

Article

Mineralogy and Geochemistry of Agates from Paleoproterozoic Volcanic Rocks of the Karelian Craton, Southeast Fennoscandia (Russia)

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Abstract: Agates of Paleoproterozoic volcanics (2100–1920 Ma) within the Onega Basin (Karelian Craton, Southeast Fennoscandia) were studied using optical and scanning electron microscopy, X-ray powder diffraction, X-ray fluorescence spectrometry XRF, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and C-O isotope analysis. Agate mineralization is widespread in the lavas gas vesicles, inter-pillow space of basalts, picrobasalts, basaltic andesites, as well as agglomerate tuffs. Agates are characterized by fine and coarse banding concentric zoning; moss, spotted, veinlet, and poor-fancy texture types were identified. Agate mineralization is represented by silicates, oxides, and hydroxides, carbonates, phosphates, sulfides, and sulfates. Among the silica minerals in agates only chalcedony, quartz and quartzine were found. The parameters of the quartz structure according to the X-ray diffraction data (well-develops reflections (212), (203), (301), large crystallite sizes (C_s 710–1050 Å) and crystallinity index (CI 7.8–10.3) give evidence of multi-stage silica minerals recrystallization due to a metamorphic (thermal) effect. The decreasing trend of trace element concentration in the banded agates from the outer zone to the core suggests a chemical purification process during crystallization. C-O isotope characteristic of agate-associated calcite reflects primary magmatic origin with the influence of hydrothermal activity and/or low-thermal meteoric fluids. Agates were formed under low PT-parameters and related to hydrothermal activity on the first stage of Svecofenian orogeny within 1780–1730 Ma. Thus, it can be believed that the temporal gap between continental flood basalts outflow and agate formation is about 190 Ma.

Keywords: agates; Paleoproterozoic volcanics; Onega Basin; SEM; X-ray diffraction; LA-ICP-MS; C-O isotopes

1. Introduction

Agates are fascinating minerals that have long attracted people's attention with the beauty and uniqueness of the pattern. Agates are found in igneous and sedimentary hosts and questions of agate genesis have been asked for over 250 years [1,2]. However, there have been few answers to key questions. In particular, the agate formation temperature in basic igneous hosts has been proposed in a range of <100 to 1000 °C [3–6]. The nature of the initial silica deposit is unproven and powdered amorphous silica as gel or powder seems the most likely source [7–9]. However, silica glass has also been featured as a possible starting material [10]. Rhythmic banding is not unique to agate but it is this visual property that characterizes the mineral and provoked much discussion [7,11,12]. The question about the temporal gap between the formation of gas vesicles in volcanic rocks and their mineral infilling is under discussion [6,13]. Currently, there is no unified and consistent theory. However new mineralogical, geochemical, and isotopic data obtained over the last 40 years have made a great contribution to our knowledge of the mineralogy and genesis of agates [5,14–25].

The present paper examines the mineralogical and geochemical properties of agates from the famous agate-bearing Paleoproterozoic volcanic complex on the Southeast Fennoscandia. This complex belongs to the Ludicovian Superhorizon (LSH, ca. 2100–1920 Ma) within the Onega Basin [26,27].

Previously, the main research interest in the LSH volcanics of the Onega Basin was focused on the study of mafic and ultramafic rocks (basalts, picobasalts), as well as volcanic clastic rocks (lava breccias, clastolavas, hyaloclastites, tephroids, and tuffites) [26,28,29]. Hydrothermal mineral systems associated with the postmagmatic processes activity are less well understood [30,31]. Agates are widespread as an infill of fissures, gas vesicles in basalts, and an infill between pillow lavas (inter-pillow lava space).

The agates were initially described by the Russian geologist V. M. Timofeev in 1912 [27]. His thin section micrographs of the agates from Ludicovian basalts of the Suisari Island in Lake Onega were the earliest agate thin sections to be found in the scientific literature. Published scientific works of information about the agates of the Onega Basin are rare [32,33].

The authors started to study Onega Basin agates in 2013. The present investigation aims to highlight both the mineralogical and geochemical features of Onega agates with a reconstruction of the possible conditions of their formation. About 70 specimens of Onega agates and parent volcanic rocks were collected from outcrops for laboratory investigation. Two specimens of agate were donated to the authors by O.B. Lavrov. The collection illustrates the agate varieties available from the Ludicovian basalts within the Onega Basin. The Onega Basin experienced the Svecofennian Orogeny (~1860 Ma) [30] and the agates could provide novel information on the evolution of Paleoproterozoic magmatic complexes in the Karelian Craton.

2. Geological Setting

The Intercraton Onega Basin is located in the southeastern part of the Archaean Karelian Craton, Fennoscandian Shield within an area of more than 35,000 km² (Figure 1) [26,34]. Meso-Neoarchaean granite-gneiss and greenstone complexes are dominated within the Craton [35]. These complexes are overlapped with angular unconformity by the Paleoproterozoic volcano-sedimentary sequence (2500–1700 Ma) within the Onega Basin [29].

The LSH within the Onega Basin was initially identified in 1982 by Sokolov and Galdobina [36]. The LSH section is represented by an association of terrigenous, siliceous, carbonate rocks with high organic carbon content (up to 20%), as well as by mafic and ultramafic volcanic complexes related to continental flood basalts. These overlap the volcano-sedimentary succession of the Yatulian Horizon (2300–2100 Ma) [26].

At present, LSH is subdivided into two formations [26,28,29,34]:

- (1) Zaonega Formation (ZF) with a total thickness of about 1.8 km that is comprised of basalts, basaltic andesites with lava flows (8–35 m) interbedded with shungite-bearing basaltic tuffs, clay-carbonate rocks, dolomites. The formation was dated with 1980–2050 Ma [26,37,38];
- (2) Suisari Formation (SF) has a total thickness up to 1 km and is represented by mafic lava flows interbedded with tuffs, hyaloclastites, tuffites. The subvolcanic complex comprises dolerite and peridotite dykes and sills. A depositional age of the SF by the Sm/Nd isotopic data is 1975 ± 24 Ma [28].

Flows of pillow lava with a terrigenous component is widespread in the inter-pillow space, producing evidence of shallow-water depths conditions during the volcanics formation.

The presence of organic carbon in the inter-pillow lava space is noted. The lavas contain numerous amygdaloids and gas vesicles in top flows. The pillow cores indicate a high initial gas saturation of melt. A feature of the SF picobasalts is a specific variolitic structures in massive and pillow lavas [39–41].

The volcano-sedimentary sequence of the LSH was deformed into a system of roughly parallel, northwest-southeast trending folds that overall form a synclinorium [26]. Metamorphism and hydrothermal activity in the Onega Basin are associated with Svecofennian orogeny 1890–1790 Ma [26,30]. The initiation of shear zones (fluid channels controlling ore formation) has occurred during a longer

time-lag (>200 Ma). According to the Rb/Sr study of the Onega Basin metasomatites, three peaks of hydrothermal activity have been established (1780–1700, 1600, and 1500 Ma) [31].

