

Geology, mineralization, fluid inclusion, and stable isotope characteristics of the Sinyukhinskoe Cu-Au skarn deposit, Russian Altai, SW Siberia



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ABSTRACT

The Sinyukhinskoe deposit (> 100 t Au with average 9.2 g/t Au) is situated in the Altaid orogenic system and is part of the regional system of Devonian-Carboniferous Cu-Au to Au-Cu porphyry, skarn and other deposits. Productive plutonic suites were emplaced in a Devonian subduction-related continental magmatic arc setting, with its further evolution toward a late- and post-collisional environment in the late Devonian-Carboniferous. The deposit is related to a magnetite-series, I-type multiphase pluton, with the evolution of the intrusive phases from early gabbroic through diorite-granodiorite to the late granitic phases. The igneous rocks belong to medium-K calc-alkaline series or are transitional from medium- to high-K calc-alkaline varieties. Prior to granitic phases, this evolution was interrupted by the intrusion of intramineral high-K mafic dikes exhibiting a shoshonitic affinity.

The deposit is characterized by the development of abundant andradite-rich garnet and wollastonite in prograde and retrograde skarns, locally together with magnetite and bornite. The subsequent propylitic (epidote-chlorite-amphibole-albite-calcite-quartz, locally with clinozoisite and prehnite) alteration assemblages bear more intense Cu mineralization (chalcopryrite, bornite, locally tennantite) and high fineness (~940–910‰) native gold. Later phyllic (quartz-sericite to quartz-sericite-chlorite) alteration assemblages comprise the most intense intermediate-fineness (910–880‰) native gold and Cu (bornite, chalcocite) mineralization that is followed by low-fineness (820–760‰) native gold and telluride minerals.

The retrograde skarn was formed from a high-salinity (22–23 wt% NaCl-eq.), hot (450 ± 50 °C), high-pressure (2.5 ± 0.5 kbar) homogenous magmatic-hydrothermal fluid, under its possible direct separation from crystallizing magma. After intrusion of intramineral mafic dikes, propylitic alteration assemblages were formed from a moderate salinity (15–18 wt% NaCl-eq.) homogenous aqueous fluid at the temperatures of 380–400 °C. This fluid could be supplied by crystallizing magma, with its further mixing with heated meteoric waters. Fluid inclusions in phyllic alteration minerals indicate a new influx of homogenous, high-salinity (18 wt% NaCl, 22 wt % KCl, 10 wt% CaCl₂), high-pressure (1.3 ± 0.1 kbar), aqueous-chloride fluid at lower (~280 °C) temperatures. Elevated Bi, Hg, Te contents, as well as δ³⁴S values close to meteorite standard (0 ± 1.5‰) suggest at least partial fluid sourcing from a mantle-derived magma at the phyllic alteration stage.

1. Introduction

The Central Asian Orogenic Belt (CAOB) incorporates numerous Cu-Au porphyry deposits (e.g., Seltmann and Porter, 2005; Seltmann et al., 2011, 2014; Yakubchuk et al., 2012; Mao et al., 2014); the largest of them include the Oyu Tolgoi deposit (Mongolia), the Almayk deposit (Uzbekistan), and the Kounrad deposit (Kazakhstan) (Fig. 1). Less is known about Cu-Au skarn deposits found in this belt; notably some of them contain significant Cu and/or Au resources (e.g., Soloviev et al.,

2018). Studying of these skarn deposits reveals important features in the Au and Cu metallogeny of the region and highlights genetic links between Au-Cu skarn and Cu-Au porphyry deposits in a broader regional skarn-porphyry mineralized system (Einaudi et al., 1981; Einaudi, 1982a,b; Meinert, 1995, 1998, 2000; Meinert et al., 2003, 2005).

The Sinyukhinskoe (Sinyukha) deposit is situated in the Russian Altai, which is characterized by a great mineral endowment (e.g., Soloviev, 2010). It was discovered in 1950 and is mined since, with

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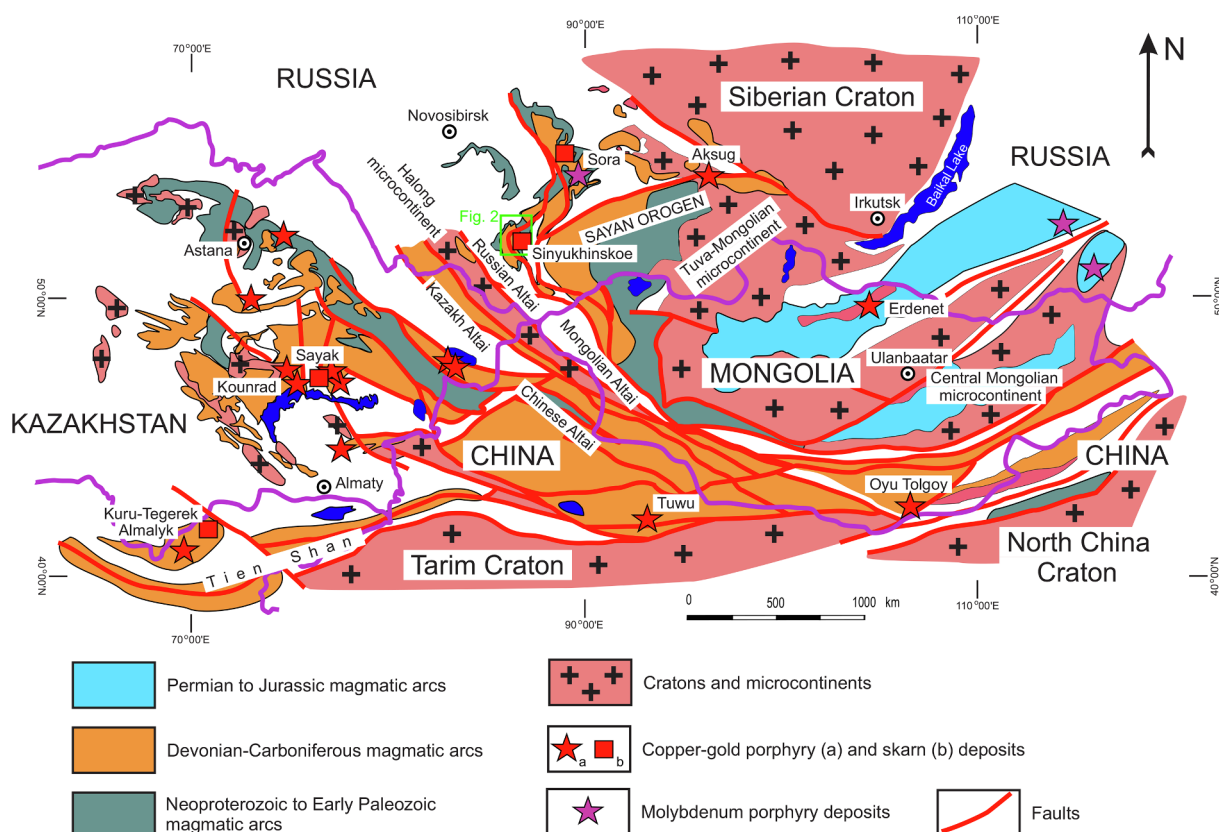


Fig. 1. Regional tectonic setting of magmatic arcs and major Cu-Au porphyry and skarn deposits in the central and western parts of the Central Asian Orogenic Belt (modified after Seltmann and Porter, 2005; Seltmann et al., 2011, 2014; Safonova, 2014; Rudnev, 2010; Buslov et al., 2013; Vladimirov et al., 2001, 2008; Berzina et al., 2016).

annual production of some 400–500 kg of gold. It currently contains reserves of ~20 t Au and resources of ~100 t, thus being one of the largest Au-Cu skarn deposits in the CAO. Average grade is 9.2 g/t Au (varying from 4 to 37 g/t Au for various resource blocks; Turkina et al., 2001) at 1 g/t Au cut-off. There are also substantial, although never delineated Cu resources, with average grades (for different resource blocks) from 0.5 to 1.8% Cu (Turkina et al., 2001). The deposit was studied in the past as a representative of a gold skarn type (e.g., Tveritinov, 1966; Vakhurshev, 1972). Then, part of the deposit (“Veselyi Mine”) was described by Ettlinger and Meinert (1991), who noted its Cu-Au skarn signatures and an affinity to the Cu-Au porphyry-skarn deposit family. Since then, more data have been obtained on its regional to local settings, age and composition of igneous suites, mineral assemblages and zonation of skarns and other hydrothermal alteration types, mineralogy of gold and sulfide mineralization (e.g., Gusev, 1994, 1998, 2007; Roslyakova and Shcherbakov, 1999; Korobeinikov and Zotov, 2006; Dvurechenskaya, 2010; Gusev and Gusev, 2012). The present study is aimed at establishing a more advanced model of the deposit formation by incorporating petrologic, mineralogical, fluid inclusion, and stable isotope data.

2. Regional tectonic and metallogenic setting

The Sinyukhinskoe deposit is situated in the Russian Altai (Fig. 1), part of the Altaid, or Central Asian, orogenic belt (CAOB), or collage (supercollage) (Sengor and Natal'in, 1996; Yakubchuk, 2004; Yakubchuk et al., 2005; Jahn et al., 2004; Safonova, 2014). This belt (supercollage) is located between the East European, Siberian, North China and Tarim cratons and extends from the Uralides in the west to the Pacific margin in the east, including orogenic areas in Russia (Altai-Sayan to Transbaikalia), Central and East Kazakhstan, Kyrgyzstan,

Uzbekistan, China, and Mongolia. The belt comprises ancient microcontinents, arc terranes, accretionary wedges, oceanic crust (ophiolites) and successions of passive continental margins. The amalgamation of these terranes occurred at different times and was accompanied by post-accretion to post-collisional granitic magmatism, large scale post-orogenic strike-slip faults and formation of post-orogenic clastic sedimentary basins (e.g., Vladimirov et al., 2001, 2008; Seltmann et al., 2011; Pirajno, 2010; Safonova et al., 2011; Safonova, 2014; Kröner et al., 2014).

The Altai orogenic system is located in south-western Siberia (Russian Altai), East Kazakhstan (Kazakh Altai), western Mongolia (Mongolian Altai) and north-western China (Chinese Altai) (Fig. 1; Safonova, 2014; Rudnev, 2010; Buslov et al., 2013; Vladimirov et al., 2001, 2008). This system comprises late Neoproterozoic to early Paleozoic oceanic and active margin units including accretionary complexes, forearc sediments, primitive- and normal island-arc rocks, which form several larger terranes separated by suture-shear zones (e.g., Buslov et al., 2002, 2004; Safonova et al., 2011; Kruk et al., 2011). Safonova (2014) distinguished four major terranes within the Russian-Kazakh Altai separated by suture-shear zones, namely, (1) Altai-Mongolian terrane, (2) Gorny Altai subduction-accretionary terrane, (3) Rudny Altai island-arc terrane, and (4) Kalba-Naryn collisional terrane, the latter two situated mostly in Kazakhstan. The deposit area is located in the Gorny Altai terrane, which was formed at an active margin of the Siberian continent and consists of (1) late Neoproterozoic-middle Cambrian subduction-accretionary complex, (2) Ordovician-early Devonian passive margin, (3) Devonian-early Carboniferous active margin, and (4) Devonian to Carboniferous-Permian collisional complex (Safonova, 2014).

The late Neoproterozoic-middle Cambrian subduction-accretionary complex comprises late Neoproterozoic ophiolites, early

Neoproterozoic-early Cambrian primitive island arc and a middle Cambrian island arc with fore-arc and back-arc basins (Safonova, 2014; Rudnev, 2010; Vladimirov et al., 2001, 2008). The corresponding volcanic-plutonic belts included multiphase gabbro-diorite-tonalite-plagiogranite intrusions; some of them, however, mark the transition to a younger accretion-collision process (Kruk et al., 2007). The Ordovician-Silurian was characterized by an accumulation of terrigenous and carbonate sediments and formation of a carbonate platform in a passive margin regime. In the Devonian, the subduction of the Paleo-Asian Ocean beneath the Siberian continent recommenced, and the geodynamic environment changed to an active continental margin, with corresponding formation of magmatic arcs and deposition of dominant rhyolite-dacitic lavas and tuffs (Safonova, 2014; Safonova et al., 2011). The plutonic rocks of the Devonian-early Carboniferous active margins are represented by granodiorite (with minor tonalite and quartz diorite, locally monzonite) suites (Buslov et al., 2013; Rudnev, 2010; Shokalsky et al., 2000; Safonova, 2014; Vladimirov et al., 2001, 2008). Then, the Devonian to Carboniferous (to Permian?) collisional (late- to post-collisional) granitoid suites were emplaced, starting with the Silurian-Devonian (~425–400 Ma) suites formed due to collision of the Altai-Mongolian and Gorny Altai terranes and continuing with the late Devonian-early Carboniferous (~370–350 Ma) and possibly younger (to Permian ?) suites formed due to collision of the Kazakhstan composite continent (including the Altai-Mongolian and Gorny Altai terranes) and Siberian craton (Vladimirov et al., 2001, 2008; Safonova, 2014).

Copper-gold mineralization in the CAOB is represented by different styles, with Cu-Au porphyry and skarn mineralization being most significant, and by different ages (from Cambrian through Devonian to Carboniferous-Permian and further to Mesozoic; Seltnann and Porter, 2005; Seltnann et al., 2011, 2014; Yakubchuk et al., 2012; Mao et al., 2014). These deposits were formed in a variety of tectonic environments spanning from subduction-related island arc and marginal continental belt terranes to the late- and post-collisional magmatic arcs. However, the Devonian (Devonian to Carboniferous) was the most productive epoch in the central part of the CAOB (e.g., Seltnann et al., 2011, 2014; Yakubchuk et al., 2012; Chen et al., 2014), where similar age, most notably, was determined for the largest Oyu Tolgoi cluster of Cu-Au porphyry deposits (Wainwright et al., 2011; Crane and Kavalieris, 2012; Porter, 2016). Correspondingly, the respective Cu-Au metallogenic belts extend together with Devonian to Carboniferous magmatic arcs within the Altai (Mongolian, Chinese, Russian and Kazakh Altai) structures, the latter spanning from those related to active subduction (mainly Devonian) to those associated with collisional (late- to post-collisional) processes.

3. District geology

The mineralized district that hosts the Sinyukhinskoe deposit is part of the north-(to north-east)-trending volcanic-plutonic belt, which extends along the eastern edge of the Gorny Altai terrane (Figs. 1 and 2) and represents a back-arc zone of the Devonian-early Carboniferous active continental margin (Shokalsky et al., 2000). In turn, the belt overprints an older regional-scale tectonic zone, which divides Neoproterozoic-Cambrian accretion-collision terrane to the west (composed of Neoproterozoic ophiolites and Neoproterozoic-Lower Cambrian turbidites, with minor carbonate units), and Ordovician-Silurian to Devonian trough to the east (composed of Ordovician-Silurian shallow-water terrigenous sedimentary rocks that are overlain by Lower Devonian red-bed and volcanic sequences) (Buslov et al., 2004, 2013). The tectonic zone comprises multiphase plagiogranite (gabbro-diorite-tonalite-plagiogranite) intrusions (e.g., Sarakokshin pluton; 516 ± 6 Ma by U-Pb method on zircon; Kruk et al., 2007).

The belt and particularly the deposit area are characterized by an intense development of various Devonian (to early Carboniferous ?) volcanic and plutonic rocks. The volcanic rocks include compositionally contrasting (from basalt-andesite-basalt to basalt-rhyolite) units that

formed due to back-arc rifting (Kruk et al., 2008). The plutonic rocks vary from gabbroic rocks through granodiorite to granite and leucogranite and, according to various authors, are subdivided into two or more suites including the early Yugalin monzogabbro-monzodiorite-granodiorite suite, and the late (younger) Turochak granite-leucogranite suite (Kruk et al., 2008; Turkin et al., 2001; Gusev, 1994; Vladimirov et al., 2001; Rudnev, 2010). These suites form large plutons (Fig. 2) that are dated at 398 ± 2 Ma to 406 ± 4 Ma (Yugalin pluton; Gusev, 2007; Gusev and Gusev, 2012) and 390 ± 6 Ma (Turochak pluton; Rudnev, 2010) by the U-Pb method on zircons. The younger Kyzyltash monzogranite-granite suite distinguished by some authors was dated at 381 ± 2 Ma for the Tsagan pluton to 340 (?) Ma for the Kyzyltash pluton (Turkin et al., 2001; Gusev and Lavinishnikova, 2011). On the other hand, the separate nearly-coeval plutons currently assigned to different suites may in fact represent a single (although complex and extended) differentiated gabbro-diorite-granodiorite-granite supersuite.

The Yugalin suite (formerly known as the Sinukha suite) is considered to be parental for the Sinukhinskoe Au-Cu skarn deposit; in the deposit area, the suite is represented by the Yugalin (Sinyukha) pluton (Gusev, 1994, 2007; Gusev and Gusev, 2012). Some intrusions of the Kyzyltash suite are similarly accompanied by Au-bearing magnetite and garnet skarns as well as by stockwork (porphyry-style) Cu-Au-Mo mineralization (e.g., Kulbich Cu-Au-Mo occurrence; Turkin et al., 2001; Gusev et al., 2011).

4. Deposit geology

The Sinyukhinskoe deposit includes a large number (at least 18; Turkin et al., 2001) of separated zones with Au-Cu or Au mineralization (Fig. 3). These mineralized zones are associated with limestone horizons found within a thick volcanic sequence that forms a large roof pendant of alternating Cambrian sedimentary and mafic to intermediate volcanic rocks that is situated above the Yugalin (Sinyukha) granitoid pluton, at a distance from the main contact of the Yugalin (Sinyukha) gabbro-monzodiorite-granodiorite pluton (Figs. 3 and 4). It appears that the larger mineralized zones are also controlled by junctions and intersections of variously oriented steeply-dipping to flat faults that are marked by variously oriented swarms of mafic to granitic dikes.

Larger and dominantly garnet-pyroxene skarn zones exhibit a stratified appearance (Fig. 4A) and replace gently-dipping to flat-lying horizons of alternating carbonate rocks and mafic volcanics (mostly andesite to trachyandesite and andesite-basalt tuffs, less typically basalt to andesite-basalt lavas). These skarn zones vary from 1 m to several tens of meters in thickness and from tens to hundreds of meters in width/length. Dominantly wollastonite-garnet to wollastonite skarns are relatively minor, possibly younger, and appear to have a more limited occurrence within a much wider halo of pyroxene- and garnet-dominant skarns (Fig. 3; Korotkikh and Voroshilov, 2011), typically at the higher levels.

