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**Organic matter and formation of buddingtonite - an example of organic-igneous
interaction from the Paleoproterozoic Volyn pegmatite, Ukraine**

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Abstract

The Volyn pegmatites from Volodarsk-Volynskiy 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 polyminerallitic pseudomorph after beryl within the breccia includes bertrandite ($\pm$ euclase) + F-muscovite (with tobelite component) + buddingtonite + OM (organic matter) + 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 atom%), Y (≤ 3 atom%), Sc (≤ 0.8 atom%), REE (≤ 0.3 atom%), Th (≤ 0.2 atom%) and U (≤ 1.25 atom%), 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.

key words: 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 $C_5H_5N_5O$, acetamide CH_3CONH_2 or urea $CO(NH_2)_2$. Under reducing conditions, NH_4^+ 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 $NH_4[AlSi_3O_8]$ and tobelite $NH_4Al_2[(OH)_2|AlSi_4O_{10}]$ are the most common and are frequently observed as a constituent in authigenic K-feldspar (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 towards 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 contamination. In combination with the N-isotopic signature it is now a well-established tracer for OM in sediments and rocks from the deep Earth (Busigny and Bebout 2013).

Here we describe the pegmatitic occurrence of complex buddingtonite-K-feldspar solid solutions coexisting with tobelite-rich mica, opal, and OM, which contains a high content of Zr and related high field strength elements (HFSE), replacing pegmatitic beryl from the late Paleoproterozoic Volyn pegmatite district from Volodarsk-Volynskyi in the Zhytomyr Oblast, northwestern Ukraine. We also provide morphological data (scanning electron microscopy SEM) of kerite, OM from the pegmatite. Data from electron probe microanalysis (EPMA), microscope infrared spectroscopy (IR), and transmission electron microscopy (TEM), with additional information from powder X-ray diffraction (XRD) and ion probe analysis of Be,

were applied to characterize the formation of the pseudomorph. Stable isotope data for C and N of buddingtonite, opal, and kerite show the biogenic origin of OM. The Volyn pegmatite represents the oldest reported buddingtonite occurrence; all others are Phanerozoic.

Geological setting and sample material

The investigated sample (stored at the mineralogical museum, TU Berlin, inv.# 2017/1) was taken at the mine tailings of the Volyn pegmatite deposit at Volodarsk-Volynskyi from pegmatite II. The kerite sample and black opal sample for stable isotope determination are from the museum collection of the National Academy of Sciences, Kyiv. The pegmatites are genetically and spatially connected with rapakivi-like differentiated granites of the Korosten pluton in the northwestern Ukrainian shield (Lazarenko et al. 1973; Koshil et al. 1991; Ivanovich and Alekseevich 2007). The Korosten pluton intruded high-grade gneisses some 1800-1760 Ma ago (Verkhoglyad 1995) and crops out over more than 15,000 km². Pegmatites are found only on the western margin of this pluton in a contact zone of hybridization between granite and gabbroic rocks over a distance of 22 km and on a width of 300 to 1500 m. These pegmatites are known as a major source of gem minerals beryl, topaz, and quartz (variety morion) and are also known for OM termed "kerite" (e.g. Ginzburg et al. 1987). Until 1996 the pegmatites were mined extensively for piezo quartz, which occurs in exceptionally large crystals (Lyckberg 2005; Lyckberg et al. 2009).

The pegmatites, typically in the range of 30 x 30 m in cross-section and 40 to 45 m high, contain meter-sized miarolitic cavities and are therefore referred to as 'chamber pegmatites' (information given here is summarized from Kalyuzhnyi 1982; Lyckberg 2005; Ivanovich and Alekseevich 2007). They belong to the category of shallow pegmatites, residual-schlieren type, fully differentiated with a distinct zonation of graphic intergrowths next to the granite body, followed by a quartz-feldspar zone and a quartz core, and are irregularly distributed in

the granites. They belong to the Nb-Y-F enriched family, the REE subclass and the miarolitic topaz-beryl interior-type (nomenclature of Černý and Ercit 2005; Černý et al. 2012). The chamber can reach a volume of ca. 40 m³, in extreme cases up to 250 m³. Large quartz crystals of 1 to 2 m size grew from the hanging wall into the chamber. Possibly due to fluid overpressure during cooling some of the chambers were destroyed. The resulting breccia consists of crystal and rock fragments, cemented by opal, chalcedony and clay minerals. The investigated sample is such a breccia, which contains a pseudomorph after beryl.

Three different types of OM were described from the Volyn pegmatite; (i) enigmatic hair-like solid material named kerite (e.g. Ginzburg et al. 1987; Luk'yanova et al. 1992; Gorlenko et al. 2000; Zhmur 2003), (ii) brown pigment in black opal (Gigashvili and Kalyuzhnyi 1969), and (iii) methane and dark matter in late low-temperature fluid inclusions in outer zones of beryl and quartz crystals (Kalyuzhnyi et al. 1971; Voznyak et al. 2012). Proshko et al. (1987) had identified buddingtonite from the Volyn pegmatites with 3-4 wt% NH₄.

Methods

Quantitative EMPA were obtained on carbon-coated samples with a field emission electron microprobe type JEOL JXA-8530F at ZELMI at TU Berlin. Common commercially available standards from Astimex were used; for N we choose boron nitride. Counting times were 10 s on peak and 5 s on background. Buddingtonite is very susceptible for beam damage, and therefore for most spots a beam diameter of 15 µm was chosen. Element mapping was carried out with dwell time 90 ms, pixel 667 x 750, step size 240 x 240 nm. Organic matter could only be analyzed with the energy dispersive method (EDS; 12 kV; 10 nA; acquisition time of ≤100 s), because it is even more susceptible for beam damage than buddingtonite. The absolute amounts of individual elements determined by EDS are uncertain, because the relative error for major elements C and O is around 10 % (as estimated by comparison of analyses on OM

and C-free minerals), but relative trends of element pairs are considered as reliable. For C, the additional effect of the carbon coating must be considered; we choose carbon coating, because coating with Au would have had a strong absorption influence on N. The EDS system is equipped with a silicon drift diode detector (model EX-94310FAL1Q) and an ultra-thin film window, and has an effective area of 10 mm² and an energy resolution of 128 eV (for Mn K α). EDS analyses were also obtained for mineral semi-characterization, especially of small inclusions. SEM images were taken with a Hitachi SU8030 instrument. Kerite was coated with a ~5 nm thick iridium layer.

Because the sum of EPMA of an originally unknown mineral (later identified as buddingtonite) was significantly <100%, we applied secondary ion mass spectrometry (SIMS) to identify the missing element, which could be Be. Analyses were carried out with a Cameca 1280-HR ion probe at GFZ Potsdam. Using bertrandite as a standard (theoretical Be-content = 31.64 wt%) the determined Be concentrations in buddingtonite and muscovite (assumed Si concentration: 46.5 wt%) are around 20 and 85 ppm, respectively. Li- and B-counts were also checked on both minerals, again indicating concentrations at the ppm-level.

Two TEM foils of dimensions 15 μ m x 10 μ m x 0.150 μ m were prepared using FIB, one (# 4467) crossing the boundary to opal, the other at the border to a vesicle (# 4461; for details of milling see Wirth 2004, 2009). They were studied in a Tecnai F20 X-Twin TEM operated at 200 kV with a field emission gun as electron source, equipped with a Gatan imaging filter GIFTM (Tridiem), a Fishione high-angle annular dark field detector (HAADF), and an EDAX X-ray analyzer with ultra-thin window. Bright field, dark field and high-resolution TEM images are usually acquired as energy filtered images applying a 20 eV window to the zero loss peak of the electron energy-loss spectrum. Counting time for EDS analyses (processed with TIATM software) in the scanning transmission mode across a pre-selected area thus avoiding mass loss during the data acquisition, was 60 to 120 s. Electron diffraction data were

acquired as selected area electron diffraction pattern (SAED) or derived from high-resolution lattice fringe images applying a fast Fourier Transform (FFT). Electron energy loss spectra (EELS; data processing with Digital Micrograph™) were acquired in diffraction mode using a camera length of 700 mm. Applying a 1 mm entrance aperture the resulting acceptance semi angle is 5 mrad. Dispersion was 0.1 eV/pixel, acquisition time was 1 s.

