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Composition of the Fluids Responsible for Gold Mineralization in the Pechenga Structure of the Pechenga-Imandra-Varzuga Greenstone Belt, Kola Peninsula, Russia

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Abstract This study presents the first fluid inclusion data from quartz of albite-carbonate-quartz altered rocks and metasomatic quartzite which host gold mineralization in the Pechenga structure of the Pechenga-Imandra-Varzuga greenstone belt. The temperature 275-370ºC, pressure 1.2-4.5 kbar, and fluid composition of gold-bearing fluid are estimated from microthermometry, Raman spectroscopy, and LA-ICP-MS of individual fluid inclusions and bulk chemical analyses of fluid inclusions. In particular Au and Ag concentrations have been determined in fluid inclusions. It is shown that albite-carbonate-quartz altered rocks and metasomatic quartzite interacted with fluids of similar chemical composition but at different physicochemical conditions. It is concluded that the gold-bearing fluid in the Pechenga structure is similar to that of orogenic gold deposits.

INTRODUCTION

According to Sundblad (2003) and Ivashchenko and Golubev (2010), gold mineralization in the Kola Peninsula is linked to Neoarchean and Paleoproterozoic greenstone belts. The Pechenga structure, reported in this paper, is a fragment of the Paleoproterozoic Pechenga-Imandra-Varzuga greenstone belt (Fig. 1). This belt extends for approximately 700 km through the Kola Peninsula from the Norwegian Caledonides in the northwest to near the White Sea in the south-east. The Gjeddevann gold prospect in Norway and some gold occurrences in the Pechenga and Imandra-Varzuga structures in Russia are located in this belt.

Hydrothermal fluids responsible for gold mineralization were studied in the highly prospective Porojarvi area, which is located in the southeastern part of the Pechenga structure near the border with Norway. The studied area may be considered as a model for the formation of gold mineralization in the southern zone of Pechenga (Voronyaeva, 2008).

GEOLOGY OF THE PECHENGA STRUCTURE

The structure and shape of the Pechenga-Imandra-Varzuga belt is the result of collision in the Late Paleoproterozoic. The main length within the belt is a monocline, formed by near concordant sedimentary and volcanic sequences bounded by thrust faults plunging to the SSW (Figs. 2, 3). The oldest sequences are located in the north (footwall) and the youngest on the southern side. Northern and southern zones are present in the Pechenga, Imandra-Varzuga, and Ust-Ponoya structures. Northern zones are characterized by weakly broken monoclinal sequences dipping at 20-60^o, in the southern zones metamorphosed sedimentary and volcanic sequences are highly folded and faulted (Fig. 2). The southern boundary of the belt is a thrust fault where the Neoarchean sequences of the Pechenga-Imandra-Varzuga belt are thrust on the Paleoproterozoic rocks of the southern zones.

The northern zone of the Pechenga structure is the best studied fragment of the Pechenga-Imandra-Varzuga belt, with the largest Cu-Ni deposits in Europe hosted in intrusions of gabbro-wehrlite. The North Pechenga Complex comprises four main units: Sariolian, Lower and Upper Yatulian, and Lyudikovian (~2550 to 1940 Ma) forming a syncline. The section is cyclic; with each group containing sedimentary and volcanic rocks in the lower and upper parts respectively. The total thickness of these volcanic and sedimentary rocks of North Pechenga reaches 11 km. The sequences are dipping at 10 to 60^o toward SW and are gradually flattening out to the core of the structure (Figs. 2, 3). This section of the North Pechenga zone is described in detail in other publications (Melezhik and Sturt, 1994; Smolkin et al., 1995).

Volcanic and tuffaceous sedimentary rocks of the South Pechenga Complex are localized within a long, but comparatively narrow tectono-stratigraphic area (Fig. 2). The South Pechenga rocks have a contact with basalts of the North Pechenga Complex in the northeast along the Poritash fault. The southeastern contact of the South Pechenga zone matches the syn-tectonic outlines of the diorite-plagiogranite cupola of the Kaskeljavr granite complex dated at ~1940 Ma (Vetrin, 1988; Skuf'in et al., 2000) and form drop-like synformal folds between the cupola (Fig. 4). The rocks are steeply dipping (40^o and higher both towards north and south) up to vertical. Poor outcrop and strongly tectonized rocks within the South Pechenga zone hamper stratigraphic breakdown of the sequences and determination of their age. Therefore, the term sequence is used instead of formation in the description of the South zone.

The Southern Pechenga zone includes two sub-zones: Shuoni-Kaskeljavr that matches the outlines of adjacent gabbro and diorite-plagiogranite cupolas and linear Porojarvi extended parallel to the boundary with the North zone (Fig. 4). The contact between these sub-zones is a thrust.

Rocks of the Shuoni-Kaskeljavr sub-zone are divided into the Talya and Peshanoozero (former tyul'pvyd and ansemjok) sequences. Sedimentary and volcanic sequences were affected by a diorite-granodiorite intrusions dated at 1940 Ma, therefore these sequences are older. The lower part of the the Talya sequence is a meta-basalt (amphibolite) of 300 to 900 m ithickness, the upper part is meta-sediments (two-mica and biotite gneisses frequently with garnet) intercalated with intermediate to felsic meta-tuffs up to 1000 in thickness. The Pschanoozero sequence is composed of schistose amphibolites, which are meta-basalts with rare intercalations of basaltic andesite, picrite, and mafic tuffs and tuffites. The thickness of this sequence is up to 1800 m. Volcanic rocks of the Talya and Peschanoozero sequences are assumed to be analogs of the Matert and/or Suppvar Formations of the Northern Pechenga zone (Skuf’in and Theart, 2005, Skuf'in et al., 2009).

The Porojarvi sub-zone comprises rocks of the Southern Pechenga Complex dated at 1.93-1.86 Ga (Skuf’in and Theart, 2005, Skuf'in et al., 2009) and the estimated total thickness ranges from 3 to 5 km. The uncertainty is caused by a system of isoclinal folds overturned to the southeast, complicated by cross breaks, concordant to general strike of the Porijarvi sub-zone. The stratigraphic section of the Porojarvi sub-zone consists of ultramafic to felsic volcanic rocks and tuffs, and meta-clastic rocks. Five sequences Kallojaur, Bragino, Mennel, Kaplin, and Kasesjoki are identified in the section and described in detail by (Skuf’in and Theart, 2005, Skuf'in et al., 2009). The Kallojaur and Bragino sequences were formed in the Kalivian and the Mennel, Kaplin, and Kasesjoki sequences were formed in the Vepsian. The Sm/Nd age of meta-volcanic rocks of the Mennel Formation at 1894 ± 40 Ma (Skuf'in et al., 2009) is consistent within uncertainty to the Rb/Sr age of these rocks 1865 ± 58 Ma (Balashov, 1996).

The rocks are intruded by large sub-volcanic and extrusive andesite and dacitic-andesite bodies of the Poritash Complex (judging from the composition, they are similar to volcanic rocks of the Kaplin sequence (Skuf'in et al., 2009)). Small sub-volcanic bodies of meta-andesite, and small bodies of meta-gabbro, meta-dolerite, meta-pyroxenite of the Bragino Complex, are presumably associated with intrusions of the Kaskam Complex.

Petrochemical and geochemical features of volcanic rocks involved of the southern limb of the Pechenga structure are described Smolkin et al. (1995), Melezhik and Sturt (1994), Skuf’in and Theart (2005) and Skuf'in et al., (2009). Ti-rich tholeiites and picro-basalts, similar to oceanic tholeiites T-MORB are predominant in the sections of the Bragino and Mennel Formations. At the same time, calc-alkaline rocks from Ti-poor basaltic andesite to rhyolite, which could be attributed to the arc series taking into account geological relationships with oceanic basalts and tuffaceous sediments are abundant in the Kallojaur and Kaplin Formations. In general, rock association of the southern limb of the Pechenga structure is comparable to that of volcanism of continental margin including an environment of back-arc spreading (Melezhik and Sturt, 1994; Mints et al., 1996).

Several stages were identified in reconstructing the geodynamic regime and the formation and evolution of the Pechenga structure (Melezhik and Sturt, 1994; Mints et al., 1996). The first stage was intra-continental rifting (> 2500 to 2390 Ma) followed by a transition from intra-continental to inter-continental rifting (2390-2100 Ma) and then an oceanic Red Sea-type stage (2100-1970 Ma) including a brief period of expanded oceanic bottom (1990-1970 Ma). The first indication of subduction (compression) appeared in the formation of aluminous abdewsite of the Porojarvi suite, which has similarities to the calc-alkaline rocks of volcanic arcs (1970-1870 Ma; Melezhik and Sturt 1994). These were metamorphosed, presumably during arc-continent collision, prior to deposition of overlapping polymictic conglomerates. Then, volcanic and sedimentary rocks of the Southern Pechenga zone were formed. These volcanic rocks also have geochemical features of calc-alkaline oceanic arcs. The rocks of the Southern Pechenga zone were metamorphosed, folded and faulted during arc-continent collision, when the Neoarchean gneiss sequences (~1.8 Ga) were thrust on them from the south.

