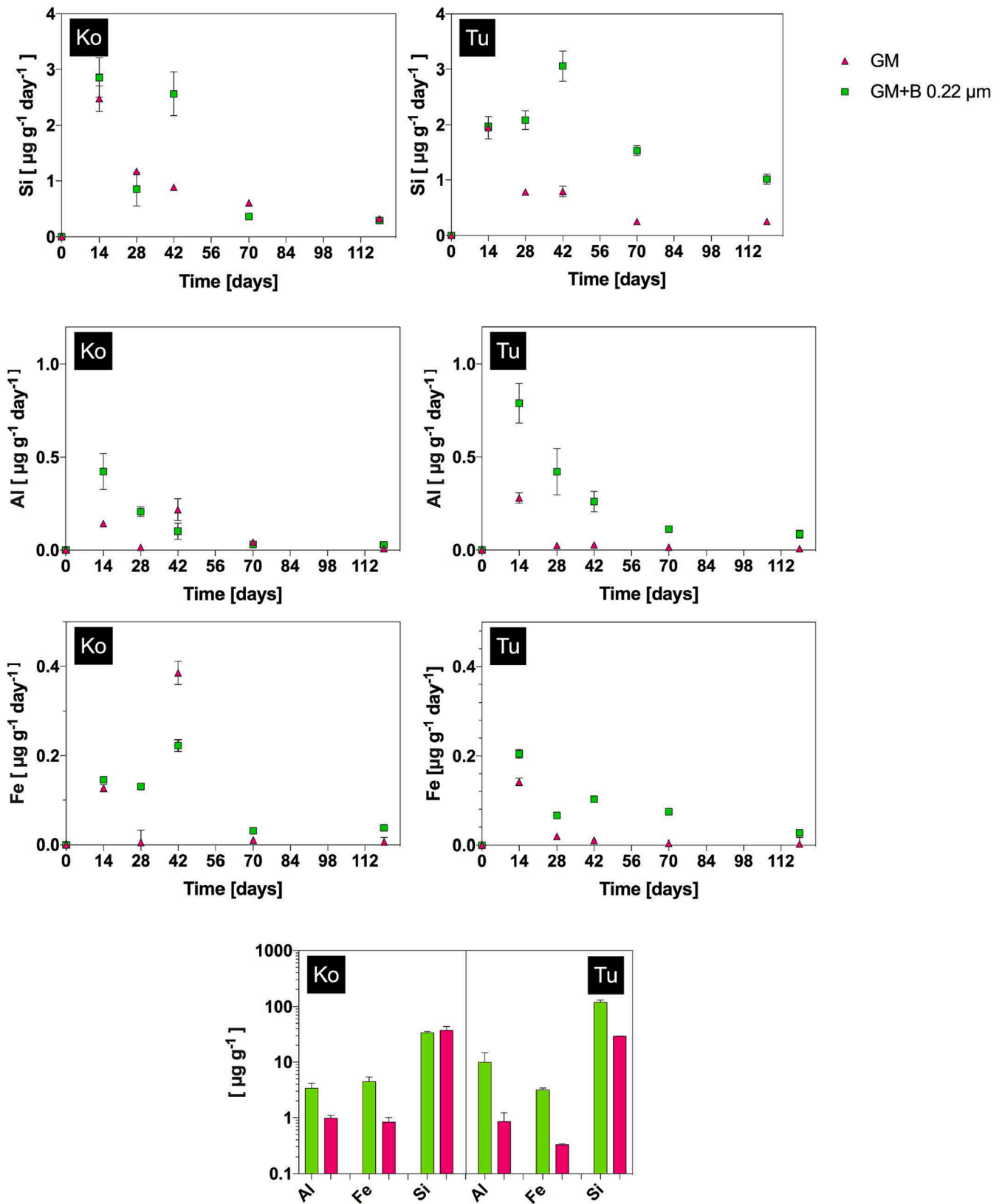


Fig. 5. Leaching rates (points) throughout the entire experiment calculated based on the concentration of elements in the leachates (GMB total: growth medium with bacteria digested; GMB: growth medium with bacteria filtered at < 0.22 μm ; GM: sterile growth medium) and total release of elements (bars) achieved after 119 days of the experiment. Continuous experiment with cubic-shaped sandstones. Error bars present standard deviation of the replicate values.

Table 2

The variability of the chemical composition of Kopulak sandstone cement with calculated statistical parameters.

	Si [wt. %]			Al [wt. %]		
	H ₂ O	GM	GMB	H ₂ O	GM	GMB
Arithmetic mean	29.48	28.10	27.03	19.52	20.94	21.58
Median	29.20	27.80	26.50	19.90	21.30	21.95
First quartile	28.60	27.60	26.10	18.90	20.90	20.80
Third quartile	30.10	28.10	27.60	20.50	21.60	22.90
Minimum	27.90	26.90	24.90	14.80	12.40	15.90
Maximum	33.60	35.80	32.30	21.40	22.10	23.70
Standard deviation	1.11	1.11	1.43	1.26	1.27	1.67

the biotic system (GMB) for all elements. The lowest value of this parameter was observed for potassium and iron content in the H₂O sample, while silicon and aluminum content showed the lowest value for abiotic weathering conditions (GM; Tab. 3). Moreover, silicon content consistently (H₂O, GM, GMB) shows a very strong to strong negative correlation with aluminum (PCC from -0.86 to -0.62) and potassium (PCC from -0.76 to -0.62) and a very weak negative correlation with iron (PCC from -0.24 to -0.02). Further, a weak positive (H₂O, GMB) to very weak negative (GM) correlation exists between aluminum and potassium (Tab. 3), while potassium and iron show a very weak (GMB and H₂O) to weak (GM) positive correlation (Tab. 3).

5. Discussion

This work evaluated the impact of bacteria on the dissolution kinetics of two different sandstones. The isolation of sandstones from bacteria (i.e., abiotic experiments) was crucial to decipher the mechanisms driving the dissolution of sandstones as well as to identify the elements that are preferentially released from sandstones, consequently clarifying the minerals prone to bacterially mediated dissolution.

Table 3

The variability of the chemical composition of Tumlin sandstone with calculated statistical parameters and Pearson's correlation matrix.

	Si [wt. %]			Al [wt. %]			K [wt. %]			Fe [wt. %]		
	H ₂ O	GM	GMB	H ₂ O	GM	GMB	H ₂ O	GM	GMB	H ₂ O	GM	GMB
Arithmetic mean	28.08	27.23	27.46	14.66	14.47	13.60	6.04	7.22	7.79	2.62	3.10	3.15
Median	27.15	26.70	26.25	15.30	14.80	14.50	6.10	7.10	7.70	2.35	2.70	2.80
First quartile	26.70	26.00	25.50	14.00	13.70	12.30	5.50	6.50	6.88	1.78	2.40	2.28
Third quartile	28.55	28.10	28.80	16.00	15.60	15.40	6.60	7.80	8.63	3.03	3.30	3.33
Minimum	24.70	24.90	22.90	7.50	8.10	6.00	3.40	4.60	4.00	1.20	1.40	1.00
Maximum	37.00	34.60	36.30	17.60	18.20	16.60	9.20	12.90	15.10	9.20	9.50	16.00
Standard deviation	2.29	1.77	2.96	2.19	1.77	2.58	1.10	1.29	1.99	1.26	1.43	1.94

5.1. Bacterially mediated dissolution of sandstones

The growth of *P. fluorescens* when bacteria were incubated with sandstones was promoted, and siderophore production was observed (Table 4). Siderophores are known for their Fe chelating properties. Therefore, using sandstones containing Fe-bearing minerals was essential to decipher the rates and intensity of sandstone dissolution under biotic and abiotic conditions. The results showed that siderophores were produced in both the Ko and Tu experiments. A quantity of $\sim 70 \mu\text{m}$ that was achieved at the initial stage of the experiment (Tab. 4) was sufficient to initiate the sandstones' dissolution (Fig. 4), proving the nutritional benefit of sandstones for bacteria (Tab. 4). This is in agreement with the study by [79] who demonstrated the nutritive potential of minerals for *Pseudomonas* spp. The bacterially mediated dissolution of sandstones was significantly higher compared to the abiotic control experiments with the growth medium and water. This is confirmed by the results of analyses of the chemical composition of the cement, which showed the greatest variability of the elemental composition for the biotic experiment (see median and standard deviation parameter differentiation, Tab. 2 and 3). Moreover, the observed highest variability in the elemental composition of the cement for biotic conditions indicates the

Table 4

Siderophore (pyoverdine PVD) concentration throughout the experiment.