Single grain IR absorption spectra were measured at room temperature in the near- and middle IR region in the spectral range 7000 to 1000 cm^{-1} , by means of a Bruker FTIR spectrometer IFS 66 equipped with an IR-microscope. All spectra were scanned with a measuring spot of 60 μm diameter, at a spectral resolution of 2 cm^{-1} . The time-averaged signal was collected over 200 scans. The reference spectra were measured in air. Areas of monomineralic buddingtonite with relatively large grains, homogeneous opal and OM were chosen from the same thin sections where microbeam analysis was carried out. Nine pieces of this buddingtonite with sufficient size for FTIR measurements were cut out from the thin sections and cleaned from resin in alcohol. Where possible, the measuring area was placed mainly in a large buddingtonite crystal. While these grains appear as fibrous polycrystalline aggregates (however with a euhedral outline; see Results) and measuring areas exceed individual fibers in the grains, spectra were measured in unpolarized light. FTIR measurements of muscovite-tobelite mica, opal and organic material were carried out in uncovered thin section. Reference spectra were taken in sample-free area of the thin section slide with thin epoxy layer.

Stable isotope analysis and concentration measurements of nitrogen and carbon were performed simultaneously with a THERMO/Finnigan MAT V isotope ratio mass spectrometer, coupled to a THERMO Flash EA 1112 elemental analyzer via a THERMO/Finnigan ConFlo IV- interface in the stable isotope laboratory of the Museum für Naturkunde, Berlin. Stable isotope ratios are expressed in the conventional delta notation

($\delta^{13}\text{C}$ / $\delta^{15}\text{N}$) relative to atmospheric nitrogen (Mariotti 1983) and VPDB (Vienna PeeDee Belemnite standard). Standard deviation for repeated measurements of lab standard material (peptone) is generally better than 0.15 per mill (‰) for both N and C. Standard deviations of concentration measurements of replicates of our lab standard are <3% of the concentration analyzed.

Results

Petrography

The handspecimen shows typical breccia phenomena (Fig. 1a) with clasts of albite, alkali feldspar, and quartz, which are embedded in a matrix of dominantly opal and vesicles. The pseudomorph after beryl is well visible with a hexagonal outline and a core-rim structure. The rim (Fig. 1b) consists of opal and bertrandite, followed by a broad zone of dominantly buddingtonite and muscovite, with minor amounts of bertrandite. The core consists of very fine-grained brownish Fe-rich muscovite, with some Fe-staining. OM is visible as an opaque, approximately 1 x 2 mm large spot within the buddingtonite rich zone. Although mostly coherent, the sample had to be embedded in epoxy resin for thin section preparation.

Mineral composition and textural relations in the beryl pseudomorph

Bertrandite and euclase. Bertrandite $\text{Be}_4\text{Si}_2\text{O}_7(\text{OH},\text{F})_2$ is the volumetrically most important Be-mineral in the pseudomorph and appears as up to almost 1 mm long euhedral, platy crystals in a matrix of F-muscovite (Fig. 2a,c), buddingtonite and opal. It was verified by powder XRD, and EDS analyses show ~2.5 wt% of F-content. Slight corrosion features are visible in contact to buddingtonite and opal. Euclase $\text{Al}[\text{BeSiO}_4(\text{OH},\text{F})]$ is rare, occurs in close association with buddingtonite (Fig. EA 1), and shows minor ZrO_2 and GeO_2 contents (≤ 1 wt%, EDS determination).

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Buddingtonite. It occurs dominantly in a network of euhedral, platy appearing crystals, together with F-muscovite and opal (Fig. 2c,d,e,f), and replacing K-feldspar (Fig. 2e) and albite (Fig. 2g). Replacement of albite results in randomly oriented crystals, replacement of K-feldspar in oriented overgrowths. Buddingtonite appears as crystals several tens of μm large with typical sector zoning (Fig. 2e; for details of sector zoning see Fig. EA 2). Euhedral appearing crystals consist of μm -sized fibers indicated by slightly different extinction position in thin section. Solid solution of dominantly $\text{NH}_4\text{-K}$ creates a strong variation in BSE contrast. There are also intermediate euhedral-fibrous textures (Fig. 2f) with clear zoning in the core, extending outwards into fibrous aggregates.

Buddingtonite was very difficult to analyze, because (i) it is not stable under a focused beam, (ii) the inherent problems of N as a light element, and (iii) the absence of appropriate standards (leading probably to a slight N over-determination). It was first analyzed without determination of N, to obtain an average value for all other determined elements. The average value for 26 analyses for SiO_2 with 67.24 wt% has only a very limited variation of ± 0.7 wt%; the same is true for Al_2O_3 with 18.95 wt% ± 0.4 wt%, with an estimated relative error of 1-2 % (Table 1; individual analyses in Appendix). Titanium, Mg, Mn, Ca, Cs and Rb are always close to or below the detection limit (≤ 0.01 wt% oxide). Fluorine was analyzed to check for overlapping analyses with muscovite and for all analyses with detectable F some overlap must be considered. Iron (average 0.08 Fe_2O_3 tot) is above the detection limit and in the formula calculation attributed to the T-site. In contrast to the constant Al-Si values, K_2O varies significantly between ~ 2 and ~ 5 wt%. Na_2O is low, maximum 0.9, average 0.3 wt%. In a second step, we analyzed especially for N and choose the average value for SiO_2 (67.24 wt%) and for Al_2O_3 (18.95 wt%) for the correction procedure (Table 1). There is no correlation between $(\text{NH}_4)_2\text{O}$ and the sum of the alkalies ($\text{K}_2\text{O} + \text{Na}_2\text{O}$) (Fig. 3a). The total of the determined wt% including N calculated as $(\text{NH}_4)_2\text{O}$ is in many analyses significantly below

100 wt%, especially for analyses with low N-content (no. 3,4 and 5 in Table 1), pointing to a significant amount of "water" compound (either H_2O or H_3O^+), which has been predicted to occur in buddingtonite and discussed by Barker (1964), Laricheva et al. (1993), and Harlov et al. (2001a). Na_2O and K_2O are also not correlated (Fig. 3b), all analyses show random scattering.

X-ray mapping (WDS) of the major components (Figs. 4, 5) highlights the zoning. There is a good positive correlation of K with Na, which are both low in the cores of the crystal (Fig. 4), but sectors enriched in K do not show Na enrichment; this might be partly due to the generally low Na-contents, but also due to complex substitution including "water". A lack of correlation is also seen in the compilation of all analyses (Fig. 3), and we conclude that from crystal to crystal and within the crystals the amount of substitution of N-K-Na in combination with H_3O^+ differs. Note that for quantitative analyses the beam diameter was 15 μm , so it averages over heterogeneities within a crystal.

White mica. Muscovite occurs as a network of platy, randomly oriented crystals with interstitial opal and vesicles (Fig. 2a,b). In areas rich in buddingtonite, K is often observed to be partly replaced by NH_4 (visible as lower BSE-contrast) parallel to the cleavage planes and outer (001) faces (Fig. 2b,d), and also when crystals are kinked. Thin plates of muscovite in a matrix of buddingtonite (Fig. EA 1) are interpreted as relicts. Quantitative analyses (Table 2) show up to 25 mol% tobelite-component. The interlayer occupancy varies from 1.7 to 2 atoms per formula unit, with two analyses >2.0 , both with high N-content, suggesting inaccurately high N. In bright areas in muscovite the N-content is below detection limit. Fluorine is variable, in some analyses with >50 mol% of the F-muscovite endmember. We checked for Be, B and Li with SIMS, but they are only present at the ppm-level. Silicon is higher than the theoretical value of 6.0, for most analyses between 6.4 and 6.8, one point with 7.3. Total Al is consistently low, on the average between 4.5 and 5.5 instead of the theoretical value of 6, and

Fig. 6

Fig. 7

the sum of octahedral occupancy is always below 4.0. Powder XRD pattern shows in addition to the muscovite peaks, a broad elevated background area between 19 and 24 °2 θ , typical for opal, and several peaks typical for tridymite. IR characteristics (see below) also confirm that it is muscovite-type mica. X-ray mapping confirms the replacement of K by N (Fig. 5); F is concentrated mostly in the inner parts of the crystals (Fig. 4).

