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Biologically mediated crystallization of buddingtonite in the Paleoproterozoic: Organic-igneous interactions from the Volyn pegmatite, Ukraine

Gerhard Franz[1,*], Vladimir Khomenko[2], Aleksei Vishnyevskyy[2], Richard Wirth[3], Ulrich Struck[4], Jörg Nissen[5], Ulrich Gernert[5], and Alexander Rocholl[3]

[1]Fachgebiet Mineralogie-Petrologie, Technische Universität Berlin, Ackerstr. 76, D-13355 Berlin, FR Germany
[2]The National Academy of Sciences, Semenenko Institute of Geochemistry, Mineralogy and Ore Formation, 34, Palladina av., Kyiv-142, 03680, Ukraine
[3]Helmholtz Centre Potsdam, GFZ German Research Centre for Geosciences, Sektion 3.1, Telegrafenberg, D-14473 Potsdam, Germany
[4]Museum für Naturkunde, Leibniz-Institut für Evolutions-und Biodiversitätsforschung, Invalidenstrasse 43, D-10115 Berlin, Germany
[5]ZE Elektronenmikroskopie, Technische Universität Berlin, Strasse des 17, Juni 135, D-10623 Berlin, Germany

Abstract

The Volyn pegmatites from Volodarsk-Volynskyi in the Zhytomyr Oblast, NW Ukraine, are associated with granites genetically related to the Paleoproterozoic Korosten pluton. Their late-stage evolution is characterized by the formation of opal-cemented breccia. A polymineralic pseudomorph after beryl within the breccia includes bertrandite (±euclase) + F-muscovite (with tobelite component) + buddingtonite + organic matter (OM) + opal (+ traces of K-feldspar, albite, columbite, FeS_2, barite, REE-minerals). Sector-zoned and platy to fibrous buddingtonite has variable (K+Na)- vs. NH_4-contents (electron microprobe analyses) and some H_2O or H_3O^+, as indicated by microscope infrared spectroscopy. We suggest that ammonium was produced by decay of OM, which is partly preserved in the pseudomorph. Energy-dispersive electron microprobe data of the OM show with increasing O–decreasing C-N-content due to degassing; the OM contains the high field strength elements Zr (≤7 at%), Y (≤3 at%), Sc (≤0.8 at%), REE (≤0.3 at%), Th (≤0.2 at%), and U (≤1.25 at%), which increase with increasing O-content. Transmission electron microscopy of the OM confirms the presence of N; Zr, Si, and O (with other HFSE) are concentrated in nanometer-sized areas and at the transition from OM to opal in nanometer-sized platy Zr-Si-O crystals. C-rich areas are amorphous but show poorly developed lattice fringes. OM is present in the pseudomorph also as brown pigmentation of opal and in pegmatitic beryl from Volyn as a component in late stage fluid inclusions, identified by C-H vibrational bands in infrared spectra. Stable isotope investigations of C and N of buddingtonite, black opal and kerite (fibrous OM known from the literature to occur in the Volyn pegmatites and interpreted as microfossils) indicate a biogenic origin of the OM. We propose that OM in the pseudomorph is condensed kerite, which achieved the high concentrations of high field strength elements via fluid-pegmatite interaction. Although no age determination of minerals in the pseudomorph is available, textural arguments and phase equilibria indicate its formation in a late stage of the pegmatite evolution, at *P-T* conditions below ~100 MPa/150 °C. We favor a conceptual model for the formation of the Volyn buddingtonite in analogy to Phanerozoic occurrences of buddingtonite, where over and around the shallow anorthosite-granite Korosten pluton hydrothermal convection cells introduced N-bearing hydrocarbons and its precursors into the cooling igneous rocks. Due to the elevated temperature, the OM disintegrated into degassing volatile and non-volatile residual components analogous to petroleum maturation. Organic N, released as NH_4, was then incorporated into buddingtonite.

Keywords: Buddingtonite, tobelite, kerite, organic matter, Volodarsk-Volynskyi pegmatite field