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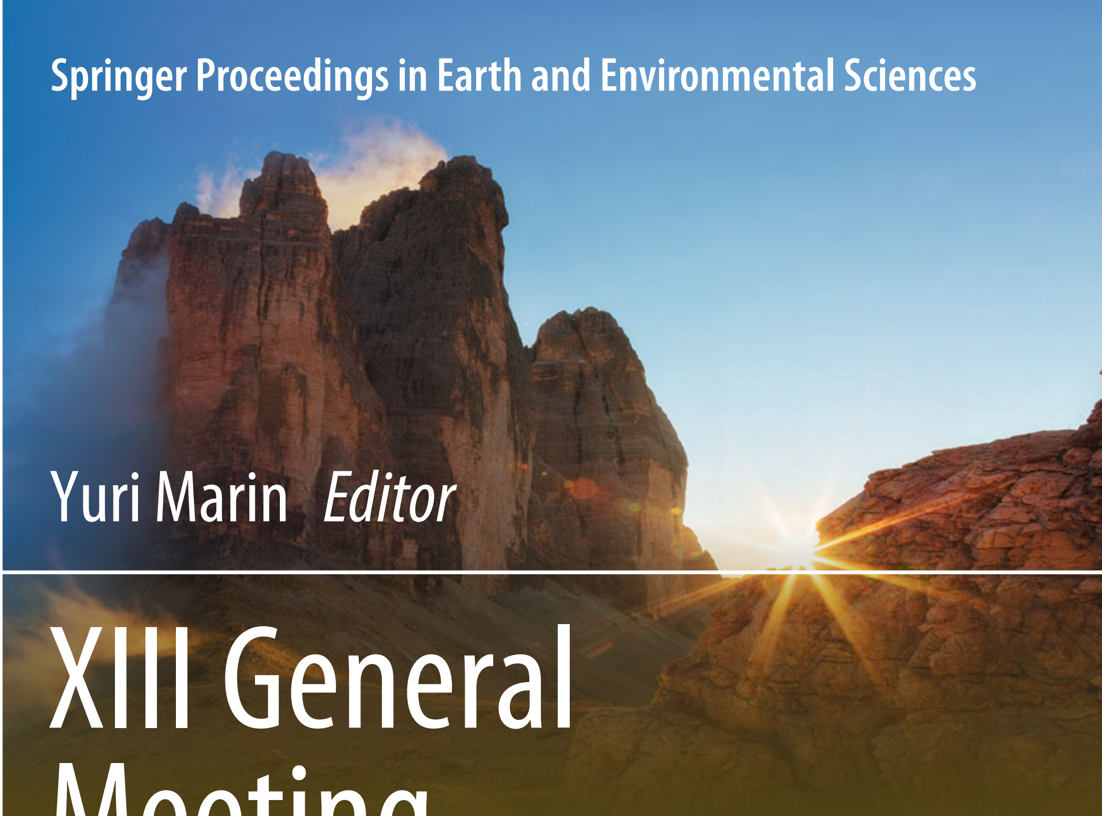

Yuri Marin *Editor*

XIII General Meeting of the Russian Mineralogical Society and the Fedorov Session

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Editor
Yuri Marin
The Russian Mineralogical Society
St. Petersburg, Russia

ISSN 2524-342X ISSN 2524-3438 (electronic)
Springer Proceedings in Earth and Environmental Sciences
ISBN 978-3-031-23389-0 ISBN 978-3-031-23390-6 (eBook)
https://doi.org/10.1007/978-3-031-23390-6

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Contents

Calcium and Cuprum Oxalates in Biofilms on the Surface of the Scoria Cones of Tolbachik Volcano

I. A. Chernyshova(✉), O. S. Vereshchagin, M. S. Zelenskaya, D. Yu. Vlasov, O. V. Frank-Kamenetskaya, and D. E. Himelbrant

Saint-Petersburg Branch of the Russian Mineralogical Society, Saint-Petersburg State University, Saint Petersburg, Russia
i.chernyshova@spbu.ru

Abstract. The study of biofilm oxalates creates the scientific basis for the development of modern nature-like biotechnologies in various fields of science and technology. Calcium (whewellite and weddellite) and copper (moolooite) oxalates in lichen thalli on scoria cones of Tolbachik volcano (Kamchatka Peninsula, Russia) were firstly found. The morphology of oxalate crystal has been described. New species of lichens (*Psylolechia leprosa, Sarcogyne hypophaea, Rinodina gennarii, Ochrolechia subplicans*) producing oxalic acid, which leads to the formation of oxalates, have been discovered. It was concluded, that in the process of biomineralization the growth of oxalate crystals alternates with their dissolution.

