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

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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 (+euclidean) + F-muscovite (with tobelite component) + buddingtonite + organic matter (OM) + opal (+ traces of K-feldspar, albite, columbite, FeS2, barite, REE-minerals). Sector-zoned and platy to fibrous buddingtonite has variable (K+Na)- vs. NH4-contents (electron microprobe analyses) and some H2O or H3O+, 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 pegmatic 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 NH4+, was then incorporated into buddingtonite.

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

INTRODUCTION

Nitrogen is an important trace element in crustal rocks, ranging from approximately 1 to 1000 ppm in igneous rocks and from ~10 ppm to 1–2 wt% in sediments, with the highest values in coal and oil shales (Holloway and Dahlgren 2002; Busigny and Bebout 2013). Nitrogen is an essential compound in organic material and therefore concentrated in biogenic minerals such as guanine C5H7N4O, acetamide CH3CONH2, or urea CO(NH2)2. Under reducing conditions, NH4+ can form from OM (organic matter); it has an effective radius of ~0.17 nm (Pöter et al. 2007) and therefore readily substitutes for K+ in many silicates (micas, feldspars, zeolites, and others). Buddingtonite NH4[AlSi3O8] and tobelite NH4[Al3[(OH)3]AlSi3O10] are the most common and are frequently observed as a constituent in authigenic K-feldspars (e.g., Harlov et al. 2001a and references therein) and illite (e.g., Nieto 2005 and references therein). Ammonium in silicates is therefore a well-established first hint toward decayed OM in their sources (Ramseyer et al. 1993), and Hall (1988) already suggested that the ammonium content in mafic magmas is an indicator for crustal