



Geology, igneous geochemistry, mineralization, and fluid inclusion characteristics of the Kougarok tin-tantalum-lithium prospect, Seward Peninsula, Alaska, USA

Serguei G. Soloviev¹ · Sergey Kryazhev² · Svetlana Dvurechenskaya²

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Abstract

The Kougarok prospect is situated in a Sn-W (±Ta, Nb, Li, Be) metallogenic belt formed in a post-collisional to within-plate tectonic environment. Crystal fractionation of granitic magma, combined with its mixing/mingling with mantle-derived mafic magma, is proposed as the major process causing the formation of the complex B-rich to Li-F-type granitic suite and associated Sn-rare metal (Ta, Nb, Li) mineralization. An intrusion of alkalic (potassic lamprophyric) mafic magma into a crystallizing biotite-tourmaline granite magma reservoir may have supplied a geochemically distinct assemblage of volatiles (F) and associated metals (Li, Ta, Nb) into the boron- and Sn-rich granitic system. An alternative model considers differentiation-driven unmixing of mafic and granitic silicate melts sequestering different volatile and mineralizing species that could also trigger magma-fluid and fluid-fluid unmixing, with separation of gaseous fluid coexisting with immiscible granitic and mafic magmas in the form of magmatic melt-fluid-crystal “suspension.” Biotite-tourmaline granite was accompanied by early quartz-tourmaline-cassiterite greisen at > 430–380 °C followed by quartz-tourmaline-chlorite-cassiterite stockwork at < 350 °C. The immiscibility of F- and B-rich fluids was followed by preferred ascent of F-rich fluids upward in the granitic magma reservoir, with its strong enrichment in F, Li, Ta, and Nb and subsequent crystallization of zinnwaldite granite at a shallower level, with separation of homogenous high-salinity magmatic fluid at ~ 600 °C. Crystallization and fluid exsolution continued at lower temperatures, followed by formation of topaz-quartz stockscheider at 550–500 °C. Ta-Nb mineralization in the uppermost part of the zinnwaldite granite appears to be associated with final episodes of magmatic crystallization, particularly W-Nb-rutile and columbite-tantalite with a higher Nb content. Some Ta-Nb minerals, such as columbite-tantalite with a higher Ta content, appear to be also stable during the post-magmatic stage, in quartz-tourmaline±topaz greisen and higher-temperature quartz-albite-Li mica alteration that replace zinnwaldite granite at ~ 500 to 400 °C. Nearly contemporaneous, lower-temperature quartz-albite-Li mica alteration and quartz-muscovite, quartz-topaz, and quartz-fluorite greisens formed from boiling fluids at 390–350 °C and caused removal of Ta-Nb minerals. Instead, fluid cooling and neutralization of boiling fluids affected Sn solubility and promoted massive cassiterite deposition in the late greisens. The latest phyllic quartz-sericite-carbonate alteration assemblage, comprising arsenopyrite, pyrrhotite, chalcopyrite and other sulfides, native Bi, and Bi tellurides, formed from boiling fluids at < 310 °C.

Keywords Li-F granite · Zinnwaldite · Topaz · Greisen · Columbite-tantalite · Cassiterite · Fluid inclusions

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✉ Serguei G. Soloviev
serguei07@hotmail.com

¹ Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry (IGEM), Russian Academy of Sciences, 35 Staromonetny Per, Moscow 109017, Russia

² Central Research Institute of Geological Prospecting for Base and Precious Metals (TsNIGRI), 1-129 Warshavskoe Chaussee, Moscow 117545, Russia

Introduction

The Kougarok prospect in Alaska is characterized by intense Ta-Nb-Li and Sn mineralization. It complements the diversity of granite-related metallogeny of Alaska and adjacent territories and belongs to the type of Sn-rare metal (Ta, Nb, Li) deposits related to Li-F type granites (Pollard 1995; Simandl 2002). Elsewhere in the world, granite-related Ta-Li-Sn deposits similar to Kougarok represent significant sources of Ta and/or Li and comprise the Orlovka and Etyka deposits in Russia (Reyf et al. 2000), Beauvoir in France (Cuney et al. 1992; Rimbault et al. 1995), Yichun in China (Yin et al.

1995), Abu-Dabbab in Egypt (U.S. Geological Survey 2015), and Cinovec deposit in Czech Republic (Štemprok et al. 1995; Rub et al. 1998; European Metals Holding Ltd. 2019). Thus, the Sn-rare metal (Ta, Nb, Li) mineralization in Alaska is important in an economic aspect highlighting the potential for Ta and Li resources in this region.

In the 1980s, the Kougarok prospect was explored by Anaconda Minerals Company (AMC; Witte et al. 1983) that outlined some 90 Kt Sn averaging 0.45–1.3% Sn and reported Ta₂O₅ grades locally exceeding 300–500 ppm (Puchner 1986; Goldfarb et al. 2016). Reid and Bergman (1982) and Puchner (1986) demonstrated a close association of Ta-Nb mineralization with apical parts of small zinnwaldite granite intrusions. Further evaluation conducted in 2001–2002 by Navigator Exploration Ltd. and Chapleau Resources Ltd. has confirmed the presence of significant Ta mineralization in local zones associated with zinnwaldite granite (Hudson 2005). Zinnwaldite granite is also considered as a potential source of lithium (European Metals Holding Ltd. 2019).

Studying complex Sn-Ta-Li deposits associated with multiphase, highly differentiated intrusions allows better understanding of granite-related mineralized systems, magmatic and related fluid evolution, magmatic-hydrothermal transition, and related mineralization processes leading to metal concentration. The petrologic and fluid inclusion data combined with geological information presented in this paper are intended to further contribute to the genetic model of granite-related Sn-rare metal (Ta, Nb, Li) deposits.

Regional tectonic and metallogenic setting

The Kougarok prospect is situated in the Seward Peninsula, westernmost Alaska (Fig. 1). The latter, along with the Russian North East, comprises a region of crustal fragments wedged between the Siberian craton to the west and the Laurentian craton to the east and consolidated by the late Late Cretaceous (Moore and Box 2016). This orogenic collage is composed of accreted fragments of igneous arcs, accretion-wedge and subduction-zone complexes, and passive continental margins and cratons overlapped by mainly Mesozoic and Cenozoic continental-margin-arc and sedimentary basin assemblages (Nokleberg et al. 2000). This assembly includes crustal fragments from the Laurentia, and from paleo-Pacific, forming the Arctic Alaska-Chukotka superterrane or microplate (Goldfarb et al. 2016; Moore and Box 2016). Following Jurassic subduction, the Mesozoic collision included development of turbidite basins, intense thrust-faulting and folding, and formation of tectonic mélanges overthrusting fragments of disintegrated ancient cratonic domains accreted to the larger cratonic blocks (Till and Dumoulin 1994). During Early to Late Cretaceous (110–90 Ma), intense granitic magmatism is associated with voluminous crustal melting in a post-collisional extensional regime that followed an earlier (Jurassic-Early Cretaceous) compressional orogen (Hudson and Arth 1983; Swanson et al. 1988; Hudson 1994; Hudson and Reed 1997; Amato et al. 2001, 2003). The granites vary in composition and sources depending on the type of the

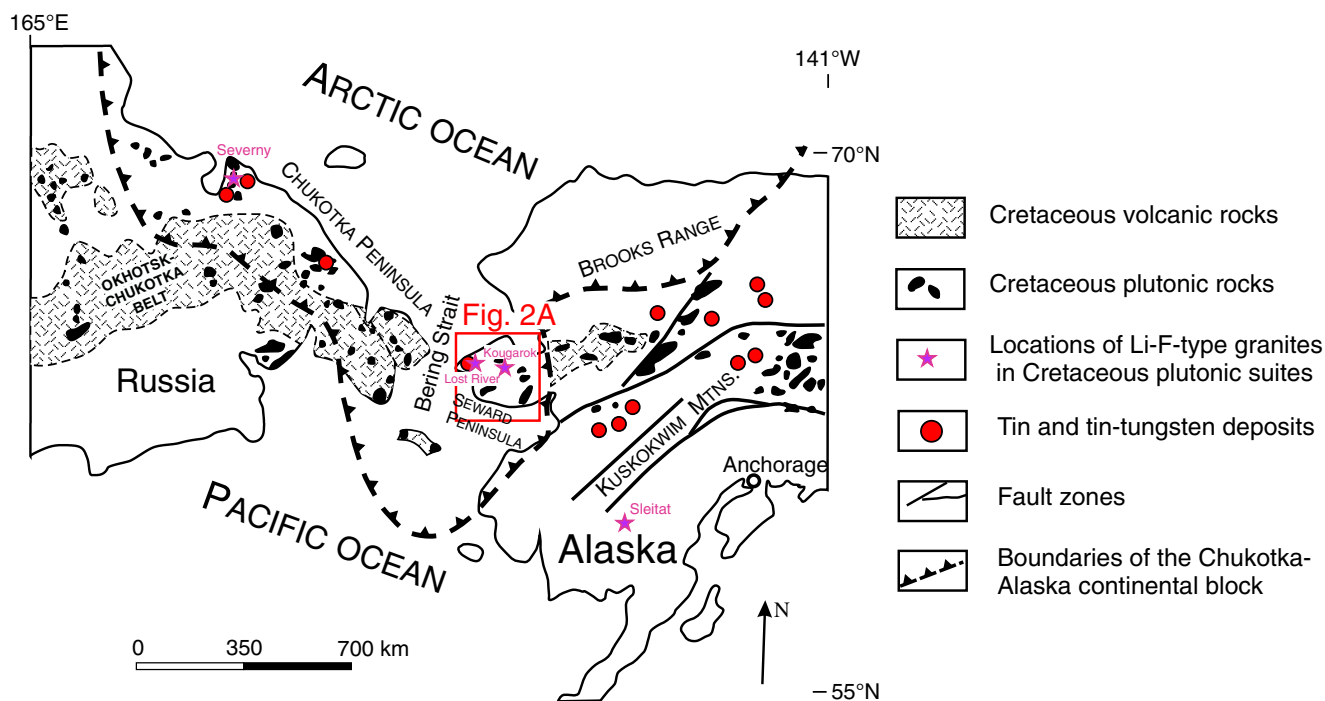


Fig. 1 Regional tectonic setting of the Kougarok and other Sn-W and Sn-Ta-Li deposits and prospects in the Alaska-Chukotka superterrane (after Nokleberg et al. 1996; Hudson and Reed 1997; Amato et al. 2001; Toro et al. 2003; Goldfarb et al. 2016; Moore and Box 2016)

basement (cratonic fragments, subduction-zone complexes, etc.) involved in generation of the magma. The latest Cretaceous (80–70 Ma) granitic intrusions were emplaced into apical parts of the Late Cretaceous granitic batholiths and are mostly mineralized in Sn and rare metals (Hudson and Reed 1997). Younger, Early Tertiary (~60–50 Ma) granitic intrusions are locally also accompanied by Sn–Li mineralization (Sleit Mountain; Burleigh 1991; Hudson and Reed 1997; Ellis 2015). Elsewhere in the North American Cordillera, similar Late Cretaceous granitic suites accompanied by Sn–W to Sn–rare metal mineralization are assigned to a within-plate tectonic regime (Ray et al. 1995; Driver et al. 2000).

The tin mineralization of Alaska is part of the Circum-Pacific “tin belt” (Sainsbury et al. 1969). It occurs at numerous typically small Sn±W deposits (Figs. 1 and 2a), with widespread veined quartz–cassiterite and greisen cassiterite (±wolframite) mineralization (Sainsbury et al. 1969; Hudson and Arth 1983; Swanson et al. 1988; Hudson and Reed 1997). The replacement-style fluorite–Sn–W–Be mineralization in skarns and limestones is known at the Lost River and some smaller deposits (Sainsbury 1969; Dobson 1982; Hudson and Reed 1997). Granite-related Sn–rare metal (Ta, Nb, Li) mineralization occurs at Kougarok, possibly Sleitat Mountain, and other locations (Puchner 1986; Swanson et al. 1988; Hudson and Reed 1997). The Sn-bearing granites and Sn mineralization of the Seward Peninsula lie at the easternmost edge of the Okhotsk–Chukotka volcanic–plutonic belt that extends for 3000 km along the western margin of the Sea of Okhotsk (Nokleberg et al. 1996). In its Russian part, the belt comprises Sn–base metal, Sn–W, and Sn–rare metal (Ta–Nb, Li, Be) deposits associated with the Late Cretaceous granitic intrusions (Nokleberg et al. 1996; Alekseev et al. 2011).

District geology and tin occurrences

The Kougarok prospect is part of the “Seward Peninsula tin granite belt” (Fig. 2a; Hudson and Arth 1983) that extends northeast–southwest for over 170 km and comprises granite plutons containing anomalous Sn, locally also Be and F. The plutons intruded Precambrian and Paleozoic metasedimentary rocks of the Nome Complex, which is composed of siliciclastic, carbonate, and graphitic rocks, some with blueschist and greenschist metamorphic fabrics (Swanson et al. 1988; Weldon et al. 2005; Ayuso and Till 2007; Till et al. 2011) (Fig. 2a). Cambrian to Devonian carbonate rocks, Late Proterozoic orthogneiss, Ordovician mafic rocks, and Middle Devonian metagranites of the Nome Complex suggest that it is a tectonic melange formed in response to tectonic piling and overthrusting (Till et al. 2011). The deformed rocks in the Seward Peninsula contain lineations, asymmetric to isoclinal folds, and microstructures that indicate north-vergent shortening and northward tectonic transport (Moore and Box 2016). The metamorphism spanned from 144 Ma to 125–109 Ma, with the peak pressure reached during

the Jurassic (Till et al. 2011). While the high-pressure blueschist facies metamorphism is attributed to subduction (Moore and Box 2016), it is overprinted by low-pressure greenschist facies metamorphism and is related to crustal extension, uplift, and unroofing, which occurred in the mid-Cretaceous in response to crustal thickening (Miller and Hudson 1991; Hannula et al. 1995; Amato et al. 2003; Till et al. 2011).

The Sn granites in the Seward Peninsula are assigned to Late Cretaceous crustal melting across central and western Alaska (80 to 69 Ma; Hudson and Arth 1983; Swanson et al. 1988). The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.708 to 0.720) for the Sn granites of the Seward Peninsula indicate a dominantly crustal source for the parent magma, with a multistage origin of the Sn granites that involved melting of sialic crust to produce batholithic plutons, and subsequent fractionation to generate smaller volumes of highly evolved residual magma (Hudson and Arth 1983). Amato et al. (2001) reported mafic calc-alkaline to potassic alkalic dikes dated at 90 to 84 Ma and intruded during the Early to Late Cretaceous (~115–75 Ma) extensional tectonic setting at the Seward Peninsula.

Within the “Seward Peninsula tin granite belt,” the Sn occurrences are associated with granitic plutons with a range of textural and alteration facies. In particular, the plutons vary from those composed of dominantly early porphyritic to seriate granitic phases (Ear Mountain, Oonatut Complex) to those with a greater role of late, highly evolved F- and H_2O -rich equigranular granitic phases (Lost River, Kougarok) (Swanson et al. 1988). In the shallow-eroded plutons with no late, highly differentiated phases, the mineralization is represented mostly by low-grade quartz–tourmaline–cassiterite veins and stockworks (Potato Mountain; Hudson and Reed 1997). In contrast, the Lost River deposit is associated with a buried granitic pluton, subvertical dikes and is represented by a combination of tin-bearing quartz, quartz–tourmaline, and quartz–sulfide (Sn, As, Pb, Zn, Cu) veins and quartz–tourmaline, quartz–topaz, and quartz–micaceous greisens overprinting skarns. Abundant fluorite in greisens and a strong enrichment of greisen micas in Li at Lost River (Dobson 1982; Alexandrov 2010) suggest that a Li–F-enriched granitic phase may be present. The Kougarok prospect corresponds to a shallow-eroded and highly differentiated granitic system (Puchner 1986; Swanson et al. 1988; Hudson and Reed 1997).