Keywords: Microbe biomineralization · Scoria cones of volcano Tolbachik · Oxalate crystallization · Whewellite · Weddellite · Moolooite

1 Introduction

In recent years, the world scientific community has shown significant interest in the mechanisms of biomineralization with the participation of microorganisms, which is associated with the study of modern mineral formation at the nano- and microlevels, as well as processes and phenomena occurring at the border of living and nonliving. These fundamental results create the scientific basis for the development of modern nature-like biotechnologies in various fields of science and technology.

Crystallization of oxalates under action of microorganisms (bacteria, microfungi, microalgae, lichens) can take place on the surface of different rocks and minerals: carbonates, phosphates, oxides, silicates and others (e.g., Gehrmann and Krumbein 1994; Purvis et al. 2008).

Only five oxalate minerals were found in biofilms with a predominance of lichens on the surface of rocks and minerals. Calcium oxalates monohydrate whewellite and dihydrate weddellite are the most common biofilm minerals. Previously, they were found on the surface of different calcium-containing rocks: carbonates (marble, limestone, dolomite), silicates (granite, serpentinite, gabbro, basalt, diabase, sandstone) and apatite-nepheline ore (e.g. Adamo et al. 1993; Ascaso et al. 1982; Bjelland et al. 2002; Bungartz

Y. Marin (Ed.): GMRMS 2021, SPEES, pp. 17–24, 2023.
https://doi.org/10.1007/978-3-031-23390-6_3

et al. 2004; Gehrmann and Krumbein 1994; Jones et al. 1980; Marques et al. 2016; Prieto et al. 1997; Ríos de los et al. 2009; Rusakov et al. 2010; Souza-Egipsy et al. 2002; Syers et al. 1967; Wilson et al. 1981). Monohydrate copper oxalate moolooite was previously found in lichen thalli of *Lecanora polytropa*, *Lecidea lactea*, *Lecidea inops*, *Acarospora rugulosa* on copper and iron sulfides (chalcopyrite, pyrite) and weathering products (attackamite, brochantite) in basaltic lavas and more siliceous volcanic rocks (Chisholm et al. 1987; Purvis 1984; Purvis et al. 2008). Dihydrate magnesium oxalate glushinskite was discovered in lichens on Mg-enriched rock (Wilson et al. Wilson et al. 1981, 1980) and manganese oxalate was found on Mn-rich rocks (Wilson and Jones 1984).

This work is devoted to the first discovery of oxalates in lichens on scoria cones of volcano Tolbachik, Kamchatka Peninsula (Fig. 1).