The metamorphic grade of the rocks within the Pechenga structure ranges from prehnite-pumpellyite to amphibolite facies increasing in grade towards the south and reaching the maximum at the southeastern flank. The majority of the structure was metamorphosed to greenschist facies. Metamorphism was polycyclic and in the Southern Pechenga zone it was related to the aforementioned collisional events. During the late stage (continent-continent collision) the area of greenschist facies metamorphism was subjected to a pressure of 4-5 kbar at 250-300^{o}C, at the southern boundary of the zone temperature exceeded 550^{o}C at similar pressures (Duk, 1977).

GOLD MINERALIZATION IN THE SOUTHERN PECHENGA ZONE

The first information on gold mineralization in the rocks of the Southern Pechenga structure was in the early1970s (works of Yu.I. Filimonov, Murmansk Exploration Expedition, 1968-1971 (Akhmedov et al., 2004). In the 1990's, the Central Kola Expedition performed additional site exploration at a 1:50000 scale in the course of which information available at that time was summarized and the geological map at a 1:50000 scale of the Southern zone of the Pechenga

Complex was revised. The Southern Pechenga zone was identified for the first time as metallogenic zone prospective for gold (Akhmedov et al., 2004).

In 2000-2004, OAO Central’no-Kol’skaya Expeditsiya prospected the Southern Pechenga zone for gold. This allowed re-evaluation of the gold content in this structure (Voronyaeva, 2008) with six main types of gold occurrences (>0.1 g/t) identified as a result of this prospecting (Akhmedov et al., 2004; Voronyaeva 2008). (1) andesitic related to the Poritash igneous complex; (2) massive pyrite-pyrrhotite ores hosted in tuffaceous and sedimentary rocks of the Kollojavr, Bragino, and Mennel Formations (massive sulfide); (3) tuffaceous-black shale related tectonized and altered carbonaceous sequences within zones of the near-meridional faults; (4) chlorite-carbonate in altered picrite, peridotite, and serpentinite; (5) carbonate-quartz veins in various sequences; and (6) in metasomatic quartzite. The last type is the most interesting. Metasomatic quartzite occurs as lenses and lenticular horizons in carbonaceous tuffaceous and sedimentary rocks of the Kollojavr, and less frequently in the Bragino and Mennel Formations (Akhmedov et al., 2004; Voronyaeva 2008).

High gold grades(up to 48 g/t) were also measured in hand specimen samples of pyrite-bearing meta-silicate and meta-basalt with sulfide-carbonate veinlets from the strike-slip zone between rocks of the Northern and Southern Pechenga zones north of the Porojarvi Lake (Balagansky and Belyaev, 2005). This gold occurrence should be attributed to the carbonate-quartz vein type. It is noteworthy that repeated float sampling and trench sampling gave gold grades of only 0.18 g/t that indicates an extremely irregular gold distribution in the rocks. Nevertheless, the gold content in the strike-slip zone between Northern and Southern Pechenga zone was identified.

DESCRIPTION OF THE POROJARVI AREA

The Porojarvi area is located in the western part of the Southern Pechenga zone south of the Porojarvi Lake and west of the Kasesjoki River (Fig. 4). The contact between rocks of the Southern and Northern Pechenga zones is in a strike-slip zone that outcrops approximately 1.5 km NW of the Porojarvi Lake. The rocks of the Northern zone are cataclasites and mylonitized meta-basalt (quartz-carbonate-actinolite-chlorite schist) of the Matert Formation, which are cut by pyrite-bearing carbonate veinlets. The Southern zone, in the outcrop, is represented by meta-sedimentary rocks of the Kollojavr Formations, which are fine-grained and banded with irregular distributions of carbonaceous matter meta-silicates with minor sericite and locally disseminated pyrite. The width of the Porojarvi Formation outcrop is approximately 4 km (Figs. 4, 5). Here, the Kallojavr, Bragino, Kaplin, Kasesjoki, and Mannel sequences were identified, the last was mapped at the western shore of the Porojarvi Lake, where it succeeds the Kaplin sequence along strike. The southern part of the area is occupied by an approximately 4km wide band of volcanic and sedimentary rocks of the Shuoni-Kaskeljarvi Group attributed to the Peschanoozero and Talya sequences. These sequences enclose cupola-like intrusions of the Kaskam gabbro-diorite-plagiogranite complex in the north. These intrusions near the Poroyarvi area are meta-gabbro, meta-gabbronorite, and garnet-bearing amphibolite. Metamorphosed volcanic and sedimentary sequences are intruded by small bodies and dikes of the Bragino Complex, which in the Porojarvi area are meta-gabbros and meta-dolerites.

Gold mineralization in the Porojarvi area was identified in altered rocks that replace mafic meta-volcanic and meta-sedimentary rocks of the Peschanoozero sequence. This distinguishes this occurrence from the central part of the Southern Pechenga zone, where gold occurrences were found in meta-volcanic and meta-sedimentary rocks of various sequences, most frequently in the rocks of the Bragino and Mennel sequences (Akhmedov et al., 2004). Some gold occurrences are present within the Projarvi area in metasomatic quartzite, stockwork of carbonate-quartz veinlets, and albite-carbonate-quartz altered rock. Metasomatic gold-bearing quartzite was found here in 2004-2005 as a result of exploration supervised by L.V. Voronyaeva. Locations with quartzite were named as Porojarvi (like the prospective area), Kontaktovy, Timofeevsky, Istok, and Svetlanovsky (Fig. 5). A gold grade higher than 1 g/t was only measured at the first three locations, therefore not all quartzite locations can be designated as gold-bearing.

GGUP Spetsializirovannaya Firma Mineral prospected for gold at the Poroyarvi area in 2010-2013. This work was focused on gold-bearing stockwork of quartz-carbonate veinlets at the Anomalny location and carbonate-albite-quartz altered rocks at the Zagadka occurrence.

The Peschanoozero sequence within the Porojarvi area is dominated by meta-basalt, meta-basaltic andesite and their tuffs (amphibolite, amphibole-chlorite and chlorite schist, and biotite-chlorite and carbonate-chlorite plagioschist). Horizons of metasedimentary rocks up to 100 m in thickness (Fig. 5) are present in the meta-volcanic sequence. They are composed of silty sandstone and carbonaceous meta-aleuropelite (biotite and two-mica plagioschists including their carbonaceous varieties). As rule, the rocks in such meta-sedimentary horizons are faulted concordant to the strike of the sequence.

Metasomatic quartzite and albite-carbonate-quartz alteration are governed by the intersection of northwestern-trending faults (along strike of meta-sedimentary horizons) and later northeastern-trending faults. Two quartzite zones were identified, the southern zone comprises the Timofeevsky and Kontaktovy locations (this zone also includes stockwork of the Anomalny location and gold-bearing aceite of the Zagadka occurrence) and northern zone comprises the Svetlanovsky, Istok, and Porojarvi locations (Fig. 5). Metasomatic quartzite occurs as lenticular bodies with individual lenses being less than 2 m and a maximum of 9 m in size that can traced for a few dozen meters along strike for up to 200 m (Kontaktovy location). The contacts of quartzite with the host amphibolite and carbonate-chlorite schist are sharp and frequently cut the schistosity of host rocks, whereas the contact with the carbonaceous schist can be both sharp or gradational (Svetlanovsky location). Along the strike, lenses can be replaced by zones of carbonate-quartz veinlets.

Quartzite is folded together with the host rocks and are cut by late faults. Quartzite bodies frequently have different dip and strike even when they are close to each other in outcrop, therefore it is not clear whether this is one lens or different quartzite bodies. Quartzite is light gray sometimes with a greenish, pink, yellow, or beige tint. It has a saccharoidal texture, but during extended weathering it becomes a white, loose and porous quartzite with oriented euhedral quartz grains present at some locations. Their length can up to 1 cm and 1 to 2 in width. Quartzite is nemato granoblastic, and due to the irregular distribution of silicates, ore minerals, and carbonaceous matter in quartz matrix, can be fine or coarsely banded. The mineralogy is relatively simple with quartz constituting from 80 to 98 vol % of the rock and dolomite and rare calcite comprise 1-5 vol % of the rock. Interstices between the quartz grains are filled by amphibole (actinolite or grunerite) up to 15 vol %, chamosite up to 5 vol %, plagioclase up to 5 vol %, magnetite up to 2 vol %, sulfide minerals up to 3 vol %, and less frequently carbonaceous matter. Amphibole (the most abundant), chlorite-amphibole, chlorite, and magnetite metasomatic quartzites may be distinguished by the dominant mineral.