Kougarok prospect geology

The Kougarok prospect area is underlain by the Nome Complex quartz–mica schists (“Kougarok schists”) incorporating lenses and sheets of quartzite and marble (Witte et al. 1983; Puchner 1986; Fig. 2b). The schists are composed of quartz, muscovite, and chlorite; close to the Late Cretaceous intrusions, the schists are converted into biotite hornfels and contain variable amounts of visually black (to dark-brown) tourmaline. The metasedimentary rocks were subjected to intense poly-phase folding and faulting (Puchner 1986), with the flat-lying,

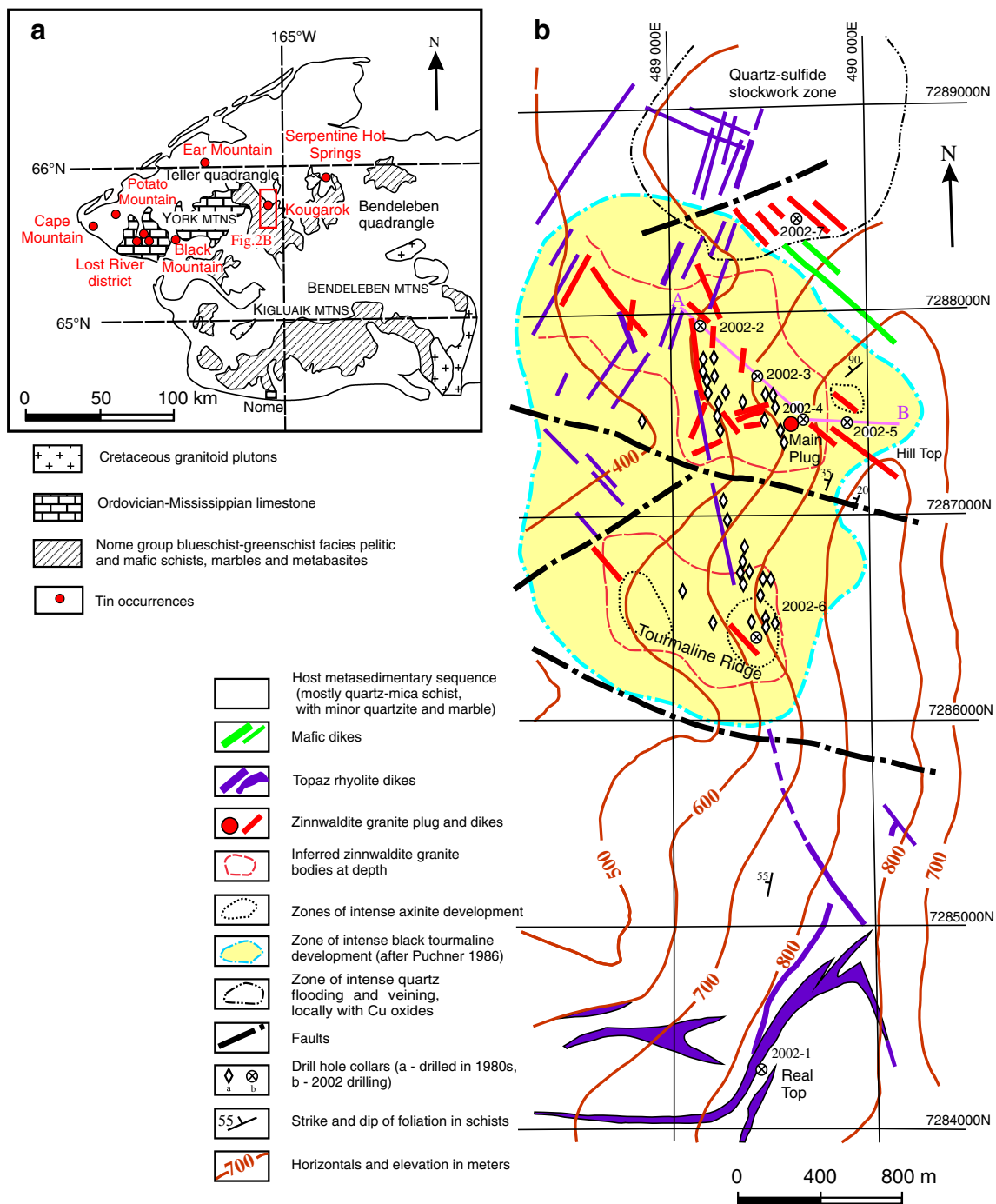


Fig. 2 Geological setting of tin mineralization in the Seward Peninsula (after Hudson and Arth 1983; Till and Dumoulin 1994; Hannula et al. 1995; Hudson and Reed 1997) (a) and geological map of the Kougarak

prospect (b); field mapping by S.G. Soloviev, using the data of Apel (1984) and Puchner (1986)

likely thrust-fault zones possibly playing a role in localizing some granitic intrusions and associated alteration zones.

The Kougarak prospect area incorporates numerous felsic dikes (Fig. 2b). There are relatively separated “magmatic centers” (~500–800 m across) with concentration of dikes, stocks, and intense hydrothermal alteration. The larger intrusions include mostly flat-lying granitic bodies from

younger intrusion phase(s) of biotite-tourmaline and zinnwaldite granites above cupola-shaped bodies of older porphyritic biotite granite (Witte et al. 1983; Reid and Bergman 1982; Apel 1984; Puchner 1986; Fig. 3). These intrusions and their apophyses outcropping at the surface are accompanied by extensive hydrothermal alteration halos including zones of quartz-tourmaline-chlorite stockworks,

evolving to zones of axinite in carbonate rocks, to greisens, and to quartz to quartz-sulfide veins in the intrusive rocks and the “Kougarok schists” (Fig. 2b).

Tin mineralization is most widespread and occurs in two principal settings (Puchner 1986). First, low-grade (typically 0.01–0.1% Sn) tin mineralization is associated with zones of quartz-cassiterite and quartz-tourmaline-cassiterite stockwork and veins over the entire extent of the alteration halo of the prospect. Second, higher-grade (typically 0.1–1% Sn, locally up to 10% Sn) tin mineralization is associated with the greisen stage in close spatial relation to the flat-lying upper contact, and subvertical apophyses, of younger granitic intrusions (Online Resource 1). Tantalum (Ta-Nb) mineralization (typically 30–300 ppm Ta) occurs in the uppermost ~30–50-m-thick part of the zinnwaldite granite body and in small subvertical apophyses of the granite (Online Resource 1). It is also found in narrow topaz rhyolite dikes. Lithium mineralization is in zinnwaldite and other Li-rich micas in the zinnwaldite granite body and in micaceous greisens overprinting the country rocks (Fig. 3).

Analytical methods

The analyses of 22 samples of igneous rocks were performed in the TsNIGRI Labs, 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. Supplementary determinations by wet chemical methods included FeO (volumetric method), Na_2O (flame photometry), F (ion chromatography), CO_2 (acidic titration), S_{total} (iodic titration), and $\text{H}_2\text{O}+$ (gravimetry). Powdered samples were digested in four acids and analyzed by ICP-ES method for trace elements. Detection limits are as follows: SiO_2 , 0.50 wt%; TiO_2 , 0.02 wt%; Fe_2O_3 and FeO , 0.25 wt%; MgO , CaO , Na_2O , K_2O , and CO_2 , 0.20 wt%; P_2O_5 , 0.04 wt%; H_2O and S_{total} , 0.10 wt%; MnO and F , 0.02 wt%; Ba, Sr, and Zr 20 ppm; Co, V, Nb, Sn, Y, and Rb 5 ppm; Li, B, Cu, Zn, Pb, and Ni 1 ppm; Be and Mo 0.1 ppm; and Bi, U, Th, REE, Hf, Cs, and Ta 0.01 ppm. Analytical errors are 0.5–5% for major elements and 1–10% for trace elements, depending on the concentrations.

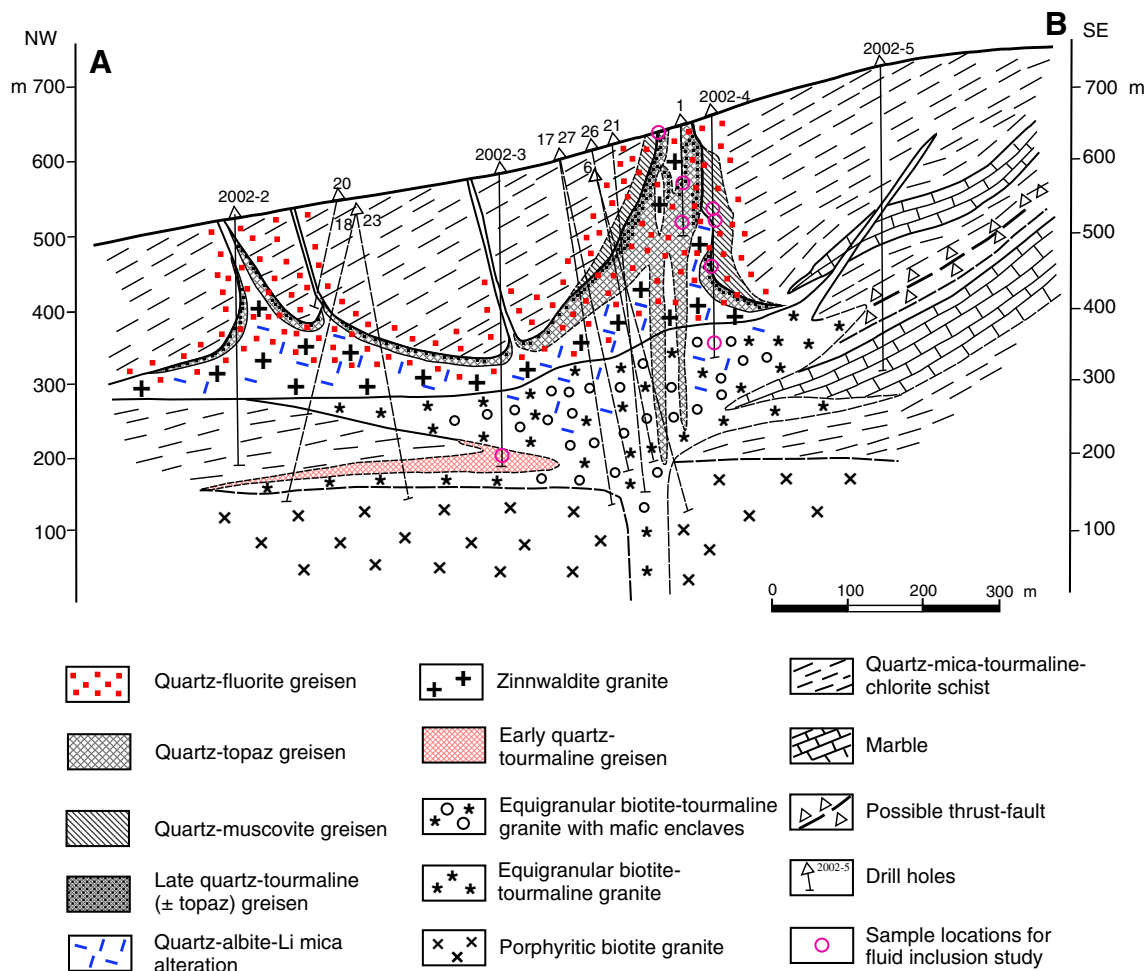


Fig. 3 Cross section of the Kougarok prospect (drill hole data from AMC and Navigator Exploration/Chapleau Resources drilling)

Minerals were analyzed using a Cameca Camebax SX50 microprobe in the GEOKHI Institute of the Russian Academy of Sciences (RAS), Moscow, under operating conditions of 15 kV accelerating voltage, 30 nA beam current, and with a beam diameter $\sim 3 \mu\text{m}$. The accuracy of element measurements was $\pm 2\%$ rel. for concentrations $> 10 \text{ wt}\%$, $\pm 5\%$ rel. for concentrations of $5\text{--}10 \text{ wt}\%$, and $\pm 10\%$ rel. for concentrations $< 5 \text{ wt}\%$. Pure Nb, Ta, and W, as well as SnO_2 , $\text{Rb}_2\text{Nb}_4\text{O}_{11}$, pyrite (Fe), rutile (Ti), and rhodonite (Mn) of known composition, were used as standards.

Twenty-six doubly polished sections of 0.3- to 0.5-mm thickness were prepared from 12 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 the observations of crosscutting trails of FIA along individual fractures, 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 based on 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, Moscow. Low-temperature measurements were conducted first. The stage is capable of attaining temperatures ranging from below -180 to over $+650^\circ\text{C}$. The stage was periodically calibrated using the boiling temperature of pure N_2 (-196°C), triple point for pure CO_2 (-56.6°C), temperatures of ice melting in standard NaCl solutions (from -18 to -1°C), and melting temperatures of AgNO_3 (210°C), K_2CrO_7 (398°C), and NaI (651°C). Final ice melting temperatures were accurate to $\pm 0.2^\circ\text{C}$, clathrate melting temperatures to $\pm 0.5^\circ\text{C}$, eutectic temperatures to $\pm 1.5^\circ\text{C}$, and homogenization temperatures to $\pm 5^\circ\text{C}$. Heating rate (at above 30°C) was $5^\circ\text{C}/\text{min}$ up to a heating limit at 650°C .

For the bulk gas chromatography analysis, 1-g quartz, topaz, and fluorite separates were prepared by handpicking under a binocular microscope. Mineral separates were crushed in an agate mortar to $0.25\text{--}0.5 \text{ mm}$, followed by sample cleaning in a HNO_3 aqueous (1:1) solution (Bottrell et al. 1988) and water-flow electrolytic cleaning in an ultrasound bath for 3 h. Samples were then dried and put into a quartz glass reactor vacuumed at 110°C and then filled with helium. Fluid inclusions were liberated by heating to 500°C . The gases were introduced into a gas chromatograph equipped with a gas flow divider to allow simultaneous determination of H_2O , CO_2 , and CH_4 . Then, the heated samples were leached with de-ionized water in an ultrasound bath for 15 min. The leachate solutions were separated by centrifuging and then analyzed by ICP-MS

(Elan-6100) for cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Mn^{2+} , Fe^{2+} , B^{3+} , Li^+) and by ion chromatography for anions (Cl^- , F^- , SO_4^{2-}). Duplicate leaching of each sample was deducted from the respective initial leachate analyses. The concentration of HCO_3^- was calculated using the cation/anion balance and all concentrations were normalized to the water content and presented in gram per kilogram H_2O values.

Minerals for isotopic analysis were extracted using a drill and/or by hand picking of chips. Sulfide mineral powders were analyzed by conventional methods (Robinson and Kusakabe 1975) by reaction with CuO at 750°C , followed by isotopic analysis of SO_2 . Analytical uncertainty of $\pm 0.2\%$ (2σ) for $\delta^{34}\text{S}$ was estimated from internal standards of homogenous pyrite from the Gaiskoe deposit in the Southern Ural ($\delta^{34}\text{S}_{\text{VCDT}} = +0.7\%$).

Igneous rocks

The earliest granitic rock forms a large pluton of porphyritic biotite granite (after Puchner 1986) or coarse-grained granite-porphyry (after Reid and Bergman 1982) situated at the deepest ($400\text{--}600 \text{ m}$) levels and outcrops as few small dikes at the surface. The rock was dated by the Rb-Sr isochrone method at $72 \pm 2 \text{ Ma}$ with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7134 (Puchner 1986). The rock is medium- to coarse-grained, with larger phenocrysts of feldspars (both K-feldspar and plagioclase) and smaller bipyramidal phenocrysts of colorless to dark-gray (“smoky”) quartz. Dark-brown biotite is found in the medium- to fine-grained groundmass composed of the same minerals (Online Resource 2 and Fig. 4a). The rock is locally affected by pervasive quartz-tourmaline replacement and is cut by quartz and dark-brown to indigo tourmaline veinlets. Rarely, porphyritic biotite granite is replaced by quartz-bluish-green tourmaline greisen, with trace fluorite and cassiterite.

A younger intrusion phase is represented by equigranular biotite-tourmaline granite forming sheet-like bodies above the roof of the porphyritic biotite granite, and rare subvertical dikes (Figs. 2b and 3), locally cutting porphyritic biotite granite (Puchner 1986). This is typically a fine-grained leucocratic rock containing reddish-brown biotite and black- to dark-brown tourmaline (Online Resource 2). Apart for intervals ($5\text{--}20 \text{ m}$ thick) of fine-grained equigranular texture, the biotite-tourmaline granite evolves to that with very variable composition and texture. In particular, it contains rounded to irregular amoeboid mafic enclaves varying from those enriched in coarser biotite and equigranular at deeper levels to those with hornfels-like fine-grained biotite-feldspar-quartz groundmass and rounded to embayed quartz phenocrysts (Fig. 4b–e), at shallower levels. Although some enclaves may be xenoliths of the “Kougarok schists” (Puchner 1986), the relationships of the most mafic enclaves and biotite-tourmaline granite suggest, rather, mixing/mingling of mafic and granitic magmas (Online Resource 3).

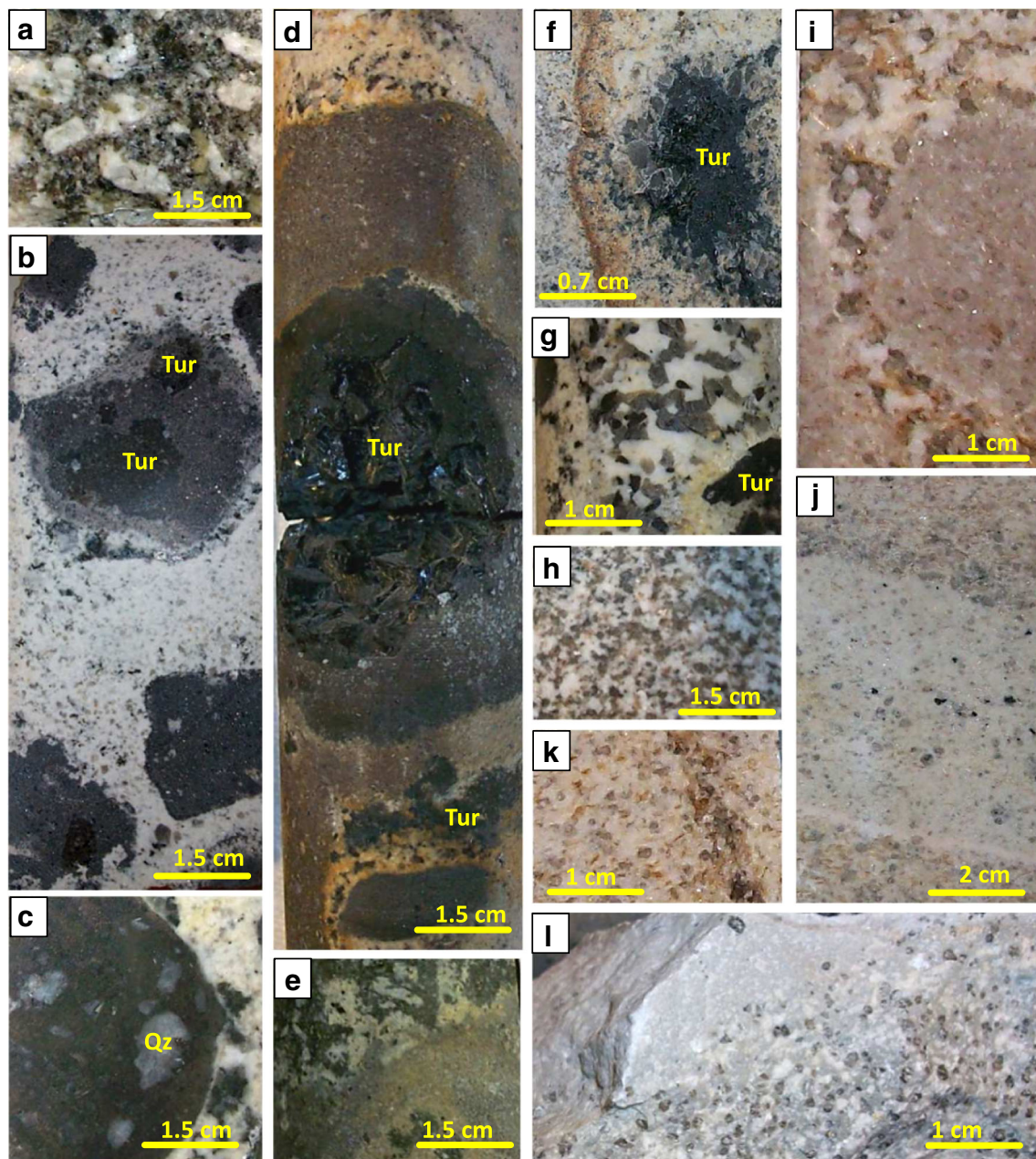


Fig. 4 Photographs showing typical features of some igneous rocks at the Kougarok prospect. **a** Porphyritic biotite granite. **b** Mafic enclaves in equigranular biotite-tourmaline granite, with black tourmaline inclusions and quartz-feldspar pegmatitic corona halos. **c** Mafic enclave with rounded droplet-like quartz inclusions. **d** Large rounded tourmaline aggregate, with a central miarolitic cavity, in mafic enclave in biotite-tourmaline granite. **e** Mafic rock similar to that in mafic enclaves in equigranular biotite-tourmaline granite, with tourmaline “droplets,” cutting the host

