Biogenic Weathering of Mineral Substrates (Review)

Natalia P. Chizhikova, Sofia N. Lessovaia and Anna A. Gorbushina

Abstract A biological impact on weathering was recognized already at the beginning of the twentieth century, when biochemical influence of the lichen growth on rocks was convincingly demonstrated. Later it was shown that the progress of solid rock weathering initiated by biological colonization was affected by the initial porosity system and sensitivity of mineral association. In the meantime a considerable amount of diverse scientific data confirm the importance of biological rock colonizers (lichens and free-living rock biofilms) in mineral material dynamics as they occur at the atmosphere-exposed rock surfaces on local as well as global scale. Subaerial rock biofilms—microbial ecosystem including free-living heterotrophic and phototrophic settlers of bare rock surfaces—are characteristic for the first stage of primary succession of terrestrial ecosystems on mineral substrates. These cultivable and free-living communities are dominated by fungi and set the stage for the later development of a lichen cover, but in comparison to lichens also represent a new tool for laboratory experimentation and thus open a new stage of work in geomicrobiology. The minerals sensitivity to microbially induced biological weathering can be demonstrated by studies of natural samples as well as by the laboratory mesocosm experiments.

Keywords Lichens · Biofilms · Minerals' transformations

N.P. Chizhikova (✉)
V.V. Dokuchaev Soil Science Institute, RAS, Moscow, Russia
e-mail: chizhikova38@mail.ru

S.N. Lessovaia
Institute of Earth Sciences, St. Petersburg State University, St. Petersburg, Russia
e-mail: s.lesovaya@spbu.ru

A.A. Gorbushina
Department of Earth Sciences, Department of Biology Chemistry Pharmacy,
Freie Universität Berlin, Berlin, Germany
e-mail: anna.gorbushina@bam.de

A.A. Gorbushina
Federal Institute of Materials Research and Testing (BAM), Berlin, Germany

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1 Introduction and Background

Mineral weathering is a sum of Earth-forming processes that start to play a role at the scale of a single mineral grain but finally express their effects at the macro-level such as ecosystem and landscape scales. A biological impact on weathering was recognized already at the begging of twentieth century (Elenkin 1901). A. Elenkin was one of the first who published a manuscript devoted to changes of a solid rock affected by lichens. Further a mechanical effect of lichens was confirmed by micro-morphological study of the rocks (sericitizated plagioclase and hornblende) in thin sections. Disintegration of the rocks in the zones of their contact with lichen hyphae has been demonstrated (Parfenova 1950). Besides that Polynov (1945) was the first who assumed a biochemical influence of the lichens on rocks based on study of granitic gneiss and miascite affected by lithophilous lichens. Not only a mechanical disintegration of rocks but also a chemical difference was identified in the studied rocks. At the same time (1940s) a selective effect of lichens on minerals in the rock was also shown. On the example of *Rhizocarpon* it was found that hyphae penetrated deeply into the grains of mica (that can be a source of nutrients, initially potassium) avoiding quartz, which does not contain nutrients (Yarilova 1947).

After these detailed first reports that were scattered over almost 5 decades, these arguments have been further developed using the advanced techniques that become available. Lichen-induced accelerated degradation of minerals has again moved the focus of attention and lichens were recognized as ideal natural microcosms in which microbially mediated mineral weathering can be studied in details (Banfield et al. 1999). Banfield et al. (1999) systematically divided the contact area between lichens and minerals into four zones: (i) zone of unweathered rock and rock incipiently weathered by inorganic reactions; (ii) zone where reactions are accelerated by dissolved organic molecules but cells are not in direct contact with reacting mineral surfaces; (iii) zone of direct and intensive contact between microbial cells, biogenic organic matrix, and mineral surfaces; (iv) zone where photosynthetic members of the symbiosis generate fixed carbon and where crystalline lichen acids precipitate. Generally at present the following zones between thallus and rock unaffected by lichens were identified: (i) a biochemical weathering where substrate is colonized by microorganisms and (ii) biophysical and biochemical weathering where thallus fixes to the substrate and contact with microorganisms (de los Ríos and Ascaso 2001; de los Ríos et al. 2002).