Most productive Cu and particularly Au mineralization post-dates intramineral mafic dikes, with their volume attaining 60% in some mineralized zones. The dikes intersect skarn zones indicating a new pulse of structural re-activation of both steep and flat faults, possibly thrust-faults (Gusev, 1998), and so are zones of quartz-sulfide veining that intersect flat-lying skarn zones at a high angle. The mineralization was formed during propylitic and phyllic alteration stages and are, in turn, associated with new pulses of structural re-activation. Consistently, mineralization is abundant in some parts of skarn zones but is absent in skarns outside such intersections (Fig. 4B). It is irregularly distributed in the skarn zones, and the outlines of mineralized zones do not repeat contours of skarn zones. Larger mineralized zones exhibit complex steeply-dipping, locally columnar (pillar-like) shape, with discontinuous high-grade pods, branching apophyses, and sub-horizontal mineralized lenses, that are separated by barren to weakly-

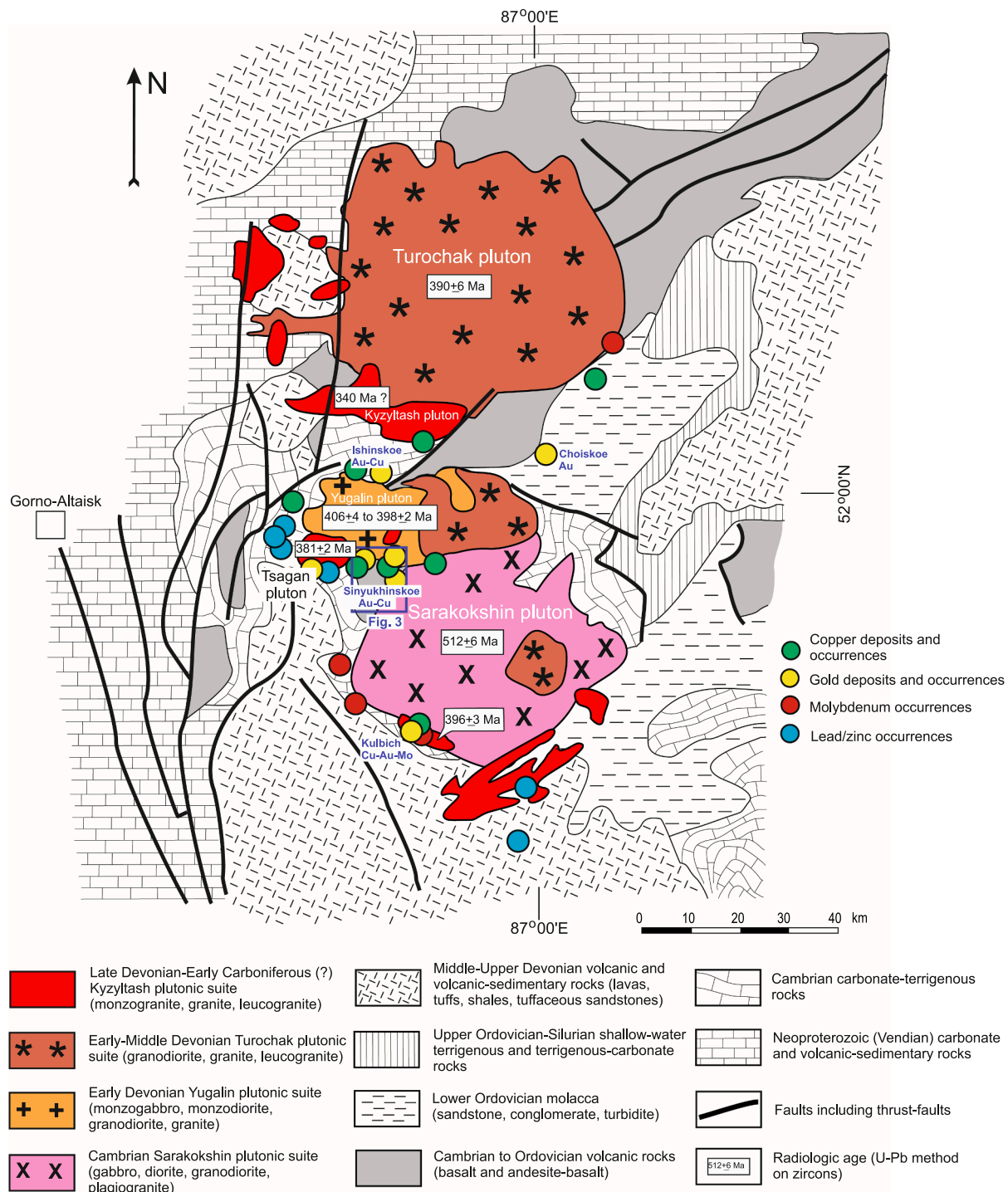


Fig. 2. Simplified geological map showing the location of the major plutons (assigned to different plutonic suites, after Gusev, 1994; Turkin et al., 2001; Kruk et al., 2008; Gusev and Gusev, 2012) in the Sinyukhinskoe deposit area (mineralized district), together with the major tectonic structures and main deposits and occurrences (modified after Gusev, 1994, 2007; Turkin et al., 2001; Kruk et al., 2008). Radiologic U-Pb zircon ages of the plutonic rocks are shown after Gusev (1994), Vladimirov et al. (2001), Turkin et al. (2001), Kruk (2015), Kruk et al. (2007, 2008), Rudnev (2010), Gusev and Gusev (2012).

mineralized domains. Larger orebodies occur in zones of wollastonite, garnet-wollastonite and garnet-pyroxene-wollastonite skarns; on the other hand, large volumes of skarns are barren, whereas some mineralized intervals are present outside skarns, particularly in limestones. Economic mineralization (referred to as the Au-Cu-skarn type) is represented by skarns altered during propylitic and phyllic stages and enriched in sulfide minerals (bornite, chalcocite, chalcopyrite) and native gold. Separate orebodies varying from 1 m to 20 m in thickness, from 10 m to 400 m along strike, and from 5 m to 150 m down dip, are

distinguished. Vertical extent of mineralization exceeds 2 km. Average Au grades in different orebodies vary from 4 to 37 g/t, and average Cu grades – from 0.5 to 1.8% (Turkin et al., 2001).

A different, Au-quartz-sulfide type of Au (with minor Cu) mineralization is represented by separate (from skarns) quartz-sulfide and quartz-K-feldspar-sulfide veining and associated phyllic alteration zones that are related to complex-shaped zones of structural complications (intervals of strike-slip faults, fault junctions and intersections, etc.). These lens-shaped zones have limited (< 10 m) thickness but

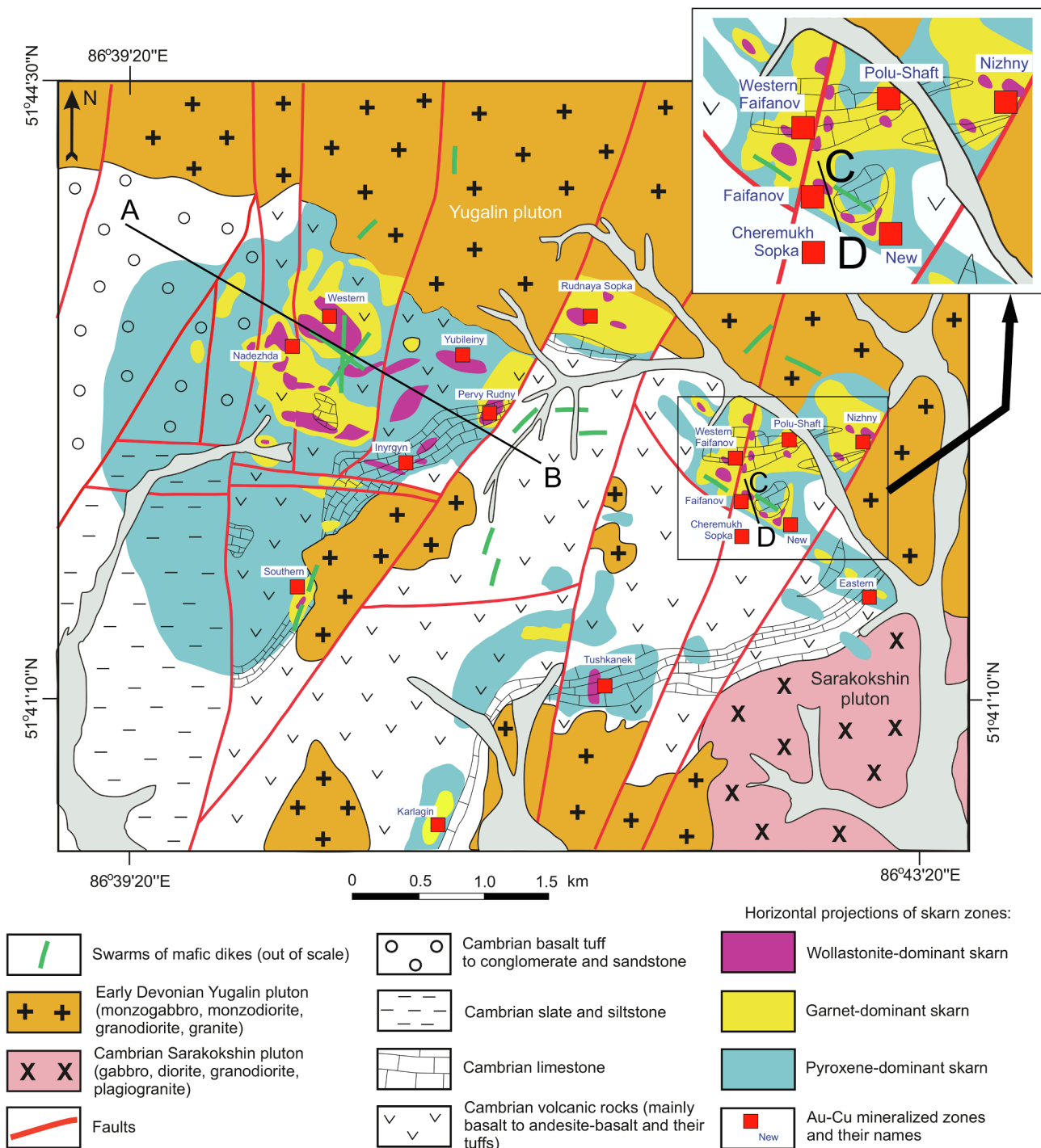


Fig. 3. Generalized geological map of the Sinyukhinskoe deposit (modified after Gusev, 1998; Korotkiikh and Voroshilov, 2011).

much greater (300–400 m) lateral and downdip extent. Average Au grades in these veining zones attain 12 g/t, average Cu grades – 1.8%. Some zones are coincident with (or overprint ?) hypothetical “feeders” of the skarn type orebodies, whereas others extend into a sedimentary-volcanic sequence and granitoid intrusions with no spatial relation to mineralized skarns. Dense quartz-sulfide veining zones locally evolve into quartz-sulfide stockworks that vary from relatively isometric to oval and linear (up to 0.25x1.5 km in areal dimensions). Average Au grades in different stockworks vary from 0.5 to 7.2 g/t but are typically around ~2 g/t (Turkin et al., 2001). These stockworks occur both proximal to the main mineralized zones of the deposit and distal, the latter inside the Yugalín pluton and at its opposite contact zones. In

many locations, they are accompanied by Au placers.

5. Analytical methods

The analyses of igneous rocks were performed in the TsNIGRI Laboratories, Moscow. SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 total, MnO, MgO, CaO, K_2O , and P_2O_5 were determined by X-ray fluorescence method using a multi-channel X-ray spectrometer. Powdered samples were digested in four acids, and ICP-ES method was used for determination of trace elements. Prior to analysis, the rock samples underwent a routine macro- and microscopic (thin section) screening procedure to avoid the effect of weathering, hydrothermal alteration, hybridization

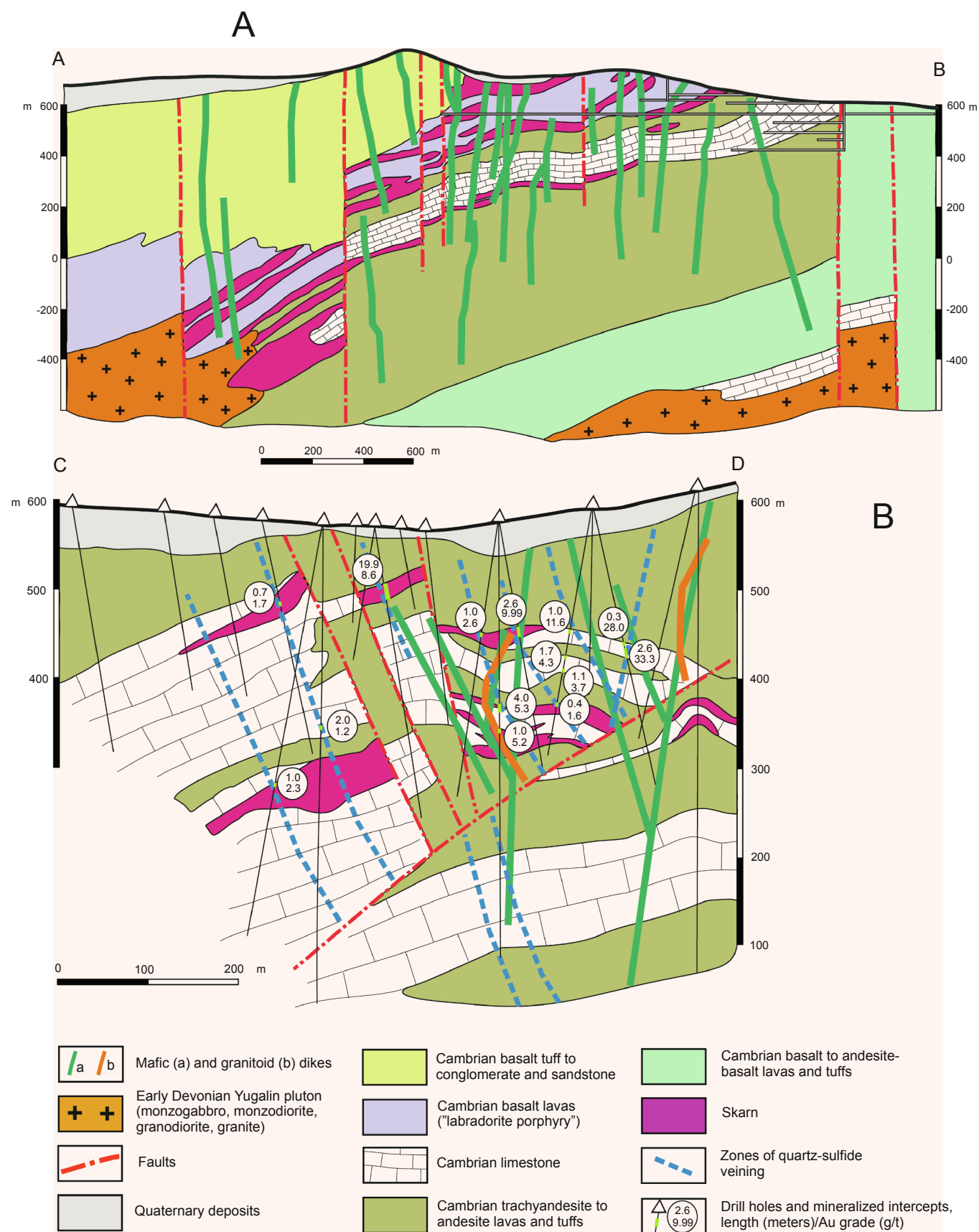


Fig. 4. Cross-sections through mineralized zones of the Sinyukhinskoe deposit. A. Generalized cross-section through the western part of the deposit (modified after Ettlinger and Meinert, 1991). B. Detailed cross-section through the eastern part of the deposit showing a transverse orientation of skarn zones and zones of quartz-sulfide veining (propylitic to phyllic alteration assemblages) associated with mafic dikes (modified after unpublished data of the Veseliy Mine).

phenomenon, and xenoliths/enclaves. Samples that returned an elevated loss on ignition (LOI) were rejected; LOIs in the majority of the remaining samples are < 2 wt%. The assay results satisfy also the criterion on essential immobility of Al and Ti thus supporting the freshness of the rocks included in the dataset (cf. MacLean and Barrett, 1993).

The analyses of minerals were performed using a Cameca SX50 electron probe microanalyser (EPMA) in the GEOKHI Institute of the Russian Academy of Sciences (RAS), Moscow, under operating conditions of 15 kV accelerating voltage, 30 nA beam current, with a beam diameter ~3 µm. The accuracy of element measurements was ± 2% rel. for concentrations > 10 wt%, ± 5% rel. for concentrations of 5–10 wt%, ± 10% rel. for concentrations of 1–5 wt%, and ± 15% rel. for concentrations of 0.1–1.0 wt%. The analyses of mineralized rocks were performed in the TsNIGRI Labs by fire assay method with gravimetric finish for Au and Ag, atomic absorption method for Cu, and ICP MS method for other elements.

Thirty doubly polished sections, 0.3 to 0.5 mm thick, were prepared from 22 individual samples for fluid inclusion petrography and microthermometry. The fluid inclusion study was focused on fluid inclusion assemblages (FIA) of closely associated groups or trails of fluid inclusions with visually similar phase ratios and shapes (Goldstein and Reynolds, 1994). The sequence of entrapment can be inferred from observations of crosscutting trails of FIA along individual fractures or rare primary inclusions distributed randomly within the core of crystals or pseudosecondary trails that are associated with healed microfractures terminated by crystal growth zones (Roedder, 1984). This also enables linking groups of fluid inclusions to various mineralizing stages on the basis of their absence in younger mineral assemblages (Masterman et al., 2005).

Microthermometric analyses were made using the UMTK-3 freezing-heating stage designed by VIMS Institute and modified by TsNIGRI Institute, to allow low-temperature experiments. Low-temperature measurements were conducted first; cooling was by liquid N₂ flow. The stage employs a chromel–alumel thermocouple and is capable of attaining temperatures ranging from below –180 to over +650 °C. The stage was periodically calibrated using the boiling temperature of pure N₂ (–196 °C), triple point for pure CO₂ (–56.6 °C), temperatures of ice melting in standard NaCl solutions (from –18° to –1 °C), melting temperatures of AgNO₃ (210 °C), K₂CrO₇ (398 °C), and NaI (651 °C). Final ice-melting temperatures were accurate to ± 0.2 °C, clathrate melting temperatures to ± 0.5 °C, eutectic temperatures to ± 1.5 °C, and homogenization temperatures to ± 5 °C. Heating rate (at above 30 °C) was 5 °C/min up to a heating limit at 650 °C.

Minerals for isotopic analysis were extracted using a drill and/or by hand picking of chips. Carbon and oxygen were obtained from calcite powder by reaction with H₃PO₄ at 75 °C using the method of McCrea (1950). Sulfide mineral powders were analyzed by conventional methods using the techniques of Robinson and Kusakabe (1975), with decomposition of sulfide minerals by reaction with CuO at 750 °C, with further isotopic analysis of SO₂. Analytical uncertainty of ± 0.2 per mil (2 σ) for δ¹³C and δ¹⁸O was estimated from the international KH-2 (δ¹³C_{PDB} = +1.97‰, δ¹⁸O_{SMOW} = +27.8‰) standard. Analytical uncertainty of ± 0.2‰ (2 σ) for δ³⁴S was estimated from internal standards of homogenous pyrite from the Gaiskoe deposit in the Southern Ural (δ³⁴S_{VCDT} = +0.7‰).

6. Devonian (to early Carboniferous ?) plutonic rocks in the deposit area

Instead of distinguishing numerous separate but nearly coeval (ca. 400–380 Ma) Devonian plutonic suites, we suggest a single gabbro-diorite-granodiorite-granite differentiation succession (a single suite or supersuite), which comprises 5–6 stages of intrusion (each in turn comprising 3–4 intrusive phases), with some compositional overlaps of different stages and phases due to a complex and extended magmatic evolution (Tables 1 and 2). The monotonous magmatic differentiation

from mafic through intermediate to granitic phases and particularly differentiation of granitoid members was interrupted (and accompanied) by the intrusions of mafic dikes.

The early (1st) intrusion stage included gabbroic intrusive phases (gabbro, monzogabbro, quartz-bearing gabbro, etc.) that form small stocks on the periphery of larger granitoid plutons. These rocks are characterized by the presence of ortho- and clinopyroxene (hypersthene and diopside-augite), locally together with brownish-green amphibole, and nearly equal amount of plagioclase (prismatic, locally zoned bytownite-labradorite with 80–50 mol% anorthite). The rock locally contains small mafic (pyroxene to pyroxene-amphibole) enclaves. Biotite and K-feldspar (microcline) are locally present but typically in minor amounts. Accessory minerals include magnetite, apatite and titanite. Turkin et al. (2001) reported small intrusives of gabbroic rocks with elevated apatite content (1.47 wt% P₂O₅), high TiO₂ (3.38 wt%) and elevated Na₂O (3.05 wt%) and K₂O (0.80 wt%) contents.

The 2nd intrusion stage included intermediate phases (monzodiorite, diorite, quartz diorite) and granodiorite; these rocks form most of the Yugalin (Sinyukha) pluton and a number of smaller plutons in the area. Turkin et al. (2001) noted gradual (facial) transition of diorite to granodiorite, whereas other authors distinguished granodiorite (locally varying to tonalite) as a separate intrusive phase. Turkin et al. (2001) also noted similarities of the granodiorite found in the Yugalin and Turochak plutons. The dioritic rocks are characterized by the presence of clinopyroxene (diopside-augite; 5–10 vol%), brownish-green amphibole (15–30 vol%) and biotite (5–10 vol%), together with zoned plagioclase (labradorite-andesine with 50–30 mol% anorthite). The rocks contain variable amounts of K-feldspar (orthoclase; 5–20 vol%) and quartz (5–15 vol%). The granodiorite exhibits a stronger porphyritic signature (with plagioclase and/or K-feldspar phenocrysts) and contains amphibole and biotite (10–15 vol% each), tabular to prismatic plagioclase (andesine-oligoclase with 45–25 mol% anorthite, occasionally labradorite with 50–55 mol% anorthite in the central parts of plagioclase crystals), K-feldspar (orthoclase; 5–20 vol%), and quartz (15–25 vol%). Accessory minerals include magnetite (up to 5 vol%), apatite, zircon and titanite. The rocks typically contain mafic (amphibole-plagioclase) enclaves.

The 3rd intrusion stage comprises the early intramineral mafic dikes, many of which crosscut the dioritic to tonalite-granodiorite rocks, although the majority of the dikes occur in the volcanic-sedimentary sequence outside of the granitoid pluton(s). Luzgin (1993) reported a number of mafic rock varieties including lamprophyre (spessartite) and andesite-porphyry. Gusev and Gusev (2012) distinguished two compositional types of the mafic dikes emplaced before the latest granitic phases, namely, (1) trachydolerite-porphyry (or monzogabbro-porphyry) and (2) trachyandesite-porphyry (or monzodiorite-porphyry). The former is characterized by plagioclase phenocrysts (up to 30 vol%) found in the fine-grained plagioclase-amphibole groundmass, which is typically altered into chlorite-epidote-calcite-sulfide aggregate; the rock has been dated at 397 ± 2 Ma by the SHRIMP method on zircon (Gusev and Gusev, 2012). The latter locally exhibits gradual transitions to the monzogabbro-porphyry but also forms separate dikes. It comprises small to large (up to 2 cm across) plagioclase (andesine, with 40–45 mol% anorthite) phenocrysts (50–55 vol%) in a fine-grained to glassy plagioclase-amphibole-clinopyroxene groundmass. Gusev and Gusev (2012) have assigned these rocks to a shoshonitic series.

The 4th intrusion stage comprises dominant granitic (granite, monzogranite and leucogranite) phases that form small to much larger plutons including parts of the Yugalin and almost entire Turochak, Kyzyltash and Tsagan plutons. The rocks are characterized by dominant biotite among mafic minerals, presence of both K-feldspar (orthoclase to microcline and microcline-perthite) and plagioclase (oligoclase), with broad occurrence of graphic and myrmekitic textures. Spherulitic granite-porphyry is locally present; spherulites form 70 to 90 vol% and are composed of a glassy material in the centers and radiating quartz-

Table 1

Major petrographic features of the Devonian (to early Carboniferous ?) plutonic rocks from the Sinyukhinskoe deposit area.