Time [days]	PVD [$\mu\text{mol L}^{-1}$]	SD $\pm$	Time [days]	PVD [$\mu\text{mol L}^{-1}$]	SD $\pm$
Kopulak			Tumlin		
14	68.4	13.7	14	66.3	8.7
28	31.3	0.1	28	28.4	0.5
42	15.4	0.3	42	22.4	8.7
56	19.6	0.5	56	9.9	0.8
70	21.5	2.1	70	19.3	1.0
84	18.5	3.0	84	14.8	4.6
98	23.2	1.6	98	12.3	0.8
119	54.7	2.2	119	118.2	9.2

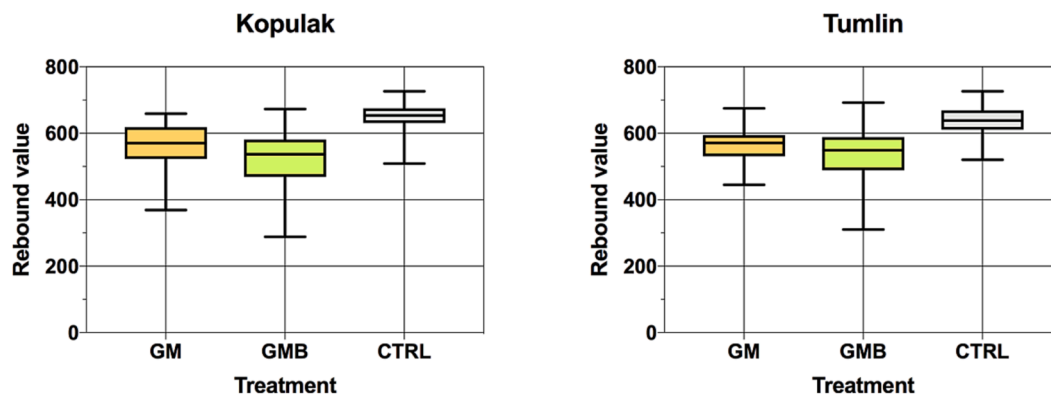


Fig. 6. Durability of sandstones based on comparison of rebound values obtained with Equotip for unweathered sandstone (CTRL) and sandstones weathered under abiotic (GM) and biotic (GMB) conditions.

heterogenic leaching of the binder. In the biotic experiment, in which pyoverdine was systematically detected (Tab. 4), the Fe and Al release was enhanced, as compared to the abiotic experiments (Fig. 4). Thus, the presence of pyoverdine (Tab. 4) had a relevant catalyzing effect on the dissolution of sandstones (Fig. 4). In terms of a 0.22- μm fraction aliquot, the lowest bacterial impact on the Fe release from sandstone was observed, which is rather surprising given the fact that siderophore is known for its high affinity to Fe [44]. Moreover, no significant bacterial uptake of Si could be observed, whereas bacteria exhibited a remarkable contribution toward Fe associated with the fraction $> 0.22 \mu\text{m}$ in the case of both sandstones and Al in the case of Tu sandstone. In terms of the total fraction, the role of bacteria in Fe acquisition is more pronounced (Fig. 4). This suggests that siderophore assisted in the Fe release from the minerals, transporting it to biofilm fraction rather than maintaining it in the fraction $< 0.22 \mu\text{m}$. Furthermore, in the initial stages of the experiments (14–28 days), Al release was promoted with respect to Fe, and Tu sandstone was found to exhibit higher dissolution rates (Fig. 4). Additionally, the association of Al with the biofilm fraction was also observed (Fig. 4). However, Al does not have any biological function in bacterial cells, therefore it can be assumed that its release from the sandstones was incidental rather than purposefully acquired by the bacteria. Nevertheless, biofilm and associated extracellular polymeric substances exhibit different properties than those observed for free bacterial cells, and consequently the bacterial incorporation of biofilm may exhibit higher tolerance to many external factors as compared to a single bacterial cell of the same strain [43]. Here, it is important to note that after the Al release from Tu sandstone was facilitated (28 days), siderophore production decreased. This is in accordance with the study by [80] who demonstrated decreased siderophore production when Al was added to the bacterial system. In this context, [81] demonstrated that siderophore production slowed the passive transport of Al at high and low concentrations of Fe. In addition, the formation constants of siderophore complexes with Al are lower than those formed with Fe [82,83], which suggests that pyoverdine could not have been the only factor contributing to the Al release. Meanwhile, other authors demonstrated that the increase of siderophore production by Al^{3+} may limit the Fe uptake or can be incorporated in *Pseudomonas* sp. using the pyoverdine pathway [84].

Furthermore, the relatively little microbial effect on the Si release (in terms of relative wt.% values, see Table 5) suggests that pyoverdine affected the mobilization of this element to lower extent as compared to Fe and Al. Therefore, complexation reactions between pyoverdine and structural Al and/or Fe promote dissolution either by a surface controlled mechanism [85] or by increasing the solubility of these

metallic elements in solution [86]. It has been shown that the general bound energy of Si to siderophore is low [87], therefore the most plausible reason for low final Si release (Tab. 5) is that Si-O bonds present in sandstones were less efficiently broken by the bacterial metabolite. Instead, the higher content of Si in the solution ($\mu\text{g g}^{-1}$) is the result of their generally higher content in sandstones and higher solution pH (discussed below). However, the susceptibility was higher for Fe and Al. Even if the affinity of Al to siderophore is lower than that of Fe, the association of both with biofilm was observed. Here, it can be assumed that extracellular polymeric substances played a predominant role. However, in this context, other sequestration mechanisms such as precipitate formation cannot be excluded. It has already been suggested in the literature that when toxicity effects are absent, the sequestration of elements on oxides may dominate over the biofilm uptake [88].

Furthermore, of a high importance is a fact that prolonged exposure of sandstones to bacteria resulted in a higher pH values in a biotic solution as compared to abiotic solution (Figure S1 Supplementary materials). The prolonged leaching of Si-bearing minerals was crucial to increase pH of the solution [89]. Bacteria indirectly created conditions favorable for enhancement of silicates dissolution kinetics. That was achieved by the siderophore excretion and withdrawal of crucial elements from sandstones. When major cations such as Fe^{2+} and Al^{3+} were leached out from the sandstone matrix and cement (Figure S1, Supplementary materials), protons were exchanged back from the medium to the solid matrix and cement to maintain the charge equilibrium, resulting in a quick pH rise from 7.0 to up to 8.8 in the presence of *P. fluorescens* [90]. As presented in Figure S1 (Supplementary materials), there is a clear shift of leaching rates as a function of pH. Thus, it can be stated that siderophores were crucial to initiate dissolution of studied sandstones, whereas further pH alteration attributed to higher dissolution under biotic conditions. It has been highlighted in the literature that organic ligands are crucial to minerals dissolution [91]. Complexing agents cause an increase of elements leaching as compared to water-mediated dissolution; as demonstrated by [92] 2–35 times higher (Si) and 3–500 times higher (Al) concentrations were observed in organic solution. In this case, element complexation by pyoverdine could also be affected by the increase of pH as at lower pH conditions protonation of the ionized chelates and competition between hydrogen ion and other elements for binding sites occurs and results in lower solubilization. In addition, it is reflected in mineralogical alterations since wide variations of Al and Si content was observed under biotic conditions which is directly associated with matrix and cement minerals dissolution. Furthermore, in this study not only dissolved microbial aliquot (leachate $< 0.22 \mu\text{m}$), but also digested fraction aliquot (including biomass GMB total) was responsible for enhanced dissolution rates. That can also be due to negatively charged biomass at higher pH values, because bacterial biomass contribution to element uptake tends to increase as pH increases [93].