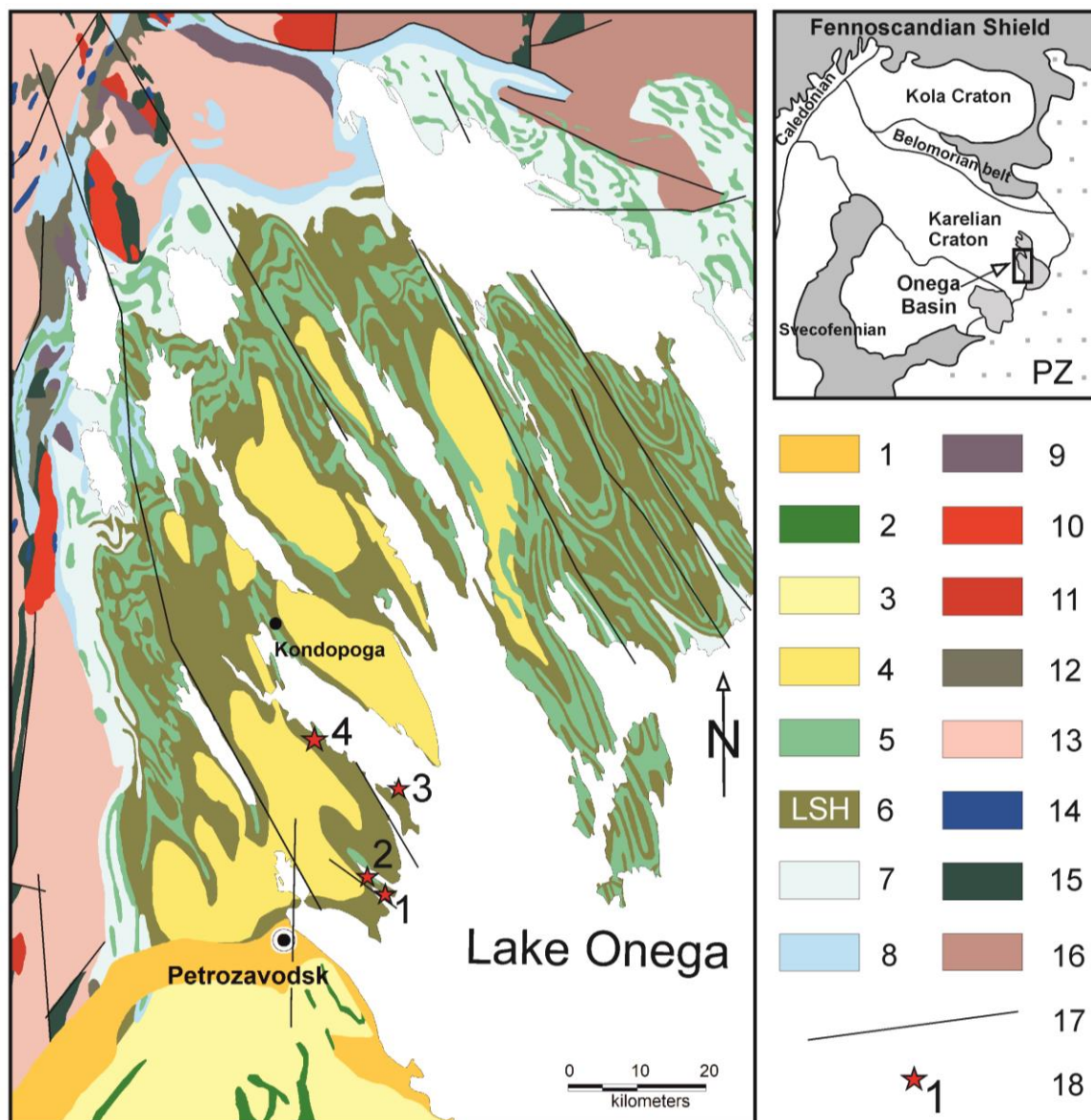


Figure 1. Simplified geological map of the northwestern part of the Onega Basin (based on [34]) and position of studied areas. Legend. Neoproterozoic: 1—ca. 635–542 Ma sandstones, siltstones, argillites, conglomerates; Paleoproterozoic: 2—ca. 1770–1750 Ma gabbro-dolerites; 3—ca. 1800–1650 Ma red quartzitic sandstones, quartzites, conglomerates; 4—ca. 1920–1800 Ma argillites, siltstones, sandstones, conglomerates; 5—ca. 1975–1956 Ma gabbroids; 6—LSH (Ludicovian Superhorizon), ca. 2100–1920 Ma picrites, picrobasalts, tuffs, tuffites, high-carbon rocks (shungites), argillites, siltstones, dolomites, basalts, basaltic andesites; 7—ca. 2300–2100 Ma dolomites, gypsum, salts, anhydrite-magnesite rocks, siltstones, basalts, dolerites; 8—ca. 2300–2100 Ma sandstones, arkoses, conglomerates, basalts; 9—ca. 2500–2300 Ma gritstones, basaltic andesites, conglomerates; Archean: 10—ca. 2740–2650 Ma granites; 11—ca. 2884–2850 Ma granites, plagiogranites; 12—ca. 2900–2800 Ma greenstone belt associations (felsic volcanics and sediments); 13—ca. 2985 Ma tonalities, granodiorites; 14—ca. 2985 Ma peridotites, pyroxenites, gabbro, diorites; 15—ca. 2940–2900 Ma komatiites, basalts, dacites; 16—ca. 3240–3220 Ma tonalities, trondhjemites; 17—faults; 18—sampling occurrences (1—Pinguba, 2—Yalguba Ridge, 3—Suisari Island, 4—Tulguba).

Dolerite sills intruded at the outset of the Svecofenian orogeny led to the initiation of the hydrothermal activity process within the LSH volcanics. For instance, the age of the Ropruchey Sill is estimated at 1770 ± 12 Ma using the U/Pb zircon method [42]. The Shunga gabbrodolerite was dated at 1746 ± 15 Ma, which is in agreement with the age of the hydrothermal zircons from the Onega Basin ore occurrences [43].

It is assumed, that the agates formation period in the Onega Basin is connected with post-magmatic hydrothermal activity initiated by the intrusion of gabbro-dolerite sills (1780–1730 Ma): 190 Ma later than continental flood basalts outflow stage [43]. The LSH volcanics within the Onega Basin were metamorphosed under the prehnite-pumpellyite facies conditions (T: 290–320 °C, P: 1–3 kbar) [32].

3. Agate Occurrences

Agates and parent volcanic rocks were sampled at the following occurrences (Figure 1):

1. Pinguba. Shore outcrops of the northern part of the Pinguba bay of Lake Onega. Here, pillow porphyric basalt lava flows attributed to the upper part of the SF were examined. The lava outcrops cover an area along the water's edge for 1 km at a width of 5–10 m. The pillows have rounded, elongated shapes, shell-like cleavage, and thin chill zones (up to 1 cm), their size ranges from 0.3×0.6 to 1.5×2.5 m. There are many gas vesicles (1–2 mm in size) filled by chlorite-carbonate-quartz in lavas. Agates form prominent nodules between pillows (Figure 2a) or fill gas cavities in pillow cores. Most agates are cone-shaped; lens-shaped bodies and veinlets are less frequent. The size of such agates ranges from 3–5 to 50 cm across. Agates also occur as rounded fragments on the shore. The frequency of agates occurrence is 3–5 per 10 m² of the lava flow surface.
2. Yalguba Ridge. The upper part of the SF section reaches 60 m in depth and is formed by massive and pillow Pl-Cpx porphyric picrobasalts. The section is well exposed in the Yalguba area of Lake Onega. The pillowed and massive lava flow interbed with tuffs with thickness up to 1–3 m. The pillows have compressed shapes, thin chill zones (up to 1 cm), their size ranges from 0.3×0.4 to 4×5 m. Some pillows have a well-developed sagging tail. Agates are present in the inter-pillow space of lava flows as large (up to 50–60 cm) segregations and veinlets varying in shape (Figure 2b). In some cases, agate mineralization is exposed in the central gas vesicles in the pillow cores. On the lava flow surface, the frequency of agates occurrence is 5–7 per 10 m².
3. Suisari Island. In the northeastern part of Lake Onega Island, numerous agates are observed in the Pl-porphyric picrobasalt lava flows. The stratigraphic attribution of volcanic rocks to ZF or SF on Suisari Island is unclear. The pillows are lightly deformed and have chill zones, their diameter ranges from 0.5 to 4 m. Agates fill cavities in the inter-pillow space of basalt flows, as well as in pillow cores (Figure 2e). These are found on the shore and underwater outcrops and can have a size of up to 50 cm. The frequency of agate occurrence is 4–6 per 10 m² of the lava flow surface. After storms, agates join the beach pebbles.
4. Tulguba. The studied area was by Lake Onega within an open-pit mine. The middle part of the SF section of the picrobasalt lava shows flows with thickness about 100–120 m. The lavas contain small (from 5 to 30 cm) and large (up to 2.5 m) pillows with chill zones (from 0.5 to 2 cm). Individual pillows have amygdalae in the top flow (Figure 2f). Some pillows have flow banding—pahoehoe. The inter-pillow space is composed of a mixture of agglutinate tuff and terrigenous material. Lenses of agglomerate tuffs (with single large volcanic bombs) overlie on the lava top flows. Most of the agates are composed of quartz and calcite. Agates are present in the inter-pillow space, in the pillow cores and tuffs as large (up to 40 cm) segregations. The frequency of agates occurrence is up to 12 per 10 m² of the lava flow surface.



Figure 2. Field outcrop photographs illustrating the occurrences of main agate mineralization types in the Paleoproterozoic volcanics of the Onega Basin LSH. (a) Agate in the inter-pillow lava space (Pinguba); (b) agates in gas vesicle and inter-pillow picrobasalt lava space (Yalguba Ridge); (c) carbonate veins in picrobasalt lavas (Yalguba Ridge); (d) scalenohedral calcite crystals from basalt fissure; (e) single agate amygdule in the pillow lava (Suisari Island); (f) agates in the inter-pillow lava space (Tulguba); (g) amygdales in the picrobasalt top lava flow (Yalguba Ridge); (h) elongated pencil-like mineralized channels in picrobasalt (cross-sectional view from (g)); (i) quartz-prehnite-carbonate (Qz-Prh-Cal) vein in basalt fissure (Yalguba Ridge). Red arrows point to the agates in gas vesicles, yellow arrows – in inter-pillow lava space.

Thus, agate mineralization in the pillow lavas of the LSH within the Onega Basin has a wide regional distribution and signifies the upper part of the volcano-sedimentary sequence.

4. Methods

Powder X-ray diffraction, XRF and LA-ICP-MS analysis, petrographical and electron microscope studies were carried out at the Institute of Geology, Karelian Research Centre, RAS (IG KRC RAS, Petrozavodsk, Russia). Thin sections were examined using Polam-211 optical microscope. The VEGA II LSH (Tescan, Brno, Czech Republic) scanning electron microscope (SEM) was equipped with energy-dispersive microanalyzer INCA Energy 350. Thin sections of agates were coated with a thin carbon layer for SEM and microprobe investigations and were examined at (W cathode, 20 kV accelerating voltage, 20 mA beam current, 2 μ m beam diameter, counting time of 90 s).