“Kougarok schist.” **f** Large miarolitic cavity filled by tourmaline in equigranular biotite-tourmaline granite. **g** Coarse-grained pegmatite-like aggregate in equigranular biotite-tourmaline granite. **h** Zinnwaldite granite. **i** Xenoliths of fine-grained zinnwaldite granite in medium- to coarse-grained zinnwaldite granite. **j** Zone of intense quartz-albite alteration in zinnwaldite granite. **k** Zinnwaldite veinlet overprinting zinnwaldite granite. **l** Porphyritic and aphanitic topaz rhyolite. Abbreviations: Qz, quartz; Tur, tourmaline

The mafic enclaves are composed mostly of fine-grained, dark-brown biotite, quartz, minor feldspars, and accessory acicular apatite. These enclaves, as well as biotite-tourmaline granites outside the enclaves, contain small to large (up to 1 cm across) rounded to “droplet”-shaped composite granular quartz phenocrystic aggregates (Fig. 5a–g) evolving to small euhedral bipyramidal to embayed quartz phenocrysts. These

“droplets” locally incorporate a central “zone” of colorless to purple fluorite and contain W-Nb-rutile (Fig. 5a–f and Table 1); cassiterite may also be present. Fluorite (small anhedral grains) as well as accessory monazite and cassiterite are also found in the fine-grained biotite-feldspar-quartz groundmass. Similar rounded to amoeboid to “droplet”-shaped black (dark brown in thin section) tourmaline

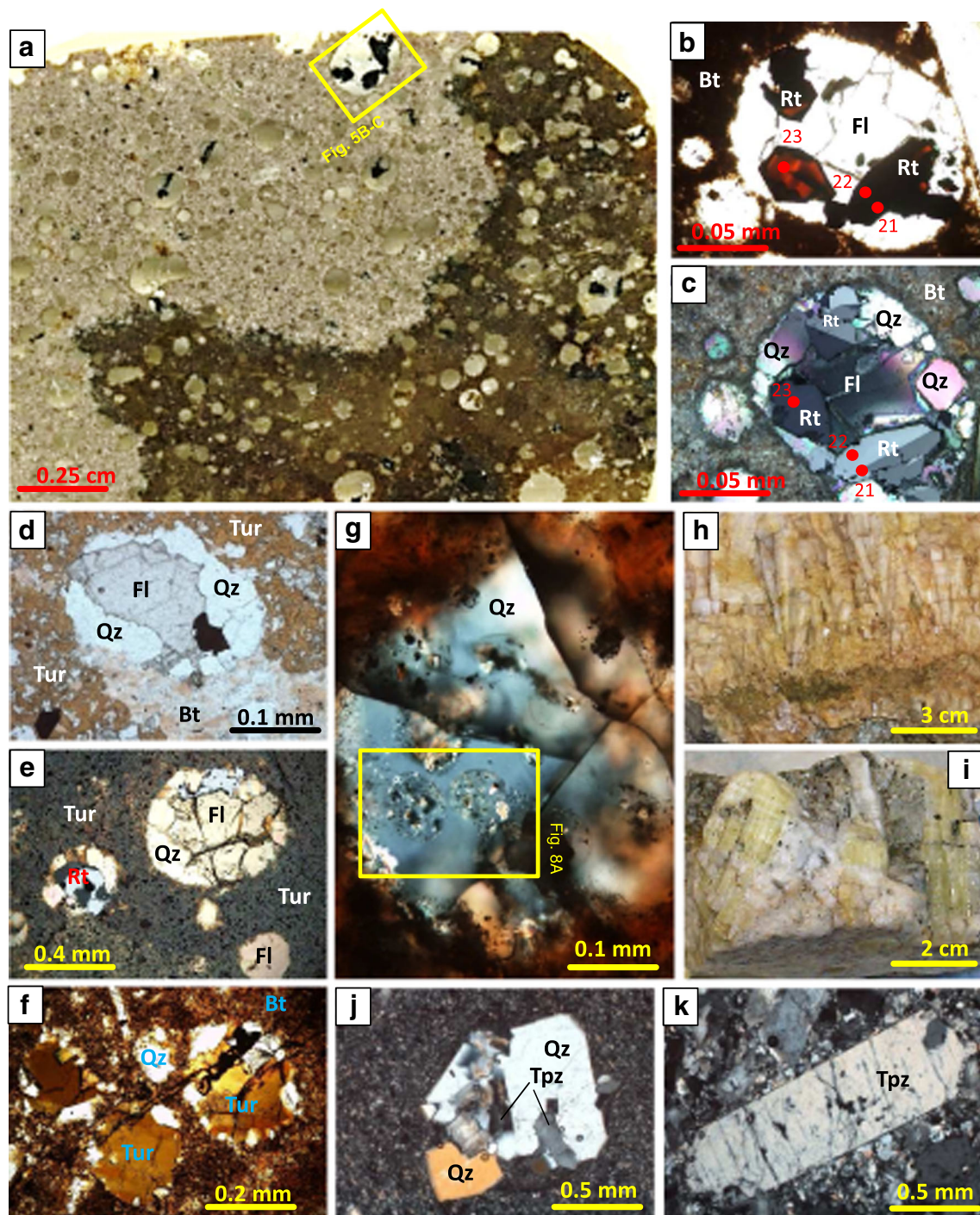


Fig. 5 Photographs showing relationships of minerals in some igneous rocks at the Kougarok prospect. **a** Quartz and quartz-fluorite “droplets” in mafic enclaves with biotite- and darker tourmaline-dominated groundmass, in equigranular tourmaline-biotite granite. **b, c** Concentric quartz-fluorite “droplet” in biotite-dominated groundmass, with rutile (thin section; **c** nicols crossed, indicating rutile twinning). Red dots show location of microprobe analyses (numbers are from Table 1). **d** Concentric quartz-fluorite “droplet” with rutile in tourmaline-dominated groundmass (thin section). **e** Fluorite and fluorite-quartz “droplets,” some with rutile, in tourmaline-dominated groundmass. **f** Quartz-tourmaline “droplets” in a finer-grained mafic (biotite-quartz-feldspar groundmass) enclave in

equigranular tourmaline-biotite granite (thin section). **g** Globular aggregates of magmatic fluid-melt-crystal “suspension” in a quartz “droplet” in a mafic enclave in equigranular tourmaline-biotite granite (polished slab, nicols crossed). **h** Topaz-quartz stockscheider, with topaz crystals elongated perpendicular to zinnwaldite granite contact. **i** Topaz-quartz stockscheider, with topaz crystals enclosed into quartz-albite-micaceous aggregate. **j** Topaz within and near quartz phenocrysts in topaz rhyolite (thin section, nicols crossed). **k** Topaz phenocryst in topaz rhyolite (thin section, nicols crossed). Abbreviations: Qz, quartz; Bt, biotite; Rt, rutile; Fl, fluorite; Tur, tourmaline; Tpz, topaz

Table 1 Chemical compositions of Ta-Nb minerals and cassiterite from the Kougarok prospect, wt. %

Reference points (Fig. 5b, c and Online Resource 7)	FeO	MnO	Nb ₂ O ₅	Ta ₂ O ₅	WO ₃	SnO ₂	TiO ₂	Total	Mineral formulae
Sample DDH Koug-1/134 m									
Columbite-tantalite mineral group									
1	1.55	17.28	58.83	17.37	1.16	0.82	2.92	99.93	(Fe _{0.08} Mn _{0.88}) _{0.96} (Nb _{1.59} Ta _{0.28} W _{0.02} Sn _{0.02} Ti _{0.13}) _{2.04} O ₆
2	4.51	14.12	56.35	20.25	2.31	0.27	2.14	99.95	(Fe _{0.23} Mn _{0.73}) _{0.96} (Nb _{1.55} Ta _{0.34} W _{0.04} Sn _{0.01} Ti _{0.10}) _{2.04} O ₆
3	9.80	7.79	33.07	42.94	2.80	0.92	2.52	99.84	(Fe _{0.55} Mn _{0.45}) _{1.00} (Nb _{1.01} Ta _{0.79} W _{0.05} Sn _{0.02} Ti _{0.13}) _{2.00} O ₆
4	3.16	16.35	54.84	19.39	1.86	0.62	3.58	99.80	(Fe _{0.16} Mn _{0.83}) _{0.99} (Nb _{1.49} Ta _{0.32} W _{0.03} Sn _{0.01} Ti _{0.16}) _{2.01} O ₆
5	10.05	8.39	43.46	32.10	3.09	0.26	2.57	99.92	(Fe _{0.54} Mn _{0.46}) _{1.00} (Nb _{1.26} Ta _{0.56} W _{0.05} Sn _{0.01} Ti _{0.12}) _{2.00} O ₆
6	10.99	6.64	31.93	43.88	2.75	1.06	2.54	99.79	(Fe _{0.62} Mn _{0.38}) _{1.00} (Nb _{0.98} Ta _{0.81} W _{0.05} Sn _{0.03} Ti _{0.13}) _{2.00} O ₆
7	1.55	16.74	59.60	17.10	1.09	0.67	3.15	99.90	(Fe _{0.08} Mn _{0.85}) _{0.93} (Nb _{1.61} Ta _{0.28} W _{0.02} Sn _{0.02} Ti _{0.14}) _{2.07} O ₆
8	7.59	11.52	54.53	23.65	1.07	0.45	1.11	99.92	(Fe _{0.39} Mn _{0.60}) _{0.99} (Nb _{1.53} Ta _{0.40} W _{0.02} Sn _{0.01} Ti _{0.05}) _{2.01} O ₆
9	9.85	7.66	30.83	45.11	2.78	1.00	2.50	99.73	(Fe _{0.56} Mn _{0.44}) _{1.00} (Nb _{0.95} Ta _{0.84} W _{0.05} Sn _{0.03} Ti _{0.13}) _{2.00} O ₆
10	1.15	16.55	52.72	24.22	0.99	1.49	2.81	99.93	(Fe _{0.06} Mn _{0.87}) _{0.93} (Nb _{1.47} Ta _{0.41} W _{0.02} Sn _{0.04} Ti _{0.13}) _{2.07} O ₆
11	1.09	17.83	62.57	13.10	1.29	0.54	3.57	99.99	(Fe _{0.05} Mn _{0.89}) _{0.94} (Nb _{1.66} Ta _{0.21} W _{0.02} Sn _{0.01} Ti _{0.16}) _{2.06} O ₆
Sample DDH Koug-1/131 m									
Columbite-tantalite mineral group									
17	1.08	17.30	60.10	14.74	2.35	0.41	3.95	99.93	(Fe _{0.05} Mn _{0.87}) _{0.92} (Nb _{1.61} Ta _{0.24} W _{0.04} Sn _{0.01} Ti _{0.18}) _{2.08} O ₆
18	1.69	16.15	59.21	16.39	1.18	1.69	3.70	100.01	(Fe _{0.08} Mn _{0.82}) _{0.90} (Nb _{1.60} Ta _{0.27} W _{0.02} Sn _{0.04} Ti _{0.17}) _{2.10} O ₆
19	0.97	15.42	50.04	23.87	2.29	0.80	6.66	100.05	(Fe _{0.05} Mn _{0.80}) _{0.85} (Nb _{1.38} Ta _{0.40} W _{0.04} Sn _{0.02} Ti _{0.31}) _{2.15} O ₆
Cassiterite									
12	0.17	0.00	0.22	0.25	1.33	98.01	0.00	99.98	(Sn _{0.99} W _{0.01} Nb, Ta, Fe)O ₂
13	0.55	0.02	0.04	0.26	0.40	98.70	0.00	99.97	(Sn _{0.99} Fe _{0.01} Nb, Ta, W, Mn)O ₂
14	1.00	0.04	2.67	2.56	0.33	93.33	0.00	99.93	(Sn _{0.93} Fe _{0.02} Nb _{0.03} Ta _{0.02} W, Mn)O ₂
15	0.79	0.00	1.81	1.38	0.63	95.39	0.00	100.00	(Sn _{0.95} Fe _{0.02} Nb _{0.02} Ta _{0.01} W)O ₂
16	0.80	0.00	1.74	1.30	0.16	95.82	0.00	99.82	(Sn _{0.95} Fe _{0.02} Nb _{0.02} Ta _{0.01} W)O ₂
20	0.43	0.19	1.18	3.10	0.29	94.77	0.0	99.96	(Sn _{0.96} Fe _{0.01} Nb _{0.01} Ta _{0.02} W)O ₂
Sample DDH 2002-04-311 m									
Rutile									
21	1.446	0.52	0.32	0.03	3.27	0.15	94.21	99.96	(Ti _{0.97} Fe _{0.02} MnW _{0.01} Nb, Ta, Sn)O ₂
22	0.653	1.15	0.24	0.01	1.12	0.10	96.27	99.55	(Ti _{0.98} Fe _{0.01} Mn _{0.01} W, Nb, Ta, Sn)O ₂
23	0.667	1.02	0.19	0.01	1.15	0.10	96.22	99.35	(Ti _{0.98} Fe _{0.01} Mn _{0.01} W, Nb, Ta, Sn)O ₂

aggregates and larger-crystalline quartz-tourmaline “droplets” are found mostly within the mafic enclaves (Fig. 5e). Droplet-shaped quartz ocelli up to 1 cm long are observed in the mafic enclaves (Online Resource 3). There are silicate melt-fluid-crystal globules in the quartz “droplets”; these globules contain gas bubbles and a mix of various small crystals, the latter including biotite and tourmaline (Fig. 5g). The mafic material can form small dike-like intrusions cutting the “Kougarok schist” and cementing small zones of intrusive breccia (Fig. 4e). Biotite-tourmaline granite contains miarolitic cavities partially filled by tourmaline (Fig. 4f), granophyric quartz and coarse-grained pegmatitic aggregates (Fig. 4g), radiating pegmatitic “halos” around some mafic enclaves (Fig. 4b), and local vein- to lens-like leucocratic biotite- and tourmaline-free aggregates. Leucogranite-porphyry (Online Resource 2) is mineralogically similar to biotite-tourmaline granite but is distinctly porphyritic and forms small dikes.

The next intrusion phase is represented by zinnwaldite granite forming sheet-like bodies and small dikes above the roof of the biotite-tourmaline granite (Online Resource 2 and Figs. 2b and 3). Puchner (1986) reported crosscutting relationships to the biotite granite, as well as xenoliths of the biotite-tourmaline granite in the zinnwaldite granite. The rock was dated by the K-Ar method at 70.2 ± 2.6 Ma (Puchner 1986). There are several varieties of zinnwaldite granite (Fig. 4h, i), such as equigranular variety with mafic enclaves at deeper levels, porphyritic variety, with small to larger rounded quartz (and zinnwaldite ?) phenocrysts, and

medium- to coarse-grained pegmatitic variety, the latter showing most definite crosscutting (intrusion phase) relationships to the other zinnwaldite granite varieties (Fig. 4i). The granite contains likely both magmatic and hydrothermal zinnwaldite, the latter forming veins associated with albitic alteration (Fig. 4j, k). Snowball textures defined by oriented laths of albite in quartz and K-feldspar phenocrysts indicate the magmatic crystallization origin of at least part of the albite. Topaz is a common accessory mineral. At higher levels, coarse-crystalline marginal pegmatite (stockscheider) up to 0.7 m wide composed of pale-white to greenish-yellow topaz crystals (up to 20 cm long) banded with fine-grained topaz-quartz-albite locally occurs along zinnwaldite granite contacts (Fig. 5h). Some of these stockscheider zones resemble those distinguished elsewhere as F-rich pycnite rock (Fig. 5i), with large topaz crystals enclosed into possibly crystallized melt pockets (Thomas and Davidson 2013).