At present, there is a limited amount of information on the effect of siderophore-producing bacteria on sandstone dissolution. Therefore, this work importantly contributes to the state of the art, whereby Tu sandstone was found to be more susceptible to bioweathering as compared to Ko sandstone (Fig. 4). Thus, based on this experimental work, new insight into the mechanisms of sandstone weathering is provided. Particularly, this experimental approach demonstrated the role of Fe chelating compound siderophores in the weathering of these materials.

5.2. Comparison of continuous and dynamic experimental systems—implications for sandstone exposure in a real environmental weathering system

In this study, two types of dynamic versus continuous leaching experiments aimed to demonstrate the two bioweathering scenarios. The former simulated several events of intensive bacterial activity interacting with sandstones, whereas the latter simulated the long-term

Table 5

Relative values of released elements after 119 days, calculated based on concentration of elements in the leachates and the bulk composition of the studied sandstones (GMB total: growth medium with bacteria digested; GMB: growth medium with bacteria filtered at $< 0.22 \mu\text{m}$; GM: growth medium; H_2O : ultra-pure water).

	Ko	SD $\pm$	Tu	SD $\pm$
Al				
GMB	0.348	0.021	2.618	0.321
GMB 0.22	0.184	0.012	1.123	0.204
GM	0.060	0.009	0.115	0.010
H_2O	0.110	0.012	0.332	0.013
Fe				
GMB	0.548	0.005	3.666	0.572
GMB 0.22	0.160	0.018	1.305	0.166
GM	0.052	0.015	0.510	0.046
H_2O	0.079	0.028	0.421	0.091
Si				
GMB	0.183	0.007	0.164	0.007
GMB 0.22	0.180	0.003	0.159	0.002
GM	0.072	0.001	0.071	0.000
H_2O	0.024	0.001	0.042	0.013

exposure of sandstones to bacteria, assuming that under such conditions, greater secondary-phase precipitation may occur. In the end, both experiments revealed higher leaching rates under biotic conditions as compared to abiotic conditions, highlighting the accelerating role of *Pseudomonas fluorescens* in sandstone deterioration. When bioleaching rates were compared for Ko sandstone, the maximum rate achieved for Si in the dynamic experiment was $7.1 \mu\text{g g}^{-1} \text{day}^{-1}$, whereas the maximum rate achieved in continuous leaching was $2.9 \mu\text{g g}^{-1} \text{day}^{-1}$. Likewise, for Tu sandstone, Si leaching rates were $6.4 \mu\text{g g}^{-1} \text{day}^{-1}$ in the dynamic versus $3.0 \mu\text{g g}^{-1} \text{day}^{-1}$ in the continuous experiments. Moreover, discrepancies between biotic leaching under dynamic and continuous conditions for Fe were $0.2 \mu\text{g g}^{-1} \text{day}^{-1}$ versus $0.2 \mu\text{g g}^{-1} \text{day}^{-1}$ and $0.5 \mu\text{g g}^{-1} \text{day}^{-1}$ versus $0.2 \mu\text{g g}^{-1} \text{day}^{-1}$ for Ko and Tu, respectively. The Al release was 0.5 versus $0.4 \mu\text{g g}^{-1} \text{day}^{-1}$ for Ko and $2.2 \mu\text{g g}^{-1} \text{day}^{-1}$ versus $0.8 \mu\text{g g}^{-1} \text{day}^{-1}$ for Tu. This comparison enables the statement that Ko sandstone was less sensitive to changed bioweathering conditions since the difference between dynamic and continuous weathering was lower than that observed for Tu sandstone. However, Tu sandstone was characterized by higher porosity compared to Ko sandstone (Tab. 1).

5.3. Susceptibility of sandstone components to the bioweathering

Based on geochemical data, the overall weathering intensity can be ranked as follows: GMB > GM > H₂O, with the last being the least intense. This is reflected in the variability of the elemental composition of the cement, which is the largest in the GMB system (Tab. 2 and 3). Moreover, it is most emphasized by the median content of silicon and aluminum in sandstone cement, which is generally the highest in abiotic samples and the lowest in samples subjected to bio-weathering. Further, biotically- and/or chemically-mediated damage of sandstone is an irreversible reaction due to the dissolution of the main minerals. Abiotic weathering was found to be less intensive when compared to biotically-mediated weathering. Therefore, the activity of heterotrophic bacteria on sandstone micro-surfaces should not be neglected when considering the durability of sandstones. The size of bacteria *P. fluorescens* is $0.5 \mu\text{m}$ in width and $2\text{--}2.5 \mu\text{m}$ in length that enable the entrance of the bacterial cells between the pores of sandstones (up to $1.1\text{--}2.6 \mu\text{m}$ [70]) and cell attachment may promote biofilm formation [5,94]. More specifically, Tu sandstone characterized by higher porosity (19.1 %, see Tab. 1) that was found to reveal higher bioweathering susceptibility. This difference does not result from the distinct compaction or grain size distribution, but from the different structure of the cement (pore-lining cement versus pore-filling cement). As a result, this differentiation has a significant effect on the permeability of the rock [95] thereby the availability of water, which is necessary for biocolonization [7]. In the experimental weathering, complete sandstone immersion was maintained throughout the experiment, and therefore high porosity enabled deep water penetration, which could, in turn, favor microbial colonization. This porosity feature is also important for in-situ weathering. However, here, the size of pores would play a predominant role rather than general porosity: small pores would enable longer water retention [7], which, would, in turn, favor microbial colonization unlike large-pore sandstones, where water retention is shorter and microbial colonization may be prevented [96].

The cumulative leaching results were also recalculated into percentage values (Tab. 5), as these are believed to represent the susceptibility of sandstones to dissolution. According to the obtained results, Tu sandstone revealed higher susceptibility to dissolution as compared to Ko sandstone. In particular, this tendency can be observed based on Al and Fe release that reached up to 2.6 % and 3.7 %, respectively, for Tu sandstone and only 0.3 % (Al) and 0.5 % (Fe) for Ko sandstone. Moreover, the main Al-bearing phase in Ko sandstones is kaolinite, while in Tu, it is illite.

Additionally, the samples also differ in Fe-bearing components. Sandstone Ko mainly contains hematite, whereas sandstone Tu is mainly

made up of goethite. Our results suggest that the different releases of Fe and Al can be assigned to the varying susceptibility of these minerals to biodissolution. As demonstrated by [97], *Pseudomonas* sp. prefers to attach to goethite rather than kaolinite. This could explain why Al was released to a lower extent (0.3 %) than Fe (0.5 %) from Tu even if kaolinite (the main Al bearing phase) is present in a volumetrically higher proportion than goethite. Other reasons include the higher complexing ability of siderophore towards Fe than Al as well as the greater susceptibility to leaching of illite as compared to kaolinite. This may be due to the different crystallographic forms of these minerals and the different surface areas exposed to weathering. Moreover, kaolinite occurs as relatively large (up to $4\text{--}5 \mu\text{m}$) euhedral flakes, while illite is filamentous and much smaller (below $1 \mu\text{m}$). In this context, a higher susceptibility of Tu sandstone to serve as an Fe source for bacteria suggests that goethite is more susceptible to bioweathering than hematite. This is in accordance with the study by [79] who demonstrated the same tendency of *Pseudomonas* sp. Additionally, these authors pointed out that Fe acquisition may have been independent of the surface area exposed to weathering. Meanwhile, kaolinite dissolution by *Pseudomonas* sp. has already been reported [98,99].