Powder XRD used a Thermo Scientific ARL X'TRA diffractometer (CuK α -radiation, voltage 40 kV, current 30 mA, analyst I.S. Inina), Thermo Fisher Scientific, Ecublens, Switzerland. All samples were scanned for review in the 2–156° 2 θ range at a scanning step of 0.6° 2 θ /min. Diffractograms in the 66–69° and 25–28° 2 θ ranges were recorded at a scanning step of 0.2° 2 θ /min for more precision measurements of parameters of diffraction reflections. X-ray phase and structural analyses were carried out using by program pack Win XRD, ICCD (DDWiew2008). Agate samples were hand ground to obtained grain sizes <50 μ m.

The chemical composition of the basalts host rocks was determined by XRF analyses. For XRF measurements, the powdered sample was mixed and homogenized with Li-tetraborate and analyzed using an ARL ADVANT'X-2331 spectrometer in the IG KSC RAS.

Trace and rare-earth elements in agates were identified by the LA-ICP-MS method on an X-SERIES-2 Thermo scientific quadrupole mass-spectrometer (Thermo Fisher Scientific, Bremen, Germany) with an UP-266 Macro Laser Ablation attachment (New Wave Research) at the IG KSC RAS following the method [44]. A section was cut perpendicular to the agate banding for analysis.

The Nd:Yag laser operates with a wavelength of 266 nm and energy output of 0.133 mJ (scan speed 70 μ m/sec and impulse frequency 10 Hz). Measurements were made along with the profile as a series of three laser shots for each analyzed point. During ablation craters with a size of 100–150 $\times$ 50 μ m and depth up to 70 μ m to are formed (Figure 3). Later, crater morphology was controlled using a SEM VEGA II LSH. Crater relief mapping was performed by 3D laser scanning microscope VK-9710 (Keyence, Osaka, Japan) equipped with a surface analysis module. Under laser sampling splashing of matter and formation of high, wide (or excessively deep) crater cones were prevented. The following isotopes were measured: ^7Li , ^9Be , ^{24}Mg , ^{39}K , ^{45}Sc , ^{47}Ti , ^{51}V , ^{52}Cr , ^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{65}Cu , ^{66}Zn , ^{69}Ga , ^{72}Ge , ^{75}As , ^{85}Rb , ^{88}Sr , ^{89}Y , ^{90}Zr , ^{93}Nb , ^{95}Mo , ^{107}Ag , ^{115}In , ^{118}Sn , ^{121}Sb , ^{138}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{172}Yb , ^{175}Lu , ^{178}Hf , ^{181}Ta , ^{182}W , ^{208}Pb , ^{232}Th , ^{238}U . All measurements were carried out with identical parameters. Standard NIST 612 was used for calibration procedures. Calibration procedures were made at the beginning and the end of the measuring cycle and after analyzing five spots. The measured trace element concentration values are characterized following parameters of relative standard deviation (RSD): for transition metals (Co, Mn, Cr, V) <15%, for LIL (Ba, Sr, Rb) <12%, for HFS (U, Th, Y) <15%, for REE (La, Ce, Eu) <20%, for FME: Li <8%, Be <22%, As <20%. These values are obtained from the results of 50 measurements of the standard and are shown in Table S1.

Isotope studies were performed at the Centre for Collective Usage «Geoscience», Institute of Geology, Komi Scientific Center, Uralian Branch, RAS (IG Komi SC UB RAS, Syktyvkar, Russia). The decomposition of calcite in phosphoric acid and the C-O isotopic composition measurement by flow mass spectrometry (CF-IRMS) were carried out on the Thermo Fisher Scientific analytical complex, which includes a Gas Bench II sample preparation and injection system connected to a mass spectrometer DELTA V Advantage. The $\delta^{13}\text{C}$ values are given in per mille relative to the PDB standard, $\delta^{18}\text{O}$ —the SMOW standard. The international standards NBS 18 and NBS 19 were used for calibration. The analytical precision for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ was ± 0.15 ‰ (1 σ).

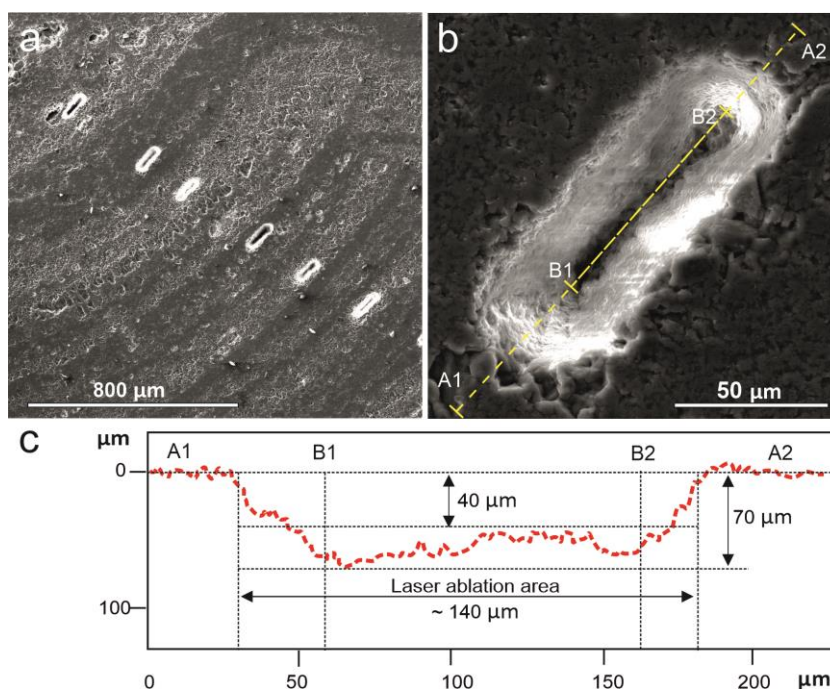


Figure 3. Surface topography of Onega agate samples and laser ablation (LA) crater character: (a) BSE image of laser sampling points in banding agate (#SvE-A1, Pinguba); (b) BSE image of the typical crater produced with 3 successive laser shots; (c) relief profile of ablation crater.

5. Results and Discussion

5.1. Host Rock Characteristic

The examined volcanics are fine-grained, greenish-gray to dark grey. Clinopyroxene (augite), albitized and saussuritized plagioclase (oligoclase-andesine), magnetite are the major rock-forming minerals of LSH volcanics. A secondary assemblage is presented by actinolite, chlorite, epidote, quartz, calcite, sericite, stilpnomelane, biotite. Ilmenite, apatite, titanite, and sulfides are accessory minerals. The primary glassy matrix of lava with a spilitic structure is replaced by a chlorite-actinolite. Plagioclase and pyroxene microliths are replaced by chlorite, actinolite, and calcite-epidotic aggregates. The obtained data on composition and texture of clinopyroxene phenocrysts together with the crystal size distribution analysis suggests that crystallization of the massive lavas mainly involves fractionation in a closed magmatic system, whereas the crystallization of the variolitic lavas is determined by processes in an open magmatic system. The study of pyroxene phenocrysts zoning from SF picrobasalts (Yalguba Ridge) has shown that the evolution of magmatic systems involved complicated processes such as fractional crystallization, magma mixing, and crustal contamination [41]. The vesicular basalts (mandelstones) are locally observed within the flows. Gas vesicles in it are mainly filled with macro crystalline quartz, chalcedony, or calcite. Inside individual pillows, elongated pencil-like mineralized channels are oriented perpendicular to the boundaries (Figure 2h) are observed forming small rounded amygdals on the surface (Figure 2g).

Using the SiO_2 and $\text{Na}_2\text{O} + \text{K}_2\text{O}$ content, volcanic rocks relate to picrite, basalt, basaltic andesite group of normal alkalinity and potassic series (Table 1).

Table 1. Chemical composition of agate-bearing volcanics from the LSH, Onega Basin, wt%.