Intrusion stage	Rocks (intrusion phases)	Petrography
1	Gabbro, monzogabbro, quartz-bearing gabbro, monzodiorite	Medium- to fine-grained, equigranular to weakly porphyritic (locally glomeroporphyritic) melanocratic (dark-grey to dark greenish-grey) rock composed of ortho- and clinopyroxene (hypersthene and diopside-augite, ~10 vol% each), typically together with brownish-green amphibole (25–45 vol%), and nearly equal amount of plagioclase (prismatic, locally zoned bytownite-labradorite with 80–50 mol% anorthite; 40–50 vol%). Amphibole aggregates are locally replaced by clinopyroxene. The rock locally contains small mafic (pyroxene to pyroxene-amphibole) enclaves. Biotite and K-feldspar (microcline) are locally present but typically in minor amounts (0–5 vol% each). Accessory minerals include magnetite, apatite and titanite.
2	Monzodiorite, diorite, quartz diorite, tonalite and granodiorite	Medium- to coarse-grained, equigranular to weakly porphyritic mesocratic (grey to greenish-grey and pinkish-grey) rock composed of clinopyroxene (diopside-augite; 5–10 vol%), brownish-green amphibole (15–30 vol%), brown biotite (5–10 vol%), together with zoned plagioclase (labradorite-andesine with 50–30 mol% anorthite) (40–60 vol% in the dioritic rocks). The rocks contain variable amounts of K-feldspar (orthoclase; 5–20 vol%) and quartz (5–15 vol%). The granodiorite exhibits a stronger porphyritic (locally glomeroporphyritic) signature (with plagioclase and/or K-feldspar phenocrysts, the latter containing poikilitic inclusions of plagioclase) and contains brownish-green amphibole and brown biotite (10–15 vol% each to 10–15 vol% biotite and 0–10 vol% amphibole). Tabular to prismatic plagioclase phenocrysts are zoned from labradorite with 50–55 mol% anorthite in the central parts to andesine with 30–50 mol% anorthite in the outer rims, whereas plagioclase in the groundmass is represented by andesine-oligoclase with 25–35 mol% anorthite. K-feldspar is orthoclase (10–20 vol%); quartz content is higher (15–25 vol%). Accessory minerals include magnetite (up to 5 vol%), apatite, zircon and titanite. The rocks contain mafic (amphibole-plagioclase) enclaves.
3	Early intramineral mafic dikes: monzogabbro- to monzodiorite-porphyry	Fine-grained mafic (black to dark greenish-grey) weakly to strongly porphyritic rock containing plagioclase phenocrysts (up to 30 vol%) found in the fine-grained plagioclase-amphibole groundmass, which is typically altered into chlorite-epidote-calcite-sulfide aggregate (monzogabbro-porphyry). The monzodiorite-porphyry locally exhibits gradual transitions to the monzogabbro-porphyry but also forms separate dikes. It comprises small to large (up to 2 cm across) plagioclase (labradorite, with 50–55 to 60–65 mol% anorthite) phenocrysts (50–55 vol%) in a fine-grained to glassy plagioclase-amphibole-clinopyroxene groundmass (Gusev, 1994; Gusev and Gusev, 2012). Accessory minerals include magnetite, apatite, zircon and titanite.
4	Granite, monzogranite and leucogranite	Fine- to medium-grained leucocratic (pink to pinkish-white to grayish-white) weakly to strongly porphyritic rock composed of feldspars including K-feldspar – both orthoclase and microcline to microcline-perthite (15–25 vol%), and plagioclase – oligoclase (35–45 vol%), quartz (25–35 vol%), brown biotite (5–8 vol%) and trace green amphibole (0–2 vol%). Graphic, micropegmatitic and myrmekitic textures are common. Accessory minerals include magnetite (up to 3 vol%), ilmenite, apatite, titanite, in the most leucocratic varieties – also allanite, fluorite and garnet (Turkin et al., 2001; Kruk et al., 2008). Spherulitic granite-porphyry contains 70–90 vol% spherulites that are composed of a glassy core and radiating quartz-plagioclase aggregate on the periphery that are surrounded by fine-grained quartz-feldspar groundmass (Luzgin, 1993).
5	Late intramineral (?) to post-mineral mafic dikes (dolerite to microdolerite)	Mafic (dark greenish-grey to black), weakly-porphyritic to almost aphyric rock composed of very small pyroxene (augite) phenocrysts surrounded by fine-grained plagioclase-pyroxene groundmass. Plagioclase is represented by labradorite with 60–70 mol% anorthite. Accessory minerals include magnetite (up to 5 vol%), ilmenite, apatite, zircon, and titanite.

plagioclase aggregate on the periphery (Luzgin, 1993). Accessory minerals include magnetite (up to 3 vol%), ilmenite, apatite, titanite, in the most leucocratic varieties – also allanite, fluorite and garnet (Turkin et al., 2001; Kruk et al., 2008).

Finally, there are late mafic dikes that post-date granitic intrusions and possibly include the late intramineral and postmineral phases, the latter apparently classified as dolerite (Gusev and Gusev, 2012). These rocks contain small pyroxene (augite) phenocrysts surrounded by fine-grained plagioclase-pyroxene groundmass. Plagioclase is andesine with 40–50 mol% anorthite. Accessory minerals include magnetite (up to 5 vol%), ilmenite, apatite, zircon, and titanite. The youngest aphyric dolerite dikes have been dated at 268 ± 2 Ma by the SHRIMP method on zircon (Gusev and Gusev, 2012) and are likely unrelated to the previous intrusions.

The major and trace element compositions of the intrusive rocks are presented in Table 2. On the total alkalis vs. SiO_2 diagram (Fig. 5A), the rocks plot in the calc-alkaline field, as defined by Middlemost (1997). The intermediate rocks are mostly transitional between the high-K and medium-K calc-alkaline fields (Fig. 5B), although with Na_2O consistently higher than K_2O ; granitic rocks have elevated K_2O content corresponding to the high-K calc-alkaline field. Some early intramineral mafic dikes have higher K_2O content and are plotted in the shoshonitic field (Fig. 5B). All rocks are metaluminous to weakly peraluminous (14–17 wt% Al_2O_3 ; Fig. 5C) and correspond mainly to the I-type granites, with a few varieties approaching the peraluminous I-type granites (cf. Chappell and White, 1992; Chappell et al., 2012). They are

characterized by elevated $\text{Fe}_2\text{O}_3/\text{FeO}$ varying from 0.73 to 2.24 (Table 2); these ratios and presence of magnetite indicate that they are members of the magnetite-series granitic rocks (Ishihara, 1981). On the Rb vs. Y + Nb diagram (Fig. 5D), less fractionated rocks plot as volcanic arc types, whereas more fractionated rocks move toward the syn- and post-collisional granite field (Pearce, 1996), thus displaying the pattern, which reflects the magmatic fractionation (Pearce et al., 1984). The discrimination diagram of Muller and Groves (2019) designed for high-K igneous rocks (Fig. 5F) indicates the continental subduction-related to post-collisional affinity of the rocks. The rocks are moderately enriched in CaO and plot mostly in the “calc-alkalic” to “alkali-calcic” fields on the $\text{Na}_2\text{O} + \text{K}_2\text{O}-\text{CaO}$ vs. SiO_2 diagram (Fig. 5D; Frost et al., 2001). Gusev (1994) reported low $^{87}\text{Sr}/^{86}\text{Sr}$ values for tonalite (0.70513) and granodiorite (0.70528). The granitoid rocks of the Yugalin pluton are moderately enriched in LREE (La_N/Yb_N varies from 7 to 5–6), with weak Eu anomalies (Kruk et al., 2008).

7. Hydrothermal assemblages and mineralization

There has been a complex development of skarn and post-skarn hydrothermal alteration and related mineralization occurring contemporaneously with magmatic evolution (Fig. 6). In particular, prograde calcic skarn of different types occurs in the broad contact halo of the Yugalin pluton, which comprises igneous rocks of the 1st and 2nd intrusive stages. This suggests genetic links of prograde skarns to the 2nd stage rocks (forming the most of the pluton), although some of their

Table 2
Chemical composition of the Devonian (to early Carboniferous ?) plutonic rocks from the Sinyukhinskoe deposit area (wt%, ppm).

Intrusion stages		2nd stage										
Rocks (intrusion phases)	1st stage		2nd stage									
	Monzogabbro to monzodiorite		Monzodiorite to monzonite to diorite									
	1	2	3	4	5	6	7	8	9	10	11	
<i>wt percent</i>												
SiO ₂	50.41	51.12	52.56	53.81	55.85	56.18	57.11	61.75	64.52	65.31	67.19	
TiO ₂	1.10	1.28	1.32	1.26	1.20	1.18	0.94	0.62	0.63	0.61	0.56	
Al ₂ O ₃	16.72	16.02	16.17	15.98	15.21	14.92	16.42	15.13	14.98	14.48	13.62	
Fe ₂ O ₃	5.34	5.12	4.60	6.61	5.91	4.99	4.49	4.02	2.95	2.79	2.53	
FeO	5.71	5.40	4.89	5.71	3.00	4.42	2.94	3.04	3.04	3.01	3.04	
MnO	0.18	0.21	0.16	0.17	0.19	0.20	0.10	0.14	0.10	0.12	0.06	
MgO	5.75	6.13	6.60	4.02	3.74	4.10	3.50	3.04	2.56	2.30	2.01	
CaO	8.12	8.64	8.06	6.75	6.18	6.14	4.70	5.12	3.44	2.98	3.60	
Na ₂ O	3.74	3.60	3.62	4.50	4.82	4.15	4.76	4.03	3.19	3.77	3.47	
K ₂ O	1.65	1.42	1.25	2.91	2.64	2.67	2.52	2.43	3.04	3.14	3.02	
P ₂ O ₅	0.18	0.24	0.26	0.20	0.18	0.21	0.20	0.18	0.21	0.18	0.16	
LOI	0.72	0.55	0.62	0.58	0.60	0.51	1.65	0.38	0.54	0.61	0.52	
Total	99.62	99.73	100.11	99.73	99.52	99.67	100.54	99.75	99.20	99.30	99.78	
<i>ppm</i>												
Ba	344	370	222	360	341	334	547	306	382	340	296	
Sr	531	515	306	440	534	496	319	472	293	199	202	
Co	30	64	33	26	38	42	26	25	17	12	26	
Ni	56	91	119	41	46	54	24	78	24	20	41	
V	98	152	159	88	120	120	137	131	98	101	70	
Cr	84	124	216	52	54	65	18	106	38	35	40	
Li	13	17	21	12	11	17	20	21	27	23	32	
Rb	31	42	39	48	50	58	73	62	94	87	104	
Cs	0.5	0.6	0.5	0.7	0.5	1.0	1.0	1.1	1.1	1.2	1.2	
Be	1.0	2.6	1.4	1.3	1.2	2.2	2.4	3.7	1.4	1.5	4.4	
Zr	68	106	161	74	76	145	150	232	232	240	265	
Nb	16	10	10	11	12	4.8	12	7.1	12	10	8.5	
Ta	0.3	1.0	2.8	1.1	0.8	0.7	1.0	1.3	1.2	1.2	1.4	
Hf	2.4	3.2	4.1	2.2	2.4	1.9	2.0	1.6	2.3	1.8	3.2	
Sc	34	21	37	14	18	16	20	22	20	11	11	
Y	29	36	41	31	26	28	36	27	43	45	29	
U	2.7	3.0	4.1	3.1	2.9	2.6	3.0	4.7	2.4	3.2	5.0	
Th	4.3	5.1	5.6	3.8	4.1	4.0	8.0	6.2	6.4	5.9	6.2	
Sn	1.2	1.8	2.4	1.8	2.1	2.0	2.5	3.7	5.4	3.7	2.9	
Mo	< 0.5	2.5	1.3	< 0.5	1.3	2.1	1.2	1.5	3.2	4.1	3.1	
W	1.0	1.2	2.1	1.8	1.5	1.7	1.0	1.9	2.1	2.0	1.8	
Cu	54	60	88	91	58	45	458	61	73	32	128	
Zn	< 10	48	< 10	22	31	31	102	25	25	22	31	
Pb	11	91	84	26	40	32	< 10	84	50	65	64	

Intrusion stages		4th stage										
Rocks (intrusion phases)		Granite to leucogranite										
		12	13	14	15	16	17	18	19	20	21	22
Early intramineral mafic dikes (monzogabbro- to monzonidiorite-porphyr)												
<i>wt percent</i>												
	SiO ₂	49.01	49.56	50.22	50.45	53.11	51.60	52.20	69.76	70.28	72.44	75.16
	TiO ₂	1.34	1.28	1.43	1.12	1.29	0.96	0.98	0.30	0.34	0.38	0.30
	Al ₂ O ₃	16.89	16.80	16.95	16.67	16.59	16.51	16.77	14.81	13.53	12.61	13.05
	Fe ₂ O ₃	4.19	4.03	6.18	4.23	4.81	3.17	3.48	1.71	1.52	1.41	1.02
	FeO		4.77	6.60	4.50	5.19	3.65	4.19	1.67	1.19	1.02	0.78

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Table 2 (continued)

Intrusion stages		4th stage										
		Granite to leucogranite										
Rocks (intrusion phases)		Early intramineral mafic dikes (monzogabbro- to monzodiorite-porphyry)										
		12	13	14	15	16	17	18	19	20	21	22
MnO	0.19	0.18	0.06	0.18	0.05	0.16	0.21	0.05	0.05	0.10	0.10	0.04
MgO	8.00	6.89	4.15	7.19	3.89	6.20	6.18	0.68	1.10	1.26	1.26	0.08
CaO	9.13	9.01	5.02	8.89	6.30	7.81	7.67	1.88	1.97	1.10	1.10	0.50
Na ₂ O	3.31	3.00	5.79	3.02	6.04	3.67	3.30	4.39	3.34	4.31	4.31	4.82
K ₂ O	1.65	2.19	0.97	3.10	0.90	4.01	3.19	3.35	4.63	4.18	4.18	4.05
P ₂ O ₅	0.28	0.30	0.40	0.26	0.39	0.33	0.27	0.11	0.09	0.09	0.09	0.03
LOI	1.63	1.56	2.06	1.71	0.95	1.68	1.48	1.93	1.61	0.52	0.52	0.61
Total	100.10	99.57	99.83	100.32	99.51	99.75	99.92	100.64	99.65	99.42	99.42	100.30
ppm												
Ba	1973	1818	417	1432	262	1543	1137	485	359	385	385	362
Sr	1037	954	229	907	479	996	860	206	109	201	80	80
Co	22	38	24	28	22	15	17	< 10	< 10	< 10	< 10	< 10
Ni	32	54	17	39	20	23	21	< 10	17	12	12	< 10
V	162	172	104	134	226	147	121	33	23	31	31	< 10
Cr	53	69	< 10	71	39	67	42	< 10	< 10	31	31	42
Li	22	33	20	14	18	19	12	18	19	22	16	16
Rb	82	90	68	81	24	99	106	119	30	85	103	103
Cs	0.5	0.5	1.0	0.6	0.5	1.8	1.2	2.1	2.0	1.8	1.8	1.6
Be	1.0	1.2	1.4	1.0	1.1	1.1	1.2	1.9	2.2	2.8	2.2	2.2
Zr	120	92	146	88	136	109	102	157	175	64	111	111
Nb	5.9	7.2	12	4.5	7.0	3.7	7.0	15	13	28	15	15
Ta	0.4	0.5	0.6	0.2	2.4	0.2	0.4	1.3	1.5	1.8	1.8	1.0
Hf	2.2	2.4	2.0	2.8	2.2	2.5	2.3	2.4	2.6	2.5	7.0	7.0
Sc	30	28	24	26	20	21	23	12	14	8.6	3.4	3.4
Y	28	25	32	34	46	51	44	28	42	45	65	65
U	4.3	2.3	2.2	2.7	2.6	3.1	2.4	3.8	3.6	4.6	4.4	4.4
Th	6.2	4.3	6.0	5.4	4.8	6.0	5.4	12	19	11	15	15
Sn	1.2	1.0	1.2	1.1	1.1	1.0	1.2	3.2	2.9	2.1	1.7	1.7
Mo	< 0.5	1.2	1.0	1.4	1.8	2.6	< 0.5	1.4	2.1	1.2	< 0.5	< 0.5
W	1.0	1.1	1.0	1.0	1.2	1.7	1.5	1.0	1.2	1.4	1.0	1.0
Cu	28	39	1133	121	22	116	44	14	12	21	18	18
Zn	18	< 10	63	12	33	11	14	47	34	22	< 10	< 10
Pb	43	55	< 10	81	< 10	93	24	34	65	55	33	33

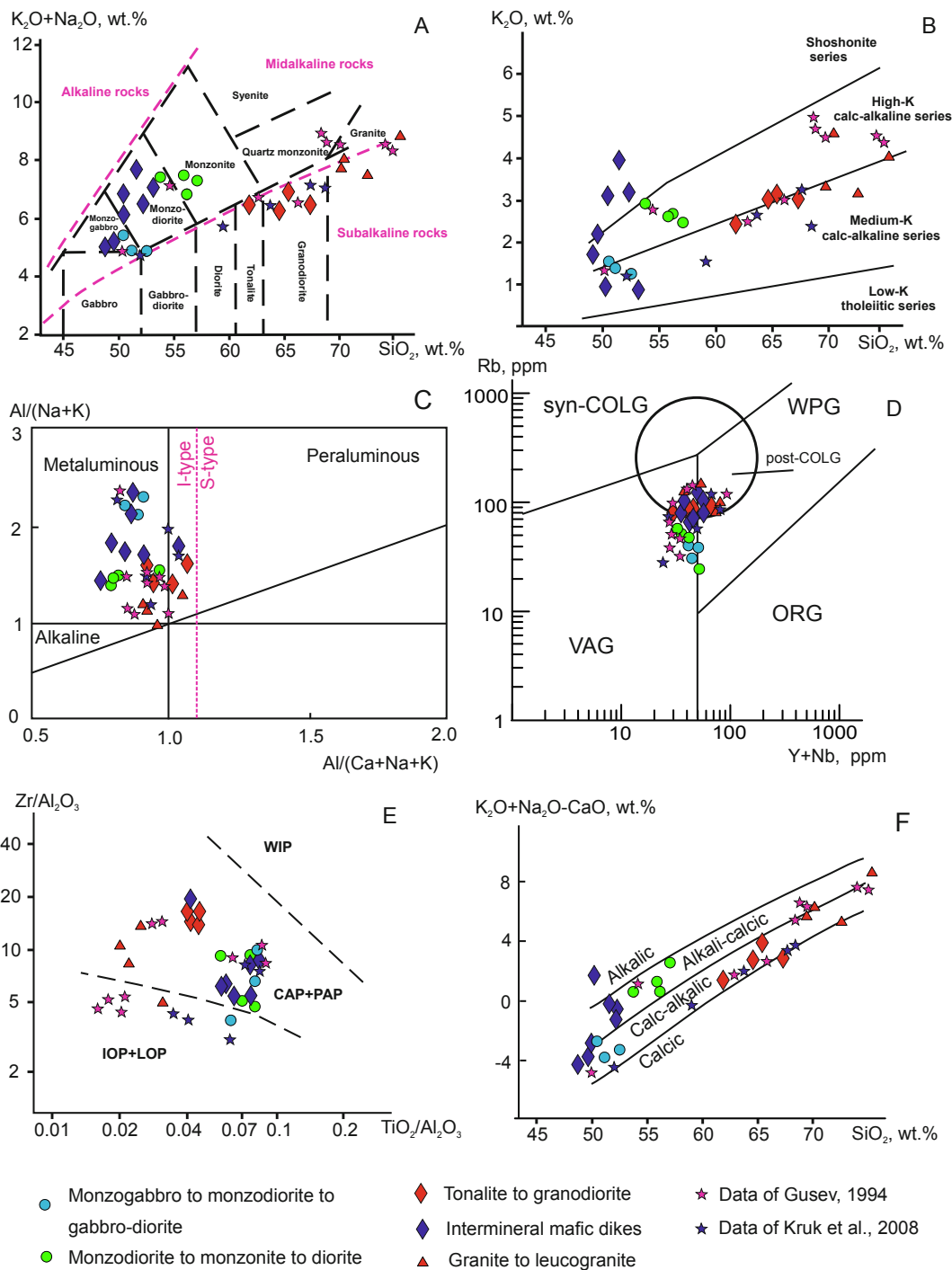


Fig. 5. Classification diagrams illustrating the chemistry of igneous rocks from the Sinyukhinskoe deposit area. (A) SiO_2 vs. $(\text{K}_2\text{O} + \text{Na}_2\text{O})$ diagram for chemical compositions of intrusive rocks (after Le Maitre et al., 1989; Middlemost, 1997). (B) SiO_2 vs. K_2O diagram (Peccherillo and Taylor, 1976; Le Maitre et al., 1989). (C) Molar $\text{Al}/(\text{Na} + \text{K})$ vs. $\text{Al}/(\text{Ca} + \text{Na} + \text{K})$ diagram defining alkaline, *meta*-aluminous and peraluminous igneous rocks (Maniar and Piccoli, 1989). (D) Rb vs. $(\text{Y} + \text{Nb})$ diagram showing compositional fields of granitic rocks formed in *syn*-collisional (syn-COLG), post-collisional (post-COLG), volcanic arc (VAG), within-plate (WPG), and oceanic ridge (ORG) tectonic environments (Pearce, 1996). (E) Discriminant diagram showing compositional fields of shoshonitic rocks formed in within-plate (WIP), continental arc (CAP) and post-collisional arc (PAP), initial oceanic arc (IAP) and late oceanic arc (LOP) tectonic environments (Muller and Groves, 2019). (F) $(\text{K}_2\text{O} + \text{Na}_2\text{O} - \text{CaO})$ vs. SiO_2 diagram defining alkalic, alkali-calcic, calc-alkalic and calcic igneous rocks (Frost et al., 2001).

younger phases may have an “intraskarn” emplacement. Prograde skarns are intersected by the early intramineral mafic dikes and then by granitic rocks of the 4th stage.