Bodies of metasomatic quartzite are weakly zoned, with in some cases, the cores being coarser-grained and nearly mono-mineralic. The zoning of quartzite is more frequently caused by the distribution of amphibole, chlorite, and carbonate and the composition of these minerals. For example, at the Porojarvi location, in the outer zone amphibole is colorless fine-fibrous actinolite (previously it was identified as sillimanite and therefore sillimanite type of quartzite was distinguished) and calcite, whereas in the core the minerals are grunerite and dolomite (Table 1). Grunerite is colorless, pale green to yellowish occurring as regular rhombic crystals and asterisk-like aggregates. In one of the quartzite bodies from Porojarvi, amphibole crystals grow up to 2 cm.

Amphibolite, biotite-chlorite and two-mica schists hosting quartzites are locally carbonated, with newly formed chlorite and biotite, also amphibole (actinolitic hornblende) porphyroblasts are present in them. At the Timofeevsky and Porojarvi locations, host rocks contain porphyroblastic garnet. These rocks may be considered as basification zones related to quartzite. There are zones of weak alteration a few10’s of meters thick and the thickness of highly altered zones, resulting from basification is up to one meter. For example, discontinuous zones of carbonate-chlorite altered rocks with carbonate veinlets was observed at the boundary between chlorite-amphibole quartzite and host carbonate-chlorite schist at the Porojarvi location. A zone of carbonate-chlorite rock with porphyroblasitc hornblende was observed at the boundary with quartzite at the Timofeevsky location.

Some quartzite bodies contain altered xenoliths of host schists and amphibolite. These are carbonate--actinolite rocks with occasional amphibole asterisks. Such xenoliths are lenticular and folded together with quartzite. Quartzite bodies are frequently cut by quartz and carbonate-quartz veins and several generations of veinlets. Complex quartz veins ranging from a few cm to one meter are the most abundant. Quartzite is recrystallized adjacent to the quartz veins, lineation disappears and quartz becomes mosaic and the size of arsenopyrite crystals increases up to 4-5 mm (Timofeevsky and Kontaktovy locations). Late carbonate-quartz and quartz-carbonate veinlets a few mm thick fill fractures and cut both quartzite and earlier quartz veins.

Material migration during the formation of metasomatic quartzite is illustrated by the Timofeevsky location (Table 2, Fig. 6). The formation of quartzite is caused by intensive input of silica. Therefore, quartz content in altered rocks increases up to 90%. Other petrogenic components (Ti, Al, Na, Ca, Mg, K) are nearly removed, their contents in quartzite decrease down to nearly zero. Biotite, muscovite, plagioclase, hornblende, and ilmenite disappear. Only the Fe content does not change during quartzite formation, this element is redistributed into newly formed Fe-rich amphibole (grunerite) and chlorite (chamosite) and in addition, an oxide-sulfide assemblage composed of pyrrhotite, arsenopyrite and/or magnetite was formed. The CO_2 content is 2-3 times more from the outer to inner zone of the alteration column owing to the formation of ankerite-dolomite solid solution series. Sulfur accumulates in outer zone and decreases towards inner zone (Fig. 6).

In the basification zone, the Fe, Mg, Ca, and CO_2 contents increase in the carbonate-chlorite schist with amphibole porphyrobasts against decreasing silica content (Table 1).

According to bulk chemical and spectral quantitative spectral analyses, the contents of minor elements in quartzite are, ppm: up to 140 Cu (up to 520 at Svetlanovsky), up to 110 Ni, below 10 Pb, up to 80 Cr, and below 10 V. These values are lower, as rule, than those in host meta-volcanic rocks.

Oxide-sulfide mineralization was observed in quartzite from all locations except with the Porojarvi location. Minerals are disseminated in quartzite (veinlet-disseminated mineralization was identified only at the Svetlanovsky location). Banded distribution frequently highlights the mineralization. The mineral assemblage is composed sulfides, pyrrhotite, chalcopyrite, pyrite, arsenopyrite, sphalerite, and molybdenite (two last minerals are sporadic) and oxide minerals magnetite, ilmenite, rutile and also native gold was indentified. Pyrrhotite is the dominant mineral, but locally magnetite is more abundant. Arsenopyrite is observed only in the southern band of quartzite (Timofeebsky and Kontaktovy locations) and is extremely irregularly distributed in the rock. It forms chains of crystals within narrow lenticular zones up to 2 cm in thickness and a few 10's cm in length concordant to linearity. In addition arsenopyrite is present in carbonate-quartz stockwork at the Anomalny occurrence. Fine anhedral grains and coarse euhedral crystals are present, the latter are typical of the recrystallized quartzite at the contact with quartz veins and veinlets (Timoveevsky and Kontaktovy locations). The morphology and chemical composition of arsenopyrite has been described in detail by Kalinin et al. (2014).

Gold grades above 1 g/t were measured in the southern quartzite zone at the Timofeevsky and Kontaktovy locations, whereas in the northern zone these grades were only found at the Porojarvi location. At all three locations, gold is related to amphibole quartzite (Table 2). At the Timofeevsky deposit, elevated gold grades were measured in both zones in association with arsenopyrite and quartzite, where only pyrrhotite as sulfide mineral is present. At Porojarvi, gold was identified in sulfide free quartzite (according to whole geochemical analysis, the sulfur content in the rock is below 0.1 wt %). We suggest that this is free gold that fills the interstices between quartz crystals in quartzite. Visible native gold was found at the boundary between scorodite and quartz in the sample with oxidized arsenopyrite. The silver grade, in gold-bearing samples of quartzite, is 0.1-0.5 g/t (Table 1). No significant correlation is observed between gold and silver grades. The Au:Ag ratio in the samples, with gold grade above 0.5 g/t, ranges from 4:1 to 10:1. Inclusions of gold, up to 5 μm in size, were found in arsenopyrite from the carbonate-quartz stockwork in the sample with gold grade 0.5 g/t taken from the Anomalny location (Kalinin et al., 2013). The gold composition was measured on a Leo-1450 scanning electron microscope equipped with a Bruker XFlash-5010 EDS using standard-free method and the QUANTAX 200 program (analyst E.S. Savchenko) is wt %: 79.5 Au and 20.5 Ag, minor elements were not detected.

Albite-carbonate-quartz altered rock at the Zagadka location forms a horseshoe body with the section area of 4 × 5.5 m. This body hosted in carbonate-chlorite schist in the axial part of open antiform that plunges towards the south, with the schist in the core of the metasomatic body. At the surface the dip of host schist in the core drastically changes from near vertical to near horizontal overlapping the southern part of metasomatic body.

The alteration body is zoned: plagioclase-calcite-chlorite schist (initial rock) → biotite-carbonate (calcite and dolomite)-chlorite altered rock → biotite-plagioclase-carbonate and biotite-plagioclase altered rock → dolomite-albite-quartz altered rock → albite-quartz altered rock. The contact of the biotite-plagioclase and dolomite-albite-quartz altered rocks is sharp, caused by not only by a change in mineralogy but by the conversion of schist to massive rock. The boundaries between other zones are gradual. The thickness of individual zones does not exceed a few 10's cm in the southern part of the body and at the inner side of the horseshoe zones of biotite-bearing altered rocks are reduced.

Mica in the altered rocks is hydrobiotite. Interstratified biotite and vermiculite layers result in a low K_2O content in this mineral (Table 2). The chlorite of host rock is chamosite, whereas in altered rocks it is clinochlore. The carbonate of host schist is calcite, whereas in altered rocks calcite is replaced by dolomite (Table 2). Muscovite replacing biotite and tourmaline (schorl) occurring as crystals up to 1 mm in size and oriented along the schistosity are present in the biotite-plagioclase-carbonate alteration.

The change in the chemical composition of rock during the formation of albite-carbonate-quartz alteration is reflected in a regular increase in Si content and decrease in the Na, K, and Al contents, going from the initial rock to outer zone of metasomatic column (Fig. 7). The Mg, Ca, and CO_2 contents increase in the inner zone, caused by dolomitization and then they decrease in the albite-quartz and quartz alterations. The content of minor elements in the altered rocks of the Zgadka location is, ppm: below 100 Cu, Ni, and Zn, below 10 Pb, up to 270 Cr, and up to 80 V. In other words, metasomatic process resulted in the removal of ore elements.