Sample	SiO ₂	Al ₂ O ₃	FeO _{tot}	Na ₂ O	CaO	K ₂ O	MgO	MnO	TiO ₂	P ₂ O ₅	S	LOI	Σ
Pinguba													
BP-1 *	57.73	12.32	9.05	3.97	3.33	0.39	7.34	0.10	1.55	0.15	0.08	3.87	99.88
BP-2 *	53.87	13.69	9.04	3.94	3.82	0.80	7.96	0.10	1.49	0.15	0.07	5.10	100.03
BP-3 *	49.88	15.01	11.22	4.16	2.62	0.34	8.75	0.12	1.64	0.20	0.07	5.36	99.37
BP-4	50.48	13.92	9.85	4.37	4.00	0.55	9.12	0.11	1.61	0.15	0.08	5.85	100.09
BP-5	49.09	14.33	10.62	4.39	3.22	0.28	9.49	0.10	1.65	0.17	0.07	6.33	99.74
Yalguba Ridge													
BYa-1 **	39.32	9.30	7.47	0.23	16.01	3.62	7.81	0.15	1.11	0.10	0.07	14.34	99.53
BYa-2	45.91	11.49	14.47	0.13	9.58	0.56	10.82	0.21	1.50	0.14	0.08	4.96	99.85
Suisari Island													
BC-1	54.78	12.27	8.45	4.59	7.43	0.34	8.14	0.13	1.54	0.17	0.08	1.93	99.85
BC-2	61.08	13.26	8.30	3.66	2.27	1.26	4.89	0.08	1.73	0.23	0.07	2.95	99.78
Tulguba													
S20-19	47.61	13.19	12.31	1.91	8.00	1.95	9.97	0.14	2.10	0.18	0.00	2.38	99.74
S20-21	48.48	12.44	11.81	2.53	8.78	0.62	10.13	0.17	2.06	0.19	0.00	2.22	99.43

Measurements were obtained using XRF analysis. Samples: BP (1–5)—basalts, basaltic andesites; BYa (1,2)—picrobasalts; BC (1,2)—basaltic andesites; S20 (19,20)—picrobasalts. Vesicular volcanics with gas vesicles filled by (*) silica and (**) calcite.

The geochemical differentiation of the studied volcanic rocks is variable. Yalguba Ridge and Tulguba sections are represented by picrites; Pinguba and Suisare Island—by basalt, basaltic andesite. All volcanic rocks (except for #BC-2) are characterized by high MgO contents (7.34–10.8 wt%), as well as moderate FeO* (7.47–12.31 wt%) and Al₂O₃ (9.3–15.01 wt%). The Yalguba Ridge vesicular picrite variety is enriched in CaO (9.58–16.01 wt%), which is probably caused by a local hydrothermal alteration of the agate-containing volcanic rocks. This observation is confirmed by the anomalously high LOI values (up to 14.34 wt %, at conventional values 1.93–5.36 wt%).

The geochemical composition of the LSH volcanics gives evidence of the intraplate character of magmatism (continental flood basalts), that took place within the Onega Basin (ca. 2100–1920 Ma). The ZF undergo significant crustal contamination at the initial magmatic stage. Basaltic complexes were formed. This was followed by picrobasaltic complexes of the SF with more primitive compositions. These were comparable with those of modern plume-derived lavas.

5.2. Morphology, Coloration, and Anatomy of Agates

Agates mostly occur in the inter-pillow lavas space as lenses, cone-form segregations, as well as are gas vesicle infill. Agates frequently contain cavities in their geometrical center (initial void relicts). Cavities commonly are incrustated by quartz (Figure 4i,j) or calcite druses, or sinter chalcedony.

Veinlet forms of agates are widespread. They infill tectonic cracks which cut massive lavas (Figure 2c). The thickness of the cracks ranges from a few mm to 10–20 cm. Frequently cracks are composed of scalenohedral crystals of calcite as druses (Figure 2d).

The agates exhibit fine and coarse banded concentric zoning; moss, spotted, poor-fancy varieties are present (Figure 4). No horizontal banded agates were found.

Macro crystalline quartz and chalcedony are the major minerals in Pinguba and Suisari Island agates. Calcite contents prevail over the silica minerals contents in Yalguba Ridge and Tulguba agates.

Silica minerals content in agates is increasing from bottom to top along the Yalguba Ridge section. In the lower section, tectonic cracks and agate segregations are mainly filled with calcite (Figure 2c). In the medium section level where agate mineralization is most widespread, agates have an outer silica layer and massive central calcite cores. Paleocavities and cracks in rocks filled with homogeneous chalcedony are observed in the upper level section. Radial-fibrous crystals of prehnite form kidney-shaped aggregates in agates and layers in veins crosscutting picrobasaltic rocks within the Yalguba Ridge (Figure 2i).

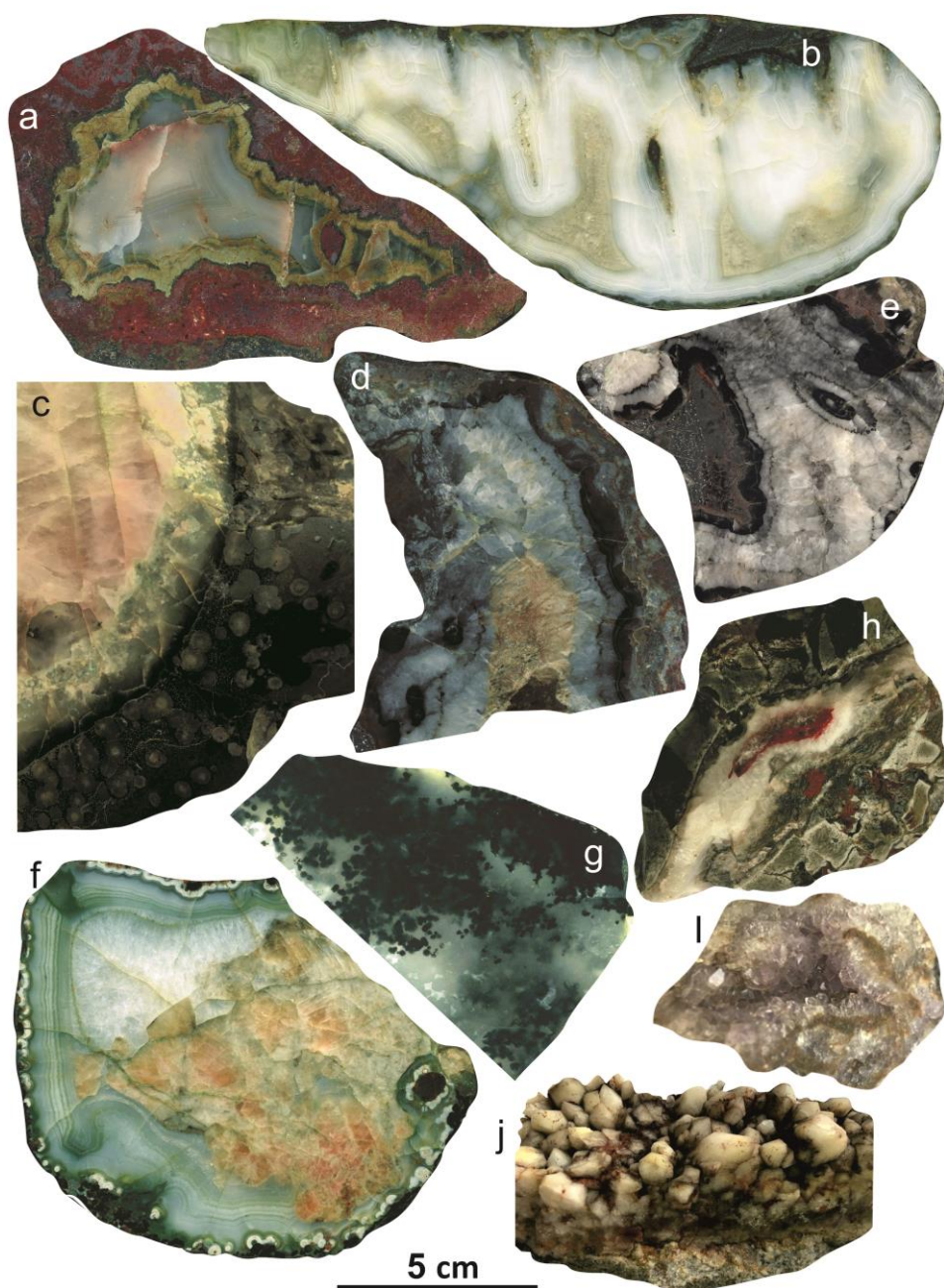


Figure 4. Macrophotographs of Onega agates: (a) concentrically zoned agate with green-colored chlorite pigment in the outer layer (Pinguba); (b) pseudostalactites of chalcedony in agate amygdale (Suisari Island); (c) chalcedony/calcite agate amygdale in variolitic picrobasalt lava (Yalguba Ridge); (d,e) quartz/chalcedony agates with black-and-white graphic ornament (Suisari Island); (f) concentric zoned agate with rosy calcite and quartz crystals in the core (Tulguba); (g) moss agate with carbon-bearing inclusions (Suisari Island); (h) agate with finely dispersed hematite in core in a lava-breccia vesicle (Tulguba); (i) amethyst geode from basalt vesicle (Tulguba); (j) druse of milky quartz crystals covered Fe-hydroxide film from a fissure in basalt (Tulguba).

Agates of the studied occurrences are characterized by peculiar color due to the composition of minerals involved in their matrix.

The Yalguba Ridge agates are either colorless or smoky with a characteristic mint-green pigment in the outer layers. This is due to mica, epidote, and chlorite inclusions in the silica matrix (Figure 4c). The Tulguba agates macroscopically like those from Yalguba Ridge (Figure 4f). Frequently, they contain

rosy and smoky-violet calcite crystals in the inner zones. The amethyst druses occur in the basalt cavities (Figure 4i).