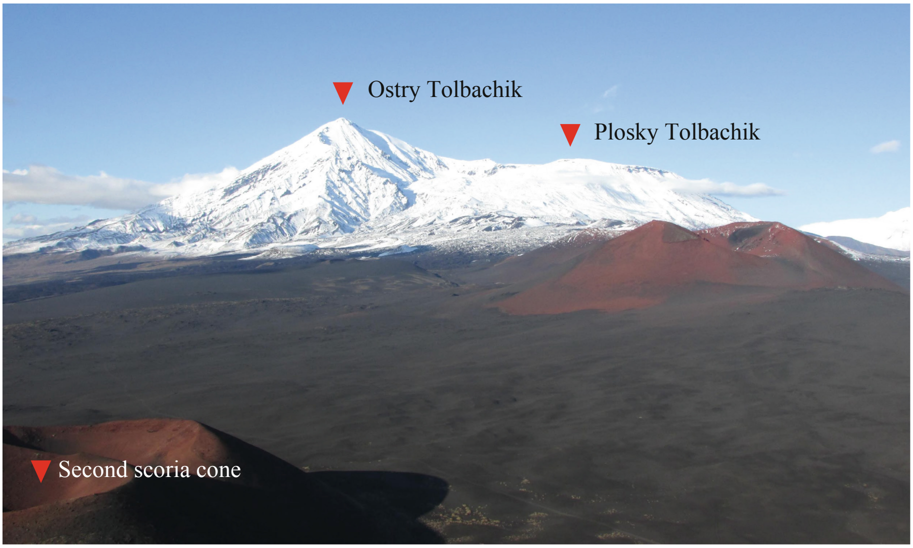

Fig. 1. Volcano Tolbachik and it's scoria cones

Volcano Tolbachik is located in the southern part of the Klyuchevskaya group of volcanoes, at the northern end of the Kuril-Kamchatka volcanic belt, near the intersection of the Kuril–Kamchatka and Aleutian Island arcs (Fedotov 1984). Tolbachik consists of three main parts: two cones Ostry Tolbachik and Plosky Tolbachik and Tolbachinsky Dol – lava-pyroclastic plain adjacent to the southern slopes of Plosky Tolbachik. Ostry and Plosky Tolbachik began to form about 7–10 thousand years ago (Churikova et al. 2013).

The first large scoria cones were formed 2000–1500 years ago and composed mainly of magnesian basalts (for example, the Mountain 1004 scoria cone). Paleofumarolic fields of Mountain 1004 bears rich Cu and Pb mineralization including tenorite, anglesite, atacamite, antlerite, pyromorphite, etc. (Pekov et al. 2018b; Serafimova et al. 1994).

The largest eruptions with the formation of scoria cones in recent years took place in 1975–1976 (the Great Tolbachik Fissure Eruption, GTFE) and 2012–2013 (Tolbachik

Fissure Eruption, TFE). They were predominantly basaltic, with two types distinguished - high-magnesian and high-alumina basalts. During the early eruption of 1975 (Northern Breakthrough, scoria cones I, II, III), pyroclastic ejections predominated, in composition corresponding to magnesian basalts. Their main minerals are olivine ($Fo_{85–99}$), diopside, diopside-augite ($Ca_{42–45}$-$Mg_{44–50}$-$Fe_{7–11}$) and plagioclase (An_{74} – An_{55}). In the main stage of the eruption of 2012–2013 (e.g., scoria cone Naboko), basaltic lavas predominated (Volynets et al. 2013). Compositionally plagiogclase of Naboko vent lavas ranges from $An_{70–72}$ to $An_{80–80}$, olivine (mainly found as microphenocrysts) ranges from Fo_{64} to Fo_{75}, clinopyroxene ranges from augite to salite (Volynets et al., 2015).

Fumarole activity of GTFE and TFE continues until the present (e.g., Vergasova and Filatov 2012). The fumaroles of the scoria cones are characterized by a wide variety of minerals and mineral-forming elements. A great number of new minerals were discovered there (e.g., Pekov et al. 2018a; Siidra et al. 2017; Vergasova and Filatov 2012).

Lichens are widespread on the Kamchatka Peninsula (Himelbrant et al. 2009, 2014; Khodosovtsev et al. 2004; Kukwa et al. 2014), which are among the first living organisms to grow on volcanic formations (Kukwa et al. 2014). The predominant group is crustose lichens (Himelbrant et al. 2009, 2014), which are well known for their ability to colonize stony substrates of various chemical compositions. Due to their active metabolism, they interact with bedrock minerals, which can lead to the oxalates formation (e.g., Frank-Kamenetskaya et al. 2019; Purvis et al. 2008; Rusakov et al. 2010).

2 Methods and Approaches

Biofilms with a predominance of lichens were sampled during field work in the fall of 2019 from the scoria cones of Tolbachik Volcano. A total of 119 samples were collected: 43 samples from ancient scoria cone (Mountain 1004), 56 samples from scoria cones of 1975–1976 eruption (I, II and III scoria cones) and 20 samples from scoria cones of 2012–2013 eruption (Naboko scoria cone).

The morphology, color and lichen/rock interface were studied using a Leica DM 2500P polarising light microscope. Lichen thalli and apothecia (spore-producing structure) were examined using a MZ16 Leica stereo microscope and Leica DM300 LED microscope. Lichen apothecia were studied by scanning electron microscopy (SEM). SEM studies of carbon-coated, unpolished samples were carried out by means of a HITACHI TM 3000.