Sulfide mineralization in altered rocks is lacking, with the S content of a few hundredths of a percent. Occasional grains of pyrite (up to 0.3 mm), arsenopyrite (up to 0.7 mm), chalcopyrite, and pyrrhotite (replaced by pyrite) are observed. In the northern part of the horseshoe, the number of specks of gold seen in hand specimen samples (up to 3 kg in weight) reaches a few hundred (up to 400; S.M. Karpov, pers. comm.), whereas in the southern part there are less than 10 specks of gold . This indicates an extremely irregular distribution of gold.

A sample of albite-carbonate-quartz rock consisting of quartz (65%), carbonate (20%), albite-oligoclase (10%), biotite (1-2%), muscovite (< 1%), ore mineral (< 1%) and accessory apatite, tourmaline, rutile, and anatase was taken for isotopic study from the Zagadka location. The Sm-Nd isotopic study of the whole rock, rock-forming and accessory minerals allowed construction of isochron corresponding to an age of 1888 ± 22 Ma (Kalinin et al., 2013), which is consistent, within uncertainty, with that of the meta-volcanic rocks of the Mannel sequence in Southern Pechenga (Skuf'in et al., 2009). This age is also close to the Rb-Sr date of volcanic rocks of the Bragino (1865 ± 58 Ma) and Kaplin (1855 ± 54 Ma) sequences, which likely corresponds to the age of metamorphism. The εNd value of albite-carbonate-quartz rock is positive and indicates mantle (DM) source for initial magmatic melt. On a εNd versus 1/Sr plot (Faure, 1986), the compositions fall into the field of continental basalts.

METHODS

Fluid inclusions were studied with a Linkam THMSG-600 freezing/heating stage equipped with an Olympus BX51 optical microscope, videocamera, and computer at the Institute of Geology of Ore Deposits, Mineralogy, Geochemistry, and Petrography, Russian Academy of Sciences, Moscow, Russia. This allows measurements of phase transition temperatures in inclusions between -196 and 600ºC, observation at high magnification and digital photographs. The composition of salts in fluid inclusions was estimated from the eutectic temperature (Borisenko, 1977) and the salinity was estimated from final melting temperatures of ice according to experimental data of the NaCl-H_2O system (Bodnar and Vityk, 1994). The salinity the aqueous solution in the CO_2-H_2O inclusions was estimated from melting temperature CO_2 hydrates (Collins, 1979). The CO_2 and CH_4 concentrations were estimated from volumetric ratios of phases and the densities of CO_2 and CH_4 in gas phase. Pressure was determined for immiscible fluids from the intersection of the isochore and isotherm (Kalyuzhny, 1982). The salinity and pressure of the fluid was calculated with the FLINCOR program (Brown, 1989).
Bulk inclusion analysis was carried out according to the techniques reported by Kryazhev et al. (2006) at the Central Institute of Geological Exploration for Base and Precious Metals, Moscow, analyst Y.V. Vasyuta. The analyzed samples were 0.5-g of crushed quartz and sphalerite (0.25- to 0.5-mm sieve fraction). Inclusions in quartz and sphalerite were opened at 500 and 350ºC, respectively. The water content was determined on a Tsevet -100 gas chromatograph to calculate the concentration of elements in the hydrothermal solution. In addition, the concentration of CO_2 and CH_4 was determined. Concentrations of Cl, SO_4 and F were determined in solution with ion chromatography on a Tsevet-3006 chromatograph with detection limit of 0.01 mg/L. Concentrations of K, Na, Ca, Mg, and other elements in the water extracts were measured using an Elan 6100 ICP-MS. The gas composition in individual inclusions were determined using Raman spectroscopy with a Jobin Yvon LabRAM HR800 spectrometer at the Institute of Mineralogy and Petrography, Siberian Branch Russian Academy of Sciences in Novosibirsk.

Individual quartz-hosted fluid inclusions were ablated using a Lambda Physik 193 nm ArF excimer laser coupled with an Agilent 7500c ICP-MS Quadrupole instrument at the University of Leeds, Great Britain. The diameter of ablation crater was 25 or 50 μm depending on inclusion size. Fluid inclusions were ablated until the signal from inclusion content returned to background. The laser pulse rate was 5 Hz and the energy on the sample surface was 10 J/cm^2. The ablated material was analyzed on an Agilent 7500c ICP-MS mass spectrometer, which successively analyzed each chosen element. The measurement time (dwell time) for Na, Si, Mg, K, and Ca was 10 ms, for Ag, 20 ms, and for Au, 40 ms. The longer dwell time for Ag and Au was required to attain a better sensitivity for measurements of these elements. The data obtained was processed using the SILLS program (Guillong et al., 2008). Silicate glass standards, NIST 610 and 612, were used for calibration of the chosen elements. Allan et al. (2005) showed the validity of these standards and this approach for the analysis of fluid inclusions.

FLUID INCLUSION STUDY

Fluid inclusions hosted by quartz from the Zagadka, Timofeevsky, and Porojarvi locations were studied. In general the inclusions were larger than 10 μm which makes them suitable for microthermometry. Quartz-hosted inclusions were related to both albite-carbonate-quartz alteration and metasomatic quartzite from various locations.

Three types of fluid inclusions were indentified in quartz (Fig. 8): (1) CO_2-H_2O fluid inclusions, (2) vapor-dominated inclusions, and (3) two-phase liquid-vapor aqueous inclusions. Primary fluid inclusions of types 1 and 2 locally co-exist, which indicates quartz crystallization from, and trapping of, an immiscible fluid.

The microthermometric data from 275 quartz hosted fluid inclusions are summarized in Table 3 and Figs. 6 and 10. The homogenization temperature of the type 1 and 2 primary fluid inclusions in quartz, from the albite--carbonate--quartz altered rock at the Zagadka location (gold grade 5.0 g/t), ranges from 342 to 370°C. The salinity of these inclusions is 0.6-1.0 wt % NaCl equiv. The CO_2 and CH_4 concentrations is between 5.3-8.8 and 0.6-1.1 mol/kg of solution, respectively. The density of the CO_2-H_2O fluid is between 0.97-1.00 g/cm^3. The eutectic temperature of the aqueous fluid at c.-29°C, indicates a predominantly Na dominated fluid with possible K in addition. The eutectic temperatures (too high) are not consistent with significant amounts of Mg, Ca or Fe in the fluid.

The CO_2 phase in primary type 1 and 2 inclusions homogenized to liquid from -30.5 to +11.5°C, and the solid CO_2 melting temperature ranges from -57.4 to -60.2°C. Solid CO_2 melting temperatures below the melting point of pure CO_2 (-56.6°C) indicates the presence of other gases. Raman data shows the presence of minor N_2 and CH_4 up to 14.9 and 1.8 mol %, respectively. Density of vapor phase is 0.85-1.08 g/cm^3.

Fluid pressure estimated from the co-existing types 1 and 2 inclusion in quartz is between 2130-4550 bar and temperatures between 342-370°C.

Secondary fluid inclusions in healed fractures in quartz contain CH_4, which homogenizes between -85.5 to -88.8°C corresponding to a density of 0.23-0.26 g/cm^3.

Secondary type 3 fluid inclusions homogenize between 149-275°C and contain an aqueous solution dominated by Na, but with additional doubly charged cations, possibly Mg, based on a eutectic temperature between -36 and -38°C. The fluid salinity and density are 1.3-5.9 wt % NaCl equiv and 0.76-0.96 g/cm^3, respectively.

The bulk chemical composition of fluids in inclusions from quartz of carbonate-quartz altered rock at the Zagadka location are given in Table 4 and Fig. 11.

The contents of the major cations in the fluid are, g/kg of H_2O: 7.1 Na, 8.0 Ca, and 6.5 Mg. Potassium is minor, 0.75 g/kg of H_2O. The appreciable concentrations of the following constituents were measured, g/kg of H_2O: 77.5 HCO_3^{2-}, 166 CO_2, 8.5 CH_4 (8.5), 0.9 B, and 0.05 Br. In addition, many minor elements were measured, g/kg of H_2O: 52 As,1.9 Li, 4 Rb, 0.66 Cs, 39 Sr, 2.1 Mo, 1.26 Sb, 0.71 Cd, 0.07 Bi, 0.47 Ga, 1.26 Ge, 23.9 Mn, 0.43Co, 4.7 Ni,0.52 Cr, 0.02 Y, 0.07 Zr, 0.24 Sn, 4.4 Ba, 3.6 W, 0.617 Au, 0.22 Tl, and 0.006 REE.

The homogenization temperature of the type 1 and 2 primary fluid inclusions in quartz from metasomatic quartzite at the Timofeevsky and Porojarvi locations (gold grade 8.1-36.6 g/t) ranges from 242 to 336°C. The salinity of solutions from these inclusions is 0.4-3.8 wt % NaCl equiv. The CO_2 and CH_4 concentrations in mineralizing fluid reached 4.6-7.3 and 0.6-0.9 mol/kg of solution, respectively. Density of CO_2-H_2O fluid is 0.98-1.07 g/cm^3. Based on the eutectic temperature (-29 to -33°C), Na and other cations such as K and possibly Mg chlorides are present in mineralizing fluid.