The agates from Pinguba differ from those described above. Pinguba agates are brownish-red and pistachio-green in color. The colors are due to finely dispersed hematite and chlorite in some agate layers (Figure 4a). Separate zones with a homogenous black color or black-and-white pattern cause specific decorative effect of Suisari Island agates (Figure 4d,e).

Moss agates are represented by colorless chalcedony with dispersed carbonaceous black particles (Figure 4g). The mineral composition of Onega agates is listed in Table 2.

Table 2. Mineral composition of Onega agates.

Occurrences	Main Minerals	Accessory Minerals
Pinguba	quartz	calcite, chlorite, epidote, hematite, goethite, pyrite
Yalguba Ridge	calcite, quartz	chlorite, epidote, phengite, prehnite, apatite, titanite, leucoxene, albite, covellite, pentlandite, bornite, chalcocopyrite, pyrite, hematite
Suisari island	quartz	calcite, chlorite, epidote, K-feldspar, titanite, barite, carbonaceous phases
Tulguba	calcite, quartz	chlorite, epidote, mica, titanite, chalcocopyrite, chalcocite, bornite, hematite, magnetite

5.3. Optical Microscopy

Microscope investigation of fine-banded agates has shown that visible silica layers are present by inequigranular quartz aggregates, fine-flake, and fibrous chalcedony, quartzine (Figure 5a,b). Spherulites composed of fibrous chalcedony or quartzine occurs in the outer zones of agates (Figure 5c). The growth of multiple spheres and semispheres of fibrous chalcedony around detached host rock fragments and the smallest particles is also common. Inclusions of epidote, mica or Fe-oxides developed at the edges of quartz grains emphasize agate zoning (Figure 5d).

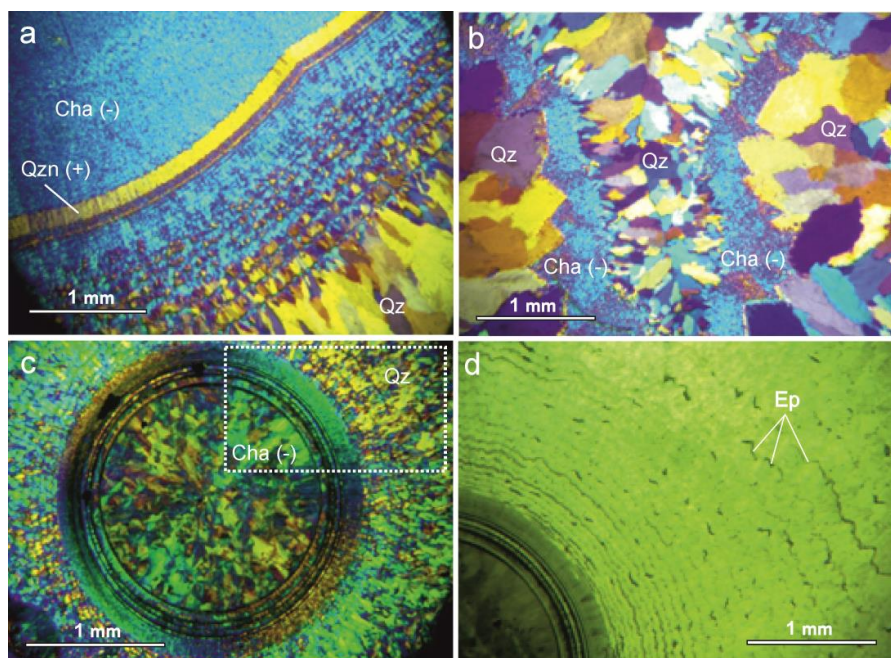


Figure 5. Microphotographs of Onega agates: (a) alternating zones of fibrous and flaked chalcedony, quartzine, and inequigranular quartz in concentric zonal agate (Pinguba); (b) internal part of the agate formed by euhedral quartz grains and flaked chalcedony (Pinguba); (c) spherulite of chalcedony in microcrystalline quartz matrix (Tulguba); (d) epidote inclusions developed at the edges of quartz grains (corresponds to dotted field in figure (c)). Cha(-): chalcedony, Qzn(+): quartzine, Qz: quartz, Ep: epidote. (a–c)—polarized light, crossed nicols, compensator plate; (d)—transmitted light, parallel nicols.

Vesicular volcanics contain mineralized vesicles filled mainly with silica. These vesicles often exhibit concentric zoning structures presented as alternating zones of quartz, chalcedony, or quartzine (Figure 6a,c,e). In the Yalguba Ridge occurrences, vesicular volcanics with calcite amygdalites are widespread (Figure 6b,d,f). The small amygdalites are usually rounded, while large ones have irregular shapes or shapes of coalesced amygdalites. In large amygdalites, several carbonate generations are distinguished: a fine-grained, fan-shaped, and usually a large single crystal in the center formed possible after quartz crystals (Figure 6f).

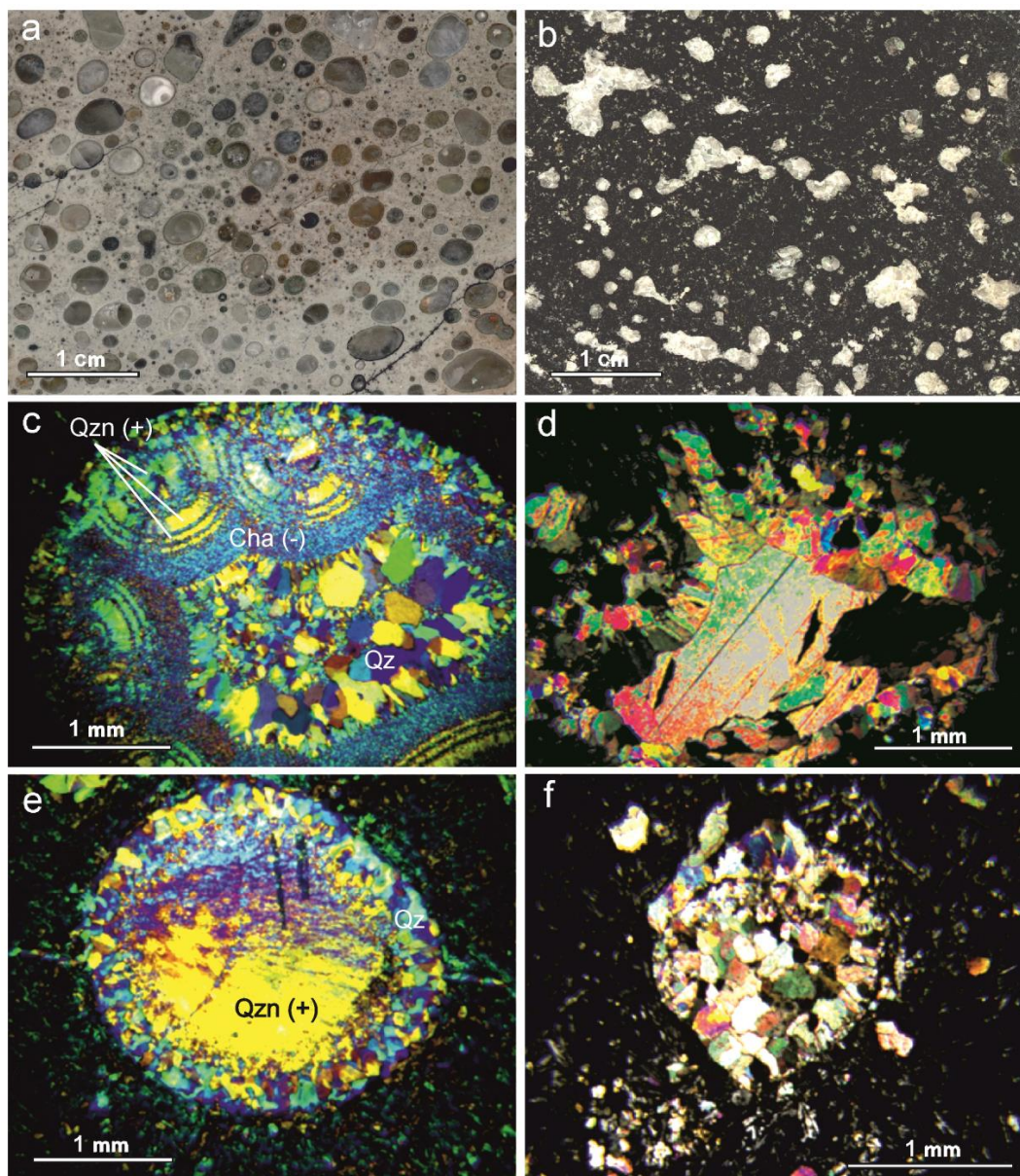


Figure 6. Vesicular basalts (mandelstones) from the LSH of the Onega Basin: Pinguba occurrence (left column, a,c,e), Yalguba Ridge occurrence (right column b,d,f). Polarized light micrographs (crossed nicols, compensator plate) of concentrically zonal amygdalites (c,e) filled by fine-flaked and fibrous chalcedony Cha(-), fibrous quartzine Qzn(+), and inequigranular quartz (Qz). Transmitted light micrographs (crossed nicols) of calcite amygdalites (d,f) filled by fine-grained, fan-shaped, and crystalline calcite.