A distinct intrusion phase is represented by topaz rhyolite (ongonite) forming numerous thin (from < 1 to 5–7 m) but extended (locally > 500 m) dikes over the area (Online Resource 2 and Figs. 2b and 3; Apel 1984). We observed no crosscutting relationships of this rock with other intrusive phases and assume that at least some of topaz rhyolite dikes may represent distal but coeval dike facies of the zinnwaldite granite. The rock is sharply porphyritic, with rounded to embayed phenocrysts of quartz and feldspars in fine-grained groundmass, to porcelain-like aphyric and aphanitic; this transition can occur in a single dike (Fig. 4l), or different dikes can be either porphyritic or aphyric. The rock

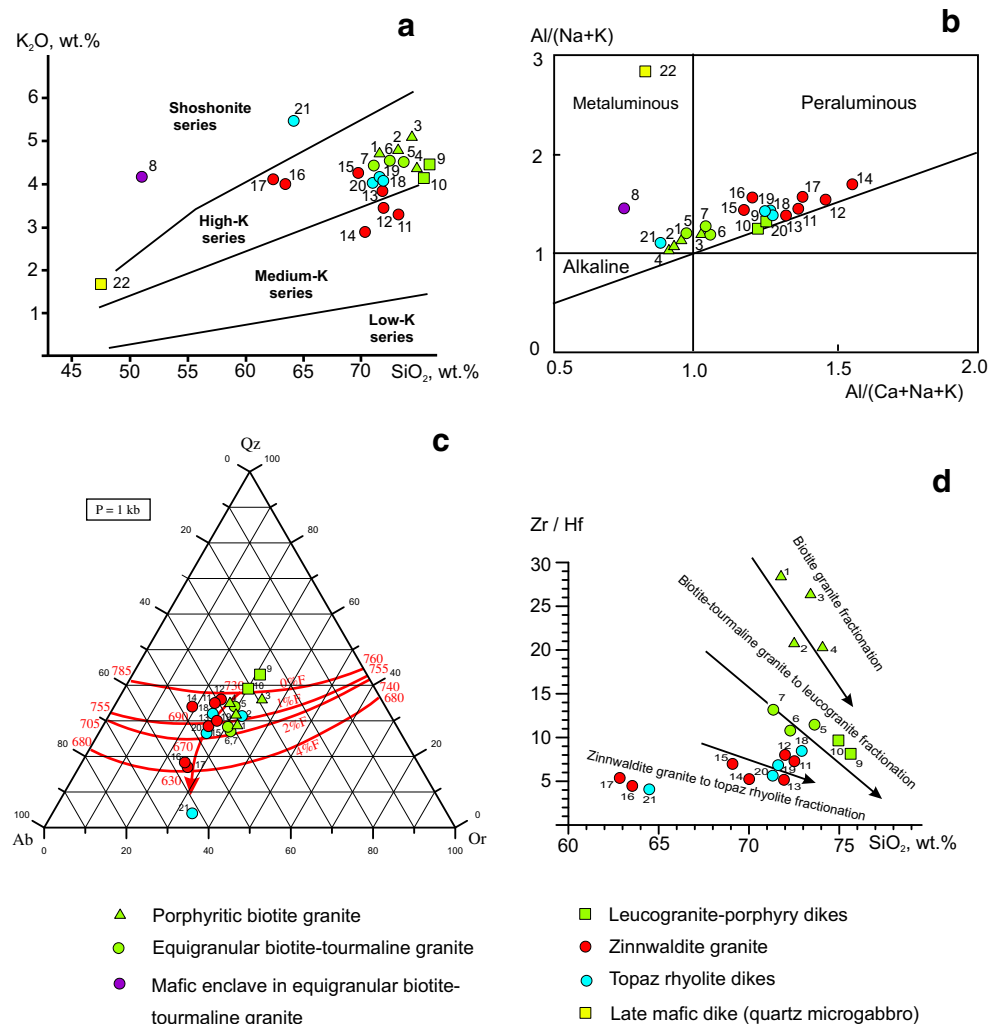
from different locations varies also in quartz/feldspar ratio of the phenocrysts. Magmatic topaz forms small crystals associated with glomeroporphyry aggregates of quartz and/or feldspars (Fig. 5j) and larger prismatic phenocrysts (Fig. 5k). The rock contains white mica, muscovite, or/and zinnwaldite.

The igneous rocks have distinct geochemical signatures (Online Resource 4). First, there are two groups of rocks distinguished by K_2O/Na_2O ratio. The earlier biotite granite and biotite-tourmaline granite, also mafic rock from the enclaves, are potassic (Fig. 6a), whereas the later zinnwaldite granite and topaz rhyolite are enriched in sodium ($Na_2O > K_2O$) (Online Resource 4). Second, there are three groups of rocks distinguished by Li and F contents. The earlier biotite granite and biotite-tourmaline granite contain minor to moderate Li and F, the mafic enclaves in biotite-tourmaline granite contain little Li but very high F (2.80 wt%), and the later zinnwaldite granite and topaz rhyolite are strongly enriched in both Li and F. Distribution of B and Sn is somewhat opposite to that of F, reaching maximum values in biotite-tourmaline granite, but being low in zinnwaldite granite and topaz rhyolite. There is a positive correlation of B and Sn values. An exception is

represented by the mafic enclaves in biotite-tourmaline granite containing both very high F and B values (Online Resource 4). Hydrothermal alteration of zinnwaldite granite caused a sharp increase in Li values due to micaceous greisen replacement as well as in B (tourmaline) and Sn (cassiterite). In contrast to tin, rare element (Ta, Nb, Cs) contents are higher in the younger zinnwaldite granite and topaz rhyolite, with Cs values correlating to these of Li suggesting Li and Cs are concentrated in white micas, and Ta-Nb values related mostly to columbite-tantalite. High Ta concentrations in the marginal (aphanitic) zone of topaz rhyolite (Online Resource 4) resemble similar feature noted for Ta concentration in the roof and apical zones of the zinnwaldite granite (Puchner 1986). The granitic rocks belong to the low-P type (Taylor 1992), whereas the mafic enclaves in biotite-tourmaline granite contain 0.5 wt% P_2O_5 .

The rocks evolve from marginal metaluminous biotite granite and biotite-tourmaline granite to strongly peraluminous zinnwaldite granite and topaz rhyolite (Fig. 6b), which contain normative corundum. The rocks are characterized by $Fe_2O_3/FeO < 0.4$, which, with the dominance of ilmenite among accessory minerals, indicates that the rocks belong to the ilmenite

Fig. 6 Plots illustrating the chemistry and mineralogy of igneous rocks from the Kougarok prospect. **a** SiO_2 vs. K_2O diagram (after Le Maitre et al. 1989; Peccerillo and Taylor 1976). **b** $Al/(Na + K)$ vs. $Al/(Ca + Na + K)$ diagram defining the alkaline, meta-aluminous, and peraluminous igneous rocks (after Maniar and Piccoli 1989). **c** Quartz (Qz)–albite (Ab)–orthoclase (Or) ternary diagram showing CIPW-normative (wt.%) mineralogy. Cotectic curves for this system with excess water at 1 kbar and 0%, 1%, 2%, and 4% added fluorine (labelled as 0%, 1%, 2%, and 4% F, respectively) are shown after Manning (1981); corresponding thermal minimum points indicate a shift from $Qz_{37}Or_{29}Ab_{34}$ at 730 °C and F = 0% to $Qz_{15}Or_{27}Ab_{58}$ at 630 °C and F = 4 wt.%. **d** SiO_2 vs. Zr/Hf diagram showing trends of crystal fractionation. Numbers (1–22) of the compositions shown are from Online Resource 4



series (Ishihara 1981). Elevated to high Ta and Nb contents define the within-plate type of the rocks (Pearce et al. 1984). On the quartz-albite-orthoclase diagram (Fig. 6c), the rocks form a trend toward higher albite contents, consistent with F and B being important volatile components, where most compositions correspond to F contents of 0.5–1.5 wt% (Manning 1981). Progressively decreasing Zr/Hf ratio indicates subsequent fractionation of biotite granite (Zr/Hf from 29 to 20), biotite-tourmaline granite (Zr/Hf from 13 to 10), zinnwaldite granite, and topaz rhyolite (Zr/Hf from 9 to 4) (Online Resource 4) (Fig. 6d). The biotite granite has low $La_N/Yb_N = 2.3–9.4$, whereas other granites have $La_N/Yb_N = 0.5–3.0$ and strong positive Eu anomaly (Online Resource 4).

Hydrothermal assemblages and mineralization

Early quartz-tourmaline alteration

Small zones of early quartz-tourmaline greisen are closely related to biotite-tourmaline granite contacts, where the greisen replaces the granite and the “Kougarok schists.” Tourmaline is black (dark-brown to dark indigo-blue in thin sections). Away from the granite contacts, the greisen is overprinted by quartz-tourmaline+chlorite+axinite alteration occurring most widely in the “Kougarok schists,” in biotite granite, and in biotite-tourmaline granite. This alteration varying from stockworks of linear quartz-tourmaline veinlets, zones of pervasive alteration, to dissemination is present almost over the entire prospect area but most intensely occurs in its west-central part (“Tourmaline Ridge”) (Fig. 2b). The assemblage containing minor fine-disseminated cassiterite replaces biotite-quartz-feldspar hornfels. Dark-green chlorite locally replaces biotite of the protolith hornfels in the outer zones of quartz-tourmaline veins. Axinite is locally abundant, replacing lenses of carbonate rocks, where almost monomineralic axinite zones up to 1 m thick are found.

Quartz-albite-Li mica alteration

Quartz-albite to quartz-albite-Li mica alteration occurs mostly in zinnwaldite granite (Fig. 3) and topaz rhyolite, where these minerals occur in addition to primary-magmatic albite and zinnwaldite. This assemblage is locally developed over biotite-tourmaline granite as variably thick, generally lens-shaped zones of pervasive replacement. Series of subparallel zones, roughly concordant to intrusive contacts, are characteristic for zinnwaldite granite. Fine-grained albite occurs with Li-micas or alone. Fine-grained cassiterite is locally present in this assemblage overprinting biotite-tourmaline granite, whereas both cassiterite and columbite-tantalite are locally present in albitic (+Li mica) rocks overprinting zinnwaldite granite, where Ta-Nb contents are particularly high locally exceeding 300 ppm (Online Resource 5). However, there is no prospect-scale correlation between the intensity of albitization and Sn grade. Thick (tens of meters) intervals of almost complete

albitic replacement (~80–90 vol.% albite) contain just trace cassiterite and no Ta-Nb minerals.

Late greisens

These greisens include several mineral assemblages replacing zinnwaldite granite and immediately adjacent country rocks and include the “inner” and “outer” greisen zones (Fig. 3; Davis and Williams-Jones 1985). Quartz-tourmaline+topaz greisen appears to be the earliest and occurs in the endocontact zone of zinnwaldite granite, both in the flat-lying body and the Main Plug. Tourmaline forms acicular bluish-green to green crystals. Quartz-muscovite greisen forms the outermost zone of the composite greisen halo in the exocontact of the Main Plug (Fig. 3), locally replacing part of the quartz-tourmaline greisen, and is also present at deeper level of the Main Plug, where it replaces zones of quartz-albite alteration. Quartz-topaz greisen (Online Resource 5) replaces both quartz-tourmaline and quartz-muscovite greisens and forms the innermost subvertical vein zones in the center of the Main Plug (Fig. 3). Quartz with colorless, light-green, and most abundant dark-purple fluorite is typically finely disseminated replacing all other greisen types as well as zones of quartz-albite (+Li mica) alteration. Purple fluorite is also found in the “Kougarok schists” adjacent to the zinnwaldite granite intrusions. Minor beryl and helvite are associated with purple fluorite.

The uppermost parts of the zinnwaldite granite body including the Main Plug and other parts with intense quartz-albite (+Li micas) replacement, as well as those overprinted by quartz-tourmaline+topaz and quartz-topaz greisens, contain Ta-Nb and Sn mineralization (Online Resource 5). Ta-Nb contents in quartz-tourmaline+topaz and quartz-topaz greisens are lower than those in quartz-albite (+Li micas) alteration of zinnwaldite granite but attain some > 100–200 ppm (locally up to 300 ppm) of each element. However, Ta-Nb grades sharply decrease in muscovite-dominant greisens, to below 100 ppm. Sn grades are variable (from < 100 ppm to several percent) and occur in quartz-tourmaline+topaz and quartz-muscovite but mostly in quartz-fluorite greisens.

Quartz-sericite+carbonate+sulfide (phyllitic) alteration

This alteration assemblage overprints greisen and adjacent metasedimentary and intrusive rocks, forming a wide halo both above and below the greisen zones. The fine-grained white mica referred to as sericite (Puchner 1986) replaces albite and primary-magmatic feldspars of intrusive rocks and coarser-grained micas of quartz-albite-Li mica and greisen alteration assemblages. Chlorite is locally abundant in the outer zones of this alteration assemblage. Disseminated arsenopyrite, pyrrhotite, sphalerite, galena, chalcopyrite, as well as native Bi and Bi tellurides are associated with this assemblage (Fig. 7 and Online Resource 6).

Ta-Nb and Sn minerals

Columbite-tantalite is present in zinnwaldite granite including its strongly altered varieties (Online Resource 1). According to Reid and Bergman (1982), it is subhedral to euhedral and opaque, except at grain edges where it is a translucent burgundy red, with grain sizes ranging from 0.01 to 0.08 mm and averaging about 0.06 mm. It is represented by the variable ferroan (from 1 to 11 wt.% FeO), manganian (from 6.6 to 17.8 wt.% MnO), and titanium (from 1.1 to 6.6 wt.% TiO₂) varieties and contains 14 to 45 wt.% Ta₂O₅ (31.9 to 60.1 wt.% Nb₂O₅), with low (< 1.5 wt.%) SnO₂ (Table 1). There is a zonation of the mineral grains, with more Nb-rich (columbite) compositions in the grain core and more Ta-rich (tantalite) compositions closer to the grain edges (Table 1 and Online Resource 7). Reid and Bergman (1982) reported also a possible presence of other Ta-Nb phases such as microlite and struverite. The latter is consistent with the presence of W-Nb-rutile (Table 2) in the equigranular biotite-tourmaline granite at the lower levels.

Cassiterite occurs in the biotite-tourmaline and zinnwaldite granites and their altered varieties as well as in altered host metamorphic rocks (Online Resource 1). It forms individual dark-brown to red-brown, euhedral, zoned, and generally very

small grains or small grain clusters (Reid and Bergman 1982) and is most abundant in quartz-muscovite and quartz-fluorite greisens, where it forms large, irregular clusters and bands of coarse, disseminated, euhedral, zoned crystals. Two generations are recognized, one with low-Ta (0.25–1.38 wt.% Ta₂O₅) and another with high Ta (2.6–3.1 wt.% Ta₂O₅) contents, respectively (Table 1 and Online Resource 7). Reid and Bergman (1982) reported values up to 6 wt.% Ta₂O₅. The high-Ta varieties contain higher Nb, Fe, and occasionally Mn contents, whereas the low-Ta cassiterite is occasionally W-rich (Table 1).

Fluid inclusions

Fluid inclusions in quartz and quartz-fluorite “droplets” in biotite-tourmaline granite

The oldest primary fluid inclusions are represented by gaseous (type 1) inclusions that are present in the magmatic melt-fluid-crystal “suspension” globules in quartz from quartz and quartz-fluorite “droplets” (Fig. 8a–c and Table 2). These fluid inclusions also occur separately as isolated individuals in small quartz phenocrysts. Gaseous phase occupies 70–90 vol.%. A younger fluid inclusion population preserved as

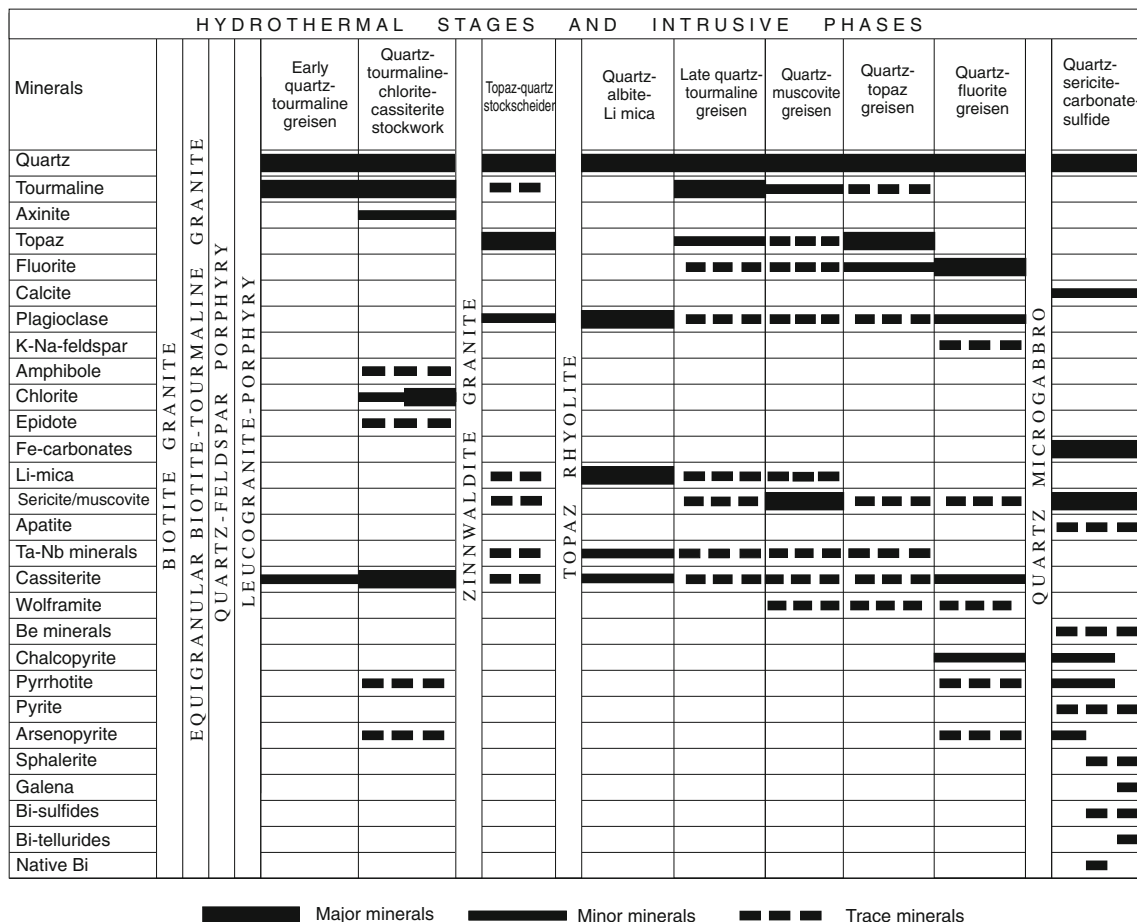


Fig. 7 Sequence of hydrothermal alteration assemblages and intrusive phases at the Kougarok prospect

