PROTEROSOIC QUARTZ-PORHYRY ASSOCIATED WITH RAPAKIVI GRANITES (SALMI BATOLITH)

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This work contains new data about quartz-porphyry associated with the Salmi batholith, which belongs to anorthosite-rapakivigranitic complexes (ARGC) of rocks. We have identified: the absolute age of the rocks by the zircon U-Pb method; the composition of the captured melt silicate inclusions, including their trace element composition; temperature of rock formation by various mineral thermometers; the presence of sulfide melt in the formation of rocks.

Introduction. At the end of the paleoproterozoic – the beginning of the mesoproterozoic (1.8-1.5 Ga), wide effused intraplate felsic magmatism of increased alkalinity took place on Earth. These events occurred on the site of stabilized early paleoproterozoic orogens. Large non-metamorphosed intrusions of anorthosite-rapakivigranite complexes (ARGC) are associated with the belts of this magmatism. Biotite-hornblende granites (rapakivi) are the earliest felsic rocks included in the ARGC. These rocks are rich in K, Fe, F, and oxygen fugacity during their formation was below the FMQ buffer. These granites have the largest area of distribution among the acid rocks of the ARGC. Effusive formations associated with rapakivi granite are known, but rare, often strongly altered, some of them are described in (Belyaev, 2013; Ehrlich et.al, 2013; Vorma, 1975; Kisvarsanyi, 1972). Effusive and sub-effusive formations, due to the more rapid formation compared to intrusions, can be a source of information about events that can be obscured or destroyed as a result of prolonged crystallization. Such information may be the mode of volatile components, the presence of such phase concentrators of the ore substance as sulphide or other non-silicate melt. Also, an extremely urgent task is to establish the relative temporal relationships of the rocks belonging to the ARGC, since often their absolute ages overlap within the limits of analytical errors. This work will discuss sub-effusive formations - igneous breccias with cement represented by quartz-porphyry.

Geological essay. The batholith is a member of the ARGC (Sharkov, 2005), located in South Karelia on the eastern shore the Ladoga lake at the junction of the Svekofen crust and the Karelian craton (Larin, 2011), formed in the range of 1549-1537 Ma (Amelin et al., 1994; Neymark et al., 1997). In the southwestern extremity of the Lupikko gneiss-granite dome (AR_2-PR_1), some researchers noted quartz-porphyry and magmatic breccia outcrops (Trustedt, 1907; Sviridenko, 1968; Sviridenko, 1984; Belyaev, 1985).

Quartz-porphyry are the series of backstage-like dikes located in the south-eastern tip of the Lupikko gneiss-granite dome (Sviridenko, 1968). Unfortunately, at the moment, quartz-porphyry outcrops noted earlier in the literature, are not available for observation, since are located at the bottom of a quarry flooded with water. Not altered quartz-porphyry were found in dumps along the quarry walls, and altered (potassic alteration) were found in the outcrop in the immediate vicinity of the dumps. The investigating sample of breccia consisting from cement represented by quartz-porphyry and fragments of host rocks. Xenoliths: gneisses of domes (AR_2-PR_1), amphibolites and mica schists (PR_1), and earlier granite phases: biotite-amphibole rapakivi granites with a texture of "rapakivi" (wiborgites), biotite fine-grained granites (their confinedness with the granites of the Salmi batholith is not currently defined), as well as altered xenoliths with clinopyroxene relics (magnesian skarn?).

Petrography. Quartz porphyry is a gray rock with a porphyritic structure due to the presence of resorbed quartz phenocrysts up to 6–8 mm in cross-section (1st Q generation) and iridescent potassium feldspar (Kfs) crystals up to 4 mm. Quartz and Kfs phenocrystals are unevenly distributed throughout the rock. The ground mass is represented by a fine-crystalline aggregate of, Kfs, albite and idiomorphic quartz crystals 100-300 μm in cross-section (2nd Q generation). Dark-colored silicates are represented by amphibole and biotite. Accessory mineralization: zircon, apatite, ilmenite, rutile, pyrrhotite, chalcopyrite, sphalerite, galena. Quartz, Kfs, zircon - contain numerous silicate melt inclusions, also, inclusions of sulfide melts were found in quartz and zircon.