CO_2 in primary inclusions of type 2 syngenetic to the type 1 fluid inclusions homogenized into liquid at -12.2 to +18.3°C. $CO_{2,}$ ice melting temperature ranges from -57.1 to -60.9°C. As before temperatures lower than the melting point of pure CO_2 (-56.6°C) indicates other minor gas components in CO_2. Raman data (Table 5) show minor N_2 and CH_4 up to 17.3 and 1.9 mol %, respectively. The density of vapor phase is 0.79-1.00 g/cm^3. The fluid pressure estimated from co-existing type 1 and 2 inclusions trapped from immiscible fluid in quartz of metasomatic quartzite is between 1200-2580 bar and 242-336°C.

Secondary type 1 fluid inclusions found in quartz from the Porojarvi location homogenize between 149-275°C and the fluid salinity is 3.2 wt % NaCl equiv. The CO_2 and CH_4 concentrations in these fluids are 1.5 and 0.1 mol/kg of solution, respectively and the density of CO_2-H_2O fluid is 1.04 g/cm^3. The eutectic temperature (-33°C), is the same as the primary fluid inclusions and indicates similar cation and anion components.

Secondary fluid inclusions of type 3 in quartz from the Timiveevsky location homogenize at 153°C, but here the eutectic temperature (-49°C) is significantly lower. The fluids will again be dominated by Na but there may be appreciable amounts of Ca present in addition. The fluid salinity and density are 17.1 wt % NaCl equiv and 1.04 g/cm^3, respectively.

The bulk chemical composition of fluids in inclusions from quartz of the metasomatic quartzite is given in Table 4 and Fig. 11.The major cations in the fluid are, g/kg of H_2O: 12.5-6.2 Na, 4.2-1.1 Ca, and 2.3-1.2 Mg, K is low, 0.3-0.2 g/kg of H_2O. Appreciable amounts of the following were also present, g/kg of H_2O: 7.5-0.3 Cl^-, 45.0-25.6 HCO_3^{2-}, 661-277 CO_2, 11.5-1.7 CH_4, 0.45-

0.29 B, and 0.33-0.32 Br. In addition, other minor elements were measured, g/kg of H_2O: 41-14 As, 0.9 Li, 2.0-0.5 5 Rb, 0.32-0.2 Cs, 53-24 Sr, 5.0 Mo, up to 0.15 Cu, up to 0.03 Ag, 0.50-0.42 Sb, 0.31-0.12 Pb, 0.02 Bi, 0.01-0.004 U, 0.10 Ga, 0.86-0.68 Ge, 13.3-2.2 Mn, up to 8.3 Fe, 0.09-0.07 Co, 1.9 Ni, up to 0.32 V, 0.32 Cr, 0.05 Y, 0.02 Zr, 0.15 Sn, 16.0-15.4 Ba, 7.3-3.3 W, 0.22-0.06 Hg, 0.03 Tl, and 0.04 REE.

The LA-ICP-MS data for 43 individual fluid inclusions of type 1 from metasomatic quartzite are given in Table 6. The ablation profile across one inclusion is shown in Fig. 12. Concentrations of the major cations are, ppm: 983-4001 Na, 1055-6075 K, 59-294 Mg, and 442-3176 Ca. Concentrations of Ag and Au are 11.0-34 and 4.6-202 ppm, respectively.

DISCUSSION

The chemical composition, mineralogy, and zoning of carbonate-albite-quartz bodies suggest they had a hydrothermal metasomatic origin. Strongly elongate crystals of quartz,up to 1 cm long, suggests their formation was under compression at the prograde stage, or peak of regional metamorphism. This is supported by folding of both metasomatic units and host rocks. As is known ductile deformation usually occurs during retrograde metamorphism. The dating of albite-carbonate-quartz altered rock at the Zagadka occurrence (1888 ± 22 Ma, Kalinin et al., 2013) and fluid inclusion data, which gives trapping PT-conditions close to those of regional metamorphism in the Pechenga structure are consistent with the formation of these altered rocks during prograde metamorphism.

The characteristic feature of the rock chemical composition evolving during the formation of acidic alteration is highly mobile nature of Ti and Al, which are typically immobile in metasomatic processes (Zharikov et al., 1998). The TiO_2 content is three to four times lower in the acidic altered rocks, but is higher in the basification zoned. The Al_2O_3 content in metasomatic quartzite and albite-carbonate-quartz rock is highly depleted, almost completely removed, and two times lower when compared to the primary rocks. This feature of the chemical composition of the altered rocks may be caused by acidic hydrothermal solutions. It was established that Al_2O_3 solubility is six orders greater when the solution acidity increases from near-neutral to extremely acidic, whereas the SiO_2 solubility only slightly increases (Zharikov et al., 1998).

On the basis of the data obtained (evolution trends of salinity and pressure depending on temperature) all the gold occurrences at Porojarvi are part of the same hydrothermal system. Slightly higher-temperature gold-bearing albite-carbonate-quartz altered rock was formed from the least mineralized fluids at the highest pressure. Fluids responsible for the formation of albite--carbonate-quartz altered rock at the Zagadka occurrence are enriched in HCO_3^{2-}, K, Ca, Mg, As, Li, B, Rb, Cs, Sb, Cd, Ge, Co, Ni, Cr, Au, and Tl and are depleted in CO_2, Cl, Br, and Ba when compared to those responsible for the formation of metasomatic quartzite. In contrast, the last are enriched in Br, Ag, Sr, Mo, Cu, Pb, Fe, V, W, Hg, and REE.

The formation of these gold occurrences in volcanic and sedimentary rocks during regional metamorphism, during the continent-continent collision, an absence of obvious association with any magmatic complexes, the relation of gold occurrences to faults, a high Au:Ag ratio and the content of other metals (gold-only type) would be most consistent with these occurrences being classified as orogenic type of gold deposits (Groves et al., 1998). The specific feature of the studied occurrences is the association of gold mineralization with the altered rocks rather than carbonate-quartz veins (with the exception of the Anomalny occurrence). Orogenic style gold mineralization in greenschist facies metamorphic rocks is usually associated with carbonate-quartz veins, whereas the gold-bearing metasomatic zones are hosted in higher grade metamorphic rocks.

The mineralizing fluids at the Porojarvi area (Fig. 13) are consistent with those commonly found in metamorphic orogenic gold deposits. The chemical composition, low salinity, high CO_2 content, and physicochemical parameters what are found elsewhere (Ridley and Diamond, 2000; Bodnar et al., 2014). The Au content in the fluids (4.6--202 ppm) is higher than the most values published for the gold deposits worldwide (Naumov et al., 2014; Garofalo et al., 2014), but it should be noted that here the gold is present as gold particles and not now in solution. LA-ICP-MS ablation of the inclusion shows a spikey signal for gold (indicating particles), therefore during analysis these may be ablated without being measured and the data give low ppm values. Where the particles are ablated during the measurement period the concentration will be higher. Therefore, we suggest gold concentrations towards the higher values may be more representative of what is in the inclusions. Prokofiev et al. (2016) also reported high gold concentration (300-1500 ppm) in deep fluids from the Kola Superdeep Borehole located close to Porojarvi. Such high Au concentration cannot be present in regular solution (Pokrovski et al, 2014) and again the LA-ICP-MS signal indicated ablation of particulate gold. However, high gold concentrations are very real in colloidal solution of gold (Saunders and Burke, 2017). It is possible that deep-seated gold-bearing fluids at the bottom of the Kola Superdeep Borehole were the source for gold in the gold occurrences of the Pechenga structure.