5.4. X-Ray Powder Diffraction

The phase composition and structural parameters of minerals formed inner agate zones (silicate and carbonate) were examined by the X-ray powder diffraction method. Reflections corresponding to

α -quartz only have been identified on the X-ray diffraction patterns of the powder silicate samples. No other silica phases (opal, cristobalite, tridymite, and moganite) have been established. The absence of these phases is typical for agates from old volcanic host rocks [23]. The unit cell parameters of quartz are stable, fluctuations of a and c values do not exceed 0.0006 Å (Table 3).

Table 3. Unit cell parameters of quartz and chalcedony from Onega agates.

Sample		$a \pm \Delta a$, Å	$c \pm \Delta c$, Å	V , Å ³	C_s , Å	CI
Pinguba						
A4x1	Wall-lining chalcedony	4.9131 ± 0.0001	5.4048 ± 0.0002	112.98	1047	8.5
A9x	Quartz from agate core	4.9133 ± 0.0001	5.4051 ± 0.0001	113.00	922	9.1
A10x	Chalcedony from the outer layer of agate	4.9137 ± 0.0001	5.4054 ± 0.0001	113.02	922	8.7
A10k	Quartz from agate core	4.9137 ± 0.0001	5.4054 ± 0.0001	113.02	934	9.1
A11x	Wall-lining chalcedony	4.9137 ± 0.0001	5.4052 ± 0.0001	113.02	848	8.7
Yalguba Ridge						
QYa-1	Quartz from agate core	4.9133 ± 0.0001	5.4050 ± 0.0002	113.00	908	10.3
QYa-2	Quartz from agate core	4.9136 ± 0.0001	5.4051 ± 0.0002	113.02	817	10.2
Suisari island						
QC-1	Quartz from agate core	4.9134 ± 0.0001	5.4050 ± 0.0002	113.00	709	9.7
QC-2	Chalcedony from the outer layer of agate	4.9136 ± 0.0001	5.4050 ± 0.0002	113.01	763	7.8
Tulguba						
QT-2	Quartz from agate core	4.9137 ± 0.0001	5.4050 ± 0.0001	113.02	801	10.1
QT-3	Quartz from agate core	4.9137 ± 0.0001	5.4051 ± 0.0001	113.02	749	10.2
Ref. std.	Quartz crystal	4.9133 ± 0.0001	5.4052 ± 0.0001	113.00	935	10

The mean crystallite size (C_s) of agate samples was determined by the Scherrer equation: $C_s = K\lambda/(\beta \cos \theta)$. The shape factor K was taken as 0.9, λ is the wavelength of Cu- $K_{\alpha 1}$ radiation (1.540562 Å), β is the full width at half maximum (FWHM) of the peak (101) in $2\theta \approx 26.6^\circ$. C_s (101) is taken to be representative of the average crystallite diameter. Mean crystallite sizes in agate quartz/chalcedony range in 710–1050 Å (Table 3), with much more values (364–567 Å) obtained for agates from young igneous hosts (38–1100 Ma) of various regions [45]. The mean value ~860 Å for Onega agates corresponds to those of agates from close to age Proterozoic and older Archean metamorphosed hosts from western Australia [21]. It is assumed that high crystallite size is the result of the transformation of fibrous to granular α -quartz during late metamorphic alteration [22].

Well-developed reflections [(212), (203), (301)] corresponding to macrocrystalline quartz were fixed on the all diffractograms of the Onega agates (Figure 7). The quartz crystallinity index (CI) of agate is defined following Murata and Norman [46] from the peak resolution in the (212) reflection at $2\theta \approx 67.74^\circ$ as $CI = 10Fa/b$ (Figure 6). A quartz crystal from hydrothermal metamorphogenic veins of the Subpolar Urals (Russia) [47] served as a reference standard with $CI = 10$. All studied samples of quartz and chalcedony from Onega agates are characterized by high values of the crystallinity index >7.8 (Table 2), which is usually typical for macrocrystalline quartz [Murata and Norman, 1976]. Quartz from the agates cores is characterized by higher CI values (9.1–10.3) as compared to chalcedony from the outer rim CI (7.8–8.7). Thus, high values of crystallinity size and crystallinity index, well-developed 2 θ reflections (212), (203), (301), and the absence of moganite evidence suggest a multistage silica minerals recrystallization due to a metamorphic (thermal) effect [22].

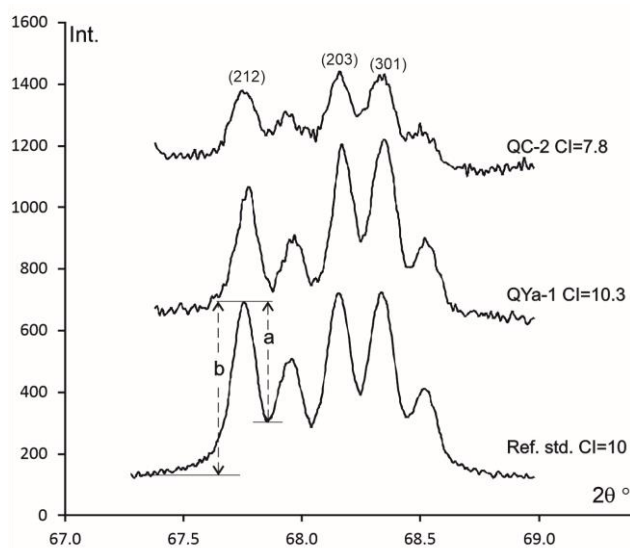


Figure 7. Diffractograms from chalcedony (QC-2, Suisari island), quartz (QYa-1, Yalguba Ridge), and quartz crystal (Ref. std., Subpolar Urals) of the $2\theta \approx 68^\circ$ quintuplet. *a* and *b* parameters are measured for Crystallinity Index (CI) calculation.

Calcite that formed in Yalguba Ridge and Tulguba agates is found as large rhombohedral crystals of varying color (colorless, smoky, and rosy). X-ray diffraction shows that crystalline calcite is free of other mineral phases. The unit cell parameters (Table 4) are close to the reference values. However, are variable depending on color: smoky calcite is characterized by higher values (*a*: 4.9865–4.9907 Å, *c*: 17.056 Å–17.065 Å, *V*: 367.3–368.1 Å³) in comparison with colorless and rosy (*a*: 4.9810–4.9867 Å, *c*: 17.028 Å–17.057 Å, *V*: 365.9–367.3 Å³). The lower parameters compared to the reference value probably points to ions with a smaller ionic radius than that of Ca²⁺, which are incorporated into the calcite structure (examples, Mn²⁺, Fe²⁺). In addition, microprobe analysis data indicated the enrichment of colored calcite samples with manganese, magnesium, and iron oxides (up to 1 wt%), which explains the nature of their coloration.

Table 4. Unit cell parameters of calcite from Onega agates.

Sample		<i>a</i> ± Δ <i>a</i> , Å	<i>c</i> ± Δ <i>c</i> , Å	<i>V</i> , Å ³
Tulguba				
CT-1	Colorless crystals	4.9851 ± 0.0003	17.050 ± 0.002	366.9
CT-2	Smoky crystals	4.9872 ± 0.0002	17.057 ± 0.002	367.4
CT-4	Smoky crystals	4.9865 ± 0.0004	17.057 ± 0.002	367.3
CT-5	Smoky crystals	4.9876 ± 0.0004	17.056 ± 0.002	367.4
CSh-2	Rose crystals	4.9865 ± 0.0004	17.057 ± 0.004	367.3
Yalguba Ridge				
CYa-1	Colorless crystals	4.9867 ± 0.0004	17.041 ± 0.002	367.0
CYa-3	Smoky crystals	4.9907 ± 0.0004	17.065 ± 0.002	368.1
CYa-6	Rose crystals	4.9810 ± 0.0004	17.028 ± 0.002	365.9
CYa-7	Colorless crystals	4.9848 ± 0.0005	17.053 ± 0.002	367.0

5.5. SEM and Microprobe Investigation

Microscopic and microprobe investigation of Onega agates revealed numerous mineral and micromineral inclusions. (Table 2). The most frequent inclusions were identified as chlorite (Mg-Fe variety). The flake chlorite clusters were responsible for the green color (Figure 8a,g). Microinclusions of iron oxides and hydroxides are also characteristic for these agates. The minerals are represented by idiomorphic (up to 200 μm) and needle-like crystals (Figure 8a,b).