Research methods. Quartz-porphyry cement, for further study was cutted out from samples of breccia using a diamond circular saw. Petrochemistry of quartz-porphyry has been studied by XRF and ICP-MS. Transparently polished slide and polished slide were made from the obtained material for studying by optical microscopy and X-ray microanalysis (RSMA).

For isotope studies, zircons were separated from the rock. For the composition study of melt inclusions in minerals, zircons and two generations of quartz were separated from rock. Zircons from the rock were separated by dissolving the rock in HF and subsequently separation in heavy liquids. Due to the longer dissolution of quartz in HF compared to feldspars, idiomorphic quartz crystals 100–300 μm in diameter were also separated along with zircon. The larger resorbed quartz phenocrysts were cutted from sample by a thin (0.1 mm) diamond saw.

Quartz crystals with melt inclusions were heated with visual control on a «Linkam 1500» thermal cell at atmospheric pressure, but all inclusions were opened. After that, a series of experiments were carried out at the "gas-bomb" (UVGD-10000) in platinum ampoules with added or absence deuterium water. The pressure in the experiment was taken with a "margin", since the modern erosion section of the granitoid rocks of the Salmi batholith corresponds to depths with pressures up to 200 MPa (Rub et al., 1986; Poutiainen, Scherbakova, 1998). The experiments were carried out at temperatures: 850-875-900-950-1000 ^{o}C. Exposure from 3 to 20 hours, followed by rapid quenching, was made by dropping the ampoule into the cold zone. The products of the experiments were studied by RSMA, SIMS. Isotopic and geochemical zircon studies were carried out using LA-ICP-MS.

Estimation of the temperatures of mineral formation and capture of melt inclusions was carried out by evaluating the occurrence of Ti in quartz and zircon (Wark et al., 2008; Watson et al., 2006), as well as by evaluating the solubility of Zr in the melt (Watson, Harrison, 1983).

The resulting data. The age of the U-Pb method for zircons was determined (31 analyzes, concordia, LA-ICP-MS): 1541 +/- 9.4 Ma (MSWD 1.7). This data is close to the age of the "third magmatic impulse" (Larin, 2011), with the formation of rapakivi granites -1540-1538 Ma (Amelin et al., 1994, Neymark et.al., 1997).

The geochemistry and the distribution of REEs spectra of studied quartz-porphyry to be close to rapakivi granites of the Salmi batholith. The age of rapakivi granites falls within the limits of the analytical error of a certain age, but judging by the presence of their xenoliths with the characteristic rapakivi texture in quartz-porphyry cement - they were formed somewhat before the formation of quartz-porphyry.

Even at 20 hours of exposure at 1000 °C 300 MPa not all inclusions became homogeneous, it does not correlate with the dimensions of inclusions. Practically all inclusions from small idiomorphic quartz crystals did not achieve homogeneity up to the maximum parameters for the exposure time and T-P, have significant amount of Kfs (heterogeneous capture?). In all quartz crystals, a grid of cracks is present, probably originating from the α-β transition, in large resorbed phenocrystals this is more pronounced than in small idiomorphic crystals.

According to SIMS data, it was revealed that all analyzed heated melt inclusions from 1st Q generation (5 analyzes) contain from 0.124 to 0.004% by weight of deuterium water with a total content of protium water from 4.36% to 0.935% by weight (last data with 0.004% deuterium). Melt inclusions from 2nd Q generation (5 analyzes) contain from 0.269 to 0.088% by weight of water (deuterium not added). Silicate melt inclusions in zircon are too small to be studied using SIMS, less than 30 microns.

Quartz-porhyry has a composition that corresponds to rhyolite, close to the boundary of trachyrhyolite. The compositions of melt silicate inclusions have a trend from phonolite (in 2nd Q generation) to low-alkaline rhyolite (1st Q generation). The compositions of melt inclusions of two generations of quartz intersect in the zone of trachyte/trachydacite/pantellerite/trachyriodacite. In this zone there is also the main swarm of compositions of melt inclusion in zircons. Also several compositions of melt inclusion in zircon is located in the field of phonothephrite/trachyandesite.