Opal. It is a volumetrically important phase (Figs. 6a, 2a) filling interstices between buddingtonite (Fig. 2d). Euhedral buddingtonite crystals within opal (Fig. 2a) indicate precipitation of opal slightly later or coeval with buddingtonite. Opal is strongly zoned in BSE images, outer rims with lower average atomic number point to higher water contents. Internal structures show concentric zoning and botryoidal growth. Opal is rich in nm to μ m sized inclusions (Fig. 6b); EDS analysis show FeS₂, BaSO₄ and a phosphate-silicate phase, rich in Th and Ca with minor amounts of La, Ce, Y and U (possibly brittolite-apatite).

Other minerals. K-feldspar (Fig. 2e), albite (Fig. 2a), columbite-Fe and bastnäsité-Ce are interpreted as relict minerals from the pegmatitic (transitional to hydrothermal) stage because of their typical corrosion features. Columbite (Fig. EA 3) and bastnäsité (Fig. EA 4) were identified by EDS. Bastnäsité is replaced by opal and an unidentified LREE-phosphate with botryoidal shape. Other secondary LREE-minerals were observed along dissolution features in albite (Fig. 2h) and also as overgrowths on the rims of muscovite.

Organic matter. It was found in one spot in the pseudomorph (Fig. 6c-f; see also Fig. 1), closely associated with opal. BSE images show a conspicuous pattern with variable brightness. Brighter areas have a high content of O together with Zr, Si, Y, Sc, U, Th, with minor amounts of REE and other elements, and dark areas are high in C (Table 3; Fig. 7). This points to variable degrees of degassing of the OM. Along voids and vesicles, brightness is very high towards the rim (Fig. 6b). Voids (Fig. 6c) and round vesicles of 1-2 μ m in size (Fig.

6d-f) are interpreted as degassing structures of OM. Shrinking cracks in OM are partly filled by opal, indicating the presence of the OM before precipitation of opal.

Carbon and O are negatively correlated, from <15 atom% O to up to 40 atom% O (Fig. 7a). Zirconium, which is considered as a non-organic derived HFSE, and Si (not shown) are positively correlated with O (Fig. 7b), whereas N is positively coupled with C and thus also an element lost from OM during degassing (Fig. 7c). Phosphorous and F are concentrated during degassing (Fig. 7d). Sulfur is negatively correlated with C, from ~0.1 to 0.3 atom% at high C-contents, but at lower C-contents it scatters at a rather small range of 0.35 to 0.45 atom% (Fig. 7h). Individual HFSE show a good positive correlation, e.g. between Sc and Y (Fig. 7f), Th and U (Fig. 7g), and Y and the sum of REE (Fig. 7h).

IR data

We observed two types of unpolarized IR spectra of buddingtonite aggregates; the first one represents the “pure” etalon spectrum of the tetrahedral ammonium molecule, whereas spectra of the second type represent a combination of NH_4^+ and H_2O (or H_3O^+) vibrations (Fig. 8a). The spectra of water-free buddingtonite are dominated by bands of the asymmetric bending mode ν_4 at 1430 cm^{-1} and both symmetric ν_1 and asymmetric ν_3 stretching vibrations at 3050 and 3268 cm^{-1} . The latter two form envelopes together with a first overtone of ν_4 at 2846 cm^{-1} . Weak bands are also clearly resolved at 1680 and 4715 cm^{-1} . In comparison to synthetic buddingtonite we assigned them to symmetric bending ν_2 and a combination of $\nu_3 + \nu_4$ vibrations, respectively (Table 4).

Unpolarized IR-spectra of ammonia-bearing muscovite, measured in uncovered thin section, show in addition to weak NH_4 bands those of OH at 3330 cm^{-1} and OM at $2950\text{--}2870\text{ cm}^{-1}$ (Fig. 8). For comparison spectra taken in basal sections of single crystals of natural NH_4 -bearing muscovite (California) and pure muscovite (Polar Ural; both from own collection) are

Fig. 8

shown (for band assignment, see Table 4). In IR spectra of brown opal (Fig. 8c), measured in uncovered thin section and in a free thin slab of opal on the border of buddingtonite aggregates, the area of C-H vibration is superimposed by a broad, H₂O-dominant stretching vibrations' envelope ($\nu_1 + \nu_3$) at ca. 3400 cm⁻¹ and a weak H₂O combination band ($\nu_2 + \nu_3$) at 5200 cm⁻¹. The IR spectra of OM was measured in uncovered thin section and shows characteristic bands for C-H vibrations between ~2800 and 3000 cm⁻¹, together with broad absorption in the range from 3000 to 3650 cm⁻¹ caused by O-H bonds (Fig. 8d).

TEM

Two FIB-foils were cut, one over the boundary from OM to opal, the other one in OM with a vesicle. The foil over the boundary from OM to opal (Fig. 9a) shows an approximately 500 nm wide area, where platy crystals of Zr-silicate are concentrated near to the OM. In the HAADF image opal shows ~5 nm large bright areas (Fig. 9b), where besides Si and O small amounts of Ba, Fe, C, S, Cl, and K could be detected (spectra in Figs. EA 5, 6). The presence of C confirms the IR-data about OM incorporated into opal. In the Zr-silicate also small amounts of Y, U, Ca, Sc and Fe were detected by EDX. Opal and the OM are essentially amorphous but with ~5 nm areas with a slight indication of lattice fringes (Fig. 9c,d).

The HAADF image (Z-contrast) of the FIB-foil cut over the boundary from the OM to a vesicle (Fig. 10a) shows an approximately 50 nm wide rim towards the vesicle with high contrast (Fig. 10b), where Zr, O, and Si are enriched together with some Al, Ca, Th, U, and Y; darker areas have a higher C and lower O content. A 150 nm wide scanned EDX profile (Fig. 10e) in the rim shows parallel enrichment of Zr, O, and Si, and independent variation of C. EELS mappings of C and O show an irregular distribution of ~10 to 30 nm wide areas, where high C-contents are correlated with low O-contents and vice versa. EELS analysis in both FIB-foils confirm the presence of N with a N-K edge at 400 eV.

Fig. 9

Fig. 10

Kerite characterization and C-N stable isotopes

Kerite is brownish-black and SEM images show typically branched fibers several 100 μm in length and approximately 3 μm thickness, with a very smooth surface (Fig. 11), but with no indications for segmentation. Fibers are brittle and broken cross sections show a hollow core of variable diameter, but typically in the range of 250 nm x 500 nm. Unbroken fibers end in a smooth round tip. The only clear indications for diagenetic alteration are mineral grains (feldspar, mica, clay minerals) on the surface.

Stable isotope determination of buddingtonite concentrate (+ opal, white mica) from the pseudomorph and from black opal yielded positive $\delta^{15}\text{N}$ (vs air) values between 1.0 ‰ and 2.9 ‰ (± 0.15 ‰); negative $\delta^{13}\text{C}$ (VPDB) values between -25.7 ‰ and -26.9 ‰ (± 0.15 ‰; Table 5; Fig. 12). Kerite has a slightly higher $\delta^{15}\text{N}$ of 2.9 - 3.5 ‰ and an extremely low value of -40.6 ‰ for $\delta^{13}\text{C}$.

Discussion

P-T-X-conditions

The formation of buddingtonite in the Volyn pegmatite requires strong interaction of biogenic material with the igneous rocks. To discuss this process, it is first necessary to estimate the physicochemical conditions *P-T-X* of the pseudomorph formation. From the Volyn pegmatites, Lazarenko et al. (1967) and Bartoshinskyi et al. (1969) first described bertrandite in a pseudomorph after beryl. They argued for a reaction of beryl with a K-bearing fluid to form bertrandite with muscovite and silica. The K-bearing fluid that caused the reaction was ascribed to the low-temperature hydrothermal period of pegmatite evolution.