Prograde skarns are partially to entirely replaced by mineralized retrograde skarn, propylitic and phyllic alteration assemblages. There appears to be a close relationship, possibly genetic links between at least propylitic alteration and the early intramineral mafic dikes: this

alteration occurs after the emplacement of these dikes and in close spatial proximity. Phyllic alteration assemblages have been developed after the intrusion of granitic rocks of the 4th stage and possibly also after intrusion of some late (late intramineral) mafic dikes; instead, the latest (postmineral) mafic dikes cut zones of phyllic alteration (Fig. 6).

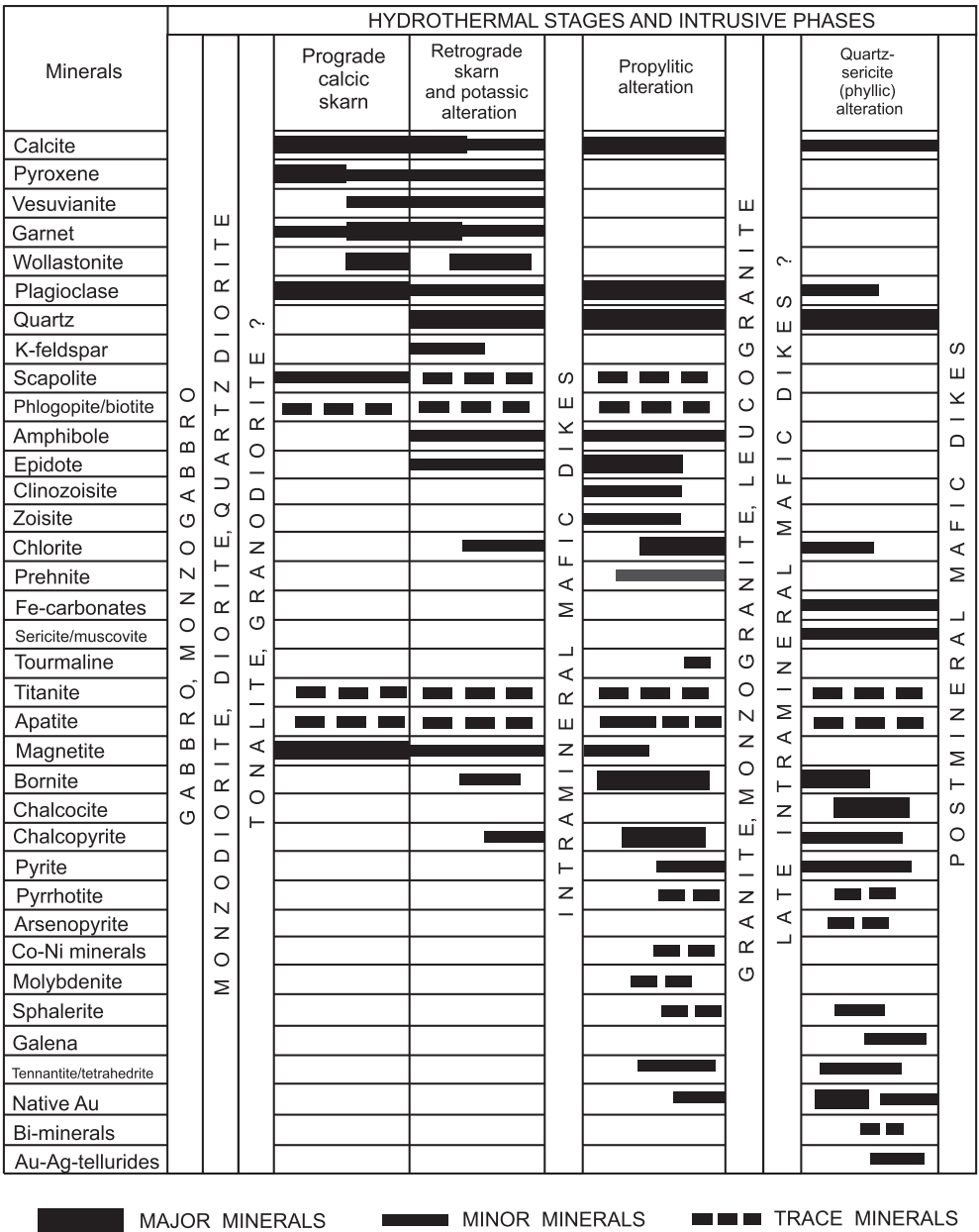


Fig. 6. Sequence of hydrothermal alteration assemblages and intrusive phases at the Sinyukhinskoe deposit.

7.1. Prograde calcic skarns

Prograde calcic skarn occurs in the volcanic-sedimentary sequence, replaces alternating marble and volcanic units, and is represented by two varieties. The early prograde skarn replaces the alternating units along their contacts (Fig. 7A) and is composed of fine-grained isotropic light pale-brown to pale-brown grossular-andradite garnet (10–30 mol % andradite; Table 3), greenish-white to green pyroxene (5–20 mol% hedenbergite; Table 3), Ca plagioclase (60–70 mol% anorthite), and minor magnetite. It exhibits a distinct zonation, where plagioclase (locally with scapolite), plagioclase-pyroxene and pyroxene zones are endoskarn replacing volcanic rocks, whereas garnet and magnetite zones are exoskarn replacing marble. This skarn is referred to as the diffusion-bimetasomatic to diffusion-infiltration skarn (Zharikov, 1970). The late prograde skarn is composed essentially of brown to dark-brown andradite-grossular garnet (30–60 mol% andradite) and wollastonite, locally with pyroxene (15–35 mol% hedenbergite; Table 3) and vesuvianite. Gusev (1998) noted ferrobustamite in close

association with pyroxene, and bustamite and rhodonite in association with wollastonite. The skarn occurs along gently-dipping, bedding-parallel fractures that follow contacts of volcanic-sedimentary units and the early prograde skarn zones, or forms “pivot” zones in the core parts of the early skarn. Wollastonite skarn is locally abundant within carbonate units, particularly at the uppermost deposit levels. In addition, the late prograde skarn locally cuts across the early prograde skarn and forms irregularly-shaped, vein-like to stockwork zones, the latter comprising branching, pinching-and-swelling skarn veinlets (Fig. 7B-C). This skarn is referred to as the infiltration skarn (Zharikov, 1970).

7.2. Retrograde skarn and potassic (calc-potassic) alteration

Retrograde skarn is defined as a series of assemblages containing both anhydrous minerals of the calc-silicate skarn paragenesis (pyroxene, garnet, plagioclase, wollastonite, etc.) and coexisting hydrous minerals (amphibole, etc.) that replaces prograde (typically anhydrous) skarn. These assemblages are most developed in garnet- and/or

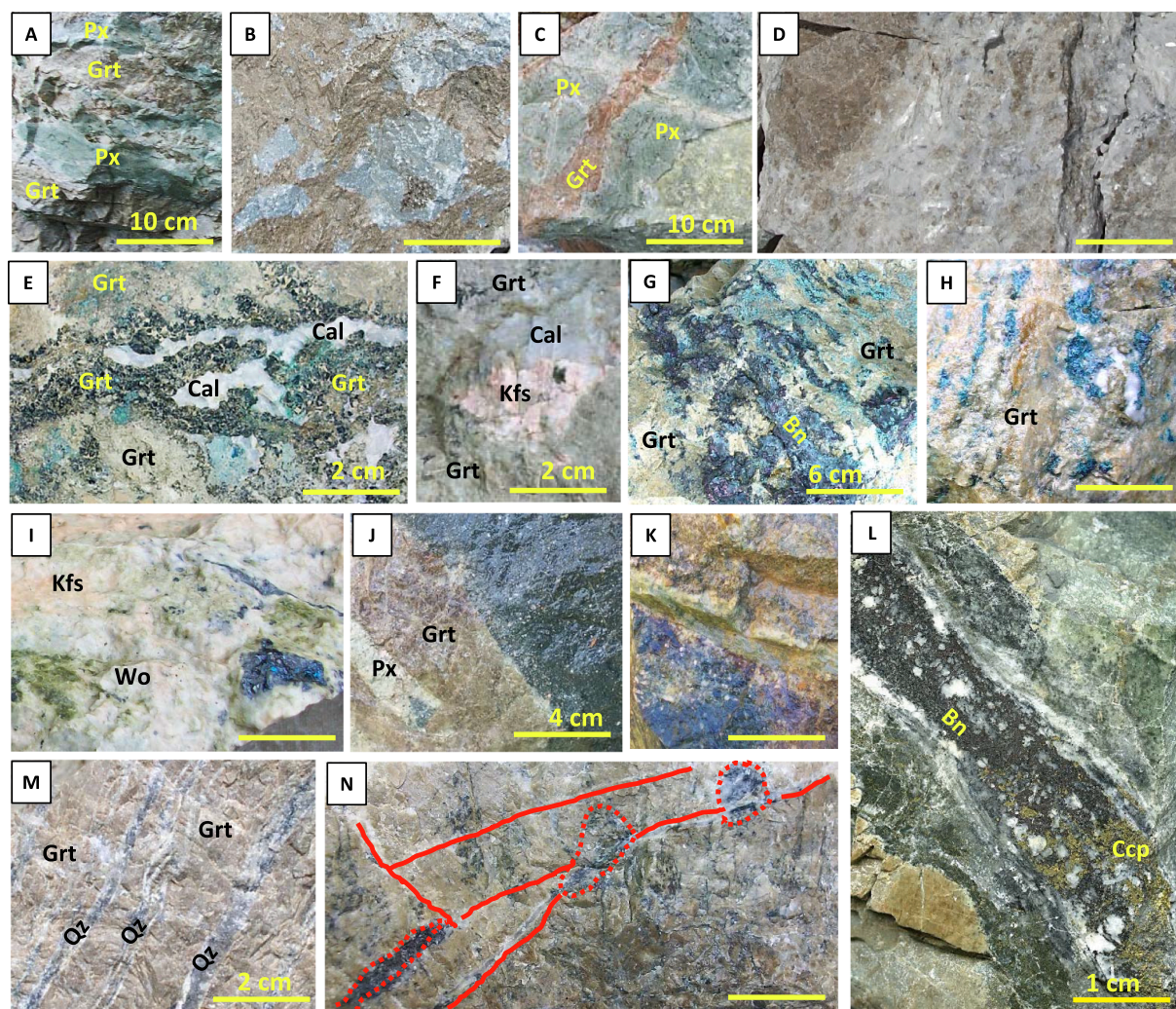


Fig. 7. Photographs showing typical features of hydrothermal alteration assemblages at the Sinyukhinskoe deposit. A. Early prograde calcic skarn (alternation of garnet and pyroxene zones). B. Branching late prograde garnet skarn replaces marble. C. Garnet veinlet of the late prograde calcic skarn intersects pyroxene zone of the early prograde calcic skarn. D. Coarse-grained retrograde wollastonite skarn replaces brecciated garnet skarn. E. Retrograde skarn (green garnet, calcite, quartz, and bornite) replaces prograde garnet skarn. F. Pink K-feldspar with calcite and quartz in retrograde skarn replacing prograde garnet skarn. G-H. Abundant bornite in retrograde skarn replacing prograde garnet skarn. I. Bornite in retrograde wollastonite skarn with epidote and K-feldspar. J. Early intramineral mafic dike (monzogabbro- to monzodiorite-porphyry) cuts across the late calcic skarn composed of dark-brown garnet that, in turn, intersects the early prograde garnet skarn (light pale-brown garnet). K. Epidote-chlorite-quartz (propylitic) veinlet cuts along a contact of the early intramineral mafic dike (monzogabbro- to monzodiorite-porphyry) intersecting garnet skarn. L. Chlorite-epidote-albite-carbonate-quartz (propylitic) alteration overprints retrograde skarn with bornite, the latter replaced by chalcopyrite. M. Quartz-sericite-sulfide (phyllic alteration) veinlets cut garnet skarn. N. Traces/outlines of quartz-sulfide veinlets and nest-like quartz-sulfide aggregates (phyllic alteration) cutting garnet skarn. Abbreviations: Grt – garnet, Px – pyroxene, Qz – quartz, Ep – epidote, Cal – calcite, Pl – plagioclase, Kfs – K-feldspar, Wo – wollastonite, Bn – bornite, Ccp – chalcopyrite. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

wollastonite-dominant prograde skarn and include (1) garnet-calcite-quartz $\pm$ vesuvianite, (2) wollastonite-quartz $\pm$ garnet $\pm$ vesuvianite, (3) epidote-garnet-quartz-calcite, and (4) K-feldspar-quartz-epidote + magnetite (Fig. 7D-E), with minor but ubiquitous amphibole, epidote and/or chlorite that are associated with quartz and emphasize the retrograde character of this skarn. The replacement of prograde skarn starts with the development of dissemination of these minerals, grading into patchy and then pervasive replacement and/or re-crystallization of garnet, wollastonite, vesuvianite and locally pyroxene into euhedral crystals and larger-crystalline aggregates, with interstitial quartz, calcite, bornite and minor chalcopyrite. The retrograde skarn garnet is dark-green to dark-brown and andradite-rich (70–100 mol%; Table 4), with minor grossular component (0–25 mol %), oscillatory zoned and optically anisotropic (birefringent in concentric and/or sectorial zones). Pyroxene-dominant prograde skarn is replaced by pyroxene-garnet-quartz to pyroxene-quartz assemblage,

which contains hedenbergite-rich pyroxene (80–95 mol% hedenbergite; Table 3). The coarse-grained wollastonite skarn, with coarse parallel to radiating and sheaf-like crystals and their aggregates, was noted by Ettlinger and Meinert (1991) as a typical retrograde skarn at Sinyukhinskoe. K-feldspar forms patches with calcite and quartz replacing prograde skarn, typically of garnet- to wollastonite-dominant composition (Fig. 7F).

Potassic (calcic-potassic) alteration assemblage has minor development, and occurs replacing igneous protolith, locally overprinting also prograde skarn; thus, it likely has a similar timing with the retrograde skarn (cf. Atkinson and Einaudi, 1978). In the igneous rocks, it comprises quartz, biotite, and K-feldspar, and forms scattered small merging veinlets, patches, and zones of pervasive replacement (Luzgin, 1987). Minor oligoclase, dark-green amphibole, epidote, calcite, magnetite, bornite, and trace dark-brown andradite garnet are also present.

Sulfide minerals formed at the retrograde skarn stage appear to be

Table 3

Representative microprobe analyses of pyroxene and garnet from prograde and retrograde skarns at the Sinyukhinskoe deposit, wt%, mol%.

	1	2	3	4	5	6	7	8	9	10	11	12	13
SiO ₂ , wt%	54.14	53.96	52.84	52.40	37.33	37.89	37.55	36.54	36.43	35.81	35.63	35.73	35.98
TiO ₂ , wt%	0.46	0.24	0.18	0.06	0.39	0.47	0.12	0.35	0.30	0.10	0.12	0.09	0.13
Al ₂ O ₃ , wt%	0.29	0.48	0.41	0.10	21.03	17.12	15.02	8.96	7.41	2.95	1.87	1.50	1.00
FeO, wt%	3.18	2.74	2.40	5.45	5.42	8.32	11.44	18.67	20.54	25.26	26.82	27.48	27.19
MnO, wt%	0.20	0.25	0.18	0.48	0.11	0.10	0.09	0.12	0.13	0.32	0.37	0.42	0.44
MgO, wt%	15.34	16.01	17.31	16.11	0.56	0.34	0.30	0.32	0.21	0.42	0.40	0.32	0.26
CaO, wt%	25.18	25.98	25.76	25.12	34.05	34.86	33.98	33.15	33.25	32.62	32.34	32.03	32.62
Total, wt%	99.79	99.66	99.08	99.72	98.89	99.10	98.50	98.11	98.27	97.48	97.55	97.57	98.12
	Di 89	Di 90	Di 92	Di 83	Alm 1	Alm 1	Alm 2	Alm 2	Alm 2	Alm 0	Alm 1	Alm 2	Alm 1
	Hd 10	Hd 9	Hd 7	Hd 16	Adr 14	Adr 24	Adr 32	Adr 57	Adr 64	Adr 84	Adr 89	Adr 89	Adr 92
	Jo 1	Jo 1	Jo 1	Jo 1	Grs 83	Grs 74	Grs 65	Grs 40	Grs 34	Grs 14	Grs 9	Grs 9	Grs 5
					Prp 2	Prp 1	Prp 1	Prp 1	Prp 1	Prp 2	Prp 2	Prp 2	Prp 1
					Sps 0	Sps 0	Sps 0	Sps 0	Sps 0	Sps 1	Sps 1	Sps 1	Sps 1

Hd = hedenbergite, Di = diopside, Jo = johannsenite, Alm = almandine, Adr = andradite, Grs = grossular, Prp = pyrope, Sps = spessartine.

1–4 – pyroxene (prograde calcic skarn), 5–13 – garnet (5–7 – light pale-brown to pale-brown garnet from early prograde calcic endo- and exoskarn, 8–9 – brown garnet from late prograde calcic skarn, 10–11 – dark-brown garnet from retrograde skarn, 12–13 – dark-green garnet from retrograde skarn).

limited to bornite (“bornite-0”; Table 5) occurring in the interstitions of coarse-grained retrograde skarn garnet (with epidote, calcite, quartz) and wollastonite aggregate; garnet and other skarn minerals are euhedral relative to bornite indicating at least their simultaneous formation (Fig. 8A–B). Minor chalcopryite is also present; it, however, typically replaces bornite and can be younger. Larger patches of massive bornite are present (Fig. 7G–I), and retrograde skarn with Cu mineralization is widespread but appears to contain no Au without superimposed younger alteration assemblages (Table 4). Also, much larger skarn masses are barren and considered for selective mining of pure wollastonite.

7.3. Propylitic alteration

Propylitic alteration has distinct development in linear zones crosscutting and overprinting skarns, where it forms variously-oriented

linear veinlets, and in wider zones of pervasive alteration, particularly occurring in close proximity to and overprinting the early intraminal mafic dikes (Fig. 7J–I). It comprises quartz, calcite, epidote, amphibole, chlorite, and oligoclase-albite, locally also scapolite, apatite, minor magnetite and/or hematite, and sulfide minerals. Most widespread assemblages are epidote-rich (epidote-plagioclase-calcite-quartz, epidote-magnetite-plagioclase-quartz, epidote-chlorite-calcite-quartz, typically also with clinozoisite, zoisite and/or prehnite; Fig. 7K), whereas amphibole- and/or chlorite-dominant assemblages are less abundant.

Propylitic alteration comprises significant sulfide and Au mineralization including the assemblage of chalcopryite-Fe bornite + tennantite and high-fineness (~940–910‰) native Au (“gold-1”; Table 5; Figs. 8C–D 9). These sulfides intersect, corrode and replace retrograde skarn minerals (Fig. 8E) and occur most broadly in altered garnet and pyroxene skarns (Fig. 8F–H), to less extent in wollastonite skarn. In magnetite-rich skarns, propylitic alteration contains abundant

Table 4

Representative analyses of skarns and post-skarn hydrothermal alteration assemblages from the Sinyukhinskoe deposit (ppm).