Table 2 Types of fluid inclusions (FI) from the Kougarok prospect

Mineral (number of FI measured)	FI type	FI size	FI content	T_m CO ₂ , °C	T_m eu., °C	T_m (ice, hh, h, cl) °C	Homogenization, T_h , °C	Estimated salinity, wt.%	Estimated CO ₂ /CH ₄ ratio ^f	Estimated pressure, kbar
Quartz and quartz-fluorite "droplets" from mafic enclaves and biotite-tourmaline granite										
Quartz (7)	1	5–15 µm	Gaseous-liquid, 70–90 vol.% gas	–38...–36	–23...–22 (ice) to +30...+31 (h)	Liquid to gas at > 500		NaCl 18–20, MgCl ₂ 8–7 ^d	~0.5/0.5	< 1.8 ^g >> 0.5–0.7 ^h
Quartz (10)	2A	5–15 µm	Multisolid, 50–70 vol.% gas, 1–3 small anisotropic solids	–60...–59	–38...–36	Liquid to gas at 490–570				
Quartz (10)	2B	5–20 µm	Multisolid, 40–50 vol.% gas, 1–3 small anisotropic solids		–38...–36	Gas to liquid at 490–570		NaCl 15±0.5, MgCl ₂ 10±0.5 ^d		> 0.4 ^h
Quartz (8)	2C	5–20 µm	Multisolid, 30–40 vol.% gas		–38...–36	Gas to liquid at 450–470		NaCl 17±0.5, MgCl ₂ 9±0.5 ^d		> 0.2 ^h
Fluorite (12)	2D	5–20 µm	Liquid-gaseous, 25–30 vol.% gas, 1–3 small anisotropic solids		–28...–27	Gas to liquid at 370–380		NaCl-eq. 7.2–7.9 ^a		
Early quartz-tourmaline greisen associated with biotite-tourmaline granite										
Quartz (8)	3A	5–15 µm	Gaseous, 100 vol.% gas	–98...–94	–29...–27	Gas to liquid at 380–430		NaCl-eq. 10.2–10.5 ^a	0.05/0.95	< 0.9 ^g >> 0.2 ^h
Quartz (8)	3B	5–20 µm	Liquid-gaseous, 30–40 to 20–25 vol.% gas, 0–3 occasional small anisotropic solids							
Quartz-tourmaline-chlorite-cassiterite stockwork associated with biotite-tourmaline granite										
Quartz (24)	4	5–20 µm	Liquid-gaseous, 20–30 vol.% gas	–31.4...–31.0	–8.5...–4.8 (ice)	Gas to liquid at 255–315		NaCl-eq. 7.6–12.3 ^a		> 0.1 ^h
Quartz phenocrysts in zinnwaldite granite, and topaz and quartz from the stockveider associated with zinnwaldite granite										
Quartz	5	5–40 µm	Multisolid, 5–10 vol.% gas, 70–90 vol.% solids, no halite	–25...–24	–7.2...–7.0 (ice)	Gas to liquid at 130–350, solids at 100–> 550, decrepitation at 230–550		NaCl-eq. 10.5–10.7 ^a		> 0.4 ^h
Topaz, quartz (zinnwaldite granite) (20)	6	5–20 µm	Multisolid, 10–35 vol.% gas, 2–5 solids (20–30 vol.%) with halite	–55	–42...–40 (ice)	Gas to liquid at 460–520, halite at 170		NaCl 14–15, CaCl ₂ 22–23 ^d		
Quartz-albite-Li mica alteration										
Quartz (8)	7A	5–15 µm	Gaseous-liquid, 80–95 vol.% gas	–58.5...–57.5	–0.8...–0.2 (ice)	Liquid to gas at 370–400		NaCl-eq. 0.4–1.4 ^a	0.8/0.2	< 1.0 ^g >> 0.2 ^h
Quartz (8)	7B	5–25 µm	Multisolid, numerous solids, with halite, 15–25 vol.% gas	–75	–51...–50 (hh)	Halite at 180–245		NaCl 9–15, LiCl 21–22 ^d		
Quartz (8)	8A	5–15 µm	Gaseous, 95–100 vol.% gas	–60.5...–59.5	–75	Liquid to gas at 365–405			0.5/0.5	0.2 ^f
Quartz (8)	8B	5–25 µm	Multisolid, numerous solids, with halite, 15–25 vol.% gas			Halite at 200–240, gas to liquid at 250–300		NaCl 10–15, LiCl 21–22 ^d		
Late greisens associated with zinnwaldite granite										
Quartz (quartz-- tourmaline-Ho- paz greisen) (15)	9	5–40 µm	Multisolid, 20–30 vol.% gas, 40–60 vol.% solids, with halite	–55	–50 (hh)	Gas to liquid at 320–340, sylyte at 84–85, halite at 400–415		NaCl 42–39 CaCl ₂ 15–16 KCl 15–14 ^b		0.85–0.9 ⁱ
Quartz (quartz-- muscovite greisen) (16)	10A	5–20 µm	Gaseous-liquid, 85–95 vol.% gas	–59...–58.5		Liquid to gas at 380–390			0.9...0.7/0.1...0.3	< 1.0 ^g >> 0.2 ^h
Quartz (quartz-- muscovite greisen) (16)	10B	5–15 µm	Liquid-gaseous, 40–50 vol.% gas, occasional small anisotropic solids	–21	–3.5 (ice)	Gas to liquid at 375–385		NaCl-eq. 5.7 ^a		
Quartz, topaz (quartz-topaz greisen) (14)	10A	5–20 µm	Gaseous-liquid, 85–95 vol.% gas	–59...–58.5		Liquid to gas at 380–385			0.9...0.7/0.1...0.3	< 1.0 ^g >> 0.2 ^h
Quartz, topaz (quartz-topaz greisen) (14)	10B	5–15 µm	Liquid-gaseous, 40–50 vol.% gas, occasional small anisotropic solids			Gas to liquid at 370–385		NaCl-eq. 1.5–1.9 ^e		
Quartz, fluorite (quartz-fluorite greisen) (12)	11A	5–20 µm	Gaseous, 100 vol.% gas	–60...–59	+9.0...+9.4 (cl)	Gas to liquid at 355–360			0.7–0.4/0.3–0.6	< 1.0 ^g >> 0.2 ^h
Quartz, fluorite (quartz-fluorite greisen) (12)	11B	5–15 µm	Multisolid, numerous solids, with halite, 15–40 vol.% gas	–55	–50 (hh)	Halite at 310–340, gas to liquid at 380–410		NaCl 28–31, CaCl ₂ 19–20 ^d		> 0.15 ^h
Quartz, fluorite (quartz-fluorite greisen) (10)	12	5–15 µm	Multisolid, 10–20 vol.% gas, 1–5 small anisotropic solids	–23.0...–22.5	–3.8...–3.7 (ice)	Gas to liquid at 355–360		NaCl-eq. 6.0–6.2 ^a		
Quartz from quartz-sericite-carbonate-sulfide (phyllite alteration) assemblage										
Quartz (34)	13A	5–20 µm	Gaseous-liquid, 95– 100 vol.% gas	–60.5...–60.0					0.2/0.8	< 0.7 ^g >> 0.05 ^h

Table 2 (continued)

Mineral (number of FI measured)	FI type	FI size	FI content	T_m CO ₂ , °C	T_m eu., °C	T_m (ice, hh, h, cl) °C	Homogenization, T_h , °C	Estimated salinity, wt.%	Estimated CO ₂ /CH ₄ ratio ^f	Estimated pressure, kbar
Quartz (34)	13B	5–40 µm	Multisolid, with halite, 15–25 vol.% gas	–29.5...–28.5	–35	–27.5 (ice)	Halite at 220, gas to liquid at 305–310	NaCl-eq. 33 ^b		
Quartz (16)	14	5–20 µm	Multisolid, with halite, 20–25 vol.% gas				Halite and gas to liquid at 290–305	NaCl 27–29, MgCl ₂ 11 ± 0.5 ^d		> 0.05 ^h

T_m eu. eutectic temperature (first ice melting temperature), degrees Celsius; T_m CO₂ final CO₂ melting temperature, degrees Celsius; T_m final ice (ice), hydrohalite (hh), halite (h), clathrate (cl) melting temperature, degrees Celsius

^a Salinity estimated by final ice melting temperature (Bodnar and Vityk 1994)

^b Salinity estimated by halite dissolution temperature (Bodnar and Vityk 1994)

^c Salinity estimated by clathrate melting temperature (Darling 1991)

^d Salinity estimated by halite dissolution temperature and final ice/hydrohalite melting temperatures for the NaCl–CaCl₂–H₂O, NaCl–MgCl₂–H₂O, or NaCl–LiCl–H₂O systems (Borisenko 1977; Vanko et al. 1988; Oakes et al. 1990; Dubois and Marignac 1997; Dubois et al. 2010)

^e The ratio estimated by final CO₂ melting temperature (Thiery et al. 1994)

^f The trapping pressure estimated by using the T_h of type B and the density of type A fluid inclusions trapped contemporaneously (Bakker 2003)

^g The maximal pressure estimated by using the T_h of type B and the assumed critical density of type A fluid inclusions, trapped contemporaneously (Bakker 2003)

^h The minimal trapping pressure estimated by using the T_h and salinity of type B fluid inclusions (Atkinson 2002)

ⁱ The minimal trapping pressure estimated by using the T_h and halite melting temperature (Atkinson 2002; Becker et al. 2008)

pseudosecondary inclusions in short trails in quartz and fluorite from quartz and quartz-fluorite “droplets” comprises coexisting multisolid gaseous-liquid type 2A and liquid-gaseous type 2B inclusions, both containing 1–3 small anisotropic solid phases (Fig. 8d–h and Table 2). There are separate short trails of multisolid type 2C and liquid-gaseous type 2D fluid inclusions. Type 2C inclusions contain 30–40 vol.% gas bubble and dominant solids are colorless and birefringent (Fig. 8i–k), whereas the type 2D contains a smaller gas bubble (25–30 vol.%) (Fig. 8l, m and Table 2).

On freezing/warming, the type 1 inclusions exhibit no evidence for a carbonic phase. The eutectic melting temperatures are from –38 to –36 °C, indicating MgCl₂–NaCl salt mixture (Borisenko 1977; Crawford 1981). Final ice melting temperatures are from –23 to –22 °C, and halite dissolution is from +30 to +31 °C. In the NaCl–MgCl₂–H₂O system, this yields concentration of 18–20 wt.% NaCl and 8–7 wt.% MgCl₂ (Table 2 and Fig. 10a; Dubois and Marignac 1997). On heating, homogenization of the type 1 inclusions occurs at > 500 °C to gas.

Freezing/warming of the type 2A inclusions indicates the presence of carbonic phases, with a small CO₂ phase that melts at –60 to –59 °C and which sublimates to gas. This allows estimation of CH₄ mole fraction at around 0.5 (Table 2; Thiery et al. 1994). Dissolution of some anisotropic solids observed in the type 2A inclusions occurs at 360–365 °C. The coexisting type 2B inclusions that exhibit eutectic melting temperatures from –38 to –36 °C, indicating MgCl₂–NaCl salt mixtures (Borisenko 1977; Crawford 1981), have final ice melting temperatures from –27 to –26 °C and hydrohalite melting temperatures from –8 to –7 °C. In the NaCl–MgCl₂–H₂O system, this yields concentration of 15 ± 0.5 wt.% NaCl and 10 ± 0.5 wt.% MgCl₂ (Fig. 10a; Dubois and Marignac 1997). On heating, both the type 2A and 2B inclusions homogenized at 490–570 °C, either to gas (type 2A) or to liquid (type 2B). The type 2C inclusions exhibit eutectic melting temperatures from –38 to –36 °C, indicating MgCl₂–NaCl salt mixture (Borisenko 1977; Crawford 1981) and have final ice melting temperatures from –24 to –23 °C, whereas halite dissolution occurs from +3 to +4 °C. In the NaCl–MgCl₂–H₂O system, this yields concentration of 17 ± 0.5 wt.% NaCl and 9 ± 0.5 wt.% MgCl₂ (Fig. 10a; Dubois and Marignac 1997). Homogenization of the type 2C inclusions occurs at 450–470 °C into liquid. Finally, the type 2D inclusions have eutectic melting temperatures from –28 to –27 °C, indicating dominant NaCl and KCl (Crawford 1981), and final ice melting temperatures from –5.0 to –4.5 °C. The latter, in the NaCl–H₂O system, corresponds to salinity of 7.2–7.9 wt.% NaCl (Table 2; Bodnar and Vityk 1994). Homogenization of the type 2D inclusions occurs at 370–380 °C into liquid (Table 2). No dissolution of other solid phases was observed in type 2A to 2D fluid inclusions over the entire heating temperature range.

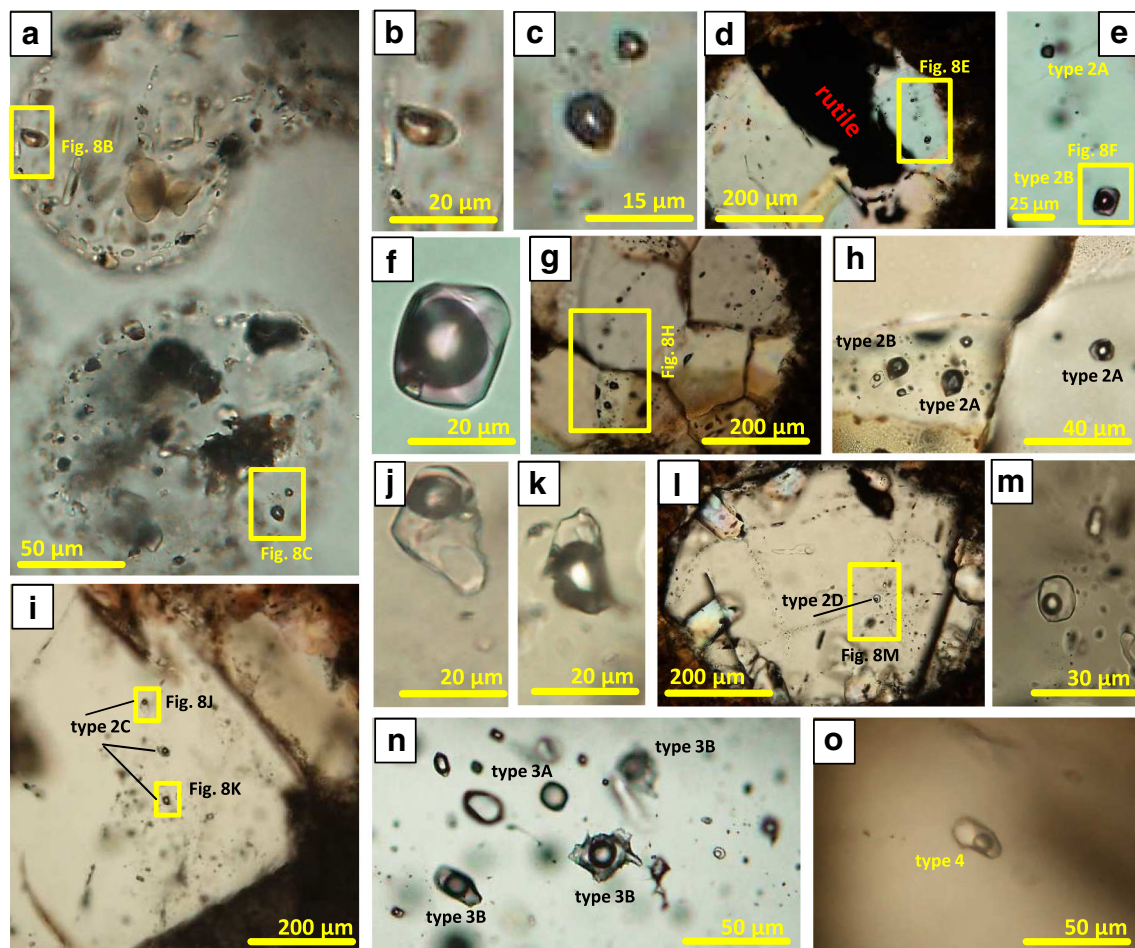


Fig. 8 Types of fluid inclusions in minerals from biotite-tourmaline granite and associated hydrothermal alteration assemblages at the Kougarok prospect. **a** Globular aggregates of magmatic melt-fluid-crystal “suspension” in quartz “droplets” in equigranular biotite-tourmaline granite and mafic enclaves (see Fig. 5g), with biotite and tourmaline crystals, possible silicate melt inclusions, and gaseous-liquid type 1 fluid inclusions. **b, c** Larger views of the type 1 inclusions. **d–m** Fluid inclusions in quartz and quartz-fluorite “droplets” in biotite-tourmaline granite and the mafic enclaves: **d–h** coexisting pseudosecondary gaseous type

2A and multisolid (type 2B) fluid inclusions in quartz droplets (**e, g, h**—larger views), **i–k** pseudosecondary type 2C fluid inclusions in quartz “droplets” (**i, j**—larger views), **l, m** primary to pseudosecondary type 2D inclusions in fluorite in quartz-fluorite “droplets” (**m**—larger view), **n** cluster of primary type 3A and 3B inclusions in quartz from the early quartz-tourmaline greisen associated with equigranular biotite-tourmaline granite, and **o** primary type 4 inclusion in quartz from quartz-tourmaline-chlorite-cassiterite stockwork associated with biotite-tourmaline granite

Fluid inclusions in quartz from early quartz-tourmaline assemblage

Primary fluid inclusions in quartz from early quartz-tourmaline greisen occur in clusters and as isolated individuals. They consist of coexisting gaseous type 3A (100 vol.% gas) and liquid-gaseous type 3B (30–40 to 20–25 vol.% gas) inclusions, the latter occasionally containing up to three small anisotropic solids (Fig. 8n). Quartz from the quartz-tourmaline-chlorite veinlets contains primary liquid-gaseous (20–30 vol.% gas) type 4 fluid inclusions, occurring mostly as isolated individuals (Fig. 8o).

Type 3A inclusions contain carbonic phases, including a small CO₂ phase that melts from −98 to −94 °C and which sublimates to gas. This indicates a high

methane content with a mole fraction of 0.95 (Thierry et al. 1994; Table 2). The coexisting type 3B inclusions yield eutectic melting temperatures from −29 to −27 °C, indicating dominant NaCl and KCl (Crawford 1981) and final ice melting temperatures from −7.1 to −6.8 °C, which, in the NaCl-H₂O system, correspond to the salinity of 10.2–10.5 wt.% NaCl-eq. (Table 2; Bodnar and Vityk 1994). Homogenization of the type 3B inclusions occurs at 380–430 °C to liquid. Type 4 inclusions have eutectic melting temperatures from −31.4 to −31.0 °C, indicating dominant NaCl but with an admixture of MgCl₂ (Crawford 1981) and final ice melting temperatures from −8.5 to −4.8 °C, which, in the NaCl-H₂O system, correspond to the salinity of 7.6–12.3 wt.% NaCl (Table 2; Bodnar and Vityk 1994). On heating, homogenization of type 4 inclusions occurs at 255–315 °C to liquid.