The content of trace elements in silicate melt inclusions. Melts during the formation of quartz porphyry are characterized by elevated concentrations of zinc, an average of 160-200 ppm, which is close to the content in the rock (194ppm). Cu and Ni contents averaged 5,8 and 2,9 ppm, which is almost by half an order of magnitude less than the content in the rock (38 and 16 ppm respectively). The content of Ta and Nb in general correlate with each other, but Ta is somewhat larger in glass (on average, 2.9 ppm Ta relative to 3,5 in rock and 37 ppm Nb relative to 48,2 in rock). This is probably due to the occurrence of Nb in ilmenite, where content of Nb according to RSMA is up to 0.4 – 0.5 wt.%. In melt inclusions from 2nd Q generation Rb is distributed higher than 2-3 times for the rock, which probably indicates a heterophase capture of a Kfs with the melt. The spectrum of Kfs was been determined by RAMAN spectroscopy in not completely homogeneous melt inclusions in 2nd Q generation.

Estimates of mineral formation temperatures. The method of incorporating Ti into zircon (Watson et al., 2006) provides estimates of the mineral formation temperatures of 700–870 °C with a distribution peak at 780–840 °C. A single grain gave an estimate of the temperature of 950 °C. The determinations were carried out using RSMA (14 measurements) and LA-ICP-MS (14 measurements).

The method of incorporating Ti into quartz (Wark et al., 2006) provides temperature estimates for quartz phenocrysts of 725-790 °C (1st Q generation, 13 measurements) and for idiomorphic quartz crystals 620-830 ° C (2nd Q generation, 7 measurements). All Ti values in quartz are determined using RSMA. In the calculations, it was assumed that $\alpha Ti = 1$.

Estimates of the capture temperature of inclusions. The Zr melt saturation method (Watson et al., 1983) showed a temperature range from 720 to 870 °C with a peak of 820-840 °C. All Zr values in melt inclusions were determined using SIMS, 6 analyzes for each inclusion in quartz (1 and 2 generations). The same method for a rough estimate of the rock formation temperature (by Zr in Rock) it gives an estimate of the temperature 914 °C.

Sulfide inclusions. Inclusions of sulphide melts were found in zircons and single inclusions in 2nd Q generation. Sulphide melt inclusions have rounded shapes, sometimes non-isometric, up to 20-25 microns in cross-section. Melt inclusions of heterophase capture of sulphide-silicate composition were also detected. Inclusions of sulphide melts are closer in composition to pyrrhotite, from the mineral phases inside such an inclusion - chalcopyrite was found. In sulphide inclusions, textures of the solid solution splitting are observed. According to RSMA, elevated concentrations of some chalcophile elements are observed: Cu, Co, Ni, Zn up to 0.2, 1, 0.25, 0.6 wt% respectively. There are references in the literature about inclusions of sulphide melts in zircons of phanerozoic quartz porphyry (Simpson, 2014).

In the study on elements-pollutants in bottom sediments of Ladoga Lake, a correlation of Cd are related to Zr and Hf was found (Ivanter et al., 2016; Slukovsky, 2013), it was concluded that the elevated concentrations of Cd is connected to zircons. Cd is cannot isomorphically icorporated in zircon due to a different valence and ionic radius. Although Cd in sulphide melt inclusions was not detected by us using RSMA, its presence is theoretically possible due to its chalcophilicity. Probably, zircon in bottom sediments of Ladoga lake contains sulphide melt inclusions or phases of sulphides. The Wyborg batholith has known preserved cover of quartz-porphyry (Belyaev, 2013; Ehrlich et al., 2012). Probably, the Salmi batholith also had effusives of quartz-porphyry in the past, destroyed by erosion with the formation of sedimentary rocks around Ladoga lake - source of zircon with Cd in modern sediments.

Conclusion. The quartz-porphyry of the Salmi batholith is 1541 +/- 9.4 Ma, their formation occurred after the formation of rapakivi granites. Their formation occurred in the range from 870 to 700-725 °C. Resorbed grains of quartz and Kfs can be associated with melting as a result of an adiabatic uplift of magma, with which droplets of sulphide melt of unknown origin were captured. The formation of these rocks occurred at fO_2 below the FMQ buffer.

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