2 Rock Weathering Initiated by Lichens—Model Studies with Natural Samples

The presence of fungal hyphae creates very special and significantly modified physicochemical conditions—as it is known for mycorrhizal root, e.g., pH value around colonized roots is significantly shifted (Rigou et al. 1995). A role of lichens as a weathering agent, which is characterized by one of the strongest effect on the substrate (Chen et al. 2000; Torbjørg and Thorseth 2002) was demonstrated in a detailed manner. It was shown that the effect of lichens leads to transformation of the rock silicates and iron extraction from silicates induced by organic acids (Wilson and Jones 1983; Prieto et al. 1994; Eick et al. 1996). In basalts, clay minerals enriched by iron disappear from the rock affected by lichens; the grains of ferromagnesian minerals and Ca feldspars are also highly sensitive to weathering based on their morphology (Jackson and Keller 1970; Jones et al. 1980). In granites the most sensitive mineral is mica, especially biotite (Varadachari et al. 1994; Ascaso et al. 1995; Silva et al. 1997). These data are in good agreement with the selective effect of lichens on rocks that was mentioned previously.

The discrepancy of data on the rate of hard rock disintegration affected by lichens is observed (Prieto et al. 1994; Sancho et al. 2003). A scheme to understand the role of a biological weathering in the Holocene accumulation of the fine earth was suggested. The findings were based on the study of rock weathering affected by pedogenesis in shallow soils mostly under lichens from East Fennoscandia (Lesovaya et al. 2008). A positive feedback was demonstrated between (i) the initial accumulation of the fine earth in the fissures and cavities and (ii) increase of biological and biochemical "impact" initiated by the predominant development of biota in these zones. As opposed to them the massive bedrock surface between the fissures is subjected by weaker action of lichens and mosses.

Additionally natural pore system in a solid rock could be considered as the prerequisite of the biological weathering processes. The interactions between primary minerals and solutions often occurring within confined or semi-confined microenvironments, such as pores, rather than in a bulk solution have been reported (Velde and Meunier 2008). Coexisting biotic and abiotic processes of rock weathering were demonstrated even for the extremely cold subarctic conditions of King George Island, Antarctica, where the initial micro-pores system in the solid rocks sets conditions for penetration of water and lichen hyphae inside the rock. Cryogenic physical weathering here is accompanied by local biochemical processes due to iron accumulation in the micro-zones of rock and lichen contacts and along the cranks (Glazovskaya 2002). In "cold" environment, freezing and thawing cycles are an additional factor of physical weathering, which results in the formation of fresh mineral surfaces that are highly susceptible to a chemical weathering (Arnaud and Whiteside 1963; Allen 2002). It can be explained by the findings that the element release from rocks depends on progress of chemical weathering on microstructure properties, characterized by nearly closed, semi-open and completely open micro-systems which are interconnected by fractures or pores (Meunier et al. 2007).

Generally the dissolution of the primary minerals in a rock creates new voids which are filled only partly by newly formed minerals. Such pore systems, which are relics of previous fluid–rock interactions, can promote further chemical weathering (Navarre-Sitchler et al. 2009). Thus, the progress of solid rock weathering initiated by lichen colonization is affected by the initial porosity system and sensitivity of mineral association.

While lichens do offer an ideal system to study rock/biota interface, these systems cannot be cultivated in the laboratory, thus limiting available experimental approaches. This drawback can be compensated for if we work with microbial associations in the form of biofilms. As biofilms were the first settlers of bare mineral surfaces at times, when the earth was inhabited only by microorganisms (while lichens appeared only in the Devonian); these communities also offer an additional advantage of an evolutionary more ancient approach.

3 Weathering Initiated by Microorganisms—A Chance to Perform Experimental Geomicrobiology

A functional role of microbes in the biosphere is based on their role in the elements' cycling. They dissolve the mineral from a colonized substrate and a set of elements such as K, Na, P, Fe, and Mg are transformed into forms that are easy available for other inhabitants of earth (Tsyurupa 1973). Several mechanisms of their effect were described: (i) oxidation of the elements with variable active valence, (ii) effect initiated by biogenic acids and alkalis, and (iii) chelation and biosorption (Zvyaginzev et al. 1999). Besides the electrochemical model of bacterial oxidation of minerals in the zones of cell / mineral contact has been reported (Ehrlich 1996; Yakhontova and Zvereva 2000). One of the results of the microbial activities can be expressed as destruction of silicates from the substrate due to metabolites effect, which is classified as chemically affected indirect process. Experimental findings showed that bacterially induced dissolution of quartz was much more active than initiated by chemical processes (Karavayko 2004). Based on experimental findings, the growth of bacterial biomass can be stimulated by adding of supplementary portions of substrate. That was shown on the example of *Rhodovulum* that the addition of volcanic ash led to formation of hard-grained micro-colonies (Naimark et al. 2009). Microbially induced biochemical transformation of minerals (Alekseeva et al. 2009) as well as mechanical disintegration of minerals (Ivanova 2013) has been reported. The latter coexists with chemical processes namely removal of elements such as K, Al, and M, shown on the example of vermiculite from Kovdor deposit.