Fluid inclusions in quartz phenocrysts from zinnwaldite granite and topaz from the stockscheider

Quartz phenocrysts in zinnwaldite granite contain primary multisolid (type 5) fluid inclusions that form isolated individuals (Fig. 9a, b). These inclusions contain relatively small (5–10 vol.%) gas bubble and numerous solid phases in total occupying 70–90 vol.%. Most solids are anisotropic and highly to weakly birefringent, and a small opaque phase is occasionally present. No

halite or sylvite was identified. Primary type 6 fluid inclusions in topaz from the stockscheider contain a small- to moderate-sized (15–35 vol.%) gas bubble and two to five solid phases, always including halite, that in total occupy 20–30 vol.% (Fig. 9c).

The aqueous phase in type 5 inclusions yields eutectic melting temperatures from -25 to -24 °C, indicating dominant NaCl and KCl (Crawford 1981) and final ice melting temperatures from -7.2 to -7.0 °C that, in the NaCl-H₂O system, corresponds to the salinity of 10.5–10.7 wt.% NaCl (Table 2; Bodnar and

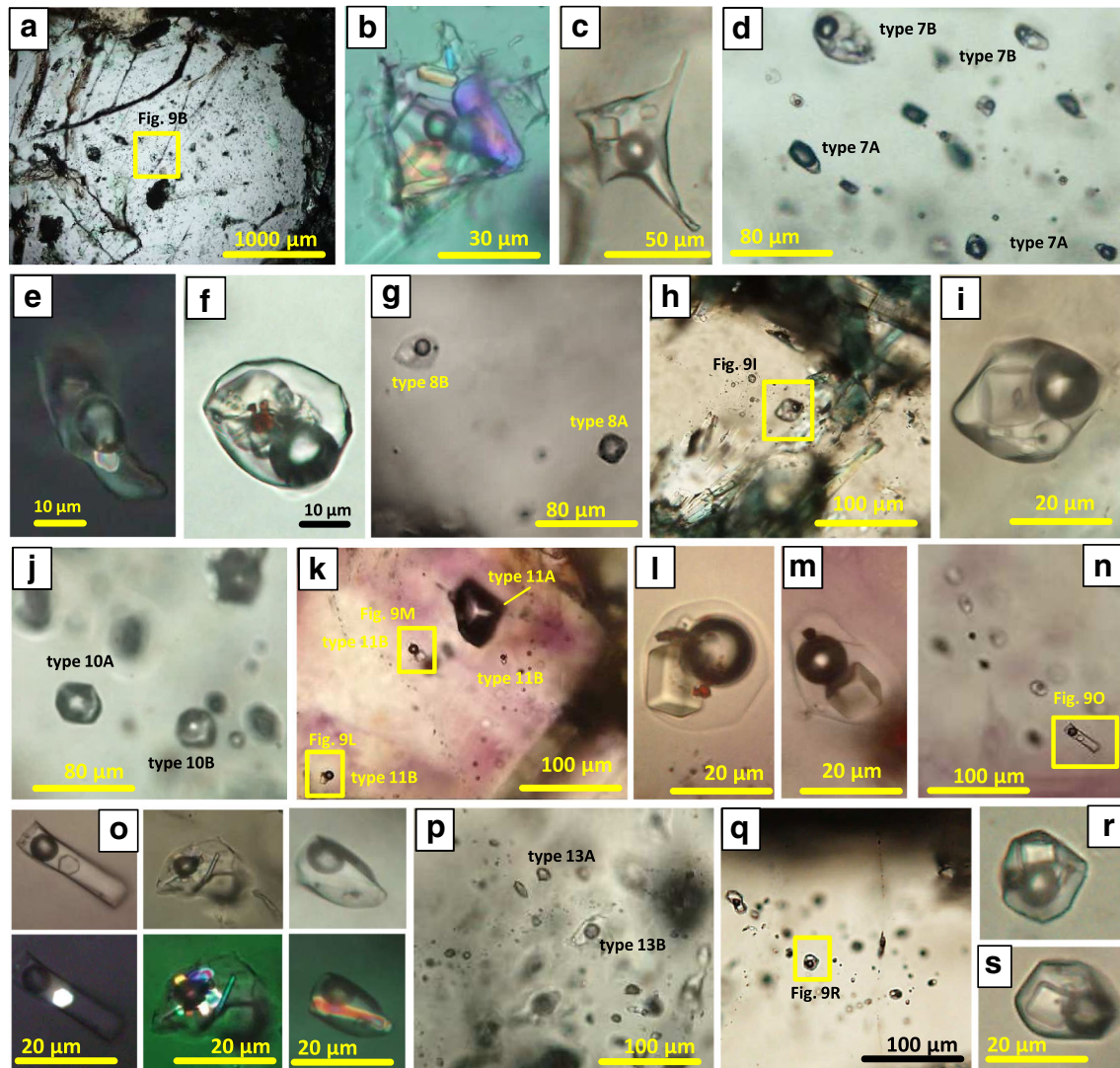


Fig. 9 Types of fluid inclusions in zinnwaldite granite, associated marginal pegmatite (topaz stockscheider), and associated hydrothermal alteration assemblages at the Kougarok prospect. **a, b** Multisolid type 5 fluid inclusions in quartz phenocryst from zinnwaldite granite (**b**—larger view, nicols crossed); **c** multisolid type 6 fluid inclusions in topaz stockscheider; **d–f** fluid inclusions in quartz from quartz-albite-Li mica alteration: **d** cluster of coexisting gaseous-liquid type 7A and multisolid type 7B inclusions; **e, f** multisolid type 7B inclusions (**e** nicols crossed, with anisotropic solids including borates, possibly sassolite; **f** with brown dendrite-like aggregate, possibly cassiterite); **g** coexisting gaseous type 8A and multisolid 8B inclusions; **h, i** multisolid type 9 fluid inclusions in quartz of quartz-tourmaline+topaz greisen (**i**—larger view); **j** coexisting

gaseous type 10A and liquid-gaseous type 10B fluid inclusions in quartz of quartz-muscovite and quartz-topaz greisens; **k–o** fluid inclusions in purple fluorite from quartz-fluorite greisen: **k** coexisting gaseous type 11A and multisolid type 11B fluid inclusions, **l, m** larger views of type 11B inclusions (**l** inclusion with brown dendrite-like aggregate, possibly cassiterite; **m** inclusions with an opaque solid phase); **n, o** pseudosecondary multisolid type 12 fluid inclusions containing highly birefringent solid phase, fluoride or borate, possibly sassolite, and their larger views in parallel and crossed nicols; **p–s** fluid inclusions in quartz from quartz-sericite-carbonate-sulfide (phyllic) alteration assemblage: **p** coexisting type 13A and 13B fluid inclusions, **q–s** multisolid type 14 fluid inclusions (**r, s**—larger views)

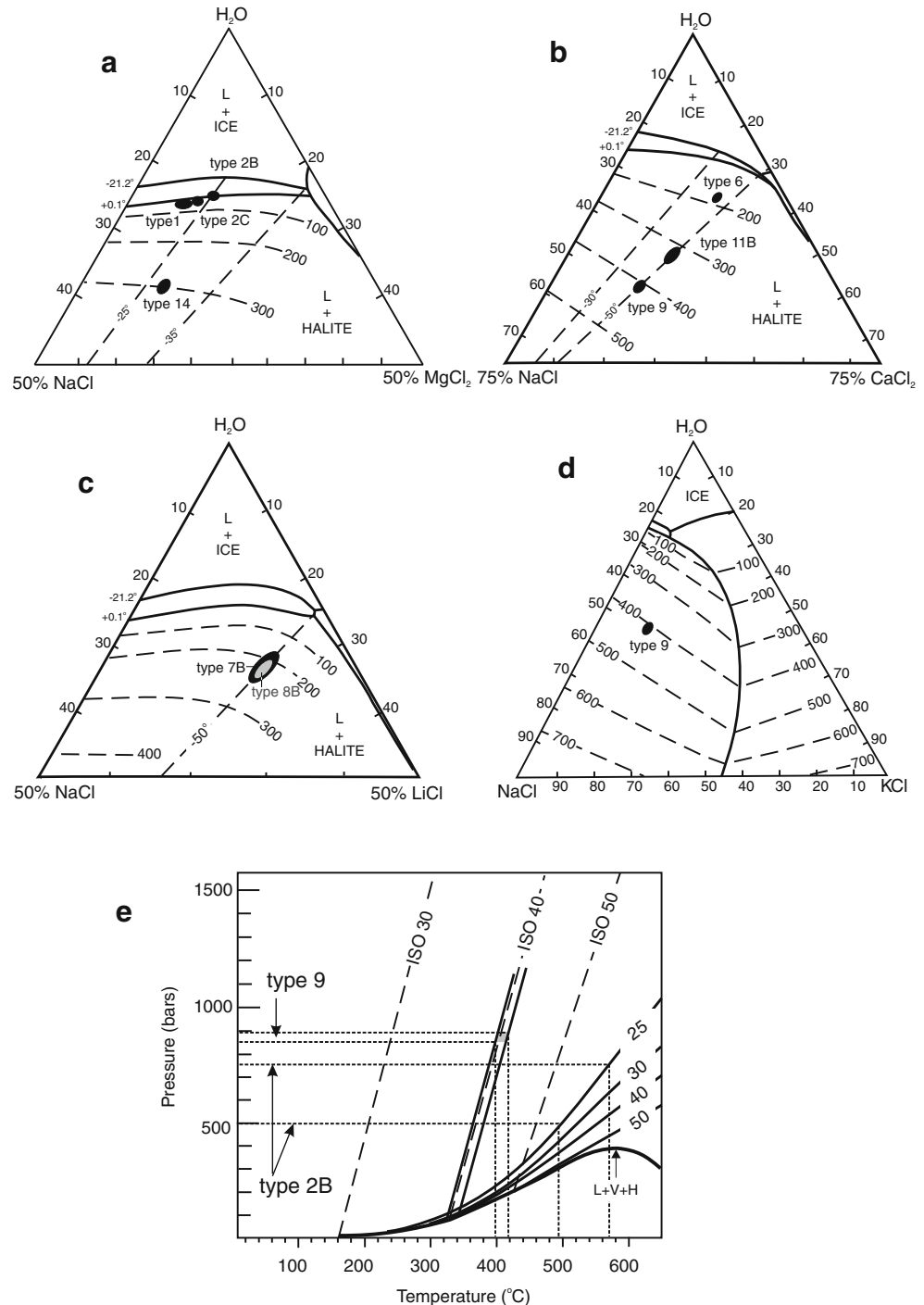
Vityk 1994). Anisotropic platy to hexagonal crystals in type 5 inclusions dissolve at 100–105 °C, whereas other solids remain undissolved over the entire range of heating. Gas bubble homogenizes to liquid at 130–350 °C. All type 5 inclusions decrepitated at 230–550 °C. Type 6 inclusions have eutectic melting temperature of –55 °C and final ice melting temperatures from 42 to –40 °C, indicating CaCl_2 – NaCl salt mixture (Crawford 1981). These inclusions show halite dissolution at around 170 °C, with the gas bubble homogenizing to liquid at

460–520 °C (Table 2). In the NaCl – CaCl_2 – H_2O system, this yields a concentration of 14–15 wt.% NaCl and 22–23 wt.% CaCl_2 (Vanko et al. 1988; Oakes et al. 1990; Fig. 10b).

Fluid inclusions in quartz from quartz-albite-Li mica alteration

Primary fluid inclusions are represented by clusters of coexisting gaseous-liquid type 7A (80–95 vol.% gas) and multisolid type 7B (15–25 vol.% gas) inclusions, with numerous solid phases, in

Fig. 10 Fluid inclusion data from various hydrothermal assemblages from the Kougarok prospect. **a** NaCl – MgCl_2 – H_2O compositions of type 1 gaseous-liquid and types 2B, 2C, and 14 multisolid fluid inclusions (phase diagram after Borisenko 1977; Dubois and Marignac 1997). **b** NaCl – CaCl_2 – H_2O compositions of types 6, 9, and 11B multisolid fluid inclusions (phase diagram after Vanko et al. 1988; Oakes et al. 1990). **c** NaCl – LiCl – H_2O compositions of types 7B and 8B multisolid fluid inclusions (phase diagram after Dubois et al. 2010). **d** NaCl – KCl – H_2O compositions of type 9 multisolid fluid inclusions (phase diagram after Roedder 1970). **e** Pressure estimates for types 9 (shaded area) and 2B fluid inclusions. Vapor-pressure curves and isochors (labeled in wt.% NaCl) and the three-phase ($L + V + H$) curve for the NaCl – H_2O system are from Atkinson (2002) and Becker et al. (2008). These vapor-pressure curves and isochors correspond to most common salinities of the halite-bearing fluid inclusions in alteration assemblages determined in this study (30–50 wt.% NaCl -eq.)



total occupying 50–70 vol.% (Fig. 9d–f). The solids include those with high birefringence similar to sassolite (H_3BO_3 ; Thomas et al. 2012) as well as brown dendrite-like aggregates, possibly cassiterite, and halite. Primary to pseudosecondary coexisting gaseous (95–100 vol.% gas) type 8A and multisolid type 8B (15–25 vol.% gas) inclusions (Fig. 9g) occur as isolated individuals, in clusters, and in short trails, the latter intersecting clusters of the type 7A and 7B inclusions.

Type 7A inclusions contain carbonic phases, including a small CO_2 phase that melts from -58.5 to -57.5 °C and sublimates to gas. This allows estimation of the CH_4 mole fraction at 0.2 (Thiery et al. 1994; Table 2). Type 7B inclusions have eutectic melting temperatures near -75 °C, indicating a LiCl – NaCl salt mixture (Dubois et al. 2010), whereas final hydrohalite melting temperatures from -51 to -50 °C. In type 7B inclusions, highly birefringent tabular to fibrous solids dissolve at 70 – 90 °C, an isometric birefringent solid phase at 160 – 165 °C, halite at 180 – 245 °C, and some other tabular anisotropic solids at 320 – 365 °C. The gas bubble homogenizes to liquid at 365 – 405 °C. In the NaCl – LiCl – H_2O system, this yields concentration of about 9–15 wt.% NaCl and 21–22 wt.% LiCl (Dubois et al. 2010; Fig. 10c).

Gaseous type 8A inclusions contain a small CO_2 with final melting temperatures from -60.5 to -59.5 °C. Homogenization of liquid CO_2 to gas at -22 to -20 °C was observed in two large type 8A inclusions, yielding a CH_4 mole fraction of 0.5 and a molar volume of $350\text{ cm}^3/\text{mol}$ (Thiery et al. 1994; Table 2). Type 8A inclusions homogenized to gas at 250 – 300 °C. The coexisting type 8B inclusions have eutectic melting temperatures near -75 °C, indicating LiCl – NaCl salt mixture (Dubois et al. 2010), and final hydrohalite melting temperatures of -51 to -50 °C. This is similar to the type 7B inclusions; however, on heating, the type 8B inclusions show dissolution of halite at 200 – 240 °C and gas bubble homogenization at 250 – 300 °C (Table 2). In the NaCl – LiCl – H_2O system, this yields concentrations of about 10–15 wt.% NaCl and 21–22 wt.% LiCl (Dubois et al. 2010; Fig. 10c).

Fluid inclusions in minerals from the late greisens

Primary type 9 fluid inclusions in quartz from quartz–tourmaline–topaz greisen contain medium-sized gas bubble (20–30 vol.%) and solid phases occupying ~40–60 vol.% (Fig. 9h, i). The solids include two isotropic to weakly anisotropic phases, including sylvite- and halite-forming cubic crystals, at least two isometric to short-prismatic anisotropic, weakly to highly birefringent phases, occasional acicular phase similar to tourmaline, and a very small opaque phase. Primary fluid inclusions in quartz and topaz from quartz–muscovite and quartz–topaz greisens consist of coexisting gaseous type 10A (85–95 vol.% gas) and liquid–gaseous type 10B (40–50 vol.% gas) inclusions, the latter containing occasional small anisotropic solid phases (Fig. 9j). Fluorite from quartz–fluorite greisen contains coexisting

primary gaseous (100 vol.% gas) type 11A fluid inclusions and multisolid type 11B fluid inclusions, the latter containing halite and a number of small colorless anisotropic solid phases, whereas some inclusions contain occasionally a brown dendrite-like mineral that could be cassiterite (Fig. 9k–m). Pseudosecondary type 12 fluid inclusions form trails intersecting inner growth zones in fluorite but terminate at outer zones. They contain one to five anisotropic phases, which are highly birefringent and likely include sassolite (Thomas et al. 2012) (Fig. 9n, o).

Type 9 fluid inclusions yield eutectic melting temperatures of -55 °C, indicating the presence of CaCl_2 (Crawford 1981), and final hydrohalite melting temperatures of -50 °C. On heating, sylvite dissolves at 84 – 85 °C, gas bubble homogenizes to liquid at 290 – 340 °C (up to 360 °C), and halite dissolves at 400 – 425 °C. In the NaCl – CaCl_2 – H_2O system, this yields concentrations of about 39–42 wt.% NaCl and 15–16 wt.% CaCl_2 (Vanko et al. 1988; Oakes et al. 1990; Fig. 10b). In the NaCl – KCl – H_2O system, this yields concentrations of about 40–42 wt.% NaCl and 14–15 wt.% KCl (Roedder 1971; Fig. 10d). Type 10A fluid inclusions contain a small CO_2 phase that melts from -59.0 to -58.5 °C and then sublimates to gas. This allows estimation of CH_4 mole fraction at 0.1 to 0.3 (Thiery et al. 1994; Table 2). Type 10A inclusions homogenized at 380 – 390 °C to gas. Type 10B fluid inclusions have eutectic melting temperatures at around -21 °C, indicating almost pure NaCl (Crawford 1981), and final ice melting temperatures near -3.5 °C. In the NaCl – H_2O system, this corresponds to the salinity of 5.7 wt.% NaCl (Table 2; Bodnar and Vityk 1994). Clathrate formation was noted on freezing in some type 10B inclusions. The clathrate melted at $+9.0$ to $+9.4$ °C, which, in the NaCl – CO_2 – H_2O system, corresponds to the salinity of 1.5–1.9 wt.% NaCl -eq. (Table 2; Darling 1991). On heating, type 10B inclusions homogenized at 370 – 385 °C to liquid.