The calculated phase diagram for beryl stability in the simplified system $\text{BeO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (Barton and Young 2002) combined with our observations provide a more quantitative background, keeping in mind that HF and CO_2 contents and especially NH_4^+ contents in the

Fig. 11 SEM kerite

Fig. 12 C-N isotopes

fluid may alter the phase relations significantly. The SIMS data show, however, that bertrandite and euclase are the only minerals, which incorporate Be on the wt% level. Muscovite textures in the pseudomorph clearly indicate that it is not a primary pegmatitic mica and its Be-, Li- and B contents are on the ppm-level and can be neglected. Therefore the relevant breakdown reaction for beryl is its lower stability limit in a hydrous fluid (Fig. 13):

At $P_{\text{fluid}} \leq 100$ MPa and $T \leq 250$ °C as estimated from Barton and Young (2002), reaction (1) crosses the stability of phenakite:

and continues to lower temperature with the formation of bertrandite:

For the F-muscovite endmember the reaction is:

Where beryl is not in contact with K-feldspar, it decomposes into bertandite + euclase (Fig. 13), as indicated by the rare presence of euclase in the pseudomorph (Fig. EA 1):

beryl fluid bertrandite euclase quartz

In the presence of an NH_4^+ -bearing fluid, K-feldspar and muscovite can equilibrate according to the exchange reactions (inset in Fig. 13), forming buddingtonite and tobelite:

For F-muscovite, reaction (7) is modified to (8), keeping in mind that the newly formed tobelite has less F:

F-muscovite fluid tobelite fluid

These reactions imply a scenario where first the pseudomorph with muscovite and bertrandite was formed; then muscovite and relict feldspar were transformed into buddingtonite and tobelite via exchange reactions with an NH_4 -bearing fluid.

However, muscovite can also be transformed into buddingtonite, as suggested by muscovite relicts in buddingtonite (Fig. EA 1):

muscovite silica fluid buddingtonite fluid

For F-muscovite, the reaction into buddingtonite is:

F-muscovite silica fluid buddingtonite fluid

Generally, in a silica-saturated environment with abundant quartz and opal the stability fields of K-feldspar, albite and muscovite are controlled by the K^+/H^+ ratio and Na^+/H^+ ratio in a fluid (Hemley and Jones 1964; Wintsch 1975). Buddingtonite with NH_4 -K-Na- H_3O solid solutions and NH_4 -K-F-bearing muscovite indicate a complex composition of the fluid. Furthermore, the presence of carbonate (bastnäsite, see Fig. EA 4) and of CO_2 -rich fluid

inclusions (Kalyuzhnyi et al. 1971) requires a certain amount of CO₂ in these fluids.

Proshko et al. (1987) determined buddingtonite from different points in a topaz-bearing chamber pegmatite from Volyn. Their observations show that buddingtonite formation via exchange of alkalis by NH₄ was not restricted to the breccia and the pseudomorph: Feldspathic rocks with buddingtonite formed under a zone of blocky pegmatite by leaching and recrystallization, substituting the high-T assemblage quartz, feldspar and mica by the low-temperature assemblage buddingtonite, albite, and hydromica.

Lazarenko et al. (1967) determined homogenization temperatures of liquid primary inclusions (L = 85-90 vol%) in bertrandite from a pseudomorph and estimated an approximate temperature of the fluid of 150 °C. The chemical composition of these late fluids is characterized by high K concentration and high pH values (Kalyuznyi and Prytula 1967; Kalyuzhnyi 1982). This is contradicting Černý's (1968, 2002) compilations that bertrandite forms in an acidic environment. A high pH is, however, indicated by the presence of ammonia. The phase assemblages of the Be-minerals indicate a maximum temperature below ~250 °C. Depending on the slope of reactions (3) and (5) at low pressure, the actual temperature was probably ≤ 150 °C (Fig. 13).

Pressure conditions are difficult to estimate. The geological framework implies an overburden, that is thick enough to create a significant lithostatic pressure for the formation of a pegmatite. The overburden must be able to seal the rock around the large chambers with a volume of tens or more m³. General estimates for the crystallization conditions of miarolitic pegmatites are between 200 and 50 MPa (at ~700 to 450 °C; London 2008; for a general discussion of chamber formation see also London 2013). The phase equilibria of the pure Be-minerals indicate a minimum pressure of ~100 MPa at 250°C (Fig. 13), which would be much lower at the assumed temperature of 150 °C.

Formation of the breccia might have occurred during cooling when the supercritical, dominantly hydrous pegmatitic fluid in the pegmatite chamber, with a significant amount of HF and saturated with Si, alkalis etc., became subcritical and separated into gas and a hydrous liquid. The gas overpressure led to escape of the gas and collapse of the chamber, and the large amount of Si in the liquid precipitated as opal cement of the breccia. In addition, significant pressure gradients are caused in the cooling igneous body itself due to the melt-crystal transition and by heating pore water in a contact aureole (e.g. Svensen et al. 2010, and references therein) leading to fracturing and mobilization of material from the country rocks into the igneous rock.

Origin of organic matter

Organic or organic-derived matter occurs as NH_4 in feldspar and mica, as C-H compounds in fluid inclusions in beryl and as pigmentation of opal, as condensed OM with a high content of HFSE in the pseudomorph, and as kerite. Kerite is considered as the original form. It occurs within the chambers, irregularly distributed, in accumulations up to 3 kg (e.g. Ginzburg et al. 1987; Zhmur 2003). The fibers have a diameter of $\sim 3 \mu\text{m}$ and are several 100 μm long, similar to what has been described as "monkey hair" in brown coal of Germany (reference Orlov and Uspenskii 1936, in Zhmur 2003). The Volyn kerite consists of amorphous graphite-type material with low structural arrangement and non-graphitized naphthenic substance (Zhmur 2003). Gorlenko et al. (2000) determined it as original biomass of cyanobacteria, although an abiotic origin was also discussed (see references in Zhmur 2003, and Gorlenko et al. 2000). The stable isotope data (Table 5) with the extremely low value of -40.6 ‰ for $\delta^{13}\text{C}$ clearly points to its biotic origin. Furthermore, the data are consistent with anoxic methanogenic bacteria (Fig. 12), typical organisms of the deep biosphere. The heavier composition of $\delta^{13}\text{C}$ in the buddingtonite concentrate (with opal) and of black opal itself is consistent with

degassing of kerite into the observed OM in the pseudomorph, where C was likely mobilized as CH₄ and NH₄.

When the breccia with the assemblage betrandite ± euclase + muscovite formed, the OM produced NH₄ to convert muscovite into the tobelite component and relict K-feldspar and albite into buddingtonite. Mäder et al. (1996) showed the relevant reactions in a schematic log activity (NH₄⁺/H⁺)-(K⁺/H⁺)-diagram (their Fig. 3; at 298.15 K/1 bar). However, due to the enlarged stability field of F-muscovite compared to pure muscovite, the topology of the system is slightly changed allowing for reaction (10), the transformation of F-muscovite into buddingtonite (inset in Fig. 13). With increasing (NH₄⁺/H⁺), F-muscovite reacts into tobelite (reaction 8) and then with further increasing (NH₄⁺/H⁺) into buddingtonite (reaction 6). Kaolinite (not observed in our sample, but described by Lazarenko et al. 1967, from a pseudomorph) is probably a later product of K-feldspar and/or muscovite alteration.

The OM in the pseudomorph is similar to kerite, but not in the typical fibrous form. We postulate that it was first incorporated into the pegmatite chamber as kerite, and then during fluid-rock interaction with fluids of the pegmatite, the kerite fibers condensed into the now observed aggregate. The liberated NH₄ converted feldspar and mica into buddingtonite and tobelite. The dominantly amorphous character of the OM is consistent with a low temperature. Kerite composition (as given by Ginzburg et al. 1987; C 60-70 wt%; H 5-7 wt%; O 9-23 wt%; N 8-9 wt%; S 2-3 wt%) in terms of C-O-N fits the general trend, which we observe, with the low O-, high C-contents (Fig. 7a; recalculated into atom%). Nitrogen is high, but fits to the trend of strongly decreasing N-contents down to a level of ~2 atom% (Fig. 7c).