Thin sections of lichenized rock samples were observed by an optical microscopy Leica DM4500P and in SEM. Chemical composition of biominerals (both polished and unpolished samples) and underlying substrate (polished rock samples) were studied in carbon-coated samples by means of a Hitachi S-3400 N SEM equipped with an Oxford Instruments AzTec Energy X-Max 20 energy-dispersive X-ray (EDX) spectrometer, with the following parameters: 20 kV accelerating voltage, 1 nA beam current and 30 s data-collection time (excluding dead time). Only semi-quantitative analysis was obtained as most of the newly formed biominerals are H_2O-rich and form small crystals (<1 μm), which size smaller than the typical EDX spot.

Powder X-ray diffraction (PXRD) of bedrocks was carried out using a Rigaku Miniflex II, Cu Ka radiation, 2-theta range 3–80°, velocity – 2°/min, step size – 0.02°. The PDXL II software was used to identify the mineral phases, accessing the ICDD database. PXRD patterns of lichens with biominerals were recorded in Debye–Scherrer geometry by means of a Rigaku RAXIS Rapid II diffractometer equipped with a curved (cylindrical) imaging plate detector (r = 127.4 mm). CoKα radiation (λ = 1.79021 Å) was generated by a rotating anode (40 kV, 15 μA) with microfocus tube optics; exposure time was set to 30 min. The data were processed using osc2xrd program (Britvin et al. 2017) and Stoe WinXPOW software (Stoe and Cie 2006).

3 Results and Discussion

According to EDX-analysis, main rock-forming minerals of volcanic rock are Ca-rich plagioclase, Ca-Mg-rich pyroxene (diopside), Mg-rich olivine and K-feldspar. Mineral amount differs from sample to sample. Secondary minerals are Mg-rich mica phlogopite ($KMg_3(AlSi_3O_{10})(OH)$) and alunite ($KAl_3(SO_4)_2(OH)_6$). Moreover, Cu, Zn and Pb fumarolic minerals were found (from Mountain 1004 only): tenorite (CuO), chalcanthite ($Cu(SO_4)\cdot 5H_2O$), atacamite ($Cu_2Cl(OH)_3$), pyromorphite ($Pb_5(PO_4)_3Cl$), linarite ($CuPb(SO_4)(OH)_2$), anglesite ($Pb(SO_4)$ and Cu, Zn-bearing diopside ($CaMgSi_2O_6$).

The following secondary minerals were found in biofilms: monohydrate and dihydrate calcium oxalates (whewellite $Ca(C_2O_4)\cdot H_2O$ and weddellite $Ca(C_2O_4)\cdot 2H_2O$) and copper oxalate monohydrate moolooite $Cu(C_2O_4)\cdot H_2O$. They were discovered in lichens from ancient (Mountain 1004) and modern (I, II. III) groups of scoria cones, whereas no oxalates were found in lichens colonized basalts from TFE (Naboko).

Whewellite was found in the lichens *Psylolechia leprosa* and *Sarcogyne hypophaea* (Fig. 2). Whewellite and Weddellite were found together in the lichen *Rinodina gennarii*. No oxalates were previously found in lichens of *Psylolechia leprosa, Sarcogyne hypophaea, Rinodina gennarii, Ochrolechia subplicans*. Whewellite accumulates in apothecia in the form of whitish masses consisting of lamellar small crystals 5–6 μ in size and their stack-like intergrowths. Weddellite forms dipyramidal crystals 2–10 μ in size. The source of calcium for the formation of oxalates are silicates pyroxene (diopside) and plagioclase (anorthite).

Moolooite was found in lichens *Acarospora squamulosa* (Fig. 3) and *Lecanora polytropa* (together with whewellite). Moolooite in the lichen *Acarospora squamulosa* was found for the first time. In the lichen *Lecanora polytropa*, the co-occurrence of moolooite and calcium oxalates has been discovered for the first time. The source of copper is tenorite, atacamite and copper-rich silicates (products of fumarolic processing of basalts). Moolooite forms lamellar crystals and intergrowths (up to 5–6 μ).