Type 11A fluid inclusions contain a small CO_2 phase that melts from -60.0 to -59.0 °C and then sublimates to gas. This allows estimation of CH_4 mole fraction at 0.3 to 0.6 (Thiery et al. 1994; Table 2). Type 11B fluid inclusions yield eutectic melting temperatures of -55 °C, indicating the presence of CaCl_2 (Crawford 1981), and final hydrohalite melting temperatures of -50 °C. In the NaCl – CaCl_2 – H_2O system, this yields concentration of 28–31 wt.% NaCl and 19–20 wt.% CaCl_2 (Vanko et al. 1988; Oakes et al. 1990; Fig. 10b). Type 11B inclusions show halite dissolution at 310 – 340 °C, and gas bubble homogenizes to liquid at 380 – 410 °C. Other solid phases remain undissolved to 650 °C, limit of heating. Finally, type 12 fluid inclusions have eutectic melting temperatures from -23.0 to -22.5 °C, consistent with the presence of NaCl – $\text{Na}_2\text{B}_5\text{O}_8$ (Borisenko 1977), and final ice melting temperatures of -3.8 to -3.7 °C. In the NaCl – H_2O system, this corresponds to the salinity of 6.0–6.2 wt.% NaCl (Bodnar and Vityk 1994). All anisotropic solid phases dissolve at 40 – 45 °C, and gas bubble homogenizes at 355 – 360 °C (Table 2).

Fluid inclusions in phyllic alteration quartz

Primary fluid inclusions occur mostly in clusters of coexisting gaseous type 13A (95–100 vol.% gas) and multisolid type 13B inclusions (Fig. 9p) that contain a small (15–25 vol.%) gas bubble and a number of solid phases including rounded to prismatic anisotropic phases and halite. Pseudosecondary fluid inclusions form short trails of multisolid type 14 inclusions that contain 20–25 vol.% gas and a number of solids including halite (Fig. 9q–s).

Type 13A inclusions contain a small CO₂ phase that melts from –60.5 to –60.0 °C and then sublimates to gas. This allows estimation of CH₄ mole fraction at around 0.8 (Thiery et al. 1994; Table 2). The coexisting type 13B inclusions have eutectic melting temperatures at –29.5 to –28.5 °C, indicating dominant NaCl (Crawford 1981). Type 13B inclusions exhibit halite dissolution at around 220 °C and gas bubble homogenization to liquid at 305–310 °C (Table 2), whereas other solids remain undissolved. In the NaCl–H₂O system, halite dissolution at 220 °C indicates a salinity of 33 wt.% NaCl (Bodnar and Vityk 1994). Type 14 inclusions have eutectic melting temperatures at –35 °C, indicating a MgCl₂–NaCl salt mixture (Borisenko 1977; Crawford 1981), and final ice melting near –27.5 °C. In the NaCl–MgCl₂–H₂O system, this yields concentration of 27–29 wt.% NaCl and 11 ± 0.5 wt.% MgCl₂ (Dubois and Marignac 1997; Fig. 10a). Type 14 inclusions show dissolution of halite and gas bubble homogenization to liquid at 290–305 °C.

Pressure estimate

Minimum pressure can be estimated for type 9 inclusions using the temperature of the gas bubble homogenization and halite dissolution (Roedder 1984). Using the isochores for a 40 wt.% NaCl solution in a H₂O–NaCl system (Atkinson 2002; Becker et al. 2008), these estimates yield minimum pressures of ~850–900 bars (Fig. 10e). This pressure corresponds to a depth of 3.3–3.5 km, assuming lithostatic conditions (Fournier 1999). In all other cases, minimum pressure can be estimated for the liquid–gaseous inclusions using liquid/vapor curve for the corresponding NaCl solution in a H₂O–NaCl system (Atkinson 2002; Fig. 10e, type 2B inclusions as an example). This method was used for the minimum pressure estimation for the types 2C, 2D, 4, 6, 14, as well as 2B, 3B, 7B, 10B, 11B, and 13B inclusions (Table 2). It should be pointed out that the latter types contain a carbonic phase; thus, the actual fluid pressure could significantly exceed the minimum pressure estimated.

The presence of coexisting “immiscible pairs” of carbonic and aqueous saline inclusions in the same clusters or trails provides additional evidence for considering them as trapped contemporaneously in the two-phase immiscible field from boiling fluids. If so, the trapping pressures for these fluid inclusions can be estimated using the respective trapping

temperatures for the high-density fluid inclusions and densities for the low-density fluid inclusions (Roedder 1984). The density of inclusions containing fractions of CH₄ in addition to CO₂ can be determined using the diagrams from Thiery et al. (1994). This method can be applied only to the type 8A + 8B inclusions, for which carbonic phase homogenization temperatures have been measured. Using the computing programs of Bakker (2003), this yields the pressures of 200 ± 20 bars at the temperatures of 250–300 °C for the mixture of carbonic phase, with a density of 350 cc/mol, and H₂O, the latter composing up to 5 vol.% of the inclusions (so that the vapor density is near 360 cc/mol). This method, applied for the “coexisting pairs” of the type 2A + 2B, 3A + 3B, 7A + 7B, 8A + 8B, 10A + 10B, 11A + 11B, and 13A + 13B fluid inclusions at corresponding trapping temperatures (Table 2), allows estimation of the maximum fluid pressure, considering the carbonic phase density was lower than the critical one. For types 2C, 2D, 4, 6, and 14 fluid inclusions, pressure corrections have to be added to the homogenization temperatures (Potter 1977).

The trapping pressures estimated in the range of 200–1000 bars (Table 2) correspond to a depth of 1–4 km assuming lithostatic conditions and to a depth of 2–10 km assuming hydrostatic conditions (Fournier 1999). A depth of some 4–10 km appears to be too great considering hypabyssal features of the Early–Late Cretaceous plutons including small zones of intrusive/eruptive breccias. On the other hand, considering that the Late Cretaceous plutons intruded a thick, possibly overthrust metamorphic sequence, with no co-genetic Late Cretaceous volcanic rocks found in the deposit area, the low pressures corresponding to a depth of < 1–2 km appear also to be unrealistic. As a result, a depth of 2–4 km seems more plausible, which suggests that the respective fluid inclusion associations formed under dominantly lithostatic conditions. Transition from lithostatic to hydrostatic conditions, with corresponding boiling, could have been caused by fracturing-related pressure drops.

Bulk fluid geochemistry

Seven samples of quartz, topaz, and fluorite from various greisens and zinnwaldite granite were analyzed by bulk fluid geochemistry (Online Resource 8). The results obtained by the bulk method are affected by the presence of secondary inclusions and must be taken with caution. Nevertheless, these results show predominance of Na among cations in fluids, and presence of CO₂ and CH₄, together with Cl. The bulk fluid geochemistry confirms elevated Ca contents in fluids conserved in quartz from zinnwaldite granite and quartz, topaz, and fluorite from related greisens. Elevated Mg, Li, and B contents defined by bulk fluid geochemistry are also consistent with the geochemical features inferred from the data on individual fluid inclusions.

Sulfur isotopes

Sulfur isotopes were measured in 12 samples of hexagonal and monocline pyrrhotite and chalcopyrite from the late greisen and phyllic alteration assemblages. The data show a uniform distribution of $\delta^{34}\text{S}$ values, with $\delta^{34}\text{S}$ varying from -3.0‰ to -0.8‰ .

Discussion

Magma sourcing and differentiation

Together with other tin deposits and occurrences in Alaska and adjacent parts of Chukotka Peninsula, the Kougark prospect is localized in the Sn-rare metal metallogenic belt related to the Late Cretaceous ilmenite-series granitoid intrusions that formed under a post-collisional to within-plate extensional tectonic regime, after cessation of active subduction (Nokleberg et al. 1996, 2000; Wirth et al. 2002). The extensional tectonic setting in the Late Cretaceous, manifested by the widespread melting of crustal rocks and emplacement of coeval peraluminous granitic suites, exhumation of high-grade metamorphic sequences, and local emplacement of alkalic (potassic) mafic dike swarms, may correspond to a possible asthenosphere uplift through a slab window formed in the subducted slab or asthenosphere mantle ascent caused by lithosphere delamination (Vaughan 1995). As a result, mingling of the ascending mafic and felsic magmas, the latter originating from the accretionary complex, can be envisioned as the major petrologic process causing formation of the complex (from B-rich to Li-F-type) granitic suites and associated Sn-rare metal (Ta, Nb, Li) mineralization in Alaska.

Granitic magma differentiation at Kougark was the main mechanism for rare metal accumulation in residual melt (Raimbault et al. 1995; Linnen and Keppler 2002; Černý et al. 2005; Linnen and Cuney 2005; London 2008; Zarsky et al. 2009; Linnen et al. 2012). It was responsible for subsequent fractionation of biotite granite, biotite-tourmaline granite, leucogranite, zinnwaldite granite, and topaz rhyolite, which is indicated by change of the Zr/Hf ratios (Online Resource 4 and Fig. 6d) and has resulted in progressing enrichment in Sn and Ta (Fig. 11). Crystal fractionation was affected and at some stages of magmatic evolution superseded by silicate melt-fluid interaction, with their combined effect influencing metal accumulation in the melt and further metal release in a magmatic-hydrothermal fluid. Notably, SiO_2 content increases during the differentiation of biotite granite and biotite-tourmaline granite, and then decreases in zinnwaldite granite, due to high F content shifting the granitic cotectic toward less silicic, more albitic compositions (Manning 1981). Fractionation toward biotite-tourmaline granite caused accumulation of Sn in residual melt that was favored by reduced, ilmenite-stable conditions and enrichment of magma in B (Lehmann 1982; Swanson et al.

1988; Taylor and Wall 1992), whereas biotite fractionation caused increases in Ta/Nb, and reduction of Ti content of the melt (Stepanov et al. 2014). Accumulation of Ta-Nb-Li during crystallization of zinnwaldite granite was favored by enrichment of magma in F and Li (Linnen 1998; Zarsky 2004).

The homogeneity of $\delta^{34}\text{S}$ values in sulfide minerals from Kougark indicates sulfur isotope homogenization in a magmatic chamber, whereas the range of $\delta^{34}\text{S}$ values is similar to those associated with ilmenite-series granitoids (Ishihara and Sasaki 2002; Seal 2006). The similarity of these values ($\delta^{34}\text{S} = -3.0\text{‰}$ to -0.8‰) to the primitive sulfur composition indicates a mixed mantle-crustal signature (Ohmoto and Goldhaber 1997; Seal 2006).

Granitic and mafic magma mixing/unmixing and related fluid immiscibility

Abundant mafic enclaves in the biotite-tourmaline granite indicate magma immiscibility (e.g., Didier and Barbarin 1991). Their origin can generally be explained by one of two models: (1) they can originate due to an intrusion of mafic magma into the granitic magma chamber, with incomplete mixing of the compositionally different magmas, or (2) they can be mafic cumulates separated in the course of within-chamber crystal fractionation or be similarly formed due to unmixing of a compositionally transitional granitoid magma into mafic and granitic melts.

Intrusion of alkalic potassic mafic magma into a crystallizing, but still liquid, granitoid magma chamber could explain some geochemical signatures. In particular, alkalic mafic magma and/or associated fluids derived from deeper sources could be supplying a geochemically distinct assemblage of volatiles (F) and associated metals (Li, Ta, Nb), as well as K, P, Ba, Sr, Ti, Co, Ni, V, and Cr, which are minor in the B- and Sn-dominated biotite-tourmaline granite. Notably, the F content in the mafic enclaves is > 10 times higher than that in the host biotite-tourmaline granite (Online Resource 4). The mafic magma intrusion, together with the incursion of associated fluids, could play a triggering role in causing silicate melt-fluid and fluid-fluid unmixing during crystallization of the biotite-tourmaline granite. A mafic intrusion into host “Kougark schists,” observed outside the granite, with small zones of intrusive breccia cemented by the mafic material, also supports this model. The role of mafic, particularly lamprophyric, magmas in the evolution of parental granites for Sn-rare metal (Ta, Nb, Li) mineralization was suggested (Muller et al. 2005; Seifert 2010; Štemprok and Seifert 2011), similar to that for granitoid-related deposits of Cu, Au, and other metals (Keith et al. 1998; Maughan et al. 2002; Muller and Groves 2019) and generally for a granite formation (e.g., Sial et al. 2011). Interaction of post-collisional crustal granitoid magmas with mantle-derived mafic potassic (lamprophyric) magmas, to form ilmenite- to transitional ilmenite-magnetite-series granitoid series, was suggested for some Late Cretaceous plutonic suites in the broader region (Mair et al. 2006, 2011). Christiansen et al.

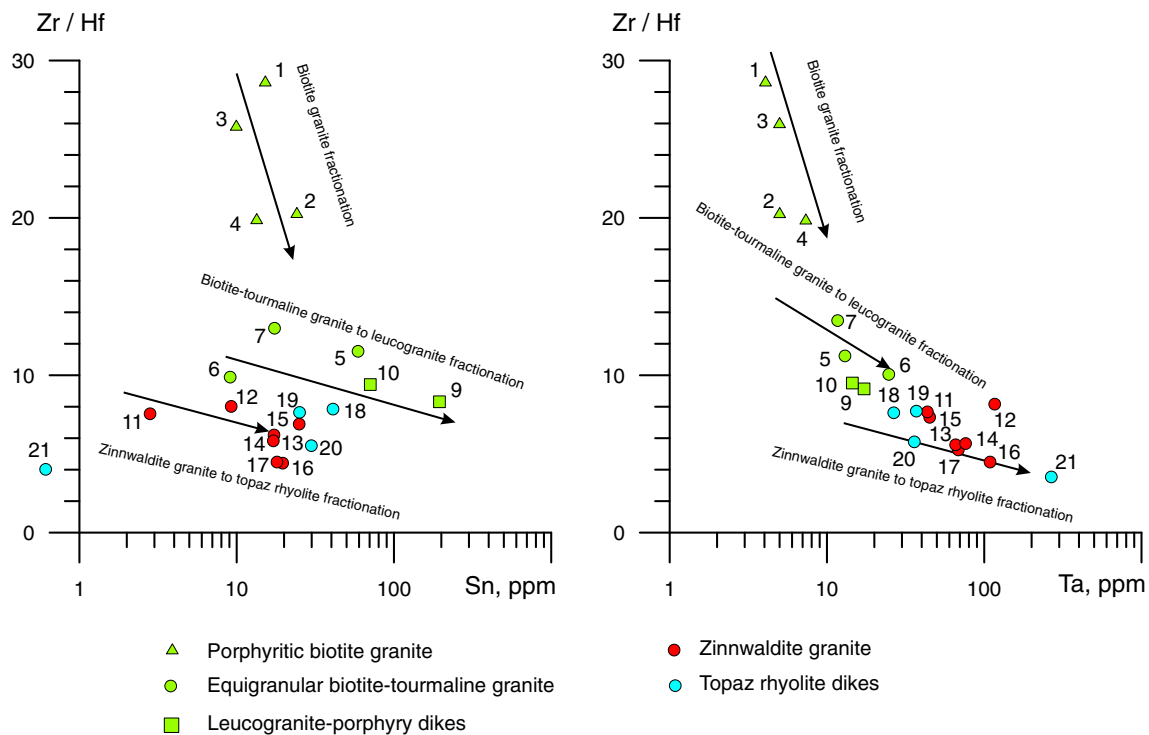


Fig. 11 Zr/Hf vs. Sn and Zr/Hf vs. Ta diagrams showing Sn and Ta accumulation in the course of crystal fractionation at the Kougarok prospect. Numbers (1–21) of the compositions shown are from Online Resource 4

(1983) considered topaz rhyolite as a product of felsic and mafic (mantle-derived) magma interaction, the latter sourcing fluorine.

Alternatively, unmixing of a less differentiated granitoid magma is plausible but requires sequestration by a mafic melt of B, P, Ba, Sr, and Ti, whereas the granitic melt should sequester Ta and Nb (Online Resource 4). Thomas and Davidson (2013, 2016) demonstrated unmixing of granitic melts at final differentiation stages, with possible separation of peraluminous and peralkaline, to nepheline syenite, melts, and their different compatibility for various fluxing and mineralizing species. It can be speculated that separated silicate melts can indicate geochemical vectors toward possible initial, compositionally contrasting, magmas that interacted at much greater depths. At Kougarok, these could be peraluminous granitoid and potassic alkalic magmas.

Immiscibility of mafic and granitic magmas as well as B-rich and F-rich fluids is inferred from the textures of biotite-tourmaline granite, such as mafic enclaves, tourmaline, and quartz-fluorite “droplets.” Pegmatitic and stockscheider aggregates indicate local H₂O as well as F and/or B saturation, possibly with second boiling/resurgent boiling, typical of epizonal intrusions (Lentz et al. 1988). It is consistent with presence of the type 1 fluid inclusions in quartz phenocrysts/“droplets” in the granite and mafic enclaves. These inclusions indicate separation of gaseous fluid coexisting with immiscible granitic and mafic magmas in the form of magmatic melt-fluid-crystal “suspension.” This further contributes to extreme heterogeneity of magmatic-hydrothermal fluid, which formed during the final stages of magmatic differentiation

(Kamenetsky et al. 2002; Davidson and Kamenetsky 2007; Kamenetsky and Kamenetsky 2010; Thomas and Davidson 2013, 2016; Wu et al. 2017). Quartz-fluorite, fluorite, and tourmaline “droplets,” particularly the quartz-fluorite with W-Nb-rutile, highlight the role of boron- and fluorine-silicate melt immiscibility in concentrating metals in granite-related system (Williams-Jones and Vasyukova 2015).