Sample numbers	36	8	60	7	39	19	73	11	16	74	9
	1	2	3	4	5	6	7	8	9	10	11
Au	< 0.2	< 0.2	< 0.2	3.7	8.72	1.0	48.3	14.9	819.7	91.0	277.6
Ag	< 5	< 5	32.0	86.0	7.0	60.0	41.0	110.0	316.0	25.5	116.0
Cu	100	2050	22,400	38,000	5500	13,200	15,700	80,000	42,600	20,200	67,000
As	65	189	133	141	154	564	183	574	183	135	141
Sb	12	0.16	59	0.60	0.82	2.07	1.65	341	1.54	2.09	1.25
Co	13	8.68	18	12	8.06	11	18	18	15	19	15
Ni	36	42	43	37	72	25	29	58	39	24	84
Mo	3.87	1.87	3.86	77	0.99	1.25	2.20	5.74	0.80	1.55	1.80
Zn	111	24	562	60	49	229	115	253	63	103	84
Pb	21	4.19	8.41	72	13	65	65	19	24	20	610
Bi	1.48	4.59	1.66	168	38	70	21	352	64	96	221
Se	3.14	2.44	13.21	32	5.70	11	31	49	37	28	89
Te	5.28	1.38	10.64	31	6.82	7.93	22	47	74	18	182
Hg	0.00	0.16	0.18	0.05	0.00	0.09	1.07	0.36	0.00	0.88	0.21
W	1.14	2.82	1.58	2.73	0.58	1.59	3.89	2.74	3.64	7.48	2.79
Sn	0.00	1.20	0.00	4.43	0.00	2.81	6.50	0.28	6.91	8.07	0.28
Cd	0.43	0.12	3.71	0.75	0.53	3.60	5.61	5.20	0.25	2.63	64
In	0.13	0.26	0.15	1.19	0.44	0.44	0.45	1.01	1.14	2.08	0.34
Ba	584	3.74	10	2.42	56	2.41	10	7.55	4.99	15	4.83
B	20	3.58	78	17	14	339	3.53	13	413	2.86	3.33
Ga	22	13	14	6.17	7.10	6.22	17	7.64	16	16	11
Ge	1.23	1.01	0.42	0.87	0.63	1.04	1.69	0.68	1.30	2.05	1.34
Pt			0.2						0.03		0.2
Pd			0.03						0.01		0.5

1 – barren prograde garnet-pyroxene skarn, 2 – weakly-mineralized garnet-pyroxene-wollastonite skarn, 3 – retrograde wollastonite-pyroxene-garnet to garnet-wollastonite skarn with quartz-calcite-chlorite to epidote-albite-quartz-calcite (propylitic alteration) overprint, 4–11 – retrograde wollastonite-pyroxene-garnet to garnet-wollastonite skarn with quartz-calcite-chlorite to epidote-albite-quartz-calcite (propylitic alteration) overprint and minor quartz-sericite (phyllitic alteration) overprint.

Table 5
Representative chemical compositions of native gold, and some sulfide, sulfosalt and telluride minerals from the Sinyukhinskoe deposit (wt%).

Mineral	Au	Ag	Fe	As	Cu	Bi	Sb	Hg	Pb	Zn	Se	Te	S	Total	Empirical formula
<i>Native gold ("gold-1") in propylitic alteration assemblage: high-fineness gold-copper association (gold-chalcocopyrite-Fe bornite assemblage)</i>															
Native Au	91.58	6.84			0.39	0.05		0.36				0.09		99.31	$\text{Cu}_{4.79}\text{Fe}_{1.10}\text{Bi}_{0.01}\text{S}_{4.10}$
Native Au	93.17	5.35			0.58	0.05		0.29				0.09		99.52	$(\text{Cu}_{15.20}\text{Ag}_{0.01})_{5.21}\text{Fe}_{0.78}\text{S}_{4.01}$
Native Au	92.54	6.04			0.54	0.00		0.04				0.16		99.32	$\text{Cu}_{5.34}\text{Fe}_{0.58}\text{Bi}_{0.01}\text{S}_{4.07}$
<i>Early native gold ("gold-2") in phyllic alteration assemblage: moderate-fineness gold-copper association (gold-chalcocite-Cu-bornite assemblage)</i>															
Native Au	89.54	8.49			0.50	0.16		0.28				0.10		99.08	$\text{Cu}_{2.00}\text{S}_{1.00}$
Native Au	87.74	11.05			0.31	0.10		0.33				0.08		99.61	$\text{Cu}_{1.91}\text{S}_{1.09}$
Native Au	88.45	10.28			0.28	0.30		0.22				0.14		99.67	$\text{Cu}_{0.99}\text{Fe}_{1.01}\text{S}_{2.00}$
Native Au	89.62	8.88			0.38	0.16		0.30				0.05		99.38	$\text{Cu}_{10.31}(\text{Zn}_{1.00}\text{Fe}_{0.83})_{1.83}(\text{As}_{3.73}\text{Bi}_{0.36}\text{Sb}_{0.03})_{4.12}(\text{S}_{12.65}\text{Se}_{0.05})_{12.74}$
<i>Late native gold ("gold-3") in phyllic alteration assemblage: low-fineness gold-telluride association</i>															
Native Au	76.77	22.12			0.46	0.43		0.03				0.09		99.90	$(\text{Cu}_{10.46}\text{Ag}_{0.05})_{10.45}(\text{Zn}_{1.50}\text{Fe}_{0.13})_{1.63}(\text{As}_{2.51}\text{Sb}_{1.51}\text{Bi}_{0.07})_{4.09}(\text{S}_{12.81}\text{Se}_{0.02})_{12.83}$
Native Au	79.13	20.49			0.02	0.07		0.00				0.17		99.88	$\text{Zn}_{1.01}\text{S}_{0.99}$
Native Au	81.22	17.50			0.78	0.32		0.04				0.07		99.93	$(\text{Zn}_{1.00}\text{S}_{0.99})_{1.00}\text{S}_{0.99}$
Native Au	81.53	17.48			0.24	0.00		0.07				0.02		99.34	$\text{Pb}_{1.00}(\text{S}_{0.98}\text{Se}_{0.02})_{1.00}$
Native Au	80.77	17.49			0.63	0.04		0.00				0.09		99.02	$\text{Pb}_{0.98}(\text{S}_{0.69}\text{Se}_{0.33})_{1.02}$
<i>Sulfide, sulfosalt and telluride minerals</i>															
Bornite-1*		0.03	12.13		60.43	0.42							26.27	99.13	$\text{Te}_{3.03}\text{Bi}_{1.97}$
Bornite-2**		0.22	8.61		64.95	0.17							25.26	99.21	$\text{Bi}_{1.99}\text{Te}_{1.93}(\text{S}_{0.88}\text{Se}_{0.20})_{1.08}$
Bornite-2**		0.10	6.41		67.04	0.30							25.76	99.49	$\text{Bi}_{2.23}\text{Te}_{2.06}(\text{S}_{0.52}\text{Se}_{0.19})_{0.71}$
Chalcocite		0.02	0.02		79.73	0.04						0.00	20.12	99.93	$(\text{Cu}_{3.05}\text{Ag}_{0.02})_{3.07}\text{Bi}_{1.00}\text{S}_{2.93}$
Chalcocite		0.23	0.00		76.60	0.08						0.03	21.86	98.97	$(\text{Pb}_{0.97}\text{Cu}_{0.03})_{1.00}(\text{Te}_{0.97}\text{Se}_{0.03})_{1.00}$
Chalcocopyrite		0.00	30.54		34.32	0.13							34.83	99.92	$(\text{Cu}_{0.95}\text{Ag}_{0.01})_{0.96}\text{Pb}_{1.04}\text{Bi}_{0.97}(\text{S}_{2.92}\text{Se}_{0.11})_{3.03}$
Tennantite		0.01	3.02	18.24	42.76	4.93	0.25			4.26	0.23		26.25	100.25	$\text{Au}_{1.22}\text{Ag}_{2.68}\text{Te}_{2.10}$
Tetrahedrite		0.36	0.45	11.92	41.97	0.93	11.67			6.21	0.11		26.08	99.70	$\text{Ag}_{1.99}\text{Te}_{1.01}$
Sphalerite***		0.03	0.15		0.68					67.36			31.69	100.34	$\text{Ag}_{5.02}\text{Te}_{2.98}$
Sphalerite****		0.00	0.03		0.00					65.24			31.86	100.11	
Galena		0.00			0.07	0.24			86.08		0.70	0.00	12.94	100.03	
Galena		0.05			0.78	1.43			77.93		10.22	0.13	8.58	99.12	
Tellurobismuthite	0.21	8.40			0.17	38.12			0.02		0.10	52.27	0.04	99.33	
Tellurobismuthite	0.00	0.29			0.17	50.73			0.11		0.16	47.79	0.06	99.31	
Tetradimitite		0.34			0.62	58.11			0.03		2.19	34.44	3.97	99.70	
Tetradimitite		0.37			0.32	60.78			0.00		1.99	34.23	2.13	99.52	
Wittichenite		0.22	0.00		38.82	42.02	0.07			0.02	0.08		18.81	100.03	
Altaite	0.25	0.31			0.88	0.77			59.49		1.09	36.51	0.05	99.35	
Alkinitite		0.14			10.30	34.65			36.60		1.43		15.94	99.06	
Calaverite	41.55	1.12			0.32	0.19			0.07		0.01	57.27	0.01	100.51	
Perzite	29.17	35.40			0.93	0.50			0.00		0.01	33.79	0.07	99.74	
Hessite	0.19	61.91			0.30	0.00			0.00		0.06	37.27	0.05	99.78	
Stutzite	0.00	58.00			0.26	0.00			0.18		0.00	40.89	0.03	99.36	

*Early high-Fe bornite, **late high-Cu bornite; ***sphalerite contains 0.43 wt% Cd and 0.00 wt% In; ****sphalerite contains 2.91 wt% Cd and 0.07 wt% In.

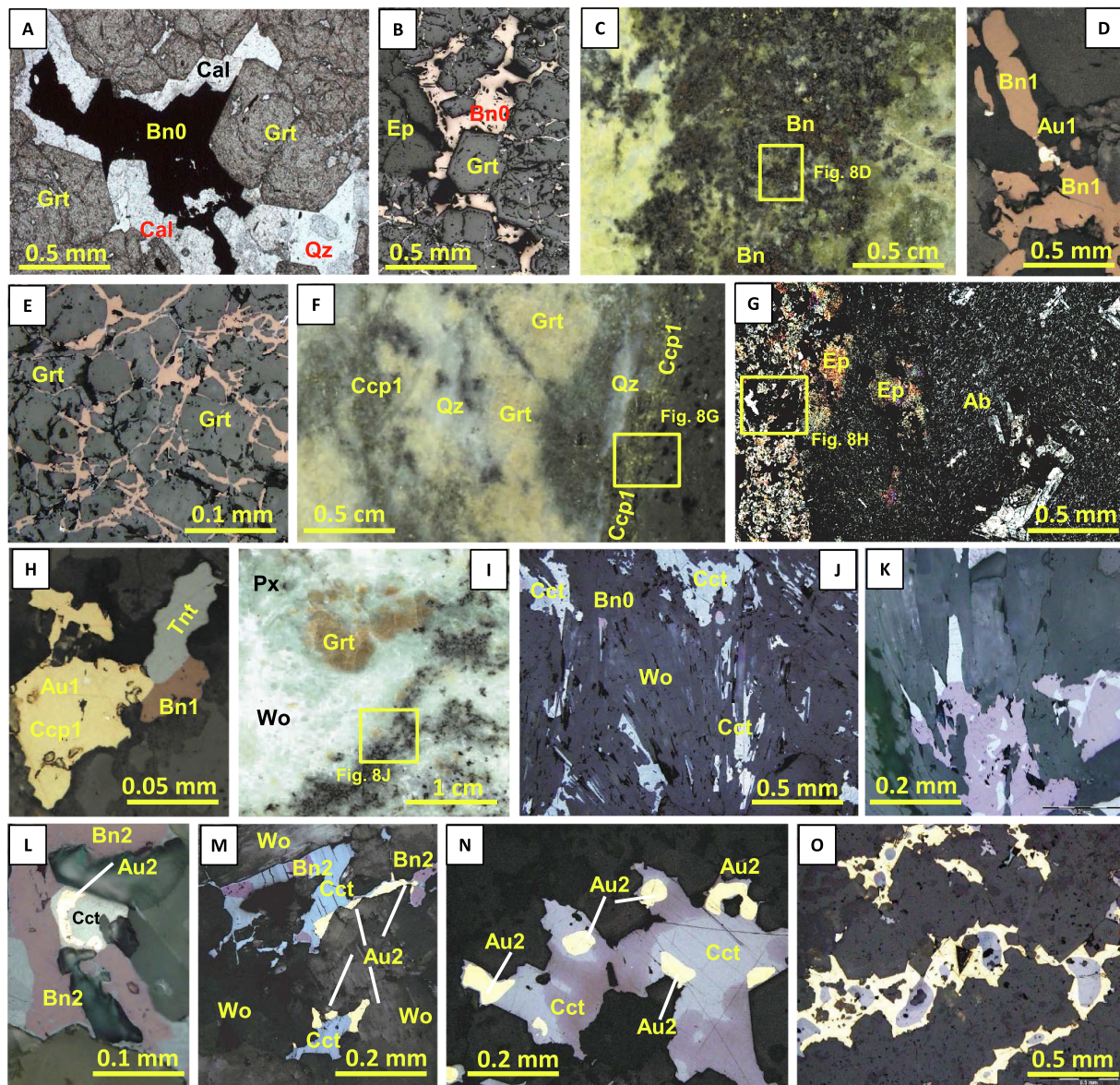


Fig. 8. Photographs and photomicrographs showing relationships of minerals at the Sinyukhinskoe deposit. A. Retrograde garnet-calcite-quartz skarn with bornite (“bornite-0”) and chalcocite (thin section). B. Retrograde garnet-epidote skarn with bornite (“bornite-0”) (polished section). C-D. Garnet-pyroxene-vesuvianite skarn is replaced by epidote-quartz-calcite (propylitic) alteration assemblage with bornite (“bornite-1”) and native gold (“gold-1”) (D – polished slab, D – polished section). E. Bornite from propylitic assemblage (“bornite-1”) forming crosscutting stockwork in retrograde skarn garnet (polished section). F-H. Monzogabbro- to monzodiorite-porphry dike intersects garnet-pyroxene skarn, and both are overprinted by epidote-chlorite-albite-quartz-calcite (propylitic) alteration with chalcopyrite, bornite, tennantite and native gold (“gold-1”) (F – polished slab, G – thin section, nicols crossed, H – polished section). I-K. Retrograde wollastonite skarn replaces prograde pyroxene-garnet skarn (remaining in small relicts) and is overprinted by Cu-Au mineralization (polished slab). J. Bornite and chalcocite in retrograde wollastonite skarn overprinted by phyllic alteration (polished section). K. Larger view showing bornite-2 and chalcocite corroding and replacing wollastonite (polished section). L. Scavenging of gold (“gold-2”) by chalcocite associated with (or replacing) bornite (polished section). M-O. Native gold (“gold-2”) associated with chalcocite (polished sections). Abbreviations: Ccp – chalcopyrite, Bn – bornite, Cct – chalcocite, Au – native gold, Tnt – tennantite, Grt – garnet, Qz – quartz, Px – pyroxene, Wo – wollastonite, Ep – epidote, Cal – calcite, Ab – albite.

magnetite, pyrite, and chalcopyrite, locally with pyrrhotite and/or sphalerite, and occasionally apatite. Sporadic Co-Ni minerals (cobaltite, siegenite, carrollite) occur together with pyrite replacing magnetite-rich skarns in zones of amphibole-chlorite-calcite-quartz alteration (Gaskov et al., 2010).

7.4. Phyllic alteration

Phyllic alteration is represented by quartz-dominant stockworks of thin variously-oriented sheeted veinlets and wider zones of incipient to pervasive replacement (Fig. 7M–N). These veinlets typically contain quartz with no alteration selvages, however, trace to minor sericite (and

occasionally much greater sericite content) are locally present, thus supporting the phyllic alteration affinity. Minor chlorite, carbonate (calcite, occasionally ankerite and/or siderite) and albite occur locally. Small breccia zones with quartz-Fe-carbonate-albite-chlorite-sericite-sulfide cement are also present.

Phyllic alteration comprises most abundant sulfide and Au mineralization represented by several assemblages, and phyllic alteration overprint of altered wollastonite, garnet-wollastonite and garnet-pyroxene-wollastonite skarns causes the highest-grade Au and Cu mineralization (Table 4). Cu-rich bornite and chalcocite dominate (Fig. 8I–K); pyrite, sphalerite, galena, arsenopyrite, pyrrhotite, tetrahedrite are minor, and altaite, hedleyite, melonite, tetradimite, wittichenite,

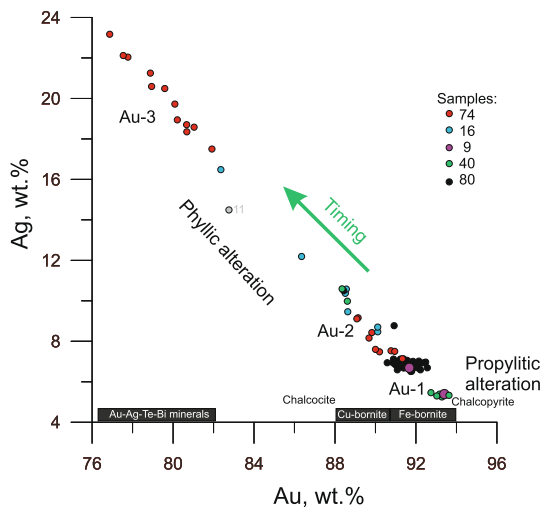


Fig. 9. Gold and silver contents in various generations of native gold at the Sinyukhinskoe deposit.

bismuthinite, petzite, calaverite, stützite and other minerals (Table 5; Fig. 10) occur sporadically and in trace concentrations. An early gold-sulfide assemblage comprises lower-fineness ($\sim 910\text{--}880\%$) native Au ("gold-2"; Table 5; Fig. 8L–O, 9) associated with Cu-bornite and chalcocite. Bornite during phyllic alteration tends to be deposited in the skarn protolith with higher Fe contents (i.e., garnet and pyroxene skarns), whereas chalcocite dominates over bornite where wollastonite skarn is replaced. Gold appears to be scavenged by chalcocite, and/or deposited in close proximity to chalcocite, the latter locally replacing earlier bornite (Fig. 8L–O). Gusev (2016) reported very high Au content in chalcocite (2475 g/t Au) as compared to that in bornite (457 g/t Au), chalcopyrite (3.8 g/t Au), pyrite (8.4–10.2 g/t Au) and magnetite (4.2 g/t Au). The latest, low-fineness ($\sim 820\text{--}760\%$) native Au ("gold-3"; Table 5; Fig. 9) is associated with tellurides and forms very fine grains and hairline to dendritic veinlets (Fig. 10K–M). Consistently, the phyllic assemblages are characterized by elevated Te grades (Table 4).

8. Fluid inclusion study

The present study was focused on fluid inclusions in hydrothermal mineral assemblages using the mineral paragenesis described above (Fig. 6). In prograde skarn minerals, we observed no fluid inclusions confidently regarded to as primary ones and without post-entrapment modifications. Consistently, fluid inclusions were studied in minerals

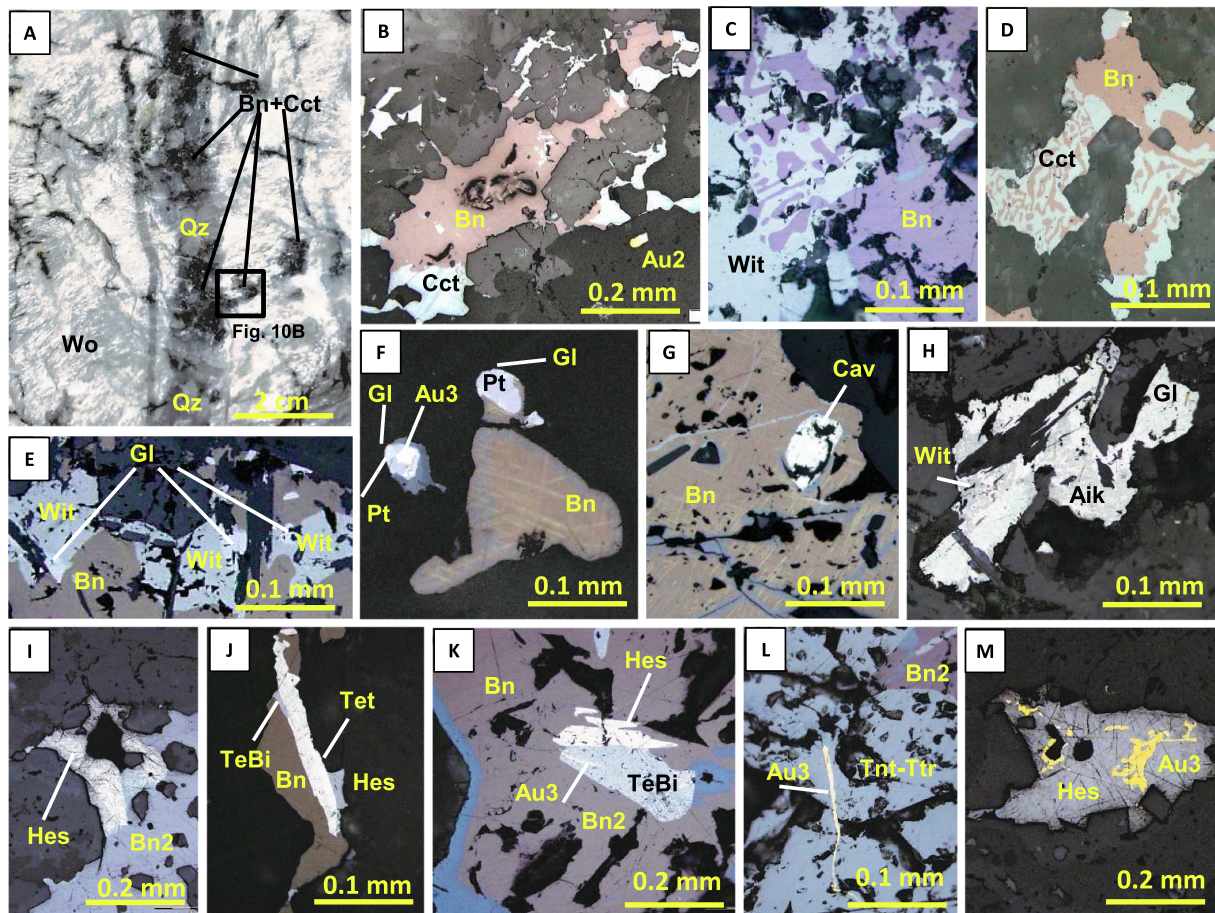


Fig. 10. Photographs and photomicrographs showing relationships of minerals in phyllic alteration zones at the Sinyukhinskoe deposit (B–M - polished sections). A. Quartz-sulfide veinlets cut wollastonite skarn. B. Bornite and chalcocite in quartz-sulfide veinlet cutting wollastonite skarn. C. Exsolution intergrowths of bornite and wittichenite. D. Mirmekitic exsolution intergrowths of bornite and chalcocite. E. Galena and wittichenite replace bornite. F. Galena, petzite and late low-fineness native gold ("gold-3") replacing bornite with chalcopyrite exsolution intergrowths. G. Calaverite replacing bornite with chalcopyrite exsolution intergrowths. H. Aggregate of galena, aikinite and wittichenite. I. Hessite replacing bornite. J. Hessite, tetradymite and tellurobismuthite replacing bornite. K. Hessite, tellurobismuthite and late low-fineness native gold ("gold-3") replacing bornite. L. Late low-fineness native gold ("gold-3") in tennantite-tetrahedrite replacing bornite. M. Late low-fineness native gold ("gold-3") in hessite. Abbreviations: Wo – wollastonite, Qz – quartz, Bn – bornite, Cct – chalcocite, Gl – galena, Au – native gold, Tnt-Ttr – tennantite-tetrahedrite, Hes – hessite, Pt – petzite, TeBi – tellurobismuthite, Cav – calaverite, Wit – wittichenite, Aik – aikinite, Tet – tetradymite.