A common feature of the morphology of oxalate crystals is the presence of rounded edges (Fig. 2, 3), which indicates the dissolution process under the influence of lichens.

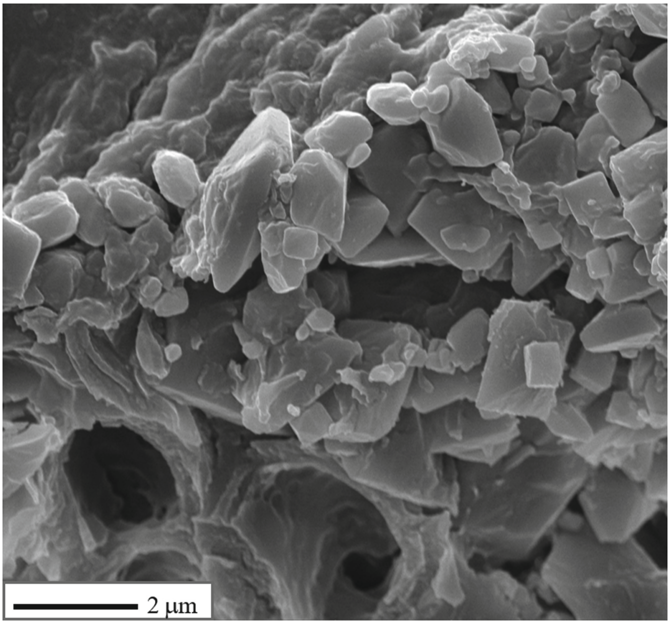

Fig. 2. Whewellite and weddellite in lichen *Sarcogyne hypophaea* (Mountain 1004)

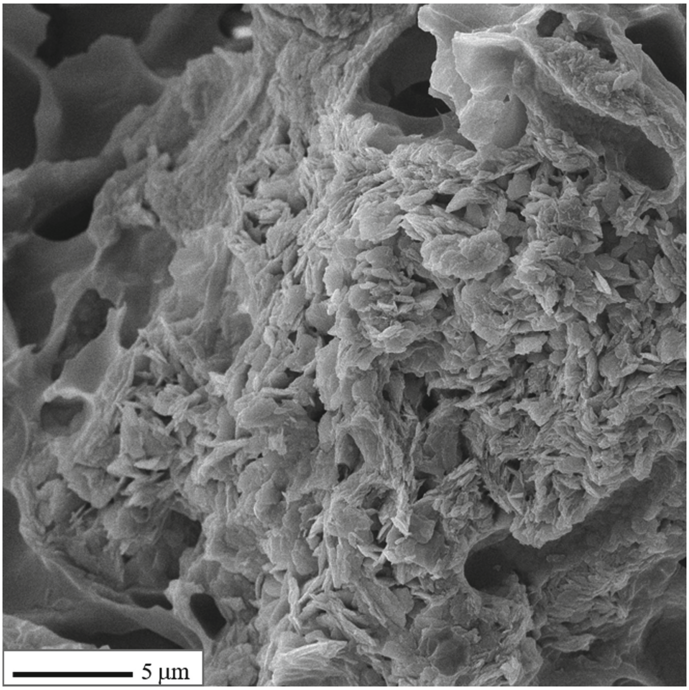

Fig. 3. Moolooite in lichen *Acarospora squamulosa* (Mountain 1004)

4 Conclusions

Oxalic acid salts (oxalates) in lichen thalli on scoria cones of Tolbachik volcano (Kamchatka Peninsula, Russia) were found for the first time. New species of lichens have been discovered, that are capable of producing oxalic acid, which leads to the formation of oxalates. The morphology of the crystals is described. Based on the analysis of the crystal morphology, it was concluded, that in the process of biomineralization the growth of crystals alternates with their dissolution.

Acknowledgements. This work was supported by the Russian Science Foundation (grant 19–17-00141). The study was carried out using the analytical capabilities of the Resource Centers of St. Petersburg State University: Centre for X-ray Diffraction Studies (RC XRD), Centre for Microscopy and Microanalysis (RC MM) and Centre for Geo-Environmental Research and Modelling (RC Geomodel).

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