F-rich fluid ascent and zinnwaldite granite crystallization

Fluorine-rich gaseous phase infiltrating upward caused F-enrichment of still liquid felsic magma in the uppermost part of the granitic magma chamber (Fig. 12). Consistently, the B-rich magmatic melt was concentrated at lower levels, whereas the F-rich melt accumulated at higher levels. Due to the greater efficiency of F (as compared to B) in lowering the density of granitic melt (Swanson and Fenn 1992; Dingwell et al. 1993), crystallization of biotite-tourmaline granite occurred faster than that of the upper part of the granitic magma chamber, where F-rich fluids are accumulating. This, in turn, resulted in early exsolution of boron-rich magmatic-hydrothermal fluid from the crystallizing biotite-tourmaline granite, causing formation of the early quartz-tourmaline greisen at temperatures > 430–380 °C (Figs. 12 and 13). High H₂O solubility in B-rich magma, combined with transition from B- and H₂O-rich silicate melt to B-rich vapor (Pollard et al. 1987; Thomas et al. 2003), is consistent with a broad range of fluids with

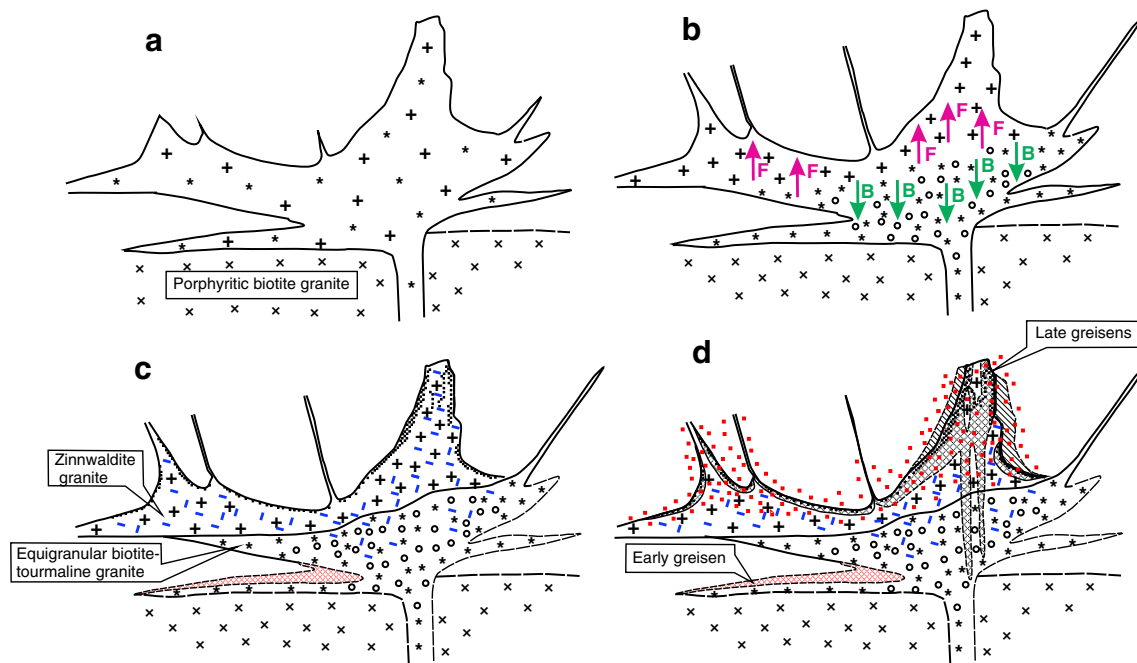


Fig. 12 Schematic model of the magmatic-hydrothermal evolution at the Kougarok prospect. **a** Emplacement of differentiated granitic magma, moderately enriched in boron and fluorine, to the upper crustal level. **b** Additional in situ differentiation of the granitic magma followed either by an external influx of incompatible volatiles or by differentiation-driven unmixing of compositionally contrasting magmatic melts and fluids, with accumulation of boron (B) and mafic components into lower levels and preferential ascent of fluorine (F), coupled with Li, Ta, and Nb, to the

higher levels. Intrusion of zinnwaldite granite and topaz rhyolite dikes into host rocks. **c** Crystallization of differentiated B-saturated biotite-tourmaline granite and F-saturated zinnwaldite granite followed by development of marginal stockscheider and early quartz-tourmaline greisen, then late quartz-tourmaline-topaz greisen and quartz-albite-Li mica alteration. **d** Development of late quartz-topaz and associated quartz-muscovite greisens, latest quartz-fluorite greisen, after full solidification of the granitic rocks. For the legend, see Fig. 3

varying water content related to degassing biotite-tourmaline granite, which formed wide quartz-tourmaline-cassiterite-chlorite stockwork halos at temperatures < 350 °C.

Protracted evolution of the upper, F-rich part of the magma reservoir was facilitated by decreasing magma crystallization temperatures to some 600 °C and perhaps lower due to the fluxing role of fluorine (e.g., Manning 1981). This caused more advanced magmatic differentiation, with a strong enrichment of crystallizing zinnwaldite granite in F, Li, Ta, and Nb, to less extent Sn. Crystallization of zinnwaldite granite involved fractionation of quartz, feldspars, Li micas, and topaz (Webster et al. 2004). High fluorine activity affected tourmaline stability resulting in tourmaline-free zinnwaldite granite, whereas decreased two-feldspar granite solidus temperature shifted the eutectics toward low-quartz and high-albite compositions (Manning 1981; Pichavant and Manning 1984; Veksler and Thomas 2002). Overall, the process of zinnwaldite granite formation features both magmatic crystallization and magmatic-stage metasomatic alteration (Haapala 1997). The magmatic-hydrothermal transition associated with zinnwaldite granite likely included separation of a highly mineralized fluid phase (type 5 fluid inclusions) that was transitional between magmatic melt and hydrothermal fluid (Li et al. 2017) and contained fluorides and fluoborates, together with chlorides. Topaz-

quartz stockscheider was formed at temperatures of 550–500 °C from a similar fluid as indicated by the type 6 fluid inclusions (Table 2).

Post-magmatic fluid evolution

Magmatic-hydrothermal evolution continued inward, from the upper contact and the footwall (Breiter et al. 2017a) with crystallization of the zinnwaldite granite body. It included quartz-tourmaline+topaz greisen and the higher-temperature quartz-albite-Li mica alteration under temperatures of ~500 to 400 °C (Fig. 13). The quartz-tourmaline+topaz greisen formed from a high-salinity fluid. Type 9 fluid inclusions homogenized by halite dissolution that indicates direct separation of high-salinity fluid from the crystallizing magma (Cline and Bodnar 1994; Bodnar 1995; Fig. 13) possibly corresponding to another “cycle” of degassing of crystallizing zinnwaldite granite (Vignerresse 2007). In contrast, the quartz-albite-Li mica alteration formed from a boiling, low-salinity fluid, with separation of gaseous (type 7A) and higher-salinity (type 7B) fluids.

Quartz-albite-Li mica alteration from a boiling fluid continued at lower temperatures (type 8A and 8B inclusions). Similarly, type 10 fluid inclusions in quartz-muscovite and quartz-topaz greisens indicate evolution of boiling magmatic-hydrothermal

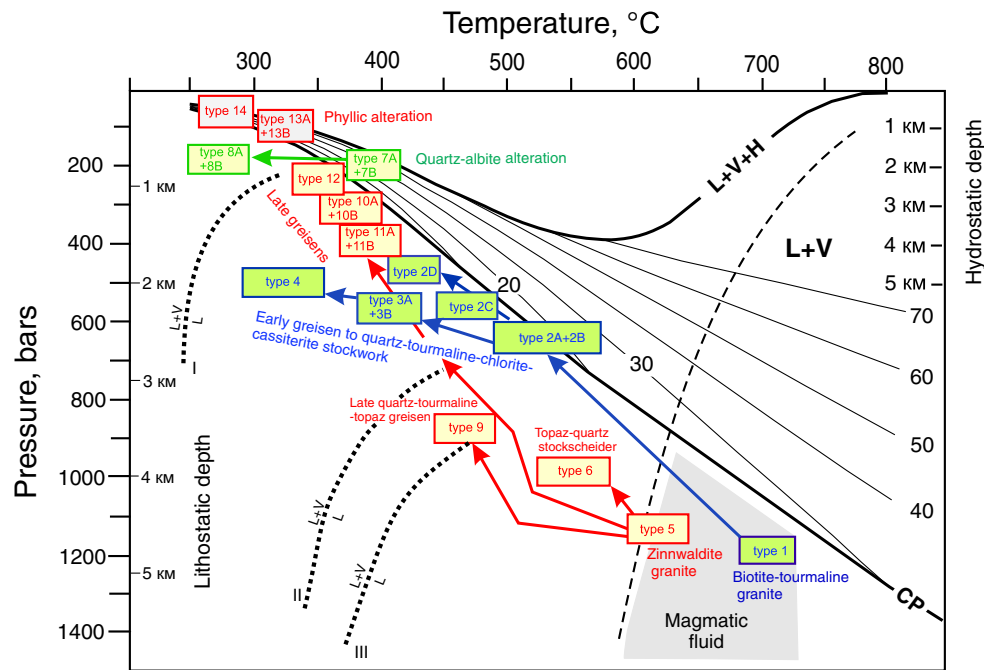


Fig. 13 Estimated pressure and temperature conditions and proposed evolution pathways for fluid inclusion types (1–14; Table 2) at the Kougark prospect, with composition of different fluid inclusion types as a function of depth and temperature (after Bodnar et al. 1985; Fournier 1999). Vapor-pressure curves for H_2O -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

solubility of a granite bearing 2 wt.% fluorine (Selby et al. 2000). The two-phase ($L / L + V$) curves (dotted lines) for H_2O -NaCl- CO_2 fluid containing 6 wt.% NaCl and 4.08 mol% CO_2 (curve I), 10 mol% CO_2 (curve II), and 21.33 mol% CO_2 (curve III) (Schmidt and Bodnar 2000) are shown. PT fields for the major fluid inclusion types and possible evolutionary paths for the fluids (arrows) are shown

fluid toward lower temperatures (Fig. 13). The transition from quartz-muscovite to quartz-topaz greisen is consistent with hydrogen metasomatism and hydrolysis reactions producing muscovite and topaz by high-acidity fluids (Burt 1981). The coexisting gaseous (type 11A) and high-salinity (type 11B) fluid inclusions in quartz-fluorite greisen also suggest fluid immiscibility at temperatures 390–380 °C to 360–350 °C (Table 2).

Finally, the quartz-sericite-carbonate-sulfide (phyllic) alteration assemblage formed from coexisting carbonic (type 13A) and saline (type 13B) fluids unmixed due to boiling and then from high-salinity sodic-magnesium chloride (type 14) fluid. The latter resembles the early magnesium-rich fluids related to biotite-tourmaline granites and suggests fluid influx from a deeper residual magmatic reservoir. The phyllic alteration assemblage is rich in sulfides and Bi, indicating metal transport and precipitation as bisulfide complexes under reduced conditions (Gammons and Williams-Jones 1997). The fluid inclusion data (Table 2) indicate the temperature of ~310–300 °C, whereas the presence of native bismuth ($T_{\text{melting}} = 271.4$ °C) indicates slightly lower temperatures.

Consistent with the ilmenite-series granites, methane was an important carbonic species in the fluids (Table 2), similarly to that at the other Sn-W and Sn-Ta deposits (Linnen and Williams-Jones 1995; Halter et al. 1998; Borges et al. 2009). The fluids that formed greisens associated with zinnwaldite granite had a higher CO_2/CH_4 ratio than the fluids that formed

the early quartz-tourmaline greisen associated with biotite-tourmaline granite. A carbonic phase likely will exsolve from granitic magma first due to lower solubility than that of H_2O , F, B, and Cl (Lowenstern 2001) but will be retained for longer in a mafic magma. Removal of carbonic phases from a magma also enhances melt-fluid partitioning of rare elements in favor of magmatic fluid (Webster et al. 1989). The fluid enrichment in carbon at Kougark is similar to that of reduced intrusion-related deposits (Baker 2002).

Magmatic to post-magmatic Ta-Nb and Sn mineralization

Ta-Nb mineralization occurs in the uppermost part of the zinnwaldite granite and is associated mostly with the final episodes of magmatic crystallization, particularly W-Nb-rutile and columbite-tantalite, with a higher Nb content, and to the late magmatic to higher-temperature post-magmatic quartz-albite-Li mica alteration. In particular, W-Nb-rutile is stable under subsolidus conditions and can evolve to ixiolite and other Nb and/or Ta phases (Černý et al. 2007). Its occurrence at a deeper level, in contrast to columbite-tantalite that is concentrated at higher levels, manifests the respective system-scale mineralogical zonation (Breiter et al. 2017b). Columbite-tantalite at Kougark exhibits a zonation, with Ta (+Fe, W) content increasing from early (core) to late (peripheral) growth zones. As shown

by Linnen (1998), Ta is retained in the melt because of high Li-F concentrations, and tantalite crystallization is delayed until Li and/or F minerals crystallize, which lowers the tantalite solubility and results in a general association of Ta with Li in mineralized granitic rocks. This is similar to the respective paragenesis in Li-Cs-Ta granitic pegmatites, where an increase in Ta with fractionation in the columbite group is explained by the higher solubility of the Ta end member relative to the Nb end member (van Lichtenvelde et al. 2007). However, Ta-Nb minerals at Kougarok appear to be also stable during the post-magmatic stage, in quartz-tourmaline+topaz greisens, which almost completely replace zinnwaldite granite. This is also consistent with partial re-mobilization and re-deposition of Ta-Nb minerals during hydrothermal alteration (Timofeev and Williams-Jones 2015; Wu et al. 2017, 2018). Furthermore, Zارايسكى (2004) and Zارايسكى et al. (2010) suggested a magmatic crystallization origin for minor Ta-Nb mineralization (< 50–100 ppm Ta and Nb), whereas much higher Ta and Nb concentrations (100–350 ppm) could be due to high solubility of Ta and Nb in aqueous fluoride fluids at 600–300 °C and 1000–500 bars. This provides a possibility for hydrothermal re-deposition of these metals, with corresponding enrichment in Ta. The data on types 7 to 8 and 9 to 11 fluid inclusions (Table 2 and Fig. 13) allow to constrain temperatures for deposition of Ta-Nb minerals during magmatic-hydrothermal evolution, from the final stages of zinnwaldite granite crystallization (~600 °C), formation of topaz-quartz stockscheider (550–500 °C) to quartz-tourmaline+topaz greisen and higher-temperature quartz-albite-Li mica alteration (~500–400 °C), in which Ta-Nb minerals appear to be stable. However, Ta-Nb minerals at Kougarok are progressively replaced by quartz-topaz, quartz-muscovite, quartz-fluorite, and lower-temperature quartz-albite-Li mica alteration assemblages, at the temperatures 390–350 °C.

The cassiterite mineralization formed at different hydrothermal stages. First, at the early quartz-tourmaline-chlorite-axinite stage accompanying biotite-tourmaline granite, the presence of chlorite suggests that tin enrichment could in part be associated with alteration of Sn-bearing Fe-Mg micas (Lentz et al. 1988). Then, during the late greisen stage, massive cassiterite deposition could be caused by neutralization of boiling fluids (Drummond and Ohmoto 1985) and/or by decreasing temperature and pressure of the fluids (Wilson and Eugster 1990; Linnen and Williams-Jones 1995; Halter et al. 1996, 1998). Loss of H₂ from a reduced, tin-rich, fluid by vapor separation could be accompanied by simultaneous reaction with aluminosilicate rocks, in total providing conditions for the formation of rich greisen-type tin deposits (Heinrich 1990).

Conclusions

The Kougarok prospect is situated in a Sn-W (+Ta, Nb, Li, Be) metallogenic belt formed in a post-collisional to within-plate

tectonic environment. The extensional tectonic regime facilitated uplift of mantle-derived mafic magma, together with widespread melting of crustal rocks and emplacement of coeval peraluminous granitic suites. Crystal fractionation of granitic magma, combined with its mixing/mingling with mantle-derived mafic magma, is envisioned as the major process causing the formation of the complex B-rich to Li-F-type granitic suite and associated Sn, Ta, Nb, and Li mineralization.

An intrusion of alkalic mafic magma into a crystallizing biotite-tourmaline granite magma reservoir may have supplied a geochemically distinct assemblage of volatiles (F) and associated metals (Li, Ta, Nb) into the boron- and Sn-rich granitic system. An alternative model of differentiation-driven unmixing of mafic and granitic silicate melts could also trigger magma-fluid and fluid-fluid unmixing, with separation of gaseous fluid coexisting with immiscible felsic and mafic magmas in the form of magmatic melt-fluid-crystal “suspension.” Crystallization of biotite-tourmaline granite was accompanied by early quartz-tourmaline-cassiterite greisen at > 430–380 °C followed by quartz-tourmaline-chlorite-cassiterite stockwork at < 350 °C.

The immiscibility of F- and B-rich fluids was followed by ascent of F-rich fluids upward in the granitic magma reservoir, with its strong enrichment in F, Li, Ta, and Nb and subsequent crystallization of zinnwaldite granite at a shallower level, with separation of moderate-salinity fluid at ~600 °C. Crystallization continued at lower temperatures due to the fluxing role of fluorine, and included separation of high-salinity magmatic fluid, with the formation of pegmatite-like topaz-quartz stockscheider at ~550–500 °C. This was followed by quartz-tourmaline+topaz greisen and higher-temperature quartz-albite-Li mica alteration, which replaced zinnwaldite granite at ~500 to 400 °C. Further nearly contemporaneous, lower-temperature quartz-albite-Li mica alteration and development of quartz-muscovite, quartz-topaz, and quartz-fluorite greisens formed from boiling fluids at ~390–350 °C. The latest quartz-sericite-carbonate-sulfide (phyllic) alteration assemblage formed from boiling fluids at < 310 °C. Methane was a dominating carbonic species in the fluids, consistent with the ilmenite-series type of the granites and reduced, pyrrhotite-stable character of the hydrothermal assemblages.

Ta-Nb mineralization is associated mostly with final episodes of magmatic crystallization at ~600 to ~550–500 °C, particularly W-Nb-rutile and columbite-tantalite with a higher Nb content. Some Ta-Nb minerals appear to be also stable at the post-magmatic stage, in quartz-tourmaline+topaz greisen and higher-temperature quartz-albite-Li mica alteration. This can be consistent with partial re-mobilization and re-deposition of Ta-Nb minerals during hydrothermal alteration at ~500 to 400 °C. However, Ta-Nb minerals at Kougarok are progressively replaced by quartz-topaz, quartz-muscovite, quartz-fluorite, and lower-temperature quartz-albite-Li mica alteration assemblages at ~390–350 °C. Fluid cooling and neutralization of boiling fluids affected Sn solubility and promoted massive cassiterite deposition in the late greisens.

Further fluid cooling and neutralization of boiling fluid under reduced conditions facilitated sulfide deposition during the phyllic quartz-sericite-carbonate alteration stage.

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