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Table 1. Electron microprobe data for metasomatic minerals of the Porojarvi gold area

Sample	P-49	P-52	732/6	732/5	P-13	P-52	P-13	735/7	P-39	P-39	P-35
Component	1	2	3	4	5	6	7	8	9	10	11
SiO_2	55.36	50.50	49.51	52.19	41.26	23.60	23.67	24.28	23.61	34.59	36.34
TiO_2	n.d.	n.d.	n.d.	0.05	0.38	n.d.	0.07	0.09	0.06	1.87	1.92
Al_2O_3	0.36	0.21	0.17	0.44	16.18	18.00	21.36	20.78	20.28	16.71	17.82
FeO	15.76	32.14	42.94	36.17	18.68	33.10	25.46	27.37	22.01	17.16	20.20
MgO	14.51	11.33	3.67	8.53	6.49	9.97	13.97	12.78	16.71	11.74	8.89
MnO	0.07	0.31	0.07	0.36	0.16	0.06	0.11	0.09	0.09	0.03	0.00
CaO	12.40	0.76	0.20	0.27	10.91	n.d.	0.03	n.d.	n.d.	0.09	0.18
Na_2O	n.d.	0.09	n.d.	n.d.	1.74	n.d.	n.d.	n.d.	n.d.	0.13	0.09
K_2O	0.02	n.d.	n.d.	n.d.	0.39	n.d.	n.d.	n.d.	0.02	8.74	9.76
V_2O_3	n.d.	n.d.	0.02	0.02	0.14	n.d.	n.d.	n.d.	0.06	0.10	0.28
Cr_2O_3	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	0.05	0.03	0.30	0.22	0.50
Total	98.48	95.37	96.58	98.03	96.34	84.74	84.72	85.42	83.14	91.38	95.98
Formula coefficients											
Si	7.98	7.94	8.08	8.07	6.33	2.72	2.60	2.67	2.60	3.04	3.08
Ti	n.d.	n.d.	n.d.	0.01	0.04		0.01	0.01	0.01	0.12	0.12
Al	0.03	0.02	0.02	0.04	1.46	1.22	1.38	1.34	1.32	0.86	0.89
Fe	1.90	4.23	5.86	4.67	2.40	3.19	2.34	2.51	2.03	1.26	1.43
Mg	3.12	2.66	0.89	1.97	1.48	1.71	2.29	2.09	2.75	1.54	1.12
Mn	0.01	0.04	0.01	0.05	0.02	0.01	0.01	0.01	0.01	n.d.	0.00
Ca	1.92	0.13	0.03	0.05	1.79					0.01	0.02
Na		0.01			0.26					0.01	0.01
K					0.04					0.49	0.53
V					0.01					n.d.	0.01
Cr									0.01	0.01	0.02

n.d. not detected. (1) Actinolite, (2-4) grunerite, (5) hornblende, (6-8) chamosite, (9) clinochlore, (10--11) hydroxtbiotite. (P-49) Calcite-actinolite quartzite, Porojarvi location; (P-52) chlorite-grunerite quartzite, Porojarvi location; (732-5, 732-6) the same, Timoveevsky location; (P-13) amphibole altered rock, Timoveevsky location; (735-7) chlorite schist, Zagadka location; (P-39, P-35) Porojarvi location. The chemical compositions of minerals were determined on a CAMECA MS-46 electron microprobe operated at accelearation voltage 22 kV, current intensity 30-40 nA, Analyst E.E. Savchenko. The following standards and analytical lines: lorenzenite (NaKα, TiKα), forsterite (MgKα), $Y_3Al_5O_{12}$ (AlKα), wollastonite (SiKα, CaKα), wadeite (KKα), chromite (CrKα), $MnCO_3$ (MnKα), hematite (FeKα), pure metal (VKα). Counting time for peak and bakground is 40 s and 20 s from each side of the peak. The formule of amphiboles, chlorites, and biotite are calculated on the basis of 23, 14, and 12 O atoms, respectively

Table 2. Chemical composition of metasomatic quartzite and albite-quartz-carbonate altered rock of the Porojarvi area (wt % and ppm for major and minor components, respectively)

Sample	732/7	P-5	P-4	P-8	P-14	P-15	732/4	P-13	P-49	P-48	P-52	735/7	735/8	P-37	735	P-38
Component	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SiO_2	66.66	87.68	91.54	90.20	92.30	89.69	65.04	44.55	87.70	89.54	89.06	42.69	57.49	60.67	66.68	81.92
TiO_2	0.43	0.15	0.07	0.11	0.00	0.17	0.82	1.73	0.12	0.12	0.14	2.36	0.57	0.54	0.64	0.15
Al_2O_3	14.86	0.00	0.00	0.00	0.20	0.00	9.86	13.00	0.10	0.00	1.01	11.18	16.91	6.43	5.72	2.95
Fe_2O_3	0.00	1.48	0.71	0.52	0.00	1.53	0.37	2.39	0.00	0.00	0.39	3.11	7.33	0.48	0.00	0.00
FeO	5.23	4.93	4.06	5.44	5.02	6.81	8.62	10.42	3.92	4.51	4.14	11.05	2.00	4.61	5.30	3.27
MnO	0.05	0.02	0.01	0.02	0.02	0.02	0.42	0.23	0.02	0.02	0.03	0.24	0.23	0.13	0.12	0.09
MgO	1.80	0.02	0.03	0.23	0.02	0.39	3.97	5.92	1.72	1.27	1.09	6.25	1.05	3.13	2.35	1.54
CaO	1.34	0.00	0.00	0.00	0.03	0.17	0.50	8.92	3.25	2.16	0.96	7.55	0.81	8.24	5.98	3.19
Na_2O	2.46	0.02	0.03	0.03	0.06	0.03	2.38	2.43	0.03	0.03	0.03	2.10	7.85	3.29	2.72	1.66
K_2O	4.04	0.01	0.01	0.01	0.01	0.01	0.14	0.30	0.04	0.02	0.02	0.15	1.27	0.27	0.21	0.12
H_2O^-	0.29	0.18	0.16	0.20	0.16	0.06	0.76	0.24	0.00	0.00	0.01	0.32	0.49	0.11	0.27	0.14
LOI + H_2O^+	2.24	3.82	0.93	1.35	0.24	0.20	5.68	3.71	0.99	0.52	1.02	5.50	2.89	1.47	2.40	1.48
S_{tot}	0.05	0.71	1.37	1.02	0.49	0.07	0.15	0.03	0.06	0.08	0.07	0.04	0.04	0.05	0.06	0.06
P_2O_5	0.09	0.03	0.03	0.02	0.00	0.02	0.06	0.22	0.03	0.03	0.04	0.19	0.06	0.23	0.05	0.14
F	0.050	0.004	0.004	0.005	0.004	0.004	0.015	0.430	0.008	0.004	0.005	0.035	0.022	0.019	0.000	0.012
Cl	0.010	0.004	000.4	0.000	0.007	0.012	0.004	0.004	0.004	0.000	0.004	0.010	0.004	0.004	0.005	0.011
CO_2	0.10	0.19	0.13	0.10	0.42	0.39	0.10	5.74	1.99	1.62	1.01	6.86	0.63	10.18	7.03	3.26
Total	99.70	99.25	99.09	99.26	98.98	99.58	98.89	100.26	99.98	99.92	99.03	99.64	99.65	99.85	99.54	99.99
Au	n.d.	6.55	0.074	0.92	1.16	0.005	0.004	0.008	0.006	0.004	2.05	0.004	0.004	<0.004	0.066	0.004
Ag	n.d.	0.56	0.28	0.25	0.26	0.12	0.20	0.18	0.07	0.09	0.11	0.15	0.11	0.10	0.18	0.11
Cu	n.d.	<100	130	100	100	<100	520	<100	100	<100	<100	<100	100	<100	<100	100
Ni	n.d.	<100	110	<100	100	100	<100	100	<100	<100	<100	<100	150	100	100	100
Co	n.d.	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
Li_2O	43.00	0.30	0.30	0.30	0.60	0.30	33.00	42.00	0.80	0.40	2.10	43.00	11.00	5.70	4.30	1.80
Rb_2O	140.00	1.60	2.50	1.80	2.20	1.20	2.00	2.10	1.30	1.30	1.30	2.40	22.00	2.40	3.30	1.90
Cs_2O	2.60	1.00	0.70	1.60	1.20	0.00	0.98	0.60	1.30	0.80	1.30	0.48	0.63	1.60	1.30	0.42

Bulk chemical analysis was performed at the analytical laboratory of the Geological Institute, Kola Scientific Center, Russian Academy of Sciences. (1-8) Timofeevsky location: muscovite--biotite plagioschist of host sequence (732/7), amphibole metasomatic quartzite (P-5-P14), magnetite metasomatic quartzite (P-15), rocks from basification zone (732/4, P-13), carbonaceous schist (732/4), and carbonate--chlorite schists with porphyroblastic hornblende (P-13); (9--11) metasomatic quartzite replacing amphibolite, Porojarvi location: actinolite (P-48, P-49) and chlorite-grunerite(P-52); (12-16) carbonate-albite-quartz altered rocks, Zagadka location: calcite-chlorite schist (primary rock) (735/7), biotite-albite altered rock (735/8), dolomite-albite-quartz altered rock (P-37, 735), and albite-quartz altered rock (P-38).