Furthermore, both sandstones revealed similar susceptibility with respect to Si release, as for both sandstones up to 0.2 % (Si) was released. Since Si-bearing minerals in both sandstones are quartz and clay minerals—kaolinite in Ko and illite in Tu—it is difficult to distinguish which mineral served as the Si input in the leachate. However, quartz is considered a relatively stable mineral under near-neutral conditions, even though the organic molecules can enhance its dissolution [100]. Therefore, we believe that most of the Si was leached from the clay cement, with quartz playing a negligible role. Thus, given that Ko sandstone is more abundant in clay minerals (kaolinite) than Tu sandstone, which contains relatively minor amounts of illite, Si release was independent of mineral abundance and its form in the sandstone. On the other hand, illite and kaolinite may show different susceptibility to leaching. Furthermore, to get a similar total Si content in leachate for Tu and Ko, different Si releases from clay minerals could be compensated using the presence of a silica cement with a low degree of crystallinity (e. g., opal) and which easily undergoes bioweathering.

5.4. Secondary phases formation in the studied (bio)weathering system

Secondary products on a sandstone surface are formed due to the release of ions (initially incorporated in minerals) in a liquid phase and the subsequent formation of secondary precipitates depending on the saturation occurring in the system. However, the secondary phase(s) coating of microcracks and fractures can inhibit the further progress of the dissolution [101]. In this study, secondary phase formation was interpreted via a geochemical model (Fig. 7). Among the phases predicted by the model, strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$), gibbsite (or other polymorphs: bayerite, doyleite, and nordstrandite), $\text{Al}(\text{OH})_3$, and goethite FeOOH were found. Generally, phosphate formation (strengite) was thermodynamically predicted in a bacterially-mediated weathering system with both Ko and Tu sandstones, whereas in an abiotic system, this phase remained undersaturated. Meanwhile, a different scenario was observed for Al-precipitates, for which saturation indices were higher in the abiotic (GM) than biotic (GMB) systems. Furthermore, goethite was a phase that was oversaturated for both sandstones and for abiotic and biotic conditions. Here, the saturation of strengite indicates that Fe solubility in the studied system was controlled by the formation of phosphate species rather than oxyhydroxides. In this context, the role of phosphates in controlling element speciation in weathering mediated by *Pseudomonas* sp. has been previously observed [90]. The Al solubility was controlled by the formation of $\text{Al}(\text{OH})_3$ with a higher saturation observed in abiotic (GM) than biotic weathering (GMB), indicating that the presence of siderophore slightly inhibited the formation of Al-precipitates in the biotic system, likely due to the formation of Al-siderophore complexes [102]. Here, it is interesting to note that even

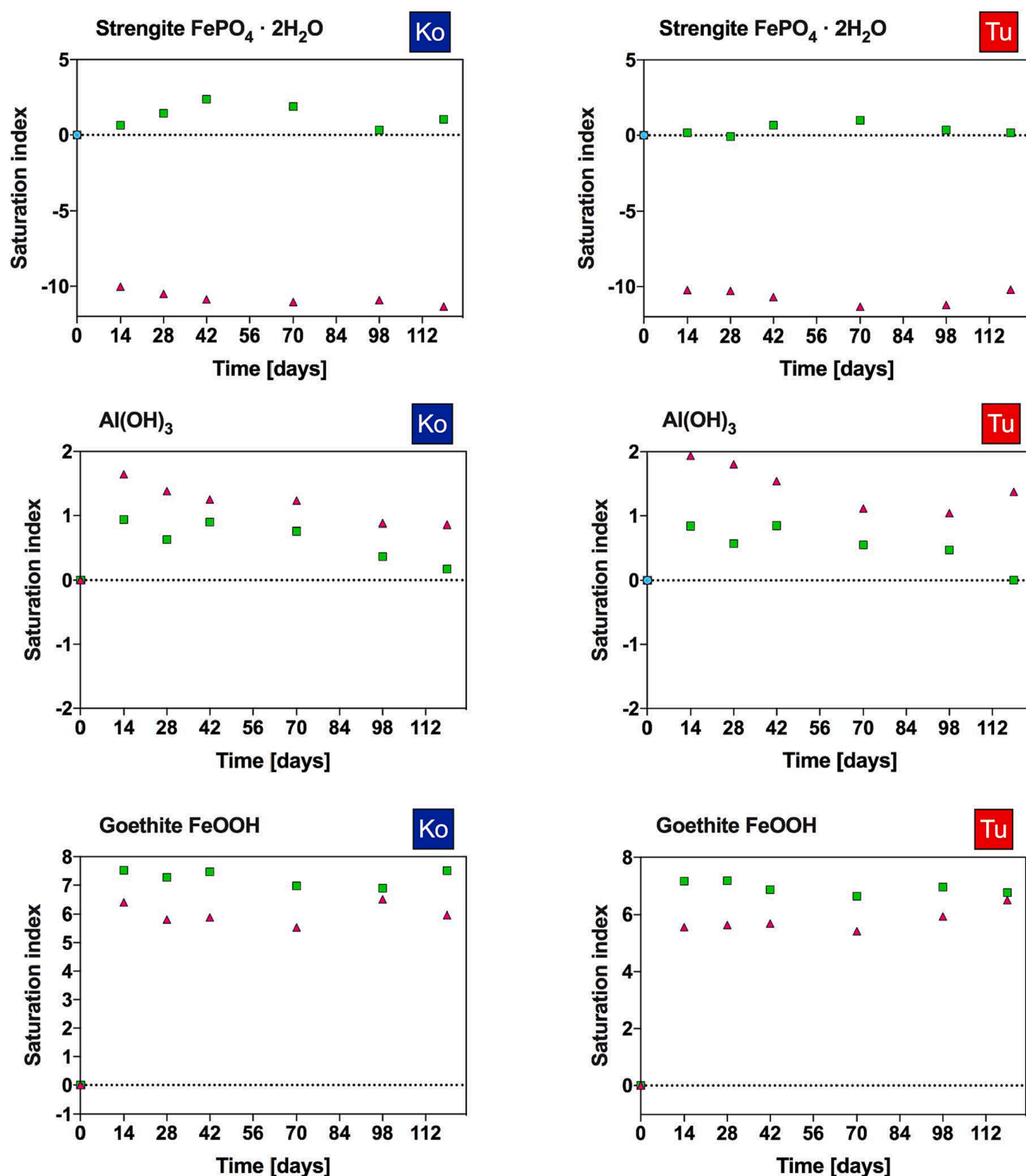


Fig. 7. Saturation indices of secondary phases controlling the solubility of Fe and Al in the studied abiotic (GM—triangle symbol) and biotic (GMB—square symbol) weathering systems.

though the siderophore produced by the bacteria is known for its high affinity to Fe, its impact on the Fe-bearing secondary phases was minor as strong goethite oversaturation was observed. This is an important finding indicating that the role of siderophore in sandstone bio-weathering is predominantly linked to controlling Al solubility rather than Fe, which was mainly controlled by the medium.

5.5. Implications of findings from this study for the durability of monuments

The results of the investigated abiotic and biotic sandstone weathering scenarios are relevant to monuments' conditions since sandstones are routinely used as building material. Therefore, their durability has to

be wisely assessed to prevent the deterioration of cultural heritage objects. However, our findings are also crucial to geomorphological research as the weathering processes influence many dynamic systems related to landscape formation [101,103,104].