Table 6

Types of fluid inclusions (FI) in minerals from various hydrothermal assemblages of the Sinyukhinskoe deposit.

Mineral (number of FI studied)	FI type	FI size, μm	FI content	T_m eu., $^{\circ}\text{C}$	T_m ice, $^{\circ}\text{C}$	Homogenization, T_h , $^{\circ}\text{C}$	Estimated salinity, wt%	Estimated pressure, bars, and T_h correction, $^{\circ}\text{C}$
<i>Retrograde skarn</i>								
Dark-brown and dark-green garnet (26)	1	< 5–30	15–20 vol% gas, 2–5 solids ~ 20–40 vol %, no halite	–36.5 to –33.5	–21.0 to –20.0	To liquid: gas at 170–180	MgCl ₂ + NaCl 18 to 23 ^a	2.5 $\pm$ 0.5 kbar ^c (220–330)
<i>Propylitic (epidote-amphibole-chlorite-quartz-calcite) alteration</i>								
Epidote, quartz, calcite (20)	2	< 5–20	20–30 vol% gas, 0–2 solids	–56.5 to –53.5	–14.4 to –11.0	To liquid: gas at 320–360	CaCl ₂ + NaCl 16 to 20 ^b	0.5–0.8 kbar ^c (40–80)
Epidote, quartz, calcite (40)	3	< 5–30	10–15 vol% gas	–28.5 to –25.0	–3.5 to –1.5	To liquid: gas at 150–215	NaCl 2.6 to 5.7 ^c	0.5–0.8 kbar ^c (40–70)
<i>Phyllic (quartz-sericite) alteration</i>								
Quartz from quartz-sulfide veinlets (20)	4	< 5–25	10–15 vol% gas, 4 solids ~ 20–40 vol%	–55...–50	–24...–25	To liquid: gas at 125–135, sylvite at 175–180, halite at 275–285	KCl 22 ^d NaCl 18 ^d CaCl ₂ 10 ^d	1.3 $\pm$ 0.1 kbar ^f (150)
Quartz from quartz-sulfide veinlets (14)	5	< 5–30	15–20 vol% gas, 0–1 solids	–55...–50	–29.5...–30.5	To liquid: gas at 150–190	KCl + NaCl 2 to 8 ^d CaCl ₂ 24 to 18 ^d	< 1.3 кбар (<150)

 T_m eu. – eutectic temperature (first melting temperature), $^{\circ}\text{C}$; T_m ice – final ice melting temperature, $^{\circ}\text{C}$;^a Salinity estimated by final ice melting temperatures for the NaCl-MgCl₂-H₂O system (Dubois and Marignac, 1997);^b Salinity estimated by final ice melting temperatures for the NaCl-CaCl₂-H₂O system (Vanko et al., 1988; Oakes et al., 1990);^c Salinity was estimated by final ice melting temperatures for the NaCl-H₂O system (Bodnar and Vityk, 1994);^d Salinity estimated by halite and sylvite dissolution temperatures for the KCl-NaCl-H₂O system (Roedder, 1971; Sterner et al., 1988) and by halite dissolution temperature and final ice melting temperatures for the NaCl-CaCl₂-H₂O system (Vanko et al., 1988; Oakes et al., 1990);^e The trapping pressure estimated by using the salinity of fluid inclusions, homogenization temperature (T_h), and the temperature of mineral formation defined by mineral paragenesis (Roedder, 1984; Bodnar and Vityk, 1994);^f The minimal trapping pressure estimated by using the gas to liquid homogenization temperature and halite melting temperature (Atkinson, 2002; Becker et al., 2008).

from retrograde skarn, propylitic and phyllic alteration assemblages (Table 6). The samples for this study were taken from the open pits (< 50 m depth) and from underground adits.

8.1. Fluid inclusions in retrograde skarn minerals

Type 1 fluid inclusions have been observed in the dark-brown and dark-green garnet of retrograde skarn, mostly as isolated individuals and in clusters. They contain a small to moderately-sized (15–20 vol%) gas bubble and 2–5 solid phases occupying 20–40 vol% (Fig. 11A–C). The solids include anisotropic highly birefringent minerals, hematite (red or orange thin plates), and rarely a small black non-magnetic opaque phase. On warming after freezing, type 1 inclusions exhibit eutectic melting temperatures of around –35 $^{\circ}\text{C}$, indicating dominant MgCl₂ and NaCl in solution (Crawford, 1981), and final ice melting temperatures of –21 to –20 $^{\circ}\text{C}$. On heating, the inclusions exhibit disappearance of a gas bubble at 170–180 $^{\circ}\text{C}$ (Table 6). Heating to higher temperatures caused decrepitation of the inclusions at 320–330 $^{\circ}\text{C}$. For type 1 inclusions, salinity estimates for the MgCl₂-NaCl-H₂O system, based on the final ice melting temperatures, indicate a salinity of 18 to 23 wt% NaCl + MgCl₂ (Fig. 12A; Table 6, Dubois and Marignac, 1997).

8.2. Fluid inclusions in minerals from propylitic alteration assemblage

Primary and pseudosecondary aqueous liquid-gaseous type 2 fluid inclusions in epidote, quartz and calcite from propylitic alteration assemblage occur as isolated individuals and in small clusters. These inclusions contain a medium-sized (20–30 vol%) gas bubble and occasionally 1–2 small anisotropic solid phases (Fig. 11D–I; Table 6). On warming after freezing, type 2 inclusions exhibit eutectic melting temperatures of around –55 $^{\circ}\text{C}$, indicating dominant CaCl₂ and NaCl in solution (Crawford, 1981), and final ice melting temperatures from –14.4 $^{\circ}\text{C}$ to –11 $^{\circ}\text{C}$. On heating, the inclusions homogenize at 320–360 $^{\circ}\text{C}$ to liquid. Heating to higher temperatures caused

decrepitation of the inclusions at 530–550 $^{\circ}\text{C}$. Salinity estimates for the CaCl₂-NaCl-H₂O system, based on the ice melting temperatures, indicate a salinity of 16 to 20 wt% CaCl₂ + NaCl (Vanko et al., 1988; Table 6; Fig. 12B).

Liquid-gaseous type 3 fluid inclusions are the most numerous in the propylitic alteration minerals and are younger than type 2 inclusions. These inclusions form trails and cloudy 3D groups, and contain a small (10–15 vol%) gas bubble (Fig. 11J–K; Table 6). On warming after freezing, type 3 inclusions exhibit eutectic melting temperatures of around –27 $^{\circ}\text{C}$, indicating a dominant NaCl in solution (Crawford, 1981), and final ice melting temperatures varying from –3.5 $^{\circ}\text{C}$ to –1.5 $^{\circ}\text{C}$. On heating, the inclusions homogenize at 150–215 $^{\circ}\text{C}$ to liquid. For type 3 inclusions, salinity estimates for the NaCl-H₂O system, based on the ice melting temperatures, indicate a salinity of 2.6 to 5.7 wt% NaCl-eq. (Bodnar and Vityk, 1994; Table 6).

8.3. Fluid inclusions in minerals from phyllic alteration assemblage

Quartz from quartz-sulfide veins crosscutting retrograde garnet and wollastonite skarn and assigned to the phyllic alteration stage contains multisolid type 4 fluid inclusions (Table 6). These inclusions occurring as isolated individuals and in small clusters contain a small (10–15 vol %) gas bubble and small amount of liquid, together with dominant solid phases (Fig. 11L). The latter include cubic to rounded isotropic crystals (halite and likely sylvite), anisotropic highly birefringent phase(s), and often a small black non-magnetic opaque phase. The solid phase thought to be sylvite, halite and anisotropic phase are systematically present in the fluid inclusions and in relatively constant volume ratios, with also constant liquid/vapor/solid ratios and coherent homogenization temperatures, and thus can be considered as daughter minerals (Roedder, 1984). On warming after freezing, the inclusions exhibit eutectic melting temperatures from –55 $^{\circ}\text{C}$ to –50 $^{\circ}\text{C}$ indicating the presence of CaCl₂ (Crawford, 1981). On heating, the inclusions exhibit disappearance of gas bubble at 130 ± 5 $^{\circ}\text{C}$, dissolution of sylvite at 175–180 $^{\circ}\text{C}$, and then dissolution of halite at 280 ± 5 $^{\circ}\text{C}$

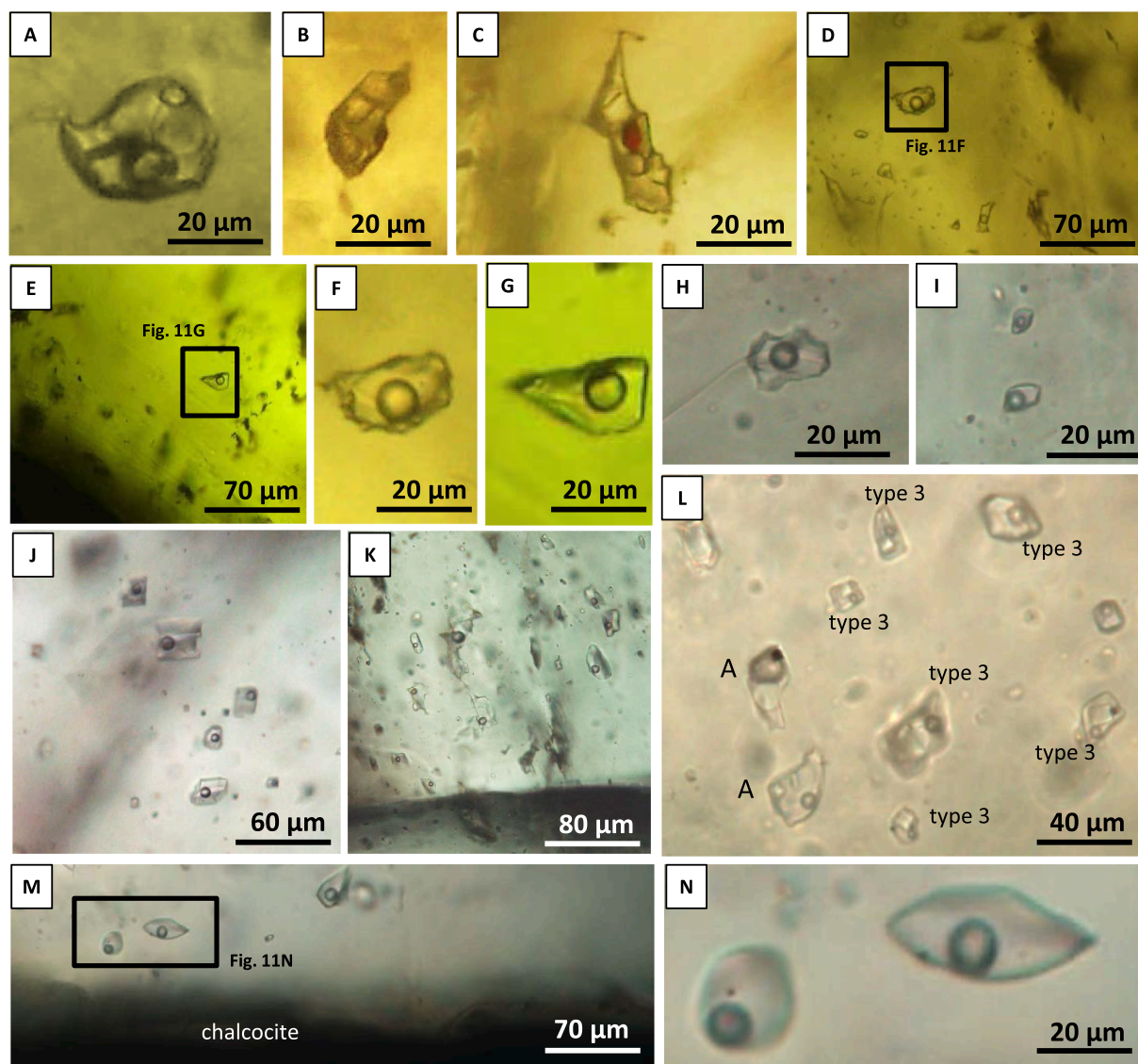


Fig. 11. Types of fluid inclusions in minerals from various hydrothermal alteration assemblages at the Sinyukhinskoe deposit. A–C. Type 1 multiphase fluid inclusions in dark-brown and dark-green garnet from retrograde skarn. D–G. Type 2 liquid-gaseous fluid inclusions in epidote from propylitic alteration assemblage (F–G – larger views). H. Type 2 liquid-gaseous fluid inclusions in calcite from propylitic alteration assemblage. I. Type 2 liquid-gaseous fluid inclusions in quartz from propylitic alteration assemblage. J. Type 3 liquid-gaseous fluid inclusions in calcite from propylitic alteration assemblage. K. Type 3 liquid-gaseous fluid inclusions in quartz from propylitic alteration assemblage. L. Cluster of type 4 multisolid fluid inclusions in quartz from quartz-sulfide veinlet cutting wollastonite skarn (see Fig. 10A). Note the two anomalous inclusions (A), probably necked down, with atypical phase volumes. M–N. Pseudosecondary type 5 aqueous liquid-gaseous (with a small opaque solid phase) fluid inclusions in quartz from quartz-sulfide veinlet with abundant chalcocite cutting wollastonite skarn (see Fig. 10A) (N – larger view). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Table 6). Heating to higher temperatures caused decrepitation of the inclusions at 430–450 °C, after significant dissolution of anisotropic solid phase. For type 4 fluid inclusions, assuming both halite and sylvite are present, salinity estimates in the KCl–NaCl–H₂O system were obtained using dissolution temperatures of sylvite and halite (Roedder, 1971; Sterner et al., 1988) (Fig. 12C; Table 6). These estimates yield a concentration of 23 wt% NaCl and 27 wt% KCl. Salinity estimates in the NaCl–CaCl₂–H₂O system yield a concentration of ~10 wt% CaCl₂ (Vanko et al., 1988; Oakes et al., 1990; Fig. 12B), and the calculated fluid salinity is 22 wt% KCl, 18 wt% NaCl and 10 wt% CaCl₂ (Table 6).

The primary and pseudosecondary aqueous liquid-gaseous type 5 fluid inclusions in quartz from phyllic alteration assemblage occur mostly as isolated individuals and in small clusters. They contain a small to moderately-sized (15–20 vol%) gas bubble and occasionally small opaque solid phase(s) (Fig. 11M–N). On warming after freezing, these inclusions exhibit eutectic melting temperatures of –55 to

–50 °C, indicating the presence of CaCl₂, NaCl and KCl (Crawford, 1981), and final ice melting temperatures of around –30 °C. These inclusions homogenize at 150–190 °C to liquid (Table 6). For type 5 inclusions, salinity estimates for the CaCl₂–NaCl–H₂O system, based on the ice melting temperatures, indicate a salinity of 18 to 24 wt% CaCl₂ and 2 to 8 wt% NaCl (+ KCl) (Vanko et al., 1988; Table 6).

9. Oxygen, carbon and sulfur isotopes

Oxygen and carbon isotopes were studied in calcite from marble (limestone) far outside skarn zones, from marble hosting skarn zones, and in calcite from prograde and retrograde skarn, propylitic and phyllic alteration assemblages (Table 7). Based on the respective temperatures of mineral formation, oxygen and carbon isotopic compositions of the fluid in equilibrium with calcite were calculated, using the oxygen fractionation equation for the CaCO₃–H₂O system (Faure, 1986)

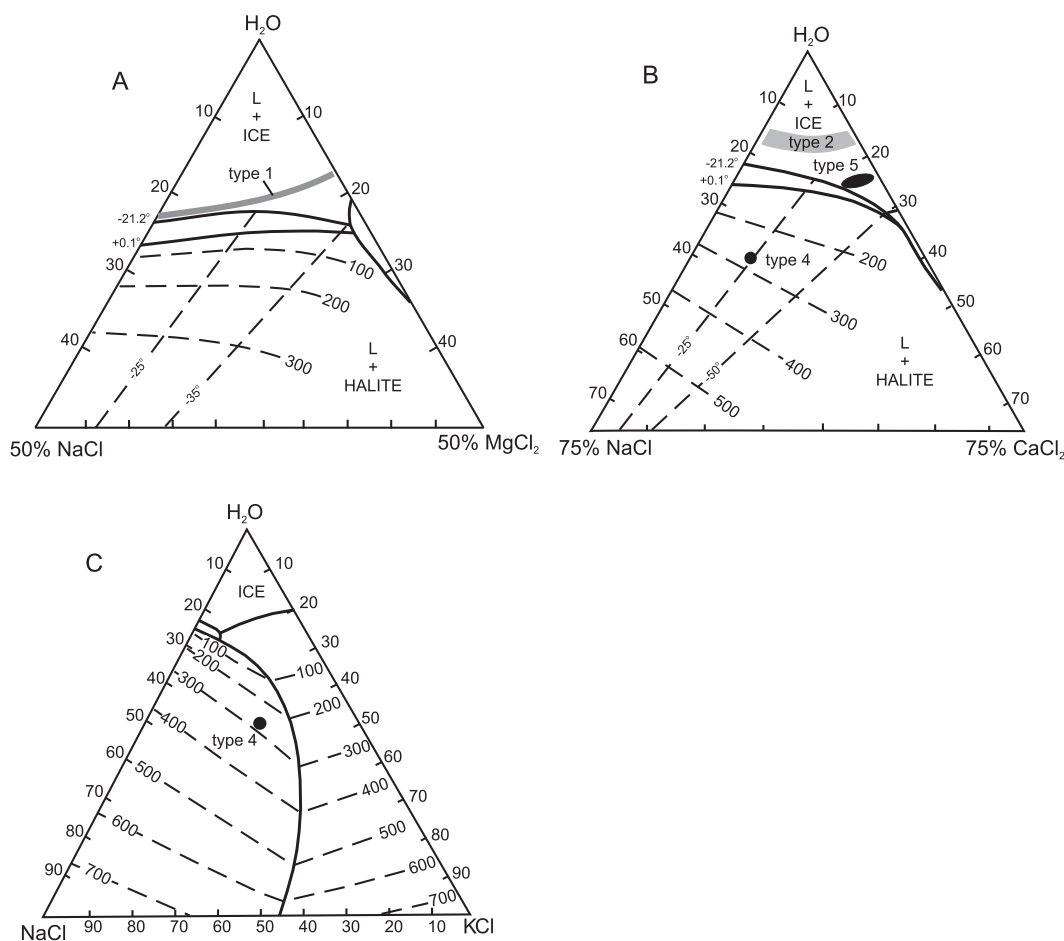


Fig. 12. Fluid inclusion data for minerals from various hydrothermal assemblages at the Sinyukhinskoe deposit. (A) NaCl-MgCl₂-H₂O compositions of type 1 fluid inclusions (phase diagram after Dubois and Marignac, 1997). (B) NaCl-CaCl₂-H₂O compositions of type 2, 4 and 5 fluid inclusions (phase diagram after Vanco et al., 1988; Oakes et al., 1990). (C) NaCl-KCl-H₂O compositions of type 4 fluid inclusions (phase diagram after Roedder, 1971; Sterner et al., 1988).

and carbon fractionation equation for the CaCO₃-CO₂ system (Ohmoto and Rye, 1979) (Table 7). These data show that the isotopic evolution of the fluid can be subdivided into several trends, which differ in relative changes of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (Fig. 13). In particular, trend 1A corresponds to the transition from limestone to marble and is expressed in decreasing both $\delta^{13}\text{C}$ (from 0.6 to -0.5‰) and $\delta^{18}\text{O}$ (from 25.9 to 14.8‰). Another trend (1B) occurs due to increasing $\delta^{13}\text{C}$ (to 1.6–2.3‰) and decreasing $\delta^{18}\text{O}$ (from 25.9 to 14.8‰) from limestone through marble to prograde skarn. During the retrograde skarn stage, trend 2A reflects decreasing both $\delta^{13}\text{C}$ (from 2.1 to -0.6‰) and $\delta^{18}\text{O}$ (from 11.2 to 8.7‰) values. This is followed by a stronger decrease of both $\delta^{13}\text{C}$ (from -0.2 to -3.2‰) and $\delta^{18}\text{O}$ (from 6.1 to 0.8‰) values during the propylitic stage (trend 3). Finally, trend 2B corresponds to the replacement of propylitic-altered skarn by phyllic alteration assemblages and shows decreasing $\delta^{13}\text{C}$ (from -0.1 to -4.2‰) values and increasing $\delta^{18}\text{O}$ (from 4.1 to 6.6‰) values (Fig. 13).