Table 3. Microthermometric data for individual fluid inclusions in quartz at the Porojarvi prospect

Number of sample	Type of inclusion *	**n**	$T_{hom.}$, °C	$T_{eut.}$, °C	$T_{ice\ melt.}$, °C	T_{melt} CO_2, °C	T_{hom} CO_2, °C	T_{melt} clathrate °C	Salinity, wt % equiv NaCl.	CO_2 mole/kg	CH_4 mole/kg	Density, g/cm^3	Pressure, bar	**(P_{H2O} + P_{vapor})/ P_{H2O}**
Zagadka (*albite-carbonate-quartz altered rock)*														
Pl 600/6	1 P	16	342-370	-29	-5.2 -4.7	-58.1	11.9… 8.1 L	9.5	0.6-1.0	8.8-5.3	1.1-0.6	0.97-1.00	2130-4550	14.9-23.0
	2 P	61	-	-	-	-57.4… -60.2	11.5… -30.5 L	-	-	-	-	0.85-1.08		
	2 S	18	-	-	-	-	-85.5… -88.9 L	-	-	-	-	0.23-0.26	-	-
	3 PS	7	275	-36	-0.8	-	-	-	1.3	-	-	0.76	-	-
	3 S	15	149	-38	-3.7	-	-	-	5.9	-	-	0.96	-	-
Timofeevsky(*metasomatic quartzite*)														
Pl 610	1 P	9	242-274	-29… -31	-4.5… -6.9	-57.6… -57.7	14.2… 17.3 L	9.6--9.8	0.4--0.8	4.6-6.2	0.6-0.8	1.02	1200-2580	38.8-47.8
	2 P	19	-	-	-	-57.9… -58.5	18.3…-12.2 L	-	-	-	-	0.79-1.00		
	3 S	12	153	-49	-13.2	-	-	-	17.1	-	-	1.04	-	--
Pl 610/2	1 P	19	276-288	-30… -33	-4.1… -5.4	-59.9	7.2… 9.2 L	10.7	0.4	5.5-5.9	0.8-0.9	0.98-0.99	1920-2270	33.4-34.3
	2 P	22	-	-	-	-59.9… -60.9	-2.1… +4.6 L	-	-	-	-	0.90-0.94		
Porojarvi (*metasomatic quartzite*)														
Pl 602/2	1 P	31	296-336	-30… -31	-6.7… -7.0	-57.1… -57.3	4.8… 13.6 L	8.1-8.7	2.6--3.8	6.5--7.3	0.7	1.04-1.07	1720-2570	19.3-22.4
	2 P	28	-	-	-	-57.1… -57.4	12.7… -0.8 L	-	-	-	-	0.84-0.93		
	3 P-S	5	176	-33	-0.5	na	24.3 L	8.4	3.2	1.5	0.1	1.04	-	-

(*) Fluid inclusion type: (1) CO_2--H_2O--salt, (2) vapor, (3) H_2O--salt. Genetic type of fluid inclusion: (P) primary, (PS) pseudosecondary, and (S) secondary. (L) CO_2 homogenization into liquid. n denotes number of inclusions. na. not analyzed

Table 4. Chemical composition of mineral-forming fluids of the Porojarvi prospect

Location	Zagadka	Timofeevsky	Porojarvi
Metasomatic rock	*Albite-carbonate quartz*	*quartzite*	
Component	PL600/6	PL610	PL602/2
Major component, g/kg H_2O			
CO_2	166.44	276.96	661.10
CH_4	8.54	11.48	1.70
Cl^-	<1.00	7.50	0.33
SO_4^{2-}	-	-	-
HCO_3^-	77.52	44.99	25.62
Na	7.14	12.49	6.23
K	0.75	0.32	0.16
Ca	7.95	4.23	1.06
Mg	6.52	2.27	1.21
Minor component, 10^{-3} g/kg H_2O			
Br	46.2	320.0	334.7
As	52.1	13.9	40.6
Li	1.9	0.9	0.87
B	909	448	293
Rb	3.99	2.00	0.55
Cs	0.66	0.32	0.26
Sr	39.0	152.3	23.7
Mo	2.09	5.02	-
Cu	-	-	0.15
Ag	-	0.03	-0
Sb	1.26	0.42	0.50
Cd	0.71	-	-
Pb	-	0.12	0.31
Bi	0.07	0.02	0.02
U	-	0.01	0.004
Ga	0.47	-	0.10
Ge	1.26	0.86	0.68
Mn	23.9	13.3	2.19
Fe	-	8.3	-
Co	0.43	0.07	0.09
Ni	4.7	1.91	-
V	-	0.32	-
Cr	0.52	0.32	-
Y	0.02	0.05	-
Zr	0.07	-	0.02
Sn	0.24	-	0.15
Ba	4.39	15.4	16.0
W	3.61	7.34	3.26
Au	0.617	-	-
Hg	-	0.22	0.06
Tl	0.22	-	0.03
REE	0.006	-	0.039
CO_2/CH_4	19.5	24.1	4.1
Na/K	9.5	38.5	39.3

K/Rb	188.1	161.5	286.7

Table 5. Raman data for vapor inclusions (mol %)

Sample, inclusion	CO_2	N_2	H_2S	CH_4	Total
Zagadka (*albite--carbonate--quartz altered rock)*					
600 1*	83.8	14.5	-	1.8	100.1
600 2*	83.9	14.9	-	1.2	100.0
600/2 1*	99.2	0.7	-	0.1	100.0
600/2 2*	99.1	0.8	-	0.1	100.0
600/2 3*	100.0	-	-	-	100.0
Timofeevsky (*metasomatic quartzite*)					
610/2 1*	80.8	17.3	-	1.9	100.0
610/2 2*	83.7	14.4	-	1.8	99.9

(*) number of inclusion

Table 6. Element ratios (wt /wt) on the basis of LA-ICP-MS data and calculated Ag and Au content (ppm) in fluid inclusions

Sample	Salinity wt. %	Na/K	Mg/K	K/K	Ca/K	Ag/K	Au/K	Ag	Au
Porojarvi (metasomatic quartzite)									
602/2 *(17)	3.2			1	0.537	<0.017	0.087	<103	536
		1.268	0.066	1	0.610	<0.006	<0.003	<38	<19
				1	0.177	<0.009	<0.005	<56	<28
		1.289	0.045	1	0.670	<0.003	<0.001	<16	<8
		0.325	0.033	1		<0.001	0.004	<9	24
				1	0.857	<0.004	<0.002	<21	<10
				1	0.625	0.004	<0.003	28	<16
				1		0.009	0.009	53	58
		0.856	0.056	1	0.257	0.007	0.024	43	151
				1	0.729	0.006	0.090	35	558
		0.345	0.024	1	0.415	0.007	0.014	43	89
		0.434		1	0.761	0.004	0.013	23	81
		0.569		1	0.670	0.004	0.004	24	24
		0.478	0.040	1	0.460	0.006	0.038	38	238
		0.509	0.047	1	0.285	0.003	0.055	21	337
		0.614	0.078	1	0.264	<0.004	0.008	<23	49
		0.559		1		<0.003	0.047	<18	290
Average		0.659	0.048	1	0.523	0.006	0.033		
Standard deviation		0.338	0.018	0	0.215	0.002	0.031		
Relative standard deviation, %		51.3	36.5	0	41.2	32.5	94.2		
Average, ppm		4001	294	6075	3176			34	202
Timofeevsky (metasomatic quartzite)									
610 *(26)	0.6	1.069	0.066	1	0.163	0.037	<0.0029	36	<3
		0.351	0.034	1	0.194	<0.001	0.0025	<1	2
		1.498	0.042	1	0.586	<0.004	<0.0020	<4	<2
				1	0.526	<0.0004	0.0006	<0.4	1
		0.323		1	0.394	<0.0004	<0.0002	<0.4	<0.2
		0.731	0.078	1	0.568	<0.003	<0.0013	<3	<1
		0.884	0.030	1	0.415	<0.002	<0.0011	<2	<1
		1.490		1	0.196	<0.0015	<0.0008	<1	<0.8
		1.113		1	0.267	<0.0007	0.0046	<1	4
				1		<0.0011	0.001	<1	1
				1	0.458	<0.0011	<0.0008	<1	<0.8
				1	0.457	<0.0011	0.002	<1	2
		0.604	0.059	1	0.357	0.001	0.0016	1	2
				1		0.025	0.010	25	10
				1		<0.0013	0.003	<1	3

		0.272	0.047	1	0.369	<0.0004	<0.0002	<0.4	<0.2
		1.102		1	0.736	<0.0008	0.0036	<1	3
				1	0.106	<0.0005	0.010	<0.5	10
		0.538	0.067	1	0.296	<0.0005	0.003	<0.5	3
		1.116		1	0.204	0.002	0.011	2	11
		0.996		1	0.485	<0.0009	0.006	<1	6
				1	0.541	0.002	0.002	2	2
				1	0.477	0.0007	0.002	1	2
			0.060	1	0.585	<0.0013	0.013	<1	13
		1.552		1	0.706	<0.0027	<0.0017	<3	<2
		1.266	0.076	1	0.544	<0.0014	<0.0009	<1	<1
Average		0.932	0.056	1	0.41	0.011	0.0048		
Standard deviation		0.4239	0.0168	0	0.1743	0.0158	0.0040		
Relative standard deviation, %		45.5	30.1	0	41.6	139.8	84.5		
Average, ppm	0.6	983	59	1055	442			11.0	4.6

*Number of studied inclusions is in parentheses.