Moreover, a comparison of the weathering conditions demonstrated that biotic factors may considerably enhance the dissolution of the minerals present in sandstones, consequently releasing elements. If the rate of dissolution achieved after 119 days proceeded further, then it is expected that decay of Ko sandstone would be likely faster than that of Tu. However, that assumption represents the worst-case scenario because the degradation rate under field conditions would undoubtedly proceed at much lower rates than at the laboratory scale. Additionally, the dissolution of cement present in sandstones is an important factor determining the durability of building materials as it causes crumbling, and the subsequent collapse of a building/monument can be expected. Meanwhile, due to seasonal changes in microbial communities that colonize sandstones [105,106], the extent to which the durability of studied sandstones changes remains to be further elucidated. This study showed that the bacterial contribution to weathering should not be ignored when sandstones are used as architectural materials.

6. Conclusions

This work is a new contribution demonstrating the impact of bacteria on the dissolution kinetics of sandstones in the presence of *Pseudomonas fluorescens* bacteria. Based on the applied geochemical approach, the following conclusions can be made:

- Considering the sandstones as a whole sample, Tu sandstone was the most susceptible to biodissolution, whereas Ko had higher durability.
- Cement and matrix minerals were found to be the most vulnerable to dissolution in the presence of *P. fluorescens*, whereas framework minerals (quartz) had much higher stability.
- The presence of pyoverdine siderophore molecules in solution improved the dissolution rate of the sandstones, promoting the release of Fe and Al.
- Goethite and illite are more susceptible to dissolution than hematite and kaolinite in the presence of *Pseudomonas fluorescens*.
- Biomass was found to play a role in capturing Al and Fe.
- Siderophore revealed an important contribution to controlling Al solubility in the studied weathering system.

CRediT authorship contribution statement

Anna Potysz: Conceptualization, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing, Funding acquisition. **Wojciech Bartz:** Conceptualization, Investigation, Methodology, Visualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This research was financed by the National Science Centre in Poland under grant agreement UMO-2018/31/D/ST10/00738 to AP. The authors would like to thank the anonymous native speakers from the commercial translating company for English proofreading. The time devoted by the editors and reviewers to evaluate our work is highly

appreciated.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.conbuildmat.2023.130584>.

References

- [1] X. Liu, R.J. Koestler, T. Warscheid, Y. Katayama, J.D. Gu, Microbial deterioration and sustainable conservation of stone monuments and buildings, *Nat. Sustain.* (2020), <https://doi.org/10.1038/s41893-020-00602-5>.
- [2] K.H. Friolo, B. Stuart, A. Ray, Characterisation of weathering of Sydney sandstones in heritage buildings, *J. Cult. Herit.* (2003), [https://doi.org/10.1016/S1296-2074\(03\)00047-5](https://doi.org/10.1016/S1296-2074(03)00047-5).
- [3] R. Snethlage, *Natural stones in architecture: Introduction*, Stone Archit. Prop. Durab. Fifth Ed. (2014), https://doi.org/10.1007/978-3-642-45155-3_1.
- [4] S. Siegesmund, R. Snethlage, *Stone in architecture: Properties, durability*, 2011. doi:10.1007/978-3-642-14475-2.
- [5] T. Warscheid, J. Braams, Biodeterioration of stone: A review, *Int. Biodeterior. Biodegrad.* (2000), [https://doi.org/10.1016/S0964-8305\(00\)00109-8](https://doi.org/10.1016/S0964-8305(00)00109-8).
- [6] H. Hu, S. Ding, Y. Katayama, A. Kusumi, S.X. Li, R.P. de Vries, J. Wang, X.Z. Yu, J. D. Gu, Occurrence of *Aspergillus allahabadii* on sandstone at Bayon temple, Angkor Thom, Cambodia, *Int. Biodeterior. Biodegrad.* (2013), <https://doi.org/10.1016/j.ibiod.2012.06.022>.
- [7] M. Steiger, A.E. Charola, K. Sterflinger, *Weathering and deterioration*, Stone Archit. Prop. Durab. Fifth Ed. (2014), https://doi.org/10.1007/978-3-642-45155-3_4.
- [8] S. Tayler, E. May, The seasonality of heterotrophic bacteria on sandstones of ancient monuments, *Int. Biodeterior. Biodegrad.* (1991), [https://doi.org/10.1016/0265-3036\(91\)90033-N](https://doi.org/10.1016/0265-3036(91)90033-N).
- [9] A. Potysz, W. Bartz, Bioweathering of minerals and dissolution assessment by experimental simulations—Implications for sandstone rocks: A review, *Constr. Build. Mater.* (2022), <https://doi.org/10.1016/j.conbuildmat.2021.125862>.
- [10] R. Prikrýl, B.J. Smith, *Building Stone Decay: From Diagnosis to Conservation*, 2007.
- [11] M. Gómez-Heras, B.J. Smith, R. Fort, Surface temperature differences between minerals in crystalline rocks: Implications for granular disaggregation of granites through thermal fatigue, *Geomorphology*. (2006), <https://doi.org/10.1016/j.geomorph.2005.12.013>.
- [12] D. Benavente, G.-G.-H. Cultrone, The combined influence of mineralogical, hygric and thermal properties on the durability of porous building stones, *Eur. J. Mineral.* (2008), <https://doi.org/10.1127/0935-1221/2008/0020-1850>.
- [13] R.B.G. Williams, D.A. Robinson, Experimental frost weathering of sandstone by various combinations of salts, *Earth Surf. Process. Landforms*. (2001), <https://doi.org/10.1002/esp.227>.
- [14] P.A. Warke, J. McKinley, B.J. Smith, Variable weathering response in sandstone: Factors controlling decay sequences, *Earth Surf. Process. Landforms*. (2006), <https://doi.org/10.1002/esp.1284>.
- [15] X. Liu, H. Meng, Y. Wang, Y. Katayama, J.D. Gu, Water is a critical factor in evaluating and assessing microbial colonization and destruction of Angkor sandstone monuments, *Int. Biodeterior. Biodegrad.* (2018), <https://doi.org/10.1016/j.ibiod.2018.05.011>.
- [16] P.A. Hale, A. Shakoor, A laboratory investigation of the effects of cyclic heating and cooling, wetting and drying, and freezing and thawing on the compressive strength of selected sandstones, *Environ. Eng. Geosci.* (2003), <https://doi.org/10.2113/9.2.117>.
- [17] Z. Zhao, J. Yang, D. Zhang, H. Peng, Effects of Wetting and Cyclic Wetting-Drying on Tensile Strength of Sandstone with a Low Clay Mineral Content, *Rock Mech. Rock Eng.* (2017), <https://doi.org/10.1007/s00603-016-1087-9>.
- [18] J. Zhang, Z. Li, L. Li, J. Liu, D. Liu, M. Shao, Study on weathering mechanism of sandstone statues in Southwest China: example from the sandstone of Niche of Sakyamuni Entering Nirvana at Dazu Rock Carvings, *Nat. Hazards*. (2021), <https://doi.org/10.1007/s11069-021-04705-w>.
- [19] M. Labus, J. Bochen, Sandstone degradation: An experimental study of accelerated weathering, *Environ. Earth Sci.* (2012), <https://doi.org/10.1007/s12665-012-1642-y>.
- [20] P.D. Sumner, M.J. Loubser, Experimental sandstone weathering using different wetting and drying moisture amplitudes, *Earth Surf. Process. Landforms*. (2008), <https://doi.org/10.1002/esp.1586>.
- [21] D.P. Halsey, D.J. Mitchell, S.J. Dews, Influence of climatically induced cycles in physical weathering, *Q. J. Eng. Geol.* (1998), <https://doi.org/10.1144/GSL.QJEG.1998.031.P4.09>.
- [22] J. Ruedrich, T. Bartelsen, R. Dohrmann, S. Siegesmund, Moisture expansion as a deterioration factor for sandstone used in buildings, *Environ. Earth Sci.* (2011), <https://doi.org/10.1007/s12665-010-0767-0>.
- [23] A. Koch, S. Siegesmund, The combined effect of moisture and temperature on the anomalous expansion behaviour of marble, *Environ. Geol.* (2004), <https://doi.org/10.1007/s00254-004-1037-9>.
- [24] M. Gomez-Heras, R. Fort, Patterns of halite (NaCl) crystallisation in building stone conditioned by laboratory heating regimes, *Environ. Geol.* (2007), <https://doi.org/10.1007/s00254-006-0538-0>.