With increasing condensation the amounts of HFSE increase (Fig. 7), best visible by the conspicuous BSE contrast pattern (Fig. 6). The OM was enriched via interaction of the hydrothermal fluids with the granitic-pegmatitic rocks, leaching HFSE, Si and other elements from the pegmatite minerals (such as bastnäsite observed as a relict in the pseudomorph; Fig.

EA 4). Mobility of the light REE is indicated by precipitation of LREE-minerals along grain boundaries (Fig. 2h). At the margin of the OM, the enrichment was large enough to precipitate nanometer-sized crystals of an unidentified Zr-silicate (Figs. 9, 10). The OM itself did not convert into graphite, as indicated by the only poorly developed lattice fringes (Fig. 10), and consistent with the low temperature at this stage. Schilling et al. (2015) reported Zr-F transport in a Be-mineralization in granite from Norway, causing precipitation of zircon in beryl-phenakite reactions. In the Volyn pegmatite, mobilization of Zr, REE, Y, Sc, U, and Th and trapping in OM (Fig. 7) via F-complexes is also a likely mechanism to concentrate these elements. Gysi and William-Jones (2013) have shown that hydrothermal mobilization of Zr and light REE in HCl-HF bearing fluids is likely controlled by pH, ligand formation, and temperature. The abundance of topaz in the pegmatites and of F in the pseudomorph minerals clearly indicates a high F activity. High Sc concentrations, such as observed in the Zr-enriched OM from Volyn (Fig. 7f) are not unusual; Cook et al. (2013) observed Sc concentrations in zircon in the same order of magnitude (up to 0.8 wt%) in a hydrothermal REE-deposit.

Opal is the latest mineral, cementing the breccia and also filling cracks in the condensed OM. Some of the opal, appearing brown in thin section, clearly contains C-H compounds (Fig. 8). According to Gigashvili and Kalyuzhnyi (1969) black opal occurs as one of the last minerals in the central pegmatite zone in voids in quartz. X-ray data indicate opal-CT. They determined the composition of gases released upon heating to 340 °C from opal and found a wide range of alkanes from methane to hexane, and possibly higher, with a mass ratio C:H = 84.7:15.3, close to natural oil. The authors speculated about deposition of OM in Volyn pegmatites simultaneously (or soon after) with coagulation of the colloidal silica solution. Hydrocarbons were also observed in a fluid inclusion in beryl on a healed crack in beryl, where a second generation of beryl was precipitated (Voznyak et al. 2012). This points to temperatures for the late stage of OM-incorporation at least in parts of the pegmatite field

above the thermal stability of beryl, depending on pressure near to ~ 150 °C (Fig. 13). Kalyuzhnyi et al. (1971) also observed OM in complex primary CO₂-inclusions and in large secondary inclusions in quartz, which contain thin crusts of material, insoluble in acids and alkalis on the walls. This substance disappears when heated in air at 340–450°C. Mass spectrometry revealed H₂, N₂, methane, ethane and other hydrocarbons of mass 80-115, similar to the analysis of black opal (Gigashvili and Kalyuzhnyi 1969).

The processes are summarized in Figure 13. It started with the igneous (transitional to hydrothermal) crystallization of beryl and K-feldspar in the chambers (stage 1). Possibly, in the surrounding and overlying rocks, bacterial life (Gorlenko et al. 2000) boomed in surficial ponds and/or sub-surface hydrothermal convection. Since kerite was observed in the chamber (Zhmur 2003; Lyckberg et al. 2009), bacterial life was apparently also present as deep biosphere; temperatures would be constrained by the thermal barrier of microbial life (stage 2). The chamber collapsed (stage 3) and in this realm, the pseudomorph with bertrandite $\pm$ euclase + F-rich muscovite formed (stage 4). The ongoing fluid circulation produced the enrichment of HFSE in the OM, which also lost its typical fibrous kerite-morphology (stage 5). The products of the degassing OM, CH₄ and higher C-H compounds, were incorporated into fluid inclusions in beryl and quartz, and transformed muscovite into tobelite and relict feldspars into buddingtonite via exchange reactions of alkalis to NH₄ (stage 6). Also, buddingtonite formed as precipitates from the fluid, as indicated by the abundant irregularly distributed buddingtonite crystals, which show no indication for replacement reactions. Further cooling led to the precipitation of opal, which also incorporated alkanes. Finally, the last hydrothermal alteration produced kaolinite (stage 7), and possibly other clay minerals, reported in the literature (e.g. Lazarenko et al. 1967).

Implications

Fig. 13

This study has shown that in a cooling granite-pegmatite system, OM can under appropriate circumstances be incorporated into a pegmatite. The general idea regarding its origin involves its incorporation into hydrothermal convection cells from ponds on the surface, where algae blooms are typical, analogous to modern formation of buddingtonite or other NH_4 -bearing minerals in volcanic settings (e.g. Krohn et al. 1993; Bobos and Eberl 2013; Altaner et al. 1988). No surrounding or overlying sediments with organic matter exist, where buddingtonite formation (due to contact metamorphism, comparable to the process postulated by Svensen et al. 2008) has also been observed (see compilation in Mäder et al. 1996).

The Volyn pegmatite represents a prime example of incorporation of OM into an igneous system and led to intense discussion of biotic versus abiotic origin of hydrocarbons (see references in Zhmur 2003). Similar scenarios, but with igneous rocks showing less obvious indications for OM, might be more common than previously thought. Due to analytical problems to identify N in silicates, small amounts of NH_4 are likely overlooked. Hydrocarbons, if not especially looked for, will also not be identified. Since kerite was observed in the collapse breccia (Zhmur 2003; Lyckberg et al. 2009), bacterial life was apparently present in the chambers; this would constrain the maximum temperatures below the thermal barrier of microbial life. The Volyn pegmatites have extraordinary large chambers, which might explain the strong enrichment of organic material, but smaller miarolitic cavities are the rule in low-pressure granitic rocks, and in basaltic rocks small vesicles due to degassing of the melt are also frequently observed. These are suitable to host the bacterial life. Fibrous fossilized microbacteria were found e.g. at the Emperor Seamounts in the oceanic deep biosphere (Ivarsson et al. 2008), however in much smaller quantities compared to Volyn and less well preserved. Interaction of organic material with igneous systems is known also from other different geological environments; Aarnes et al. (2015) have shown that in the North Sea basins, volcanic intrusive sills contain a high amount of CH_4 , generated in

sediments rich in organic carbon and incorporated into the cooling igneous rocks. Svensen et al. (2008) used N content as a tracer for fluid flow in a hydrothermal vent system around sills in the Karoo Basin, South Africa, and Hall (1988) has already proposed that the ammonium content of mafic magmas is a good indicator for crustal contamination. CH₄ and N₂ is commonly observed in gases from drill holes in Precambrian Canadian and Fennoscandian shields (e.g. Sherwood Lollar et al. 1993, and references therein), interpreted as a mixing of microbially biogenic and abiogenic derived fluids (e.g. Sherwood Lollar et al, 2006). It can be speculated that also an ancient deep biosphere such as that from Volyn might contribute to these fluids.

The formation of buddingtonite happened in the cooling Paleoproterozoic Korosten pluton. It seems unlikely that a much younger event caused the hydrothermal alteration, because no later geological activity is reported from the stable Precambrian Ukrainian shield. Weathering phenomena can safely be excluded, as indicated by the large crystals of bertrandite and muscovite in the pseudomorph and their textural relations; however the poor stoichiometry of muscovite observed here and the characterization of these as hydromica (Proshko et al. 1987) is in agreement with low temperatures. According to our literature search this is the oldest reported occurrence of the ammonium minerals, and also the oldest reported occurrence of amorphous opal. It belongs to the era of biomediated mineralogy (Hazen et al. 2008), transitional between stages 7 of Paleoproterozoic atmospheric changes and surface oxidation and stage 8 of an intermediate ocean. However, concerning the evolution of Be-minerals in Earth's history, the Volyn pegmatites do not add new information, since all observed Be-minerals are known from the Archean (Grew and Hazen 2014).

