



Ca, Cu and Pb solubilization and biomineralization by microorganisms: case study from Kamchatka, Russia

Irina Chernyshova, Oleg Vereshchagin, Zelenskaya Marina, Himelbrant Dmitry, Vlasov Dmitry, and Frank-Kamenetskaya Olga

St Petersburg State University, Institute of Earth Sciences, Crystallography, Russian Federation (i.a.chernyshova@yandex.ru)

The role of microorganisms (lichens, micromycetes and bacteria) in the formation of biominerals is widely known (Purvis, 2008; Vlasov et al., 2020). In the fall of 2019, we organized an expedition to the area of Tolbachik volcano (cones 1, 2, 3 and Mount 1004), Kamchatka, Russia, and collected 120 samples of volcanic rocks with biofilms. The volcanic cones of Tolbachik concentrate a wide variety of elements and are a type-locality of more than 300 minerals (Vergasova and Filatov, 2012; Siidra et al., 2017; Pekov et al., 2018). Lichen species are widespread in the volcanic fields of Kamchatka, Russia (Kukwa et al., 2014). The goal of this work was to search for and study biominerals associated with lichens.

As a result of our research, calcium oxalates (whewellite and weddellite) and copper oxalates (moolooite) associated with lichens were found. Whewellite was found in the lichens *Psylolechia leprosa* and *Sarcogyne hypophaea*. Whewellite and weddellite were found together in the lichen *Rinodina gennarii*. Pyroxene (diopside) and plagioclase (anorthite) sourced calcium for the oxalates formation. Whewellite accumulates in apothecia in the form of whitish masses, consisting of lamellar crystals of 5-6 microns in size and their stacked intergrowths. Weddellite forms bipyramidal crystals of 2-10 microns in size. Moolooite was found in lichens *Acarospora squamulosa* and *Lecanora polytropa* (together with whewellite). The source of copper is tenorite, atacamite and copper-rich silicates (products of basalt processing by fumaroles). Moolooite forms lamellar crystals and intergrowths up to 5-6 microns in size. An interesting feature of oxalate formations in the *Lecanora polytropa* lichen is a high lead content, which has never been previously recorded in natural oxalates. Linarite and pyromorphite are most likely the source of lead. Chemical analysis showed that "nests" of calcium oxalates can contain up to 6 wt% PbO, while "nests" of copper oxalate - no more than 1 wt% PbO. The results obtained indicate the possibility selective sorption of lead and suggest the possibility of replacing calcium with lead in the oxalates. The studies of the location forms of lead in biofilms are in progress. The exact form of lead has not yet been established. Linarite and pyromorphite are most likely the source of lead. *This research was supported by Russian Science Foundation grant (19-17-00141) and performed at the resource centers of St. Petersburg State University (MM, XRD, Geomodel).*

Fedotov S.A. (ed.). Great fissure Tolbachik eruption (1975-1976, Kamchatka) // Moscow: Nauka. 1984. 637 p.

Kukwa M. et al. // *The Lichenologist*. 2014. 46. 1. P. 129–131.

Pekov I.V. et al. // *Acta Cryst.* 2018. B74. P. 502–518.

Purvis O.W. et al. // *Mineralogical Magazine*. 2008. 72. 2. P. 607–616.

Siidra O.I. et al. // *European Journal of Mineralogy*. 2017. 29. 3. P. 499–510.

Vergasova L.P. and Filatov S.K. // *Volcanology and Seismology*. 2012. 5. P. 3–12.

Vlasov D.Yu. et al. In: *Aspergillus niger: pathogenicity, cultivation and uses*, Nova Science Publishers, New York. 2020. P. 2-121.