- [25] Q. Sun, Z. Dong, H. Jia, Decay of sandstone subjected to a combined action of repeated freezing–thawing and salt crystallization, *Bull. Eng. Geol. Environ.* (2019), <https://doi.org/10.1007/s10064-019-01490-6>.
- [26] J. Xu, H. Pu, Z. Sha, Mechanical behavior and decay model of the sandstone in Urumqi under coupling of freeze–thaw and dynamic loading, *Bull. Eng. Geol. Environ.* (2021), <https://doi.org/10.1007/s10064-021-02133-5>.
- [27] G. Khanlari, Y. Abdilor, Influence of wet–dry, freeze–thaw, and heat–cool cycles on the physical and mechanical properties of Upper Red sandstones in central Iran, *Bull. Eng. Geol. Environ.* (2015), <https://doi.org/10.1007/s10064-014-0691-8>.
- [28] S. Zhang, S. Wu, G. Zhang, Strength and deformability of a low-porosity sandstone under true triaxial compression conditions, *Int. J. Rock Mech. Min. Sci.* (2020), <https://doi.org/10.1016/j.ijrmms.2019.104204>.
- [29] P. Migoń, Sandstone geomorphology – Recent advances, *Geomorphology*. (2021), <https://doi.org/10.1016/j.geomorph.2020.107484>.
- [30] R.A.L. Wray, F. Sauro, An updated global review of solutional weathering processes and forms in quartz sandstones and quartzites, *Earth-Science Rev.* (2017), <https://doi.org/10.1016/j.earscirev.2017.06.008>.
- [31] H. Siedel, S. Siegesmund, Characterization of stone deterioration on buildings, *Stone Archit. Prop. Durab. Fifth Ed.* (2014), https://doi.org/10.1007/978-3-642-45155-3_6.
- [32] H. Siedel, S. Siegesmund, K. Sterflinger, Characterisation of stone deterioration on buildings, *Stone Archit. Prop. Durab.* (2011), https://doi.org/10.1007/978-3-642-14475-2_6.
- [33] S. Scheerer, O. Ortega-Morales, C. Gaylarde, Chapter 5 Microbial Deterioration of Stone Monuments–An Updated Overview, *Adv. Appl. Microbiol.* (2009). doi: 10.1016/S0065-2164(08)00805-8.
- [34] S. Papida, W. Murphy, E. May, Enhancement of physical weathering of building stones by microbial populations, *Int. Biodeterior. Biodegrad.* (2000), [https://doi.org/10.1016/S0964-8305\(00\)00102-5](https://doi.org/10.1016/S0964-8305(00)00102-5).
- [35] C. Urzi, M. Realini, Colour changes of Noto's calcareous sandstone as related to its colonisation by microorganisms, *Int. Biodeterior. Biodegrad.* (1998), [https://doi.org/10.1016/S0964-8305\(98\)00045-6](https://doi.org/10.1016/S0964-8305(98)00045-6).
- [36] E. May, S. Papida, H. Abdulla, S. Tayler, A. Dewedar, Comparative Studies of Microbial Communities on Stone Monuments in Temperate and Semi-Arid Climates, *Microbes Art* (2000), https://doi.org/10.1007/978-1-4615-4239-1_4.
- [37] L. Tomaselli, G. Lamenti, M. Bosco, P. Tiano, Biodiversity of photosynthetic micro-organisms dwelling on stone monuments, *Int. Biodeterior. Biodegrad.* (2000), [https://doi.org/10.1016/S0964-8305\(00\)00078-0](https://doi.org/10.1016/S0964-8305(00)00078-0).
- [38] G. Gómez-Alarcón, M.L. Muñoz, M. Flores, Excretion of organic acids by fungal strains isolated from decayed sandstone, *Int. Biodeterior. Biodegrad.* (1994), [https://doi.org/10.1016/0964-8305\(94\)90006-X](https://doi.org/10.1016/0964-8305(94)90006-X).
- [39] S. Tayler, E. May, Investigations of the localisation of bacterial activity on sandstone from ancient monuments, *Int. Biodeterior. Biodegrad.* (2000), [https://doi.org/10.1016/S0964-8305\(00\)00100-1](https://doi.org/10.1016/S0964-8305(00)00100-1).
- [40] A. Potysz, W. Bartz, K. Zbońska, F. Schmidt, M. Lenz, Deterioration of sandstones: Insights from experimental weathering in acidic, neutral and biotic solutions with *Acidithiobacillus thiooxidans*, *Constr. Build. Mater.* (2020), <https://doi.org/10.1016/j.conbuildmat.2020.118474>.
- [41] E.P. Burford, M. Fomina, G.M. Gadd, Fungal involvement in bioweathering and biotransformation of rocks and minerals, *Mineral. Mag.* (2003), <https://doi.org/10.1180/0026461036760154>.
- [42] G.M. Gadd, Fungi, rocks, and minerals, *Elements*. (2017), <https://doi.org/10.2113/gselements.13.3.171>.
- [43] H.C. Flemming, J. Wingender, U. Szewzyk, P. Steinberg, S.A. Rice, S. Kjelleberg, Biofilms: An emergent form of bacterial life, *Nat. Rev. Microbiol.* (2016), <https://doi.org/10.1038/nrmicro.2016.94>.
- [44] A. Khan, P. Singh, A. Srivastava, Synthesis, nature and utility of universal iron chelator – Siderophore: A review, *Microbiol. Res.* (2018), <https://doi.org/10.1016/j.micres.2017.10.012>.
- [45] A. Perez, S. Rossano, N. Trcera, A. Verney-Carron, C. Rommevaux, C. Fourdrin, A. C. Agnello, D. Huguenot, F. Guyot, Direct and indirect impact of the bacterial strain *Pseudomonas aeruginosa* on the dissolution of synthetic Fe(III)- and Fe(II)-bearing basaltic glasses, *Chem. Geol.* (2019), <https://doi.org/10.1016/j.chemgeo.2019.05.033>.
- [46] D.W. Collinson, The Role of Pigment and Specularite in the Remanent Magnetism of Red Sandstones, *Geophys. J. R. Astron. Soc.* (1974), <https://doi.org/10.1111/j.1365-246X.1974.tb04119.x>.
- [47] T.R. Paradise, Sandstone architectural deterioration in Petra, Jordan, in: *Proc. 9th Int. Congr. Deterior. Conserv. Stone*, 2000. doi:10.1016/b978-0-444-50517-0/50095-7.
- [48] R. Drewello, A. Schmiedinger, The sandstone of the fortress Rosenberg in Kronach between ecology and cultural heritage preservation, *Zeitschrift Der Dtsch. Gesellschaft Für Geowissenschaften*. (2007), <https://doi.org/10.1127/1860-1804/2007/0158-0895>.
- [49] K.R. McClay, M.G. Norton, P. Coney, G.H. Davis, Collapse of the caledonian orogen and the old Red sandstone, *Nature*. (1986), <https://doi.org/10.1038/323147a0>.
- [50] J.R. Underhill, N.H. Woodcock, Faulting mechanisms in high-porosity sandstones: New Red Sandstone, Arran, Scotland, *Geol. Soc. Spec. Publ.* (1987), <https://doi.org/10.1144/GSL.SP.1987.029.01.09>.
- [51] A. Ehling, F. Häfner, H. Siedel, Natural Stone and World Heritage, 2021. doi: 10.1201/9780367823061.