Although most studies of rock colonization have been naturalistic or descriptive, sufficient information has been gained to allow the selection of a few typical "rock settlers" and to study their joint development in a simple laboratory system. The sensitivity of minerals to biological weathering initiated by associations of actinomycete and cyanobacteria as well as their individual cultures was investigated experimentally (Ivanova 2013). Minerals of mica group, which are significantly different based on their stability in soil environment; Gumbrin and Oglanlinskaya bentonite clays were used as a growth medium. The growth of the cultures on the trioctahedral mica (biotite) caused to disintegration of its particles and transformation of biotite into vermiculite through mixed-layer minerals with different tendencies of layers interstratifying in crystallites. But no changes were detected in dioctahedral mica (muscovite/sericite) (Ivanova et al. 2012). Gumbrin, which is Cenomanian bleaching clay from Georgia, composed of individual smectite and cristobalite, and quartz affected by the microorganisms associations demonstrates the significantly increase of amorphous phase (based on XRD data) as a result of smectite dissolving and residual accumulation of quartz. After the experiment in Oglanlinskaya bentonite clay, which is composed of individual smectite and zeolite of clinoptilolite type, zeolite was totally collapsed. So, in zeolite a more favorable habitat for microbial communities was created, which might be explained by the frame structure of zeolite. Additionally the structure of zeolites is characterized by important property such as exchange of freely associated cations, and high content of essential nutritional elements necessary for microbes (Chizhikova et al. 2009; Zenova et al. 2009; Ivanova et al. 2009; Ivanova 2013).

There have only been rare attempts at quantification of biological weathering usually based on insufficient ecological and mineralogical background. Fewer investigations have been carried out on the qualitative and quantitative changes that rock-weathering microbial communities undergo under global climate change.

To accelerate and study weathering under laboratory conditions an in vitro model of a rock-colonizing community was suggested. The selection of organisms for the model lab system was based on the assumption that a functional rock biofilm ecosystem has to possess separate but interacting components responsible for different tasks including weathering. One model fungus is combined with a model cyanobacterium, and this dual system is used to examine the continuum of microbial interactions that leads to stable rock colonization (Gorbushina and Broughton 2009) and rock weathering. The model system used here was already demonstrated as an efficient weathering agent (Seiffert et al. 2014) and includes:

- the oxygenic photoautotrophic cyanobacterium *Nostoc punctiforme* that possesses multiple developmental states and can form nitrogen-fixing symbioses with a variety of terrestrial plants and fungi;
- a model rock inhabiting Ascomycete *Knufia petricola* (Nai et al. 2013) known for its protective pigmentation, restricted colony growth and capacity to form close inter- and intra-cellular contacts with phototrophic cells.

Morphologically simple and microbially dominated ecosystems termed "biofilms" are coupling agents between the lithosphere and atmosphere. They are interesting geobiologically as well as ecologically existing and prevailing on earth for a remarkably long period of biosphere evolution. A microbial ecosystem including heterotrophic and phototrophic settlers form on bare rock surfaces under atmospheric (subaerial) exposure. Such systems form at interfaces of solid materials with gas or liquid phases and represent a unique structure capable of multiple impacts on substrate and element cycles (Burford et al. 2003; Gorbushina 2007). These microbial structures have occurred on virtually every rock surface throughout the entire geological history of the earth and have actively participated in rock weathering. Lithobiontic communities are the primary settlers on lava following volcanic eruptions and on rocks after the retreat of glaciers. Subaerial rock biofilms represent the first stage of primary succession of terrestrial ecosystems on mineral substrates. Through occupying the fractal dimension of the rock surface, subaerial biofilms present an immense reactive surface in contact both with the atmosphere and with the underlying mineral materials. Life at the rock / atmosphere interface influences both the rock substrate and the microclimate zone above and around it.

Summarizing the microbial influence on minerals (Sokolova 2011; Gorbushina 2007) can be split into four types: (i) direct one realized in the zones of mineral and microbe contact based on reaction of anode—cathode interaction; (ii) indirect one affected by products of biological metabolism including acids, alkalis, and chelates; (iii) direct and intensive contact between microbial cells, biogenic organic matrix, and mineral surfaces where physical influences as growth pressure and desiccation/humidification movements play a role and (iv) biogenic mineral formation that results for a powerful biomineralization activity of fungi that can create new biogenic minerals from oxalates to carbonates and from oxides to sulfides (Gadd 2007). This complete spectrum of microbial influences can be most efficiently addressed with the help of reverse genetics and a model rock biofilm (Gorbushina and Broughton 2009; Seiffert et al. 2014; Noack-Schönmann et al. 2014).

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