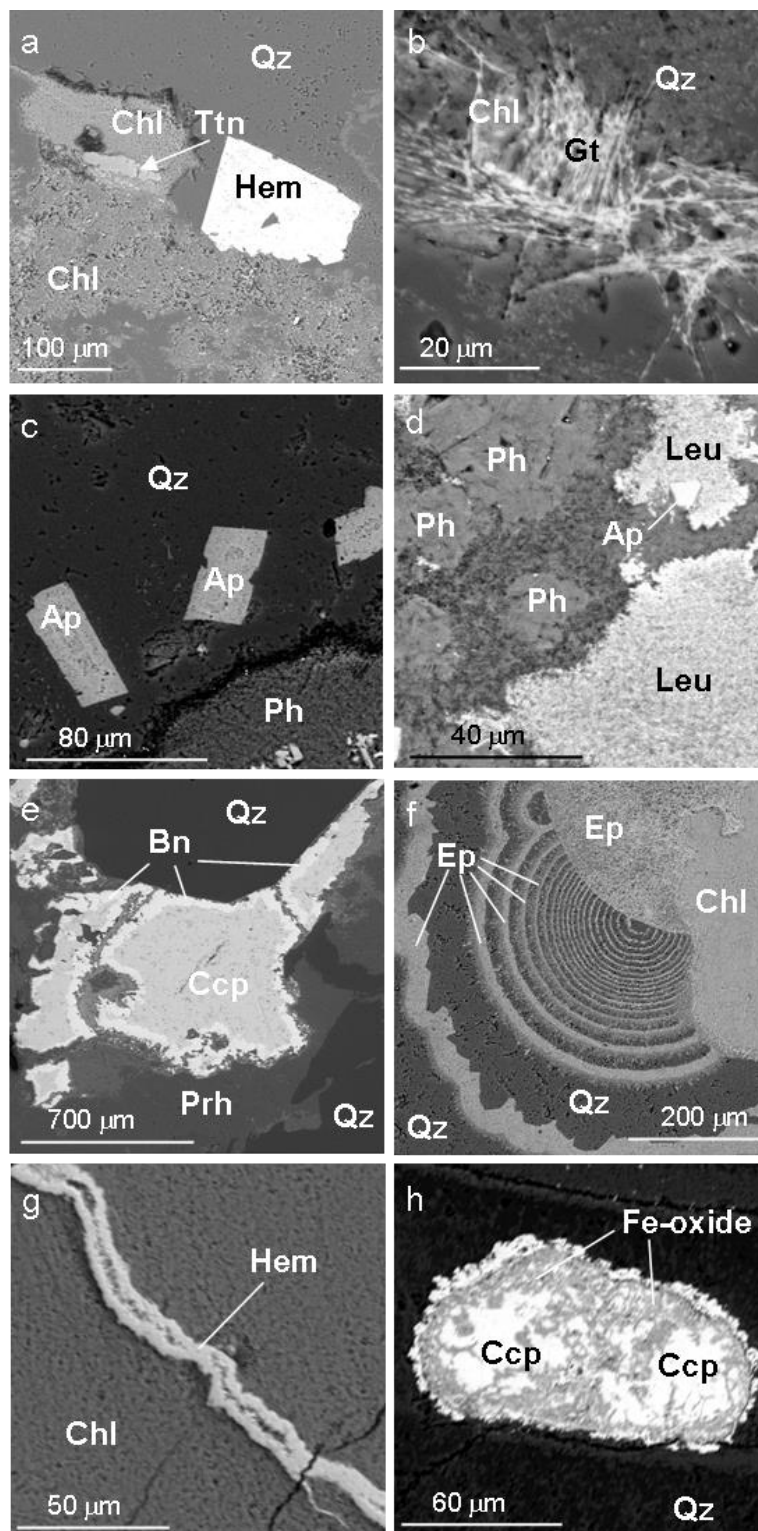


Figure 8. BSE images of microinclusions in Onega agates: (a) hematite (Hem) crystal in association with chlorite (Chl), quartz (Qz), and titanite (Ttn); (b) needle-like crystals of goethite (Gt) surrounded by silica; (c) prismatic apatite (Ap) grains and phengite (Ph) in outer chalcedony zone of agate; (d) flaked leucoxene (Leu) and phengite enclosed by chlorite; (e) chalcopyrite (Ccp) embedded with bornite (Bn) surrounded by quartz and prehnite (Prh); (f) epidote pseudomorphs after banded silica; (g) chlorite fissure filled by hematite; (h) patchy inclusion of chalcopyrite with Fe-oxide replacement zones.

Multiple epidote after silica pseudomorphs are frequently forming characteristic concentric agate textures are observed at the contact with host rocks (Figure 6f). Fine-flaked mica inclusions that correspond compositionally to phengite are present in the chalcedony and calcite matrixes of the Yalguba Ridge and Tulguba agates (Figure 8d). Various sulfides (chalcopryrite, chalcocite, pyrite, pyrrhotite, bornite) are present in forms of both macroinclusions and microinclusions. Sulfide phases have frequently microheterogeneity. As an example, the inclusions result from, chalcopryrite overgrowth by bornite, or iron oxide substitution of sulfide phase (Figure 8e,h). Hydroxylapatite clusters as flaked aggregates or individual prismatic grains up to 60 μm in size in silica matrix were identified only in Yalguba Ridge agates (Figure 8c). Titanite inclusions from 5 to 100 μm in diameter and leucosene flakes, which are products of titanate decomposition were revealed in Yalguba Ridge and Tulguba agates (Figure 8a,d). Carbonaceous microinclusions whose presence is confirmed by the previously Raman spectroscopy method were identified in Suisari Island agates only [48]. The determination of carbonaceous matter sources in Onega agates is one of the future challenges of our investigation. For the moment, we speculate that the carbonaceous matter is associated with ZF volcanogenic-sedimentary rocks containing a significant amount of organic carbon [26].

5.6. Geochemistry Investigation

Previous work using trace element analyses has been carried out by the authors on Onega agates and parent host rocks [48].

It is established that agates from Pinguba, Yalguba Ridge, and Suisari Island differ in their chemical composition (Tables S2 and S3). The quartz from Pinguba and Suisari Island agates have high Ti, Cr, Mn, Ni, and Cu (10–120 ppm) and low Li, Co, Ga, Zn, Sr, Zr, Mo, Sn (0.5–10 ppm) concentration. The total rare earth elements (REE) concentration in the quartz from Pinguba agates (3–15 ppm) is higher than that from Suisari agates (0.5–0.6 ppm). A significant difference for other elements is not observed. Heavy REE concentration in all cases is on the detection limit, which is in agreement with data on agates from other localities around the world [19]. The Yalguba Ridge agate calcite is characterized by a high concentration of Mn (1253–6675 ppm), Sn, Ti, Ni, Sr, Y, La, and Nd (5–56 ppm) and Cr, Zn, Sm, Gd, Dy (1–8 ppm). The Cr, Zn, Sm, Gd, and Dy concentrations are lower (1–8 ppm). The contents of other identified trace elements are below 1 ppm. The REE content level in calcite is similar to or slightly higher than that in host volcanics and is higher by 1–2 orders of magnitude than that in agate quartz (Tables S2 and S3). The total REE content ranges from 31–58 ppm in smoky calcite crystals to 158 ppm in colorless ones.

Additionally, we have analyzed the lateral distribution of transition metals (Co, Mn, Cr, V), large ion lithophile (LIL) elements: Rb, Ba, Sr; high field strength (HFS) elements: Y, U, Th; light rare earth (LREE) elements: La, Ce, Eu; fluid mobile elements (FME): As, Be, Li in banded agate from Pinguba occurrences using LA-ICP-MS method of local chemical analysis (Table S4). To obtain valid results, measurements were made using an enhanced field of laser sampling because certain elements occur in very low concentrations (Figure 3). However, even in this case, concentrations of some REE elements are below the detection limit of trace-element analysis. The example of certain trace elements distribution profiles is illustrated in Figure 9.

Transition metals concentrations of clear macrocrystalline quartz area (points 1–2) are low and relatively constant. Their accumulation is observed in outer and colored agate zones due to microinclusions presence (points 3–7). LIL and HFS elements content except for Y are more balanced along with the profile. The highest LREE and Li concentrations are typical for outer agates zones near the contact with host rocks. This effect can probably be resulting from host volcanic rocks alteration. Supposably it is bound with the decomposition of volcanic glass and feldspars, which could be a base source of not only Si, Al, Ca, Na, K but also LIL and HFS elements for agates.