- [52] M. Marszałek, Z. Alexandrowicz, G. Rzepa, Composition of weathering crusts on sandstones from natural outcrops and architectonic elements in an urban environment, *Environ. Sci. Pollut. Res.* (2014), <https://doi.org/10.1007/s11356-014-3312-y>.
- [53] E. Uchida, K. Ito, N. Shimizu, Provenance of the sandstone used in the construction of the khmer monuments in Thailand, *Archaeometry*. (2010), <https://doi.org/10.1111/j.1475-4754.2009.00505.x>.
- [54] E. Tolkanowicz, Czerwone piaskowce z Gór Świętokrzyskich, *Świat Kamienia*. 6 (2003) 86–91.
- [55] R. Gradziński, A. Uchman, Trace fossils from interdune deposits—an example from the lower triassic aeolian Tumlin Sandstone, central Poland, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 108 (1994) 121–138, [https://doi.org/10.1016/0031-0182\(94\)90025-6](https://doi.org/10.1016/0031-0182(94)90025-6).
- [56] M. Kuleta, G. Niedźwiedzi, T. Ptaszyński, Nowe stanowisko z tropami kręgowców z górnego pstręgo piaskowca Gór Świętokrzyskich, *Przegląd Geol.* 53 (2005) 151–155.
- [57] J. Rajchel, Kamienny wystrój Biblioteki Jagiellońskiej w Krakowie, *Przegląd Geol.* 48 (2000) 707–712.
- [58] M. Lorenc, S. Mazurek, Wykorzystać kamień, Studio JASA, Wrocław, 2007.
- [59] H. Walendowski, Minimonografie polskich kamieni budowlanych, *Piaskowce tumlińskie*, Nowy Kamieniarz. 44 (2010) 80.
- [60] J. Urban, J. Gągół, Kamieniolomy piaskowców w dawnych ośrodkach górnictwa kamiennego północnej części regionu świętokrzyskiego jako zabytki techniki i przyrody, *Przegląd Geol.* 42 (1994) 193–200.
- [61] Z. Złonkiewicz, A. Fijałkowska-Mader, Kamień w architekturze zespołu kościelnoklasztornego na Karczówce w Kielcach (Góry Świętokrzyskie), *Przegląd Geol.* 66 (2018) 421–435.
- [62] M. Kamiński, A. Kubicz, Kwasoodporność piaskowców Gór Świętokrzyskich i Dolnego Śląska na tle ich własności petrograficznych, *Biul. Inst. Geol.* 178 (1962) 1–115.
- [63] ICDD, The Powder Diffraction File., Int. Cent. Diff. Data, Newt. Square, Pennsylvania, USA. (2003).
- [64] N. Roduit, JMicroVision : un logiciel d'analyse d'images pétrographiques polyvalent, Université de Genève. (2007).
- [65] S.J. Blott, K. Pye, Gradistat: A grain size distribution and statistics package for the analysis of unconsolidated sediments, *Earth Surf. Process. Landforms*. (2001), <https://doi.org/10.1002/esp.261>.
- [66] R.L. Folk, W.C. Ward, Brazos River bar [Texas]; a study in the significance of grain size parameters, *J. Sediment. Res.* 27 (1957) 3–26, <https://doi.org/10.1306/74d70646-2b21-11d7-8648000102c1865d>.
- [67] M.C. Powers, A New Roundness Scale for Sedimentary Particles, *J. Sediment. Res.* 23 (1953) 117–119, <https://doi.org/10.1306/d4269567-2b26-11d7-8648000102c1865d>.
- [68] N.A. Riley, Projection Sphericity, *SEPM J. Sediment. Res.* 11 (1941) 94–95, <https://doi.org/10.1306/d426910c-2b26-11d7-8648000102c1865d>.
- [69] M. Rembiś, A. Smoleńska, Preservation of the selected building sandstones of southern Poland exposed to salt and the sulphur dioxide in the presence of moisture, *Geologia*. 36 (2010) 539–553.
- [70] M. Rembiś, Sandstones modified with silico-organic compounds and changes of their porosity and flexural strength under concentrated load, *Geologia*. 36 (2010) 67–108.
- [71] C.F. Tseng, A. Burger, G.L.A. Mislin, I.J. Schalk, S.S.F. Yu, S.I. Chan, M. Abdallah, Bacterial siderophores: The solution stoichiometry and coordination of the Fe(III) complexes of pyochelin and related compounds, *J. Biol. Inorg. Chem.* (2006), <https://doi.org/10.1007/s00775-006-0088-7>.
- [72] H. Aoki, Y. Matsukura, A new technique for non-destructive field measurement of rock-surface strength: An application of the Equotip hardness tester to weathering studies, *Earth Surf. Process. Landforms*. (2007), <https://doi.org/10.1002/esp.1492>.
- [73] J. Desarnaud, K. Kiriya, B. Bicer Simsir, K. Wilhelm, H. Viles, A laboratory study of Equotip surface hardness measurements on a range of sandstones: What influences the values and what do they mean?, *Earth Surf. Process. Landforms*. (2019), <https://doi.org/10.1002/esp.4584>.
- [74] T. Niedzielski, P. Migoń, A. Placek, A minimum sample size required from Schmidt hammer measurements, *Earth Surf. Process. Landforms*. (2009), <https://doi.org/10.1002/esp.1851>.
- [75] K. Wilhelm, H. Viles, Ó. Burke, Low impact surface hardness testing (Equotip) on porous surfaces – advances in methodology with implications for rock weathering and stone deterioration research, *Earth Surf. Process. Landforms*. (2016), <https://doi.org/10.1002/esp.3882>.
- [76] F.J. Pettijohn, P.E. Potter, R. Siever, Sand and Sandstone, Springer US (1973), <https://doi.org/10.1007/978-1-4615-9974-6>.
- [77] M. Földvári, Handbook of the thermogravimetric system of minerals and its use in geological practice, Geological Institute of Hungary (Magyar Állami Földtani Intézet), Budapest, 2011.
- [78] L.N. Warr, IMA–CNMNC approved mineral symbols, *Mineral. Mag.* 85 (2021) 291–320, <https://doi.org/10.1180/MGM.2021.43>.
- [79] L.E. Hersman, J.H. Forsythe, L.O. Ticknor, P.A. Maurice, Growth of *Pseudomonas mendocina* on Fe(III) (Hydr)Oxides, *Appl. Environ. Microbiol.* (2001), <https://doi.org/10.1128/AEM.67.10.4448-4453.2001>.
- [80] N. Roy, P.K. Chakrabarty, Effect of aluminum on the production of siderophore by *Rhizobium* sp. (Cicer arietinum), *Curr. Microbiol.* (2000). doi:10.1007/s002840010082.
- [81] X. Hu, G.L. Boyer, Siderophore-mediated aluminum uptake by *Bacillus megaterium* ATCC 19213, *Appl. Environ. Microbiol.* (1996), <https://doi.org/10.1128/aem.62.11.4044-4048.1996>.
- [82] A. Evers, R.D. Hancock, A.E. Martell, R.J. Motekaitis, Metal Ion Recognition in Ligands with Negatively Charged Oxygen Donor Groups: Complexation of Fe(III),