Sulfur isotopes were studied in bornite, chalcocite, chalcopyrite and pyrite from retrograde skarn, propylitic and phyllic alteration assemblages (Table 8). The data demonstrate a homogenous overall sulfur isotope composition ($\delta^{34}\text{S}$ varies from -3.6 to $+2.7\text{‰}$, with most $\delta^{34}\text{S}$ values being in the range of -1.5 to $+0.5\text{‰}$). However, there is an increase of $\delta^{34}\text{S}$ values in sulfides from prograde skarn ($\delta^{34}\text{S} = -3.6$ to -1.0‰) through those from propylitic alteration ($\delta^{34}\text{S} = -2.7$ to $+0.6\text{‰}$) to those from phyllic alteration ($\delta^{34}\text{S} = +2.7\text{‰}$).

10. Discussion

10.1. Regional tectonic and metallogenic setting

Despite of the fact that the Sinyukhinskoe deposit is mined primarily for its high Au endowment, it bears striking similarities to Cu-Au skarn deposits, which are, in turn, part of a broader Cu-Au porphyry-skarn deposit family (Ettlinger and Meinert, 1991). Consistently, this Au-Cu to Cu-Au skarn mineralization can be related to Cu-Au porphyry analogies within a larger (district- to regional-scale) skarn-porphyry mineralized system.

The Sinyukhinskoe deposit is situated in the central part of the Altaid orogenic system (CAOB), and was formed in Devonian to Carboniferous magmatic arcs that are the most productive for Cu-Au porphyry and related skarn mineralization in the region. The emplacement of the productive plutonic suites in Altai corresponded to a Devonian subduction-related continental magmatic arc setting, with its further evolution toward a late- and post-collisional regime in the late Devonian-Carboniferous. This allows the consideration of regional metallogenic links within the larger terrane of the central Altaids, with possible extension toward the Devonian-Carboniferous Oyu Tolgoi Cu-Au mineralized cluster in Mongolia. On the other hand, this further emphasizes the potential Cu-Au fertility of the Devonian-Carboniferous igneous suites in Altai.

Table 7

Oxygen and carbon isotope data for calcite and corresponding calcite-equilibrium fluids at the Sinyukhinskoe deposit.

Sample number	Description of samples	Calcite		Fluid	
		$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{SMOW}}$	CO_2 , $\delta^{13}\text{C}_{\text{PDB}}$	H_2O , $\delta^{18}\text{O}_{\text{SMOW}}$
		‰			
<i>Limestone (outside of the deposit area)</i>					
72-1	Limestone	0.8	25.9	0.8*	25.9*
72-2	Limestone	0.6	25.5	0.6*	25.5*
<i>Calcite from weakly altered marble</i>					
65	Fine- to medium-grained (0.5–2 mm) massive light-grey calcite marble with trace phlogopite	0.4	19.2	0.4*	19.2*
47	Fine-grained (0.1–0.3 mm) banded (bedded ?) light-grey calcite marble, with thin bands (beds ?) of carbonaceous material	−0.3	17.0	−0.3*	17.0*
50	Fine- to medium-grained (1–2 mm) banded (bedded ?) light-grey calcite marble, with thin bands (beds ?) of carbonaceous material	−0.5	14.8	−0.5*	14.8*
<i>Calcite from moderately to strongly altered marble (prograde calcic skarn overprint, 550 ± 50 °C)</i>					
54	Fine- to medium-grained (1–2 mm) massive light-grey calcite marble, with trace fine-grained garnet	−1.1	14.6	1.6	13.4 ± 0.5
3	Medium-grained (to 5 mm) white calcite marble, partially re-crystallized, with trace garnet and pyroxene, also phlogopite	−0.4	14.3	2.3	13.1 ± 0.5
2	Coarse-grained (1–2 cm), partially re-crystallized, massive white calcite marble, with a network of fine-grained garnet microveinlets	−0.9	13.5	1.8	12.3 ± 0.5
49	Fine- to medium-grained (1–2 mm) light-grey calcite marble, with a network of fine-grained brown garnet microveinlets	−1.0	13.2	1.7	12.0 ± 0.5
<i>Hydrothermal calcite (retrograde skarn, 450 ± 50 °C)</i>					
5	Re-crystallized coarse-grained (> 5 mm) calcite from retrograde garnet-pyroxene-wollastonite skarn	−0.6	13.6	2.1	11.2 ± 0.7
c-1	Re-crystallized calcite in retrograde garnet-pyroxene-wollastonite skarn	−1.9	14.8	0.8	12.4 ± 0.7
c12-1	Blue calcite in retrograde garnet skarn (pinkish-brown garnet) with minor pyroxene	−2.7	11.7	0.0	9.3 ± 0.7
48	Fine-grained calcite intergrowing with quartz in the interstitions of green garnet (retrograde garnet skarn with > 90 vol% garnet), with trace pyroxene, scapolite, epidote, chlorite	−3.3	11.1	−0.6	8.7 ± 0.7
<i>Hydrothermal calcite (propylitic alteration, 380 ± 20 °C)</i>					
c12-5	Calcite-quartz-epidote-prehnite alteration with sulfides replacing garnet-pyroxene skarn	−5.8	7.9	−3.2	4.2 ± 0.4
c-2	Calcite-quartz-epidote-chlorite alteration with chalcopyrite over garnet skarn	−3.6	8.5	−1.0	4.8 ± 0.4
ca-8	Calcite-quartz-epidote-chlorite alteration with hematite replacing garnet skarn	−2.8	9.8	−0.2	6.1 ± 0.4
ca-8a	Calcite from a microveinlet in the previous sample	−3.9	7.8	−1.3	4.1 ± 0.4
1	Fine-grained calcite overprinting fine-grained (0.1–0.3 mm) calcite marble	−4.5	7.0	−1.9	3.3 ± 0.4
K-6-1	Albite-chlorite-quartz alteration with quartz-calcite veinlets	−3.8	8.7	−1.2	5.0 ± 0.4
c12-8	Epidote-calcite-quartz replacement of garnet skarn, with abundant bornite and chalcopyrite	−5.1	4.5	−2.5	0.8 ± 0.4
c12-15	Quartz-calcite replacement of retrograde garnet-pyroxene skarn; sulfides (5–7 vol%) include dominant bornite and minor chalcopyrite	−4.5	5.3	−1.9	1.6 ± 0.4
58	Calcite-chlorite-quartz assemblage, with hematite and chalcopyrite	−2.5	7.8	0.1	4.1 ± 0.4
<i>Hydrothermal calcite (propylitic alteration with phyllic alteration overprint, 280 ± 20 °C)</i>					
c12-7	Epidote-calcite-quartz-magnetite replacement of garnet skarn, trace sericite	−5.9	12.4	−4.1	6.2 ± 0.7
ca-5	Epidote-calcite-quartz replacement of garnet skarn, trace sericite	−6.0	12.8	−4.2	6.6 ± 0.7

* $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{SMOW}}$ values of the fluid are equal to those of the rocks due to low fluid/rock ratio

10.2. Igneous association: Evolution and metallogenic implications

The deposit is associated with a magnetite-series (Ishihara, 1981), I-type (Chappell and White, 1992) multiphase pluton of medium-K to high-K calc-alkaline to shoshonitic igneous rocks, with the differentiation-driven evolution of the intrusive phases from early gabbroic through intermediate diorite-granodiorite to the late granitic phases. Overall, the intrusion geochemistry at Sinyukhinskoe exhibits similarities to igneous suites parental to Cu-Au porphyry mineralization elsewhere (Fig. 14; Ettlinger and Meinert, 1991; Meinert, 1995; Muller and Groves, 2019). There is particular similarity to some other Devonian-Carboniferous Cu-Au deposits in the CAO, such as the Oyu Tolgoi and Almalyk Cu-Au porphyry deposits, where medium-K to high-K calc-alkaline to shoshonitic plutonic rocks also play a significant role in the genesis of most productive mineralization (e.g., Perello et al., 2001; Kavalieris and Wainwright, 2005; Cheng et al., 2018). In a broader context, the formation of the I-type, oxidized (magnetite-series), high-K calc-alkaline to shoshonitic igneous suites can reflect the respective links to the mantle-related magmatic sources (Blevin and Chappell, 1992; Muller and Groves, 2019).

The monotonous magmatic evolution was interrupted by the intrusion of intramineral mafic dikes most distinctly exhibiting a shoshonitic affinity. The nearly-contemporaneous occurrence of calc-alkaline

and potassic (to shoshonitic) magmatism may be attributed to the respective evolution of a deep-seated magmatic source, with possible mutual influence and interaction of the different magmas. For example, a similar magmatic-hydrothermal evolution, with subsequent emplacement of low- and high-K intrusive phases, was described by McMahon (1994) for the Ertsberg Cu-Au skarn and porphyry district. This may reflect an influence of deeper-seated, mantle-related magmatic sources producing high-K mafic magmas after establishing deeper-penetrating fault zones, perhaps, due to a significant (catastrophic ?) tectonic event (cf. Richards, 2018). More importantly, the most significant Au-Cu mineralization at Sinyukhinskoe followed the intrusion of these mafic dikes, as they immediately pre-date the most productive mineralization. Thus, it appears that only following generation of higher-K to shoshonitic magmas did the system evolve to a productive metalliferous hydrothermal system capable of forming economic Au-Cu mineralization (cf. Soloviev et al., 2013). This suggests a possibility of supplying of fluids and metals (e.g., Cu, Au) from a deeper mafic magma chamber, a phenomenon reported at many Cu-Au and Cu-Au-Mo porphyry deposits, where mineralization overprints intramineral mafic dikes (e.g., Keith et al., 1998; Hattori and Keith, 2001; Maughan et al., 2002; Pollard et al., 2005; Redmond and Einaudi, 2010; Muller and Groves, 2019). The mafic dikes can also manifest a thermal rejuvenation of magmatic chamber(s), thus triggering their saturation in volatiles

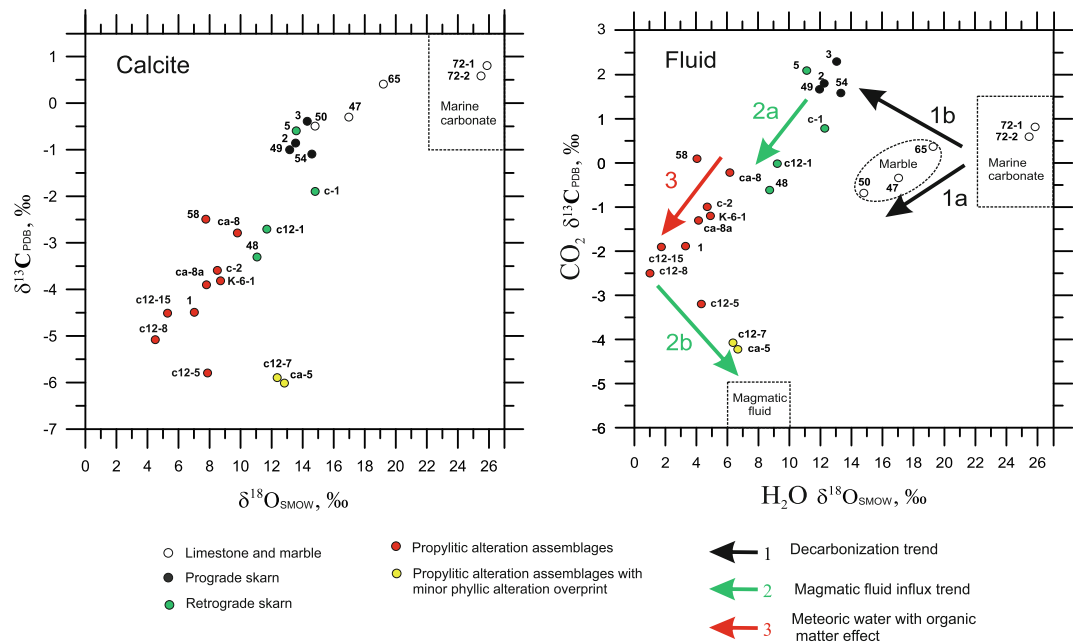


Fig. 13. $\delta^{13}\text{C}_{\text{PDB}}$ and of $\delta^{18}\text{O}_{\text{SMOW}}$ plots for calcite from various rocks and corresponding calcite-equilibrium fluids at the Sinyukhinskoe deposit. The data for marine carbonate and magmatic fluid are plotted after Hoefs (1997). The data and sample numbers are from Table 7.

(Wilkinson, 2013). Similar evolution from calc-alkaline to shoshonitic rocks was also demonstrated for the Devonian-Carboniferous Mo-dominant porphyry deposits further north (Berzina et al., 2010, 2011, 2016).

10.3. Local structural and lithological controls

Skarns and mineralization at Sinyukhinskoe are associated with

zones of structural intersections of variously-oriented, both steeply-dipping and flat faults (the latter possibly being parts of thrust-faults; Gusev, 1998). This results in a complex, mosaic-like distribution of mineralized zones at the deposit, and in the complex shapes of individual mineralized zones. Mineralization overprints parts of wollastonite- and garnet-dominant skarns in these structural intersections. Further telescoping of mineralization during multiple re-activation of pre- and *syn*-mineral fault zones or their parts in the course of later

Table 8
Sulfur isotope compositions of sulfide minerals from the Sinyukhinskoe deposit.

Sample numbers	Description of samples	Minerals	$\delta^{34}\text{S}_{\text{CDT}}$, ‰
<i>Sulfide minerals from retrograde skarn</i>			
ca-11	Retrograde garnet-epidote-calcite-quartz skarn with bornite	Bn 0	−1.5
c12-11	Retrograde garnet-epidote-calcite-quartz skarn with bornite and chalcopyrite	Ccp	−1.0
<i>Sulfide minerals from propylitic alteration</i>			
80	Prehnite -sulfide veinlets in retrograde garnet-pyroxene skarn, with abundant bornite (50 vol%) and minor chalcocite, also native Au	Bn 1	0.6
c12-15	Quartz-calcite-chlorite replacement of retrograde garnet-pyroxene skarn; sulfides (5–7 vol%) include dominant bornite and minor chalcopyrite; trace hematite is present	Bn 1	−0.5
59	Prehnite-quartz-epidote replacement of wollastonite-dominant skarn with chalcopyrite and minor bornite	Ccp	−0.5
77	Quartz-calcite-chlorite replacement of magnetite skarn, with minor chalcopyrite and sphalerite	Ccp	−0.3
c12-8	Epidote-calcite-quartz replacement of garnet skarn, with abundant bornite and chalcopyrite	Ccp	0.4
K-6-1	Albite-chlorite-quartz alteration with quartz-calcite veinlets	Ccp	−0.5
c-2	Calcite-quartz-epidote-chlorite alteration with chalcopyrite over garnet skarn	Ccp	−0.2
c12-12	Quartz-calcite-chlorite alteration with massive anhedral pyrite (65–70 vol%) and magnetite (5–7 vol%); magnetite replaces hematite; minor chalcopyrite, together with magnetite, replaces pyrite	Py	−0.2
c12-10	Quartz-calcite-chlorite alteration with massive anhedral pyrite (50–55 vol%); abundant chalcopyrite (15–20 vol%) and sphalerite (15–20 vol%) replace pyrite	Py	1.5
<i>Sulfide minerals from phyllic alteration</i>			
c12-20	Quartz - sulfide (with dominant bornite-2) replacement of garnet-pyroxene-vesuvianite retrograde skarn with epidote-calcite alteration.	Bn 2	−1.5
39	Quartz-sulfide to quartz-carbonate-sulfide replacement of retrograde wollastonite-pyroxene-garnet skarn, with chalcocite and bornite	Bn 2	−0.9
74	Quartz-sulfide to quartz-carbonate-sulfide (with minor sericite) replacement of retrograde wollastonite-pyroxene-garnet skarn, with chalcocite and bornite	Bn 2	−0.8
c-2-5	Quartz-sulfide replacement of retrograde wollastonite skarn with abundant bornite and chalcocite	Cct	0.5
c12-13	Quartz veinlet intersecting retrograde wollastonite skarn; contains abundant chalcocite and minor bornite	Cct	−1.2
16	Quartz-sulfide replacement of retrograde garnet-pyroxene-wollastonite skarn, with dominant chalcocite and minor bornite, also native Au	Cct	−2.0
19	Quartz-sulfide to quartz-carbonate-sulfide replacement of retrograde wollastonite-garnet-pyroxene skarn, with dominant chalcocite, minor chalcopyrite and bornite	Cct	−2.4
73	Quartz-sulfide replacement of retrograde garnet-pyroxene-wollastonite skarn, with dominant chalcocite, minor chalcopyrite and bornite	Cct	−2.1

Abbreviations: Bn0 – bornite from retrograde skarn, Bn 1 and Bn2 – early (Fe-rich) and late (Cu-rich) bornite from propylitic and phyllic alteration, respectively, Cct – chalcocite, Ccp – chalcopyrite, Py – pyrite.

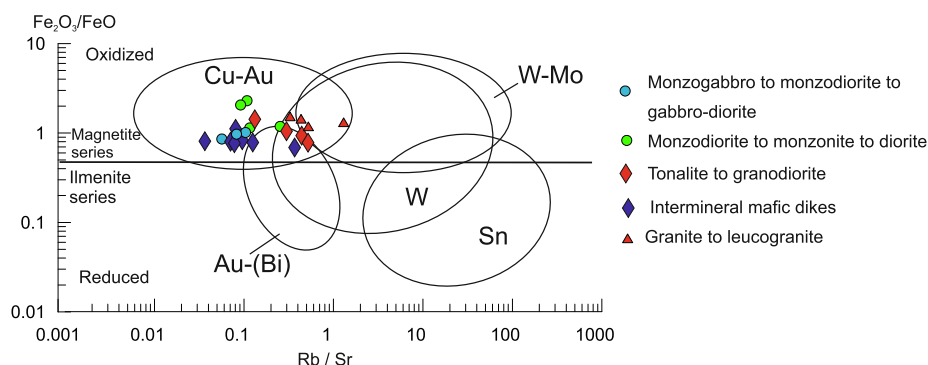


Fig. 14. Composition of igneous rock from the Sinyukhinskoe deposit shown on the plot of degree of fractionation (Rb/Sr ratio) versus the oxidation state ($\text{Fe}_2\text{O}_3/\text{FeO}$) for intrusive rocks associated with Cu-Au, W-Mo, Au-(Bi) and Sn mineralization (Baker et al., 2005). Note the rock composition plots mainly in the Cu-Au field.

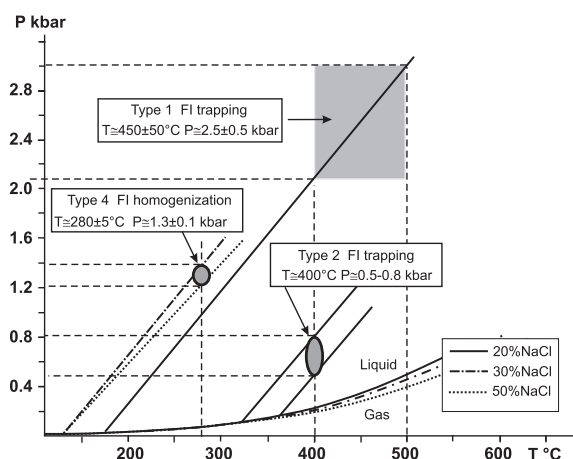


Fig. 15. Pressure estimates for fluid inclusions (FI) in minerals from retrograde skarn (type 1 fluid inclusions), propylitic alteration (type 2 fluid inclusions) and phyllic alteration (type 4 fluid inclusions) at the Sinyukhinskoe deposit. Vapor-pressure curves for H_2O -NaCl solutions and isochors are from Roedder (1984), Atkinson (2002), Becker et al. (2008) and correspond to most common salinities of fluid inclusions determined in this study (20 and 30–50 wt% NaCl-eq., respectively).

propylitic and phyllic alteration stages provided superposition of different mineral assemblages and high Cu and Au grades, rather than a temporal coincidence of skarns and mineralization. A lithological control was also important: bornite is most abundant in Fe-rich protolith (particularly in skarns with greater content of garnet and/or pyroxene), whereas chalcocite dominates over bornite in Fe-poor protolith (e.g., wollastonite skarn). An occurrence of Au mineralization outside skarn zones, specifically in limestones, shows some affinity to the Carlin-style mineralization, particularly to that associated with Au skarns (e.g., Vikentyev et al., 2019), or represents the distal carbonate-hosted Au members of oxidized Cu-Au systems (e.g., Xie et al., 2019).