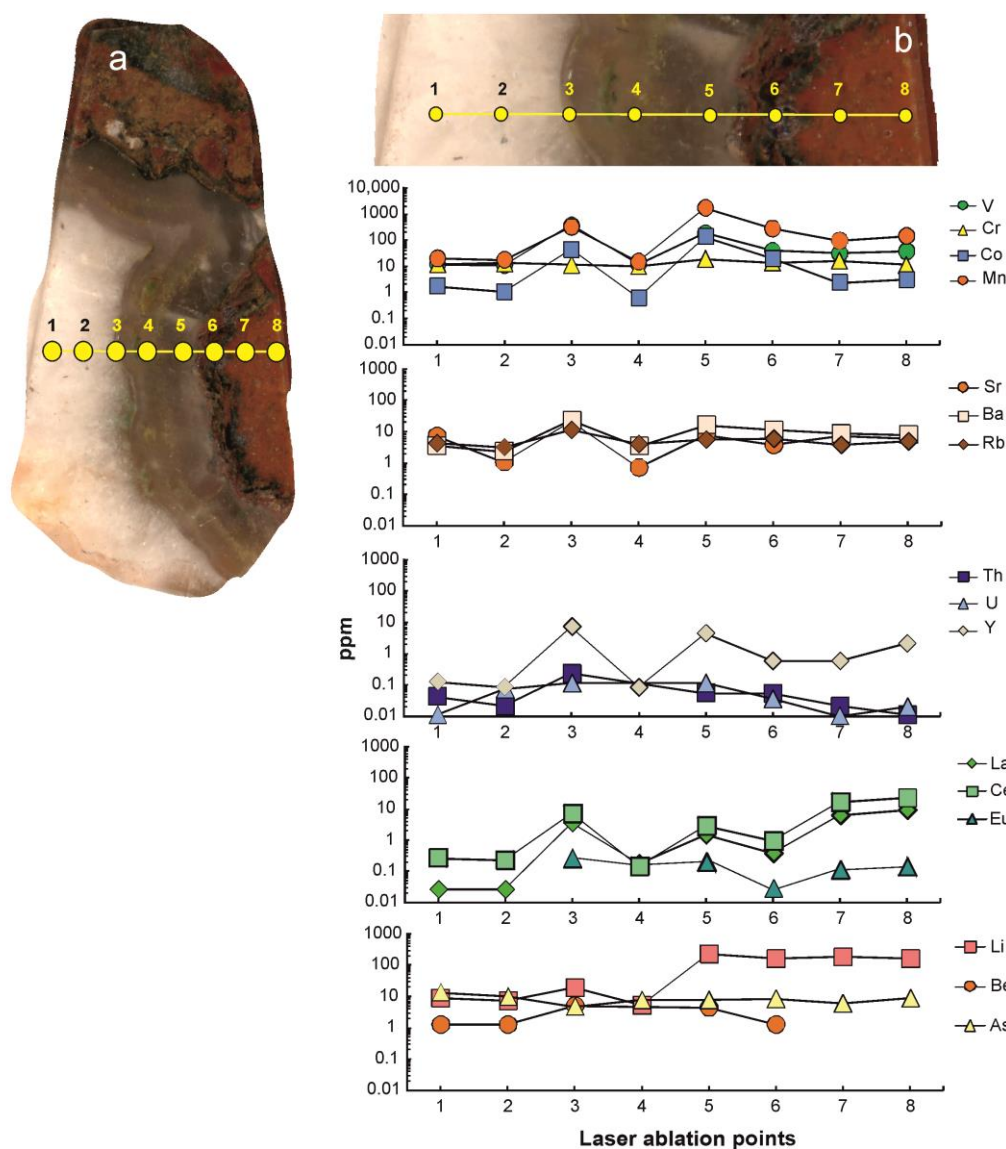


Figure 9. Micrograph of an agate from Pinguba occurrence with a profile showing the analytical points of trace element analysis by LA-ICP-MS (a); distribution profiles of certain trace elements in the investigated agate (b). Points: 1, 2—macrocrystalline area; 3–5—chalcidony zone; 6–8—outer colored zone.

Möckel et al. [12] established elevated concentrations of V, Co, Mn, Ba, Y, La, Ce, Eu, Li in chalcidonic layers of agates when compared to macrocrystalline quartz areas. This is supported by our investigation. The concentrations of Cr, As, Be, and Rb are only slightly varying along with the profile.

The observed decrease of trace element concentration in banded agates from the agate host rock to core probably reflects the chemical purification process during crystallization [12]. It is established that the chemical composition of agate layers correlate with their colors: the total concentration of trace elements in colored zones is higher than in colorless.

5.7. C-O Isotopic Composition

Preliminary stable isotope studies were carried out on agate-associated calcite samples of Yalguba Ridge occurrence (Table 5).

Table 5. Carbon and oxygen isotope composition of calcite samples from Yalguba Ridge agates.

Sample	$\delta^{13}\text{C}_{\text{PDB}}(\text{‰})$	$\delta^{18}\text{O}_{\text{SMOW}}(\text{‰})$
CYa-1	−3.31	15.67
CYa-2	−4.98	13.46
CYa-3	−5.12	12.91

Measurements have shown that calcites have a narrow $\delta^{13}\text{C}$ (−3.31 ... −5.12‰, PDB) and $\delta^{18}\text{O}$ (12.91–15.67‰, SMOW) ranges. The $\delta^{13}\text{C}$ values are significantly higher than ones for organic carbon in sedimentary rocks (−30 to −10 ‰, [49]) that indicate an inorganic carbon origin. The $\delta^{13}\text{C}$ of agate-associated calcite within the range of mantle carbonite [50] and probably reflect primary magmatic origin. In the ratio plot, $\delta^{13}\text{C}/\delta^{18}\text{O}$ markers are in the transition zone between sedimentary carbonates (normal marine limestone) and magmatic carbonates with the influence of hydrothermal or low-thermal meteoric fluids [50] (Figure 10). In the same plot area, but with a less pronounced hydrothermal trend, there are samples of agate calcite from similar genesis host rocks (Phanerozoic and Precambrian volcanic complexes) from some other locations in the world [19]. The close C–O isotopic characterization of agate calcite from different regions suggests that agates in volcanics were formed with the active participation of post-magmatic hydrothermal fluids.

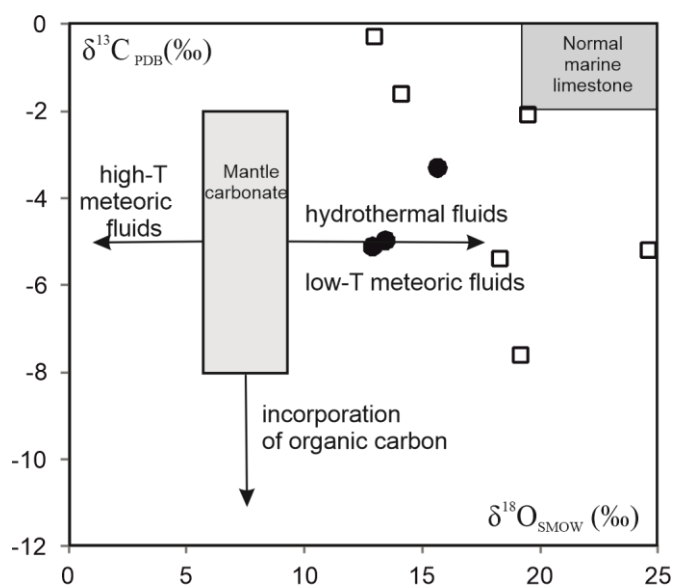


Figure 10. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ diagram for agate-associated calcite samples from: ●—Yalguba Ridge occurrences, □—other localities around the world [19]. Mantle carbonate box and arrows showing how various processes could affect the C and O isotopes of magmatic carbonates are given according to Giuliani et al. [50], normal marine limestone (part of the field)—[51].

6. Conclusions

- (1) The present study describes the key occurrences of agate mineralization in volcanic rocks of the LSH within the Onega Basin, Karelian Craton, Southeast Fennoscandia, Russia (2100–1920 Ma). Agates occur in the inter-pillow lava space, fills gas vesicles, and tectonic cracks of volcanics.
- (2) Investigations showed that this mineralization is represented by silicates, oxides and hydroxides, carbonates, phosphates, sulfides, and sulfates. Among the silica minerals in agates only chalcedony, quartz, and quartzine are found. The parameters of the quartz structure according to the X-ray diffraction data (well-develops reflections (212), (203), (301), large crystallite sizes (C_s 710–1050 Å) and CI (7.8–10.3) provide evidence for multi-stage silica minerals recrystallization due to a metamorphic (thermal) effect.

- (3) The elevated concentrations of certain elements (V, Co, Mn, Ba, Y, La, Ce, Eu, Li) in chalcedonic layers of banded agates in comparison with macro crystalline quartz areas were confirmed. The concentrations of Cr, As, Be, and Rb are only slightly varying. The observed decrease of trace element concentration in banded agates from the agate host rock to core is probably reflecting a chemical purification process during crystallization.
- (4) C–O isotope characteristic of agate-associated calcite reflects a primary magmatic origin with the influence of hydrothermal or low-thermal meteoric fluids.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/10/12/1106/s1>, Table S1. The trace elements content in the reference material NIST-612 and average measured values at 50 points by LA-ICP-MS (ppm, RSD %). Table S2: The trace elements contents of agate-bearing volcanics from the LSH, Onega Basin, Russia, on a bulk probes by ICP-MS, ppm; Table S3 The trace elements contents in agates of the LSH, Onega Basin, Russia, on a bulk probes by ICP-MS, ppm; Table S4 The trace elements contents in agates of the LSH, Onega Basin, Russia, by LA-ICP-MS, %, ppm.

Author Contributions: Conceptualization, E.N.S. and S.A.S.; methodology, E.N.S. and S.A.S.; field investigation, E.N.S. and S.A.S.; writing—original draft preparation, E.N.S.; writing—review and editing, E.N.S. and S.A.S.; visualization, E.N.S. and S.A.S. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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