The scenario implies a terrestrial environment, and therefore already at ~1.8 Ga microbial life on the continents and as deep biosphere must have been intense enough to create the conditions for formation of buddingtonite and tobelite-rich mica. Kerite, an extremely well

preserved fossil microorganism, must have been available in very large amounts to increase the activity of NH_4 to such a level that buddingtonite is stabilized (expressed as $\log a(\text{NH}_4^+/\text{H}^+)$ of approximately 10; Mäder et al. 1996). Furthermore our observations show that OM is able to concentrate large amounts of HFSE, which are generally considered as insoluble at low temperature. This has strong implications for element mobility in diagenetically overprinted organic-rich sediments.

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References

- Altaner, S. R., Fitzpatrick, J. J., Krohn, M. D., Bethke, P. M., Hayba, D. O., Goss, J. A., and Brown, Z. A. (1988) Ammonium in alunites. *American Mineralogist*, 73, 145-152.
- Barker, D. S. (1964) Ammonium in alkalifeldspars. *American Mineralogist*, 49, 851-858.
- Barton, M. D., and Young, S. (2002) Non-pegmatitic deposits of beryllium: Mineralogy, geology, phase equilibria and origin. *Reviews in Mineralogy and Geochemistry*, 50, 591-691.
- Bartoshinskiy, Z. V., Matkovskiy, O. I., and Srebrodolskiy, B. I. (1969) Accessory beryl from chamber pegmatites of Ukraine. *Mineralogicheskiy Sbornik*, 23, N4, 382-397 (in Russian).

- Bobos, I., and Eberl, D. D. (2013) Thickness distributions and evolution of growth mechanisms of NH₄-illite from the fossil hydrothermal system of Harghita Băi, eastern Carpathians, Romania. *Clays and Clay Minerals*, 61, 375-391.
- Busigny, V., and Bebout, G. E. (2013) Nitrogen in the silicate earth: speciation and isotopic behavior during mineral-fluid interactions. *Elements*, 9, 353-358.
- Černý, P. (1968) Berylliumwandlungen in Pegmatiten. *Neues Jahrbuch Mineralogie, Abhandlungen*, 108, 166-180.
- Černý, P. (2002) Mineralogy of beryllium in granitic pegmatites. *Reviews in Mineralogy and Geochemistry*, 50, 405-444.
- Černý, P., and Ercit, T. S. (2005) The classification of granitic pegmatites revisited. *Canadian Mineralogist*, 43, 2005-2026.
- Černý, P., London, D., and Novak, M. (2012) Granitic pegmatites as reflections of their sources. *Elements*, 8, 289-294.
- Cook, N. J., Ciobanu, C. L., O'Rielly, D., Wilson, R., Das, K., and Wade, B. (2013) Mineral chemistry of rare earth elements (REE) mineralization, Browns Ranges, Western Australia. *Lithos*, 172-173, 192-213.
- Ginzburg, A. I., Bulgakov, V. S., Vasilishin, I. S., Luk'yanova, V. T., Solntseva, L. S., Urmenova, A. M., and Uspenskaya, V. A. (1987) Kerite from pegmatites of Volyn. *Doklady Akademii Nauk SSSR*, 292, 188-191 (in Russian).
- Gigashvili, G. M., and Kalyuzhnyi, V. A. (1969) Black opals from Volynian pegmatites, containing organic matter. *Doklady Akademii Nauk SSSR*, 186, 1154-1157 (in Russian).
- Gorlenko, V. M., Zhmur, S. I., Duda, V. I., Osipov, G. A., Suzina, N. E., and Dmitriev, V. V., (2000) Fine structure of fossilized bacteria in Volyn kerite. *Origin of Life and Evolution of the Biosphere*, 30, 567-577.
- Grew, E. S., and Hazen, R. M. (2014) Beryllium mineral evolution. *American Mineralogist*,

99, 999-1021.

- Gysi, A., and William-Jones, A. E. (2013) Hydrothermal mobilization of pegmatite-hosted REE and Zr at Strange Lake, Canada: A reaction path model. *Geochimica Cosmochimica Acta*, 122, 324-352.
- Hall, A. (1988) Crustal contamination of minette magmas: evidence from their ammonium contents. *Neues Jahrbuch Mineralogie Monatshefte*, 1988, 137-143.
- Harlov, D. E., Andrut, M., and Pöter, B. (2001a) Characterisation of buddingtonite $(\text{NH}_4)[\text{AlSi}_3\text{O}_8]$ and ND_4 -buddingtonite $(\text{ND}_4)[\text{AlSi}_3\text{O}_8]$ using IR spectroscopy and Rietveld refinement of XRD spectra. *Physics and Chemistry of Minerals*, 28, 188-198.
- Harlov, D. E., Andrut, M., and Pöter, B. (2001b) Characterisation of tobelite $(\text{NH}_4)\text{Al}_2(\text{AlSi}_3\text{O}_{10}(\text{OH})_2)$ and ND_4 -tobelite $(\text{ND}_4)_2\text{Al}_2(\text{AlSi}_3\text{O}_{10}(\text{OD})_2)$ using IR spectroscopy and Rietveld refinement of XRD spectra. *Physics and Chemistry of Minerals*, 28, 268-276.
- Hazen, B. M., Papineau, D., Bleeker, W., Downs, R. T., Ferry, J. M., McCoy, T. J., Sverjensky, D. A., and Yang, H. (2008) Mineral evolution. *American Mineralogist*, 93, 1693-1720.
- Hemley, J. J., and Jones, W. R. (1964) Chemical aspects of hydrothermal alteration with emphasis on hydrogen metasomatism. *Economic Geology*, 59, 538-569.
- Holloway, J. M., and Dahlgren, R. A. (2002) Nitrogen in rock: Occurrences and biogeochemical implications. *Global Geochemical Cycles*, 16, doi: 10.1029/2002GB001862.
- Ivanovich P. V., and Alekseevich, D. S. (2007) Mineralogy of the Volynian chamber pegmatites. EKOST Association, Mineralogical Almanac, 12, 128 p, Moscow.
- Kalyuzhnyi. V. A., and Prytula, Z. S. (1967) Study of structural, thermodynamic and geochemical conditions of camera pegmatites' deep fluids activities. In: Study of

- geochemistry of deep fluids using carbonaceous relics and paragenetic minerals. *Geologiya i Geokhimiya Goryuchih Poleznyh Iskopaemyh*, 9, 33-54 (in Russian).
- Kalyuzhnyi, V.A., Voznyak, D.K., and Gigashvili, G.M. (1971) Mineral forming fluids and mineral paragenesis of chamber pegmatites of Ukraine. Kyiv: Naukova Dumka, 216 p (in Ukrainian).
- Kalyuzhnyi, V.A. (1982) The basis of teaching about mineral forming fluids. Kyiv: Naukova Dumka, 239 p (in Ukrainian).
- Koshil, I. M., Vasilishin, I. S., Pavlishin, V. I., and Panchenko, V. I. (1991) Wolodarsk-Wolynskii Geologischer Aufbau und Mineralogie der Pegmatite in Wolynien, Ukraine. *Lapis*, 10, 28-41.
- Krohn, M. D., Kendall, C., Evans, J. R., and Fries, T. L. (1993) Relations of ammonium minerals at several hydrothermal systems in the western U.S. *Journal of Volcanology and Geothermal Research*, 56, 401-413.
- Laricheva, O. O., Akhmanova, M. V., and Byvkhov, A. M. (1993) Low-temperature hydrothermal synthesis of buddingtonite. *Geochemistry International*, 30, 126-132.
- Lazarenko, E. K., Matkovskii, O. I., Pavlishin, V. I., and Sorokin, Ju. G. (1967) New data on morphology and mineralogy of Volyn pegmatites. *Doklady AN SSSR*, 176, N1 (in Russian).
- Lazarenko, E. K., Pavlishin, V. I., Latysh, V. T., and Sorokin, Ju. G. (1973) Mineralogy and genesis of the chamber pegmatites of Volyn. Lvov, Vysshaja shkola, 360 p (in Russian).
- Levin, L.A., and Michener, R. (2002) Isotopic evidence of chemosynthesis-based nutrition of macrobenthos: The lightness of being at Pacific methane seeps. *Limnology and Oceanography* 47, 1336-1345.
- London, D. (2008) Pegmatites. *The Canadian Mineralogist, Special Publications* 10, p 347; Québec, Canada.