- Ga(III), In(III), Al(III), and Other Highly Charged Metal Ions, *Inorg. Chem.* (1989), <https://doi.org/10.1021/ic00310a035>.
- [83] B.J. Hernlem, L.M. Vane, G.D. Sayles, Stability constants for complexes of the siderophore desferrioxamine b with selected heavy metal cations, *Inorganica Chim. Acta.* (1996), [https://doi.org/10.1016/0020-1693\(95\)04780-8](https://doi.org/10.1016/0020-1693(95)04780-8).
- [84] A. Braud, F. Hoegy, K. Jezequel, T. Lebeau, I.J. Schalk, New insights into the metal specificity of the *Pseudomonas aeruginosa* pyoverdine-iron uptake pathway, *Environ. Microbiol.* (2009), <https://doi.org/10.1111/j.1462-2920.2008.01838.x>.
- [85] C. Cocozza, C.C.G. Tsao, S.F. Cheah, S.M. Kraemer, K.N. Raymond, T.M. Miano, G. Sposito, Temperature dependence of goethite dissolution promoted by trihydroxamate siderophores, *Geochim. Cosmochim. Acta.* (2002), [https://doi.org/10.1016/S0016-7037\(01\)00780-3](https://doi.org/10.1016/S0016-7037(01)00780-3).
- [86] E.H. Oelkers, J. Schott, Does organic add adsorption affect alkali-feldspar dissolution rates? *Chem. Geol.* (1998) [https://doi.org/10.1016/S0009-2541\(98\)00082-5](https://doi.org/10.1016/S0009-2541(98)00082-5).
- [87] T. Baramov, K. Keijzer, E. Irran, E. Mösker, M.H. Baik, R. Süßmuth, Synthesis and structural characterization of hexacoordinate silicon, germanium, and titanium complexes of the *E. coli* siderophore enterobactin, *Chem. - A Eur. J.* (2013), <https://doi.org/10.1002/chem.201301825>.
- [88] T.J. Stewart, R. Behra, L. Sigg, Impact of chronic lead exposure on metal distribution and biological effects to periphyton, *Environ. Sci. Technol.* (2015), <https://doi.org/10.1021/es505289b>.
- [89] P.V. Brady, J.V. Walther, Controls on silicate dissolution rates in neutral and basic pH solutions at 25 °C, *Geochim. Cosmochim. Acta.* (1989), [https://doi.org/10.1016/0016-7037\(89\)90160-9](https://doi.org/10.1016/0016-7037(89)90160-9).
- [90] N.H. Yin, Y. Sivry, C. Avril, S. Borensztajn, J.Ö. Labanowski, V. Malavergne, P.N. L. Lens, S. Rossano, E.D. van Hullebusch, Bioweathering of lead blast furnace metallurgical slags by *Pseudomonas aeruginosa*, *Int. Biodeterior. Biodegrad.* (2014), <https://doi.org/10.1016/j.ibiod.2013.10.013>.
- [91] S.V. Golubev, A. Bauer, O.S. Pokrovsky, Effect of pH and organic ligands on the kinetics of smectite dissolution at 25 °C, *Geochim. Cosmochim. Acta.* (2006), <https://doi.org/10.1016/j.gca.2006.06.1557>.
- [92] W.D. Keller, R.F. Hanson, W.H. Huang, A. Cervantes, Sequential active alteration of rhyolitic volcanic rock to endellite and a precursor phase of it at a spring in Michoacan, Mexico, *Clays Clay Miner.* (1971), <https://doi.org/10.1346/ccmn.1971.0190209>.
- [93] J.S. Chang, R. Law, C.C. Chang, Biosorption of lead, copper and cadmium by biomass of *Pseudomonas aeruginosa* PU21, *Water Res.* (1997), [https://doi.org/10.1016/S0043-1354\(97\)00008-0](https://doi.org/10.1016/S0043-1354(97)00008-0).
- [94] Y. Nuhoglu, E. Oguz, H. Uslu, A. Ozbek, B. Ipekoglu, I. Ocak, I. Hasenekoglu, The accelerating effects of the microorganisms on biodeterioration of stone monuments under air pollution and continental-cold climatic conditions in Erzurum, Turkey, *Sci. Total Environ.* (2006), <https://doi.org/10.1016/j.scitotenv.2005.06.034>.
- [95] J.M. McKinley, P.A. Warke, Controls on permeability: Implications for stone weathering, *Geol. Soc. Spec. Publ.* (2007), <https://doi.org/10.1144/GSL.SP.2007.271.01.22>.
- [96] T. Warscheid, D. Barros, T.W. Becker, J. Braams, S. Eliasaro, G. Grote, D. Janssen, L. Jung, S.P.B. Mascarenhas, M.L. Mazzoni, K. Petersen, E.S. Simonoes, Y.K. Moreira, W.E. Krumbein, Biodeterioration studies on soapstone, quartzite and sandstones of historical monuments in Brazil and Germany: preliminary results and evaluation for restoration practices, in: *Proc. 7th Int. Congr. Deterior. Conserv. Stone Held Lisbon, Port.* 15-18 June 1992, 1992.
- [97] H. Wu, D. Jiang, P. Cai, X. Rong, Q. Huang, Effects of low-molecular-weight organic ligands and phosphate on adsorption of *Pseudomonas putida* by clay minerals and iron oxide, *Colloids Surf. B Biointerfaces.* (2011), <https://doi.org/10.1016/j.colsurfb.2010.08.035>.
- [98] P.A. Maurice, M.A. Vierkorn, L.E. Hersman, J.E. Fulghum, A. Ferryman, Enhancement of kaolinite dissolution by an aerobic *Pseudomonas mendocina* bacterium, *Geomicrobiol. J.* (2001), <https://doi.org/10.1080/01490450151079752>.
- [99] H. Wu, W. Chen, X. Rong, P. Cai, K. Dai, Q. Huang, Adhesion of *Pseudomonas putida* onto kaolinite at different growth phases, *Chem. Geol.* (2014), <https://doi.org/10.1016/j.chemgeo.2014.10.008>.
- [100] P. Bennett, D.I. Siegel, Increased solubility of quartz in water due to complexing by organic compounds, *Nature.* (1987), <https://doi.org/10.1038/326684a0>.
- [101] A.V. Turkington, T.R. Paradise, Sandstone weathering: A century of research and innovation, *Geomorphology.* (2005), <https://doi.org/10.1016/j.geomorph.2004.09.028>.
- [102] M. Gaspar, R. Grazina, A. Bodor, E. Farkas, M.A. Santos, Siderophore analogues: A new macrocyclic tetraamine tris(hydroxamate) ligand; synthesis and solution chemistry of the iron(III), aluminium(III) and copper(II) complexes, *J. Chem. Soc. - Dalt. Trans.* (1999), <https://doi.org/10.1039/a809039d>.
- [103] P. Migoń, M. Różycka, K. Jancewicz, F. Duszyński, Evolution of sandstone mesas – following landform decay until death, *Prog. Phys. Geogr.* (2018), <https://doi.org/10.1177/0309133318795837>.
- [104] F. Duszyński, P. Migoń, Sandstone Landforms of the High Weald, *World Geomorphol. Landscapes* (2020), https://doi.org/10.1007/978-3-030-38957-4_6.
- [105] X. Li, H. Arai, I. Shimoda, H. Kuraishi, Y. Katayama, Enumeration of sulfur-oxidizing microorganisms on deteriorating stone of the angkor monuments, Cambodia, *Microbes Environ.* (2008), <https://doi.org/10.1264/jsme2.ME08521>.
- [106] Y. Zhang, F. Wu, M. Su, D. He, J.D. Gu, Q. Guo, M.A. Kakakhel, Y. Yang, W. Wang, H. Feng, Spatial and temporal distributions of microbial diversity under natural conditions on the sandstone stelae of the Beishiku Temple in China, *Int. Biodeterior. Biodegrad.* (2021), <https://doi.org/10.1016/j.ibiod.2021.105279>.