FIGURE CAPTIONS

Fig. 1. Main structures in the Pechenga-Imandra-Varzuga greenschist belt, after Melezhik and Sturt (1994). (1) Polmak, (2) Pasvik, (3) Pechenga, (4) Imandra--Varzuga, (5) Ust-Ponoi. Box depicts location shown in Fig. 2.

Key:
Баренцево→Barents Sea;
100 км-->100 km;
Белое→White Sea.

Fig. 2. Scheme of main geological and structural elements of the Lapland-Pechenga district, simplified after Seismological model… (1997). (1-3) Paleoproterozoic plutons: (1) granite and granodiorite of the Araguba Complex and Vinospaa, (2) granite and granodiorite of the Kaskeljarvr, Shuini, and Ruosula Cupola, (3) Naiden granite; (4-6) Paleoproteozoic structural complexes: (4) Northern Pechenga zone, (5) Southern-Pechenga zone, (6) Lapland granulite complex; (7) Inari terrane; (8-14) Neoarchean structural complexes of the Servaranger-Kola terrane; (8) Svanvik, (9) Garsio, (10) Brannfillet, (11) Bjernvatn, (12) Varanger, Kirkenes, and Hutojavr, (13) Jarfjord-Kola, (14) Hompen; (15) thrusts; (16) steep faults; (17) line of section.

Key
25 км-->25 km
С→N.

Fig. 3. Sketch section along the Pechenga ore district, simplified from the Seismological model…(1997). (1) Proterozoic plagiogranite and granodiorite; (2-3) Sothern Pechenga zone: (2) meta-andesite, (3) meta-basalt and schists; (4--7) Northern Pechenga zone: (4) Ni-bearing gabbro-wehrlite intrusions, (5) meta-volcanics rocks of the Pilgujavr Group, (6) meta-sedimentary rocks o fthe main productive sequence, (7) metavolcanic rocks of the Kolasjok, Kuetsjarvi, and Akhmalakhta Groups; (8) Archean Complex; (9) gneisses of the Talya block; (2) faults; (13) shear zones.

Key:
ЮЗ→SW;
СВ→NE;
10 км→10 km.

Fig. 4. Geological sketch map of the Southern Pechenga zone, after Akhmedov et al. (2004) and Vorinyaev (2008). (1) Southern Pechenga Complex of small meta-gabbro, meta-dolerite, and

meta-pyroxenite bodies; (2) Poritash Complex of subvolcanic meta-andesite and meta-dacitic andesite; (3) complex of small subvolcanic meta-andesite bodies; (4) plagiogranite, granodiorite, and diorite of the Shuoni-Kaskeljavr Complex; (5) gabbro and gabbro-norite of the Kaskam Complex and amphibolite replacing them; (6) Kallojaur sequence: andesitic tuff, tuffaceous sandstone, and tuffaceous gravel-stone, sericite and sericite-carbonate schists partly enriched in carbonaceous matter and hosting lenticular andesite, basalt, and picritic basalt flows; (7) Bragino sequence: basalt, ferrobasalt, picrobasalt pillow lavas, andesitic to picrobasalt tuffs intercalated with carbonaceous carbonate-bearing schists and meta-tuffites; (8) Kaplin sequence: andesite-dacite and andesite-basalt meta-volcanics rocks intercalated with intermediate to felsic tuff, tufacceous siltstone, and tuffaceous sandstone; (9) Mennel sequence: massive and pillow lavas of tholeiite-basalt series with intercalations of tuff and carbonaceous schist; (10) Kasesjok sequence: sericite, sericite-biotite, biotite-sericite-chlorite schists with tuffaceous conglomerate at the bottom; (11) Peschanoozero sequence: schistoze amphibolite and meta-basalt with rare intercalations of basaltic andesite, picrite, tuff, and mafic tuffite; (12) Talya sequence: amphibolite-meta-basalt, two-mica and biotite gneisses (meta-sedimentary rocks) with intercalations of intermediate to felsic meta-tuffs; (13) Suppvar sequence: monotonous homogenous basalt with horizon of volcanomictic meta-sandstone; (14) Matert Formation: basalt flows with thin lenses of mafic tuffs; (15) steep faults; (16) reverse faults and thrusts; (17-20) gold mineralization in: (17) massive sulfides, (18) metasomatic quartzite and muscovite-carbonate-quartz altered rock (beresite), (19) carbonate-quartz veinlet zones; (20) albite-carbonate-quartz altered rock (aicite). Box depicts the Porojarvi area.

Key:
озеро→lake
оз→lake;
2 км→2 km;
С→N.

Fig. 5. Geological sketch map of the Porojarvi area. (1) Kaplin sequence: meta-dacitic andesite, its tuff and tuffite; (2) meta-basaltic andesite and its tuff, and partly carbonaceous meta-sandstone and meta-siltstone; (3) Kasesjok sequence: meta-sandstone, meta-siltstone, and meta-pelite;(4-5) Peschanoozero sequence: meta-basalt and meta-andesitic basalt, (5) horizons of tuffaceous and sedimentary rocks; (6) meta-sedimentary rocks of the Talya sequence: biotite and two-mica gneisses and schists; (7) meta-gabbro and meta-dolerite of the Southern Pechenga Complex of small intrusions; (8) steep faults; (9) reverse faults and thrusts; (10) locations of metasomatic quartzite; (11) locations of gold-bearing carbonate-quartz veinlets; (12) locations of

albite-carbonate-quartz altered rocks (aicite). Numerals are locations (1) Timofeevsky, (2) Anomalny, (3) Zagadka, (4) Kontaktovy, (5) Svetlanovsky, (6) Istok, and (7) Porojarvi.
Key
оз. Пороярви→Porojarvi Lake
1 км→1 km;
С→N.

Fig. 6. Migration of elements during the formation of metasomatic quartzite at the Timofeevsky location. Number of atoms of chemical elements in 10000 $Å^3$ of rock volume is shown. Calculated according to Kazitsyn and Rudnuk (1978).
Key:
общ→tot.

Fig. 7. Migration of elements during the formation of albite-carbonate-quartz altered rock Zagadka location.
Key:
общ→tot.

Fig. 8. Photomicrographs of fluid inclusions in quartz of the Porojarvi prospect. (a, b) Type 1 CO_2--H_2O inclusions: (a) +20°C, (b) +3°C; (c, d) type 2 vapor inclusions with dense CO_2: (c) +20°C, (d) -15°C; (e, f) type 2 secondary inclusions with methane: (e) +20°C, (f) -90°C; (g, h) type 3 two-phase inclusions of aqueous solutions. Scale bar 20 μm.
Key:
(а)→(a);
(б)→(b);
(в)→(c);
(г)→(d);
(д)→(e)
(е)→(f);
(ж)→(g);
(з)→(h);
20 мкм→μm.

Fig. 9. A temperature versus pressure plot for mineralizing fluids at the Porojarvi prospect. Locations: (1) Zagadka, (2) Timofeevsky, (3) Porojarvi.

Key:

Альбит→Albite-carbonate-quartz altered rock;

Метасоматические→Metasomatic quartzite;

P, бар→P, bar

Fig. 10. A temperature versus salinity plot for mineralizing fluids at the Porojarvi prospect. Locations: (1) Zagadka, (2) Timofeevsky, (3) Porojarvi.

Key

C, мас %-->Salinity, wt % NaCl equiv.

Fig. 11. Chemical composition of mineralizing fluids at the Porojarvi prospect. Locations: (1) Zagadka, (2) Timofeevsky, (3) Porojarvi.

Key:

C, г/кг→Concentration, g/kg H_2O

Fig. 12. Ablation profile of the type 1 fluid inclusion from sample 602/2 containing 21 ppm Ag and 337 ppm Au. The spikes of the gold signal indicate solid particles (gold is not in solution) and the signals are within the area of the potassium peak which indicates the ablation of the fluid inclusion contents in solution..

Key:

Сигнал→Signal;

Время→Ablation time, s.

Fig. 13. Compositions of mineralizing fluids of the Pechenga belt (asterisks) on the triangular diagram for fluid compositions of the orogenic gold deposits (Bodnar et al., 2014).

Key:

200 МПа→200 MPa.