- London, D. (2013) Crystal-filled cavities in granitic pegmatites. *Rocks and Minerals*, 88, 527-534.
- Lu'kyanova, V. T., Lobzova, R. V., and Popov, V. T. (1992) Filaceous kerite in pegmatites of Volyn. *Izvestiya Ross. Akademii Nauk Ser. Geologicheskaya*, 5, 102-118 (in Russian).
- Lyckberg, P. (2005) Gem beryl from Russia and Ukraine. In: *Beryl and its color Varieties*. Lapis Intl., L.L.C., East Hampton, CT, USA, 49-57.
- Lyckberg, P., Chornousenko, V., and Wilson, W.E. (2009) Famous mineral localities: Volodarsk-Volynski, Zhitomir Oblast, Ukraine. *The Mineralogical Record*, 40, 473-506.
- Mariotti, A. (1983) Atmospheric nitrogen is a reliable standard for natural ^{15}N abundance measurements. *Nature*, 303, 685-687.
- Mäder, U. K., Ramseyer, K., Daniels, E. J., and Althaus, E. (1996) Gibbs free energy of buddingtonite ($\text{NH}_4\text{AlSi}_3\text{O}_8$) extrapolated from experiments and comparison to natural occurrences and polyhedral estimation. *European Journal of Mineralogy*, 8, 755-766.
- Nieto, F. (2005) Characterization of coexisting NH_4 - and K-micas in very low-grade metapelites. *American Mineralogist*, 87, 205-216.
- Orlov, N.A. and Uspenskii, V.A., (1936) *Mineralogy of caustobioliths*, Moscow: Akademiya Nauk SSSR (in Russian; not seen, extracted from Zhmur 2003).
- Peterson, B.J., and Fry, B. (1987) Stable isotopes in ecosystem studies. *Annual Reviews of Ecological Systems*, 18, 293–320.
- Pöter, B., Gottschalk, M., and Heinrich, W. (2007) Crystal-chemistry of synthetic K-feldspar-buddingtonite and muscovite-tobelite solid solutions. *American Mineralogist*, 92, 151-165.
- Proshko, V. Ya., Bagmut, N. N., Vasilishin, I. S., and Panchenko, V.I. (1987) Ammonium feldspars from Volyn pegmatites and their radiospectroscopic properties. *Mineralogical Journal (Ukraine)*, 9, 67-71 (in Russian).
- Ramseyer, K., Diamond, L. W., and Boles, J. R. (1993) Authigenic K- NH_4 -feldspar in

- sandstones: A fingerprint of the diagenesis of organic matter. *Journal of Sedimentary Petrology*, 63, 1092-1099.
- Rau, G. H., Teyssie, J. L., Tassoulzadegan, R., and Rowler, S. W. (1990) $^{13}\text{C}/^{12}\text{C}$ and, $^{15}\text{N}/^{14}\text{N}$ variations among size-fractionated marine particles: implication for their origin and trophic relationships. *Marine Ecology Progress Series*, 59, 33–38.
- Rau, G. H., Riebesell, U., and Wolf-Gladrow, D. A. (1996) A model of photosynthetic ^{13}C fractionation by marine phytoplankton based on diffusive molecular CO_2 uptake. *Marine Ecology Progress Series*, 133, 275–285.
- Schilling, J., Bingen, B., Øyvind, S., Wenzel, T., Markl, G. (2015) Formation and evolution of the Høgtuva beryllium deposit, Norway. *Contributions to Mineralogy and Petrology* 170:30 DOI 10.1007/s00410-015-1179-7.
- Sherwood Lollar, B., Frape, S. K., Fritz, P., Macko, S. A., Welhan, J. A., Blomquist, R., and Lahermo, P. W. (1993)
- Simmons, W. B. (2014) Gem-bearing pegmatites. In: *Geology of gem deposits*. Mineralogical Association of Canada Short Course Series (L. E. Groat, ed.), 44, 257-304.
- Struck, U. (2012) On the use of stable nitrogen isotopes in present an past anoxic environments. In: Altenbach, A. V., Bernard, J. M. and Seckbach, J. (eds.) *Anoxia, evidence for eukaryote survival and paleontological strategies*. Book series: Cellular origin, life in extreme habitats and astrobiology, 21, 497-513, Springer, Berlin.

- Svensen, H., Aarnes, I., Podlachikov, Y. Y., Jetttestuen, E., Harstadt, C. H., and Planke, S. (2010) Sandstone dikes in dolerite sills: Evidence for high-pressure gradients and sediment mobilization during solidification in magmatic sheet intrusions in sedimentary basins. *Geosphere*, 6, 211-224.
- Verkhoglyad, V.M. (1995) Age stages of magmatism of Korosten pluton. *Geochimiya i Rudoobrazovanie*, 21, 34-47 (in Russian).
- Voznyak, D.K., Khomenko, V. M., Franz, G., and Wiedenbeck, M. (2012) Physic-chemical conditions of the late stage of Volyn pegmatite evolution: Fluid inclusions in beryl studied by thermobarometry and IR-spectroscopy methods. *Mineralogical Journal (Ukraine)*, 34, 26-38, ISSN 0204-3548 (in Ukrainian).
- Wintsch, R. P. (1975) Solid-fluid equilibria in the system $KAlSi_3O_8$ - $NaAlSi_3O_8$ - Al_2SiO_5 - SiO_2 - H_2O - HCl . *Journal of Petrology*, 16, 57-79.
- Wirth, R. (2004) Focused Ion Beam (FIB): a novel technology for advanced application of micro-and nanoanalysis in geosciences and applied mineralogy. *European Journal Mineralogy*, 16, 863–876.
- Wirth, R. (2009) Focused ion beam (FIB) combined with SEM and TEM: Advanced analytical tools for studies of chemical composition, microstructure and crystal structure in geomaterials on a nanometre scale. *Chemical Geology*, 261, 217-229.
- Zhmur, S. I. (2003) Origin of Cambrian fibrous kersite of the Volyn region. *Lithology and Mineral Resources*, 38, 55-73.

Figure captions

Figure 1. (a) Cut surface of handspecimen of breccia with the pseudomorph after beryl (outlined). The matrix consists of albite (variety cleveandite), dark quartz (variety morion),

cemented by opal and chalcedony. (b) Thin section blocks of the pseudomorph, showing a core-rim structure with a rim of opal + bertrandite (bert), a broad zone of buddingtonite (bud) + muscovite (musc), with an aggregate of organic matter (C org) and a core of very fine-grained muscovite with Fe-staining (musc + Fe).

Figure 2. BSE images of buddingtonite from pseudomorph. (a) Euhedral bertrandite (bert) in a network of F-muscovite (musc) and with albite (alb). Rectangles indicate position of enlarged parts in c, e and f, resp. (b) Muscovite partly replaced parallel to (001) and in a kink band by tobellite-rich muscovite (tob). (c) Detail of (a), fibrous buddingtonite (bud) between F-muscovite and opal. Rectangle indicates position of (d), enlarged part of fibrous buddingtonite with opal between F-muscovite. Muscovite extending into buddingtonite (tob) shows a tobellite component (lower BSE-contrast due to NH_4 -replacement for K). Small white dots in buddingtonite are due to beam damage with a focused beam, large circular areas traces of slight damage during analysis. (e) Euhedral buddingtonite crystals in opal with typical sector zoning and a relict K-feldspar (Kfsp) core. White rims on K-feldspar are enriched in Fe. (f) Buddingtonite in opal and muscovite. The central part shows a homogeneous low-contrast area with euhedral outline and sector zoning, the outer rim is fibrous with a change in low-high contrast areas. White areas with numbers 1-3 are areas of beam damage during analysis. (g) Detail of (a), albite, partly replaced by buddingtonite. (h) Detail of (a), a LREE-mineral with associated porosity (black) in albite.