10.4. Temperature and pressure constraints

The mineral paragenesis data indicate deep conditions of the deposit formation. In particular, the prograde skarns are characterized by a broad occurrence of wollastonite indicating the temperatures of 700–600 °C and low X_{CO_2} (Zharikov, 1970; Zharikov et al., 1998). Paragenesis of wollastonite + pyroxene in prograde calcic skarn is formed at 650 °C at 2 kbar (Gustafson, 1974). Stability of andradite-grossular garnet (up to 40 mol% grossular) in skarns requires temperatures of 500–600 °C and pressures of 1.5–2.0 kbar under low X_{CO_2} (< 0.1) (Taylor and Liou, 1978), and pyroxene in skarns is stable at temperatures > 450 °C (Gustafson, 1974). These data indicate the prograde calcic skarn was formed at the temperatures > 500 °C and

pressures of 1.5–2.0 kbar.

The retrograde skarn formation corresponds to a thermal decline evident by the expanded stability of hydrous silicates (amphibole, epidote, chlorite, etc.), and their occurrence with andraditic garnet (Johnson and Norton, 1985). Andradite is stable at temperatures as low as 300–350 °C (Einaudi, 1982b), whereas the stability of hedenbergitic pyroxene extends to temperatures below 400 °C (Gamble, 1982); this corresponds to the lower temperature limit of retrograde skarn formation. However, the deposit is characterized by an unusual and intense development of wollastonite in the retrograde skarn (e.g., Ettlinger and Meinert, 1991); wollastonite retrograde skarn replaces prograde garnet skarn. The latter can be explained by X_{CO_2} decrease or/and by a temperature increase, with wollastonite being stable at > 450 °C (Zharikov, 1970; Burt, 1977; Einaudi et al., 1981; Zharikov et al., 1998). A low X_{CO_2} is consistent with the lack of fluid inclusions with CO_2 , whereas a temperature increase interrupting the general retrograde trend could be caused by a magmatic intrusion, possibly an intermediate granitoid phase.

Pressure can also be estimated for type 1 fluid inclusions using isochors for H_2O -NaCl solution (Roedder, 1984) with salinities most closely corresponding to those defined in this study (20 ± 3 wt% NaCl-eq.) and the respective temperatures of mineral deposition defined by mineral paragenesis of the retrograde skarn at 450 ± 50 °C. Assuming the difference between the homogenization temperature (170–180 °C) measured, and this actual temperature (450 ± 50 °C) of mineral deposition, these estimates yield pressures of 2.5 ± 0.5 kbar (Fig. 15, Table 6), which may be higher than that at the prograde skarn stage and corresponds to a depth of ~10 km assuming lithostatic conditions (Fournier, 1999). Thus, in addition to the possible temperature increase (or at least partial temperature overlap) suggested by the presence of wollastonite in the retrograde skarn, there could also be a pressure increase, as compared to the prograde skarn formation.

Due to abundant epidote, propylitic alteration at Sinyukhinskoe corresponds to a relatively higher-temperature regime, as compared to a chlorite-dominant propylitic alteration (cf. Wilkinson et al., 2015), likely in the order of ~380–400 °C. On this basis, considering the difference between the homogenization temperature (320–360 °C) measured, and the actual temperature (380 to 400 °C) of mineral deposition, pressure can be estimated for type 2 fluid inclusions using isochors for H_2O -NaCl solution with salinities at ~20 wt% NaCl-eq. These estimates yield pressures of 0.5 to 0.8 kbar (Fig. 15; Table 6), which corresponds to a depth of ~5 to 8 km under hydrostatic conditions (Fournier, 1999). The respective pressure drop causing a transition from lithostatic to hydrostatic regime can be related to the intense faulting in the local zones that served as conduits for the mafic magma and then for development of propylitic alteration assemblages. These or similar pressures also require pressure corrections for the homogenization temperatures recorded for type 3 fluid inclusions (Table 6).

Minimum pressure can be estimated using homogenization

temperatures of multisolid type 4 fluid inclusions that homogenized by halite dissolution at $280 \pm 5^\circ\text{C}$ (Table 6). Using the isochores for a 30–50 wt%

NaCl solution (Atkinson, 2002; Becker et al., 2008), these estimates yield minimum pressures of 1.3 ± 0.1 kbar (Fig. 15; Table 6). The pressure of ~ 1.3 kbars corresponds to depths of about 5 km (cf. Fournier, 1999) assuming lithostatic conditions. This is consistent with the depths estimated for the propylitic alteration stage and corresponds to a relatively high-pressure regime indicating a significant depth of mineral deposition. These or similar pressures require significant (in the order of 100°C) pressure corrections for the homogenization temperatures recorded for type 5 fluid inclusions (Table 6).

10.5. Stable isotope data interpretation

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data for calcite and calcite-equilibrium fluid (Fig. 13; Table 7) display several evolutionary trends that reflect correspondingly different conditions of mineral deposition. In particular, trend 1A of decreasing both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ during the transition from limestone to marble can be explained by de-carbonization and/or by interaction of carbonate rocks with magmatic fluid. De-carbonization causes removal of heavy carbon and oxygen isotopes together with CO_2 , with complementary decreasing $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the rocks. Trend 1B of increasing $\delta^{13}\text{C}$ and decreasing $\delta^{18}\text{O}$ during the transition from limestone through marble to prograde skarn can reflect burial of CO_2 , obtained due to de-carbonization of limestone/marble and enriched in heavy carbon isotope, in the skarn calcite. Trend 2A of decreasing both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ during the retrograde skarn stage can correspond to a growing influence of magmatic fluid. During this evolution, $\delta^{18}\text{O}$ decreases toward typical values of magmatic water ($\delta^{18}\text{O}_{\text{H}_2\text{O}} = +8$ to $+10\text{‰}$; cf. Taylor, 1979), whereas the $\delta^{13}\text{C}$ decrease is less pronounced (is typically within the $\delta^{13}\text{C}$ values of marine carbonate, with the mean $\delta^{13}\text{C} = \sim 0\text{‰}$; Fig. 13), possibly due to low carbon content in a magmatic fluid and under a dominant carbonate rock-derived heavy carbon isotope. Trend 3 expressed in a stronger decrease of both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ during the propylitic alteration stage can be explained by a supply of heated meteoric waters, the latter being possible along zones of intense fracturing and faulting, with corresponding fluid pressure decrease toward hydrostatic conditions, i.e., toward establishing connections with the paleosurface. The direct correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ indicates a supply of light carbon isotope together with light oxygen isotope. This can be explained by the light carbon isotope sourcing from organic sedimentary matter (the mean $\delta^{13}\text{C} = \sim 25\text{‰}$; Hoefs, 1997) dissolved in the meteoric waters and oxidized to carbonate. Finally, trend 2B corresponding to the replacement of propylitic-altered skarn by phyllic alteration assemblages, with decreasing $\delta^{13}\text{C}$ and increasing $\delta^{18}\text{O}$ values, can reflect an influx of magmatic fluids enriched in heavy oxygen isotope and light carbon isotope. During this process, $\delta^{18}\text{O}$ increases to the values of magmatic water, whereas $\delta^{13}\text{C}$ values differ from those of magmatic water, the latter with the mean $\delta^{13}\text{C} = \sim -5 \pm 2\text{‰}$ (Hoefs, 1997; Ohmoto and Rye, 1979; Ohmoto and Goldhaber, 1997). This is consistent with a very little CO_2 content in the hydrothermal fluids, and with the overall dominance of heavy carbon isotope supply from carbonate rocks.

The $\delta^{34}\text{S}$ data for sulfide minerals indicates a primarily mantle/magma-derived source of sulfur ($0 \pm 3\text{‰}$; Ohmoto and Rye, 1979; Ohmoto and Goldhaber, 1997; Seal, 2006), and the homogenous style of the isotope compositions is consistent with sulfur isotope homogenization in a magmatic chamber. Gradually increasing enrichment of chalcocite in light sulfur isotope (to -2.4‰) at the phyllic alteration stage likely corresponds to a trend toward its equilibrium with $\text{H}_2\text{S}_{\text{fluid}}$ (the equilibrium fractionation of sulfur isotopes between chalcocite and H_2S is -2.5‰ at 280°C ; Ohmoto and Rye, 1979). Overall, a dominant role of homogenous mantle-related sulfur source is typical for Cu-Au porphyry deposits (e.g., Seal, 2006).

10.6. Magmatic-hydrothermal evolution

The relationships of the Sinyukhinskoe deposit with magnetite-series (after Ishihara, 1981) igneous suite explain many features of hydrothermal alteration and mineralization that are similar to those occurring in other oxidized-type, magnetite-rich Cu-Au skarn deposits (e.g., Mertig et al., 1994; Einaudi, 1982a,b; Fontbote et al., 2004; Forster et al., 2004; Meinert et al., 2005; Markowski et al., 2006; Li et al., 2014; Soloviev et al., 2013, 2018). These features include the presence of magnetite skarn, multiple generations of magnetite, abundance of garnet (versus pyroxene) in skarns, essentially andraditic composition of garnet, abundance of bornite and other signatures that are consistent with the oxidized skarn type (cf. Einaudi et al., 1981; Meinert et al., 2005). This differs oxidized Au skarn deposits from reduced Au skarn deposits related to ilmenite-series granitoids (Meinert, 1995, 1998, 2000; Mueller et al., 2004; Meinert et al., 2005; Sui et al., 2017). The high redox potential of magmatic melt coupled with high water content could also cause an early saturation of magma in Cu-sulfides (Jenner et al., 2010; Sun et al., 2015), with further release of Cu-bearing magmatic-hydrothermal fluid from a moderately-fractionated magmatic melt.

The fluid inclusions data (Table 6) indicate the involvement of low-carbonic, aqueous, dominantly magnesium-sodic-chloride, moderately-saline (20 ± 3 wt% NaCl-eq.), high-pressure ($\sim 2.5 \pm 0.5$ kbar), hot fluid (type 1 fluid inclusions) in the retrograde skarn formation. This fluid could have been originated directly from crystallizing magma (Cline and Bodnar, 1994; Bodnar, 1995), and skarn formation from high-salinity magmatic-hydrothermal fluid directly sourced from crystallizing magma is common for Cu-Au skarn deposits (Meinert et al., 2003). This fluid was likely responsible for the deposition of the early Cu mineralization (bornite, possibly chalcocite), which is associated with retrograde skarn. No boiling recorded for the fluids that formed retrograde skarn at Sinyukhinskoe, and this is consistent with relatively deep (high-pressure) conditions of the retrograde skarn formation that precluded phase separation in the magmatic-hydrothermal fluid.

Propylitic alteration is closely associated with the intramineral mafic dikes and replaces retrograde skarn, principally in the form of a garnet/pyroxene/wollastonite-destructive, epidote-chlorite-amphibole-plagioclase-quartz $\pm$ sulfide assemblage (cf. Zharikov, 1970; Einaudi et al., 1981; Wilkinson et al., 2015). Abundant epidote, clinozoisite and calcite reflect a high-Ca environment. This assemblage was formed from a moderate salinity (16–20 wt% NaCl + CaCl_2) homogenous aqueous fluid at the temperatures of $380\text{--}400^\circ\text{C}$ (Table 6; type 2 fluid inclusions). This fluid could represent a new fluid influx from crystallizing magma (Fig. 16) that followed the intrusion of intramineral mafic dikes immediately pre-dating propylitic alteration. The stable isotope data suggest a possible involvement of heated meteoric waters into the magmatic-hydrothermal system.

However, the most intense Au mineralization (moderately-high fineness native “gold-2”), together with substantial Cu mineralization, occurred at the beginning of the next phyllic alteration stage, i.e., at a lower temperature ($\sim 280^\circ\text{C}$) than that at the propylitic stage. The phyllic alteration stage followed a more advanced magmatic differentiation toward most silicic ($\sim 75\text{--}76$ wt% SiO_2) granite to leucogranite intrusions. Advanced magmatic evolution promoted enrichment of residual melt in Au that was facilitated by the low content of accessory oxides and sulfides and by elevated volatile content (Mustard et al., 2006). Consistently, type 4 fluid inclusions in phyllic alteration minerals indicate a new influx of homogenous, high-salinity potassic-sodic-calcic (22 wt% KCl, 18 wt% NaCl and 10 wt% CaCl_2), high-pressure (~ 1.3 kbar) aqueous-chloride fluid (Table 6; Fig. 16). Some data (e.g., elevated Bi, Hg, Te contents, as well as $\delta^{34}\text{S}$ values close to meteorite standard) suggest at least partial fluid sourcing from a mantle-derived magma. In this environment at the phyllic alteration stage, bornite and chalcocite precipitated, with chalcocite efficiently scavenging gold (Cook et al., 2011).

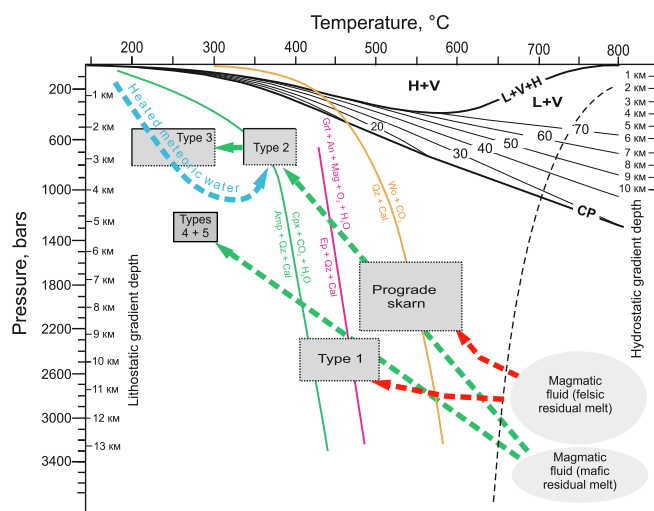


Fig. 16. Estimated pressure and temperature conditions and evolutionary paths for different fluid inclusion types in hydrothermal assemblages at the Sinyukhinskoe deposit, with composition of different fluid inclusion types as a function of depth and temperature (after Bodnar et al., 1985; Hedenquist et al., 1998; Fournier, 1999; Meinert et al., 2003; Baker and Lang, 2003). Vapor-pressure curves for H₂O–NaCl solutions at 0–70 wt% NaCl-eq. and the three-phase (L + V + H) curve are shown after Atkinson (2002) and Becker et al. (2008). Dashed line represents water-saturated granite solidus (Holtz et al., 2001). Equilibrium lines for wollastonite = quartz + calcite, garnet (40 mol% andradite) + anorthite + magnetite = epidote + quartz + calcite (at $f_{O_2} = 10^{-20}$), and clinopyroxene = amphibole + quartz + calcite are shown after Zharikov et al. (1998) for the conditions of $X_{CO_2} = 0.1$ and $X_{H_2O} = 0.9$. PT-fields for the major fluid inclusion types and possible evolutionary paths for fluids (arrows) are shown. Abbreviations: Cpx – clinopyroxene, Grt – garnet, Amp – amphibole, Ep – epidote, Mag – magnetite, Qz – quartz, Cal – calcite.

The fluid pressures both at the propylitic and phyllic alteration stages corresponding to a level of ~2 to 6 km (Fig. 16) precluded fluid boiling in zones of the most intense Cu and Au mineralization at Sinyukhinskoe. This is why other physical–chemical mechanisms that are efficient for the metal (Cu, Au) precipitation have to be considered. In this regard, possible involvement of meteoric water is suggested by stable isotope data for the propylitic alteration stage; this could contribute to pH/ f_{O_2} change during this stage. In contrast, under meteoric water influx lacking, fluid cooling was pronounceable during the phyllic alteration stage. Consistently, during these stages of the most intense Cu and Au deposition, solubility of these metals could be affected either by pH/ f_{O_2} and f_{S_2} change, or by fluid cooling, and by a combination of these processes (Gammons and Williams-Jones, 1997). This can be sufficient to substitute the lack of fluid boiling as the most efficient mechanism for metal deposition. A similar model of mixing of a relatively reduced meteoric water with an oxidized fluid derived from a mafic or mixed mafic/granitic source, followed by additional inflow of a cooler water, was proposed for some Cu–Au deposits (e.g., Haynes et al., 1995; Fekete et al., 2016). The respective fluid mixing/cooling model is also consistent with the succession of Cu and Au mineral deposition observed at Sinyukhinskoe, i.e., from magnetite through chalcopyrite to bornite (or bornite + chalcocite solid solution) (+ Au) and finally to chalcocite (+ Au) (cf. Haynes et al., 1995). An additional effect to pH and f_{O_2} change was likely provided by the neutralizing and/or oxidizing reactions of mineralizing fluids with compositionally contrasting skarn minerals (e.g., Zhou et al., 2017).

The mineral deposition during the propylitic and phyllic alteration stages differs from many Cu–Au porphyry and skarn deposits, where Cu and Au are precipitated mainly at the potassic alteration stage or in equivalent retrograde skarn (e.g., Atkinson and Einaudi, 1978; Meinert et al., 1997; Arif and Baker, 2004; Sillitoe, 2010). The latter fits to the model of early contemporaneous

introduction of Cu and Au and their late re-equilibration, with gold being initially deposited within bornite solid solution (at temperature > 350 °C to ~550 °C) that later exsolved on cooling to chalcocite-bornite intergrowths plus native gold (Redmond and Einaudi, 2000; Kesler et al., 2002). However, similar to Sinyukhinskoe, Cu and Au occur in phyllic alteration assemblages and are paragenetically late at many other Cu–Au porphyry and skarn deposits (Meinert et al., 2005; Pirajno, 2009). Consistently, this leads to another model, where Cu–Au mineralization is related to propylitic and particularly phyllic (quartz-chlorite-sericite to quartz-sericite) alteration, which overprints potassic alteration and/or retrograde skarn (Meinert et al., 1997; Hedenquist et al., 1998; Harris and Golding, 2002; Harris et al., 2005; Seedorff et al., 2005; Klemm et al., 2007; Rusk et al., 2008; Prendergast et al., 2005; Soloviev et al., 2013, 2018).

11. Conclusions

The Sinyukhinskoe deposit is situated in the Altaid orogenic system and is part of the regional metallogenic system of Devonian–Carboniferous Cu–Au to Au–Cu porphyry, skarn and other deposits. The emplacement of productive plutonic suites in Altai corresponds to a Devonian subduction-related continental magmatic arc setting, with its further evolution toward a late- and post-collisional regime in the late Devonian–Carboniferous. In this regard, the regional metallogenic links within the large terrane of the central Altaids, with possible extension toward the Devonian–Carboniferous Oyu Tolgoi Cu–Au mineralized district in Mongolia, can be considered.

The deposit is related to a magnetite-series, I-type multiphase pluton, with its evolution from early gabbroic through intermediate diorite-granodiorite to the late granitic phases. The igneous rocks belong to high-K calc-alkaline series or are transitional from medium- to high-K calc-alkaline varieties. Prior to granitic phases, the respective magmatic differentiation was interrupted by the intrusion of mafic magma exhibiting a shoshonitic affinity. These shoshonitic intrusive phases could manifest a thermal rejuvenation of magmatic chamber(s) and possibly directly source fluids, metals and/or sulfur to form most productive mineralization. The oxidized (magnetite-series) character of the igneous rocks is consistent with many features of hydrothermal alteration assemblages and mineralization that are similar to those occurring in other magnetite-rich Cu–Au skarn deposits and exhibiting links to Cu–Au porphyry mineralized systems.

The deposit is characterized by abundant andradite-rich garnet and wollastonite in prograde and retrograde skarns. The formation of wollastonite at the retrograde skarn stage manifests a temperature increase that interrupts the general temperature decline and could be caused by a magmatic intrusion (likely granodiorite). These and other retrograde skarn assemblages locally comprise also magnetite and bornite. The subsequent propylitic (epidote-chlorite-amphibole-albite-calcite-quartz, locally with clinozoisite and prehnite) alteration assemblages bear more intense Cu mineralization (chalcopyrite, bornite, locally tennantite) and high fineness (~940–910‰) native gold. Later phyllic (quartz-sericite to quartz-sericite-chlorite) alteration assemblages comprise the most intense intermediate-fineness (910–880‰) native gold and Cu (bornite, chalcocite) mineralization that is followed by low-fineness (820–760‰) native gold and telluride minerals.

The retrograde skarn was formed from a high-salinity (18–23 wt% MgCl₂ + NaCl), hot (~450 ± 50 °C), high-pressure (~2.5 ± 0.5 kbar) magmatic-hydrothermal fluid, under its possible direct separation from crystallizing magma. No fluid boiling occurred. After intrusion of intramineral mafic dikes exhibiting a shoshonitic affinity, propylitic alteration assemblages were formed from a moderate salinity (16–20 wt% NaCl + CaCl₂) homogenous aqueous fluid at the temperatures of 380–400 °C. This fluid could be supplied from crystallizing magma, with its further mixing with heated meteoric waters. Fluid inclusions in phyllic alteration minerals indicate a new influx of homogenous, high-salinity potassic-sodic-calcic (22 wt% KCl, 18 wt% NaCl and 10 wt%

CaCl₂), high-pressure (~1.3 kbar), aqueous-chloride fluid. Elevated Bi, Hg, Te contents, as well as $\delta^{34}\text{S}$ values close to meteorite standard (most $\delta^{34}\text{S}$ values are in the range of -1.5 to $+1.5\text{‰}$) suggest at least partial fluid sourcing from a mantle-derived magma.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.oregeorev.2019.103039>.

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