



Carbonate-silicate inclusions in garnet as evidence for a carbonate-bearing source for fluids in leucocratic granitoids associated with granulites of the Southern Marginal Zone, Limpopo Complex, South Africa

Oleg G. Safonov ^{a,b,c,*}, Alexander S. Mityaev ^{a,b}, Vasily O. Yapaskurt ^b, Georgy A. Belyanin ^c, Marlina Elburg ^c, H.M. Rajesh ^d, Maria A. Golunova ^a, Vasily D. Shcherbakov ^b, Valentina G. Butvina ^a, Dirk D. van Reenen ^c, Andre C. Smit ^c

^a Korzhinskii Institute of Experimental Mineralogy, Russian Academy of Sciences, Academician Ossipyan str., 4, Chernogolovka, Moscow District, 142432, Russia

^b Department of Petrology, Moscow State University, Moscow, Russia

^c Department of Geology, University of Johannesburg, Johannesburg, South Africa

^d Department of Earth and Environmental Sciences, BIUST, Botswana

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ABSTRACT

We present a study of carbonate-bearing polyphase inclusions in garnets from leucocratic granitoids intruding metapelitic granulites of the Southern Marginal Zone (SMZ) of the Neoproterozoic Limpopo high-grade complex, South Africa, during the post-peak stage (2710–2650 Ma; U–Pb ages for zircons and monazites). Ternary feldspar thermometry suggests that the granitoid magma cooled from temperatures 800–900 °C at a pressure of ca. 6.5 kbar. Abundant CO₂ fluid inclusions in quartz and T–X_{CO2} phase equilibria modeling via PERPLE_X imply action of an essentially carbonic fluid in the granitoids. Cores of almandine-rich garnet grains from the granitoids contain polyphase carbonate-bearing inclusions with a distinct negative crystal shape. The major carbonate in the inclusions is a strongly zoned magnesite-siderite variety, whereas pyrophyllite is the predominant silicate phase. Raman spectra of unexposed inclusions revealed a presence of CO₂, as well as CH₄ and H₂O. The carbonate-bearing inclusions coexist with larger polyphase inclusions composed of biotite, quartz, K-feldspar, plagioclase, sillimanite, which are interpreted as relics of granitic melts. Modeling the mineral assemblage preserved within the carbonate-bearing inclusions shows that their present mineral and chemical compositions are a product of interaction of the trapped aqueous-carbonic fluid with host garnet during cooling below 400 °C. Despite strong modifications, the inclusions bear evidence for initial saturation of the fluid with Mg-carbonate. This is taken as an evidence for an origin of the fluids by devolatilization of the Mg-rich carbonate-bearing ultrabasic greenstone rocks of the Kaapvaal Craton that were buried under the SMZ. Being generated at temperatures between 650 and 700 °C, the fluid subsequently participated in anatexis and coexisted with the granite magma during exhumation and interaction of the SMZ granulites with cratonic rocks.

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1. Introduction

Independent of their formation either under fluid-absent or fluid-present conditions (see Weinberg and Hasalová, 2015 for review), granitoid magmas usually carry a vast amount of fluids. The C–O–H species are the most important components of these fluids. In the case of granitic and rhyolitic magmas that are separated from their sources, the H₂O content varies from about 1 wt% to about 8 wt% showing a negative

dependence on the temperature of the magmas (see compilations in Clemens and Watkins, 2001; Clemens and Stevens, 2015). According to melt inclusions studies (e.g. Bartoli et al., 2014), the H₂O content for granitoid melts at their source could be up to 9 wt%. The situation for CO₂ is more debatable. In