Figure 3a,b. Chemical variation of buddingtonite, EMPA. (a) $(\text{NH}_4)_2\text{O}$ varies independently of sum of $\text{K}_2\text{O} + \text{Na}_2\text{O}$, indicating the presence of H_3O^+ . (b) Na_2O vs. K_2O shows random scattering of the data. Dots mark analyses with N-determination.

Figure 4. X-ray mapping and BSE image of aggregate of buddingtonite crystals (bud) with characteristic sector zoning. The core zone is depleted in both, K and Na. The first inner zone show two sectors enriched in K and two poor in K, but no difference in Na within these sectors. The inner zone is followed by an outer zone, poor in K, and extends towards the rim in fibrous crystals, indicated by a striped pattern of K-distribution. No difference in Na-content is obvious in these zones. Si and Al content do not vary significantly. Al- and F-mapping shows the distribution of muscovite, where F-contents are highest in central parts of the crystals.

Figure 5. X-ray mapping and BSE image of buddingtonite-muscovite, together with opal. K-mapping shows significant differences in different sectors and zones, N is homogeneously distributed. Na-contents are low and show slightly heterogeneous distributions, however not as strong as K.

Figure 6. BSE and SEM images of opal (a,b) and organic matter (c-f). Opal, replacing bertrandite (bert), with botryoidal structure and a dark rim, indicating higher water content. Arrow points to buddingtonite (bud) which appears as a small euhedral crystal in the center of botryoidal opal. (b) Botryoidal opal, interstitial between buddingtonite. Bright dots near the center of the botryoidal opal are FeS_2 and BaSO_4 . (c) Overview of the aggregate of organic matter (OM), within opal and muscovite (musc); rectangle indicates position of (d), which shows the variable BSE contrast patterns, from dark = rich in C, to very bright = rich in cations and oxygen. Arrows in (d) point to voids; around the voids the BSE contrast is higher, pointing to degassing structures in the organic matter with enrichment of cations and oxygen. Cracks in the organic matter (filled with epoxy, appearing black) are partly filled with opal. (e) Overview of typical round structures in organic matter, next to opal. (f) SE-image from a

detail of round structures along a small crack, indicating that they are vesicles, interpreted as degassing structures.

Figure 7 (a-h). Chemical variation of organic matter, plotted in atom% (EDS analyses). Carbon content decreases with increasing brightness in BSE-images (cf. Fig. 6) linearly correlated with increasing O. (b) Zr increases with O, indicating capture of Zr during degassing. (c) N-content decreases with decreasing C-content, indicating loss of N during degassing. (d) P is positively correlated with F, and negatively correlated with N (not shown), indicating enrichment of P and F during degassing. (e) S behaves irregularly, areas rich in C are poor in S, areas rich in O poor in S (see text). Y and Sc (f), Th and U (g), and Y and the summ of REE (h) are all well correlated, and also positively correlated with Zr (not shown). For comparison, the average composition of kerite (asterisk), organic matter from the Volyn pegmatites (Ginzburg et al 1987; Zhmur 2003; converted into atom%) is shown in (a, c, e).

Figure 8. FTIR spectra of (a-d) buddingtonite, NH₄-rich muscovite, brown opal, and organic matter from the beryl pseudomorph, Volyn. (a) Unpolarized FTIR spectra of crystal aggregates of buddingtonite. Spectra are shifted vertically. Lower lines, labeled with ν_1 to ν_4 , are for buddingtonite with varying amounts of K-NH₄, upper line is for hydronium-bearing buddingtonite, labeled with arrows pointing to H₃O bands, demonstrating the presence of both NH₄- and H₃O- vibrations. The modes of NH₄ vibrations are marked according to the band's assignments in Table 4. (b) Unpolarized FTIR spectra of ammonia-bearing muscovite intergrowth, measured in uncovered thin section (upper, solid line), in comparison with natural NH₄-bearing muscovite from California (middle, dashed line) and pure muscovite from Polar Ural (bottom, dot-dash line). In Volyn sample vibration bands of H₂O at 3330 cm⁻¹ and organic matter at 2950-2870 cm⁻¹ are present in addition to weak NH₄ bands. (c) FTIR spectra

of brown opal measured in thin section and a thin slab of opal material on the border of buddingtonite grain. The area of C-H vibrations is shown as well as broad H₂O-dominant stretching vibrations' band ($\nu_1+\nu_3$) at ca. 3400 cm⁻¹ and weak combination band ($\nu_2+\nu_3$) at 5200 cm⁻¹. (d) FTIR spectra of dark organic matter, measured in uncovered thin section.

Figure 9. TEM results foil #4667 of boundary between opal and organic matter (OM). (a) Detail of HAADF (Z-contrast) image. Bright area at the rim of organic matter with platy habit shows high amounts of O-Zr-Si with minor Y, U, Th, Fe, and Al contents. All EDX spectra are compiled in Figs. EA 5,6. (b) Detail of HAADF image of opal with patchy contrast. Bright areas show Ba, S, Fe, C, and minor K and Cl in the EDX spectra. (c) High-resolution image of bright area in opal, showing the dominantly amorphous character and ~5 nm wide areas with lattice fringes that indicate nanocrystalline material (arrows). (d) High-resolution image of organic matter, showing patchy distribution of ~5 nm wide areas with poorly developed lattice fringes.

Figure 10. TEM results foil # 4461 at the boundary of organic matter (OM) to a vesicle. (a) HAADF Z-contrast image of the FIB-foil. Organic matter is essentially amorphous, showing lattice fringes with spacing of ~0.33 nm in approximately 5 to 10 nm wide areas of nanocrystalline material, which is enriched in O-Si-Zr (similar as in Fig. 9d). (b) Detail of rim area of OM; HAADF image, upper part in (a). Rectangles indicate areas of EDX analyses with higher O-Si-Zr (-Th-U-Ca)-contents in the bright areas (spectra in Fig. EA 7), line indicates position of profile in (c), EDX line scan with parallel enrichment of O-Si-Zr, inversely correlated with C. (d,e) EELS element mapping of O and C of OM, confirming the irregular distribution of poorly crystalline material.

Figure 11. SEM images of kerite. a) overview, showing hair-like morphology; b) characteristic branching, c) round end of a fiber and smooth surface; rectangular dark area is artefact due to beam damage during analysis. d) Broken fiber, showing the characteristic hollow core with a width of approximately 260 x 550 nm.

Figure 12. Results of organic carbon and nitrogen stable isotope determination of kerite, opal and buddingtonite concentrate (with opal, tobelite). Fields for modern marine sediments, phytoplankton and methanogenic bacteria are summarized from Levin and Michener (2002) Peterson and Fry (1987) Rau et al. (1990, 1996) and Struck (2012).

Figure 13. Schematic *P-T* diagram, illustrating the evolution of mineral assemblages in the pseudomorph after beryl (based on Barton and Young 2002); inset shows schematic fluid-solid equilibria in the system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O-H}_2\text{O-NH}_3$ at quartz saturation and ambient conditions, based on Mäder et al. (1996), but with an enlarged field for F-muscovite instead of pure muscovite. Encircled numbers refer to reactions (see text), numbers in bold/italic to formation stages. Pegmatitic crystallization started with **1** beryl+K-feldspar; **2** in hydrothermal convections cell, bacterial life produced kerite in the chambers; **3** chamber collapse produced the breccia, in which **4** the pseudomorph formed with betrandite, euclase and F-rich muscovite; **5** fluid circulation enriched HFSE in kerite, and C-H fluids from degassing kerite were incorporated into cracks in beryl; fluid composition was enriched in NH_4 , which drove the equilibrium of muscovite-Kfeldspar **6** towards the muscovite-tobelite equilibrium (reaction 8 in inset), and with further increase in NH_4 concentration reached reactions 10 and 6. Opal precipitated as one of the last minerals; **7** late hydrothermal alteration produced kaolinite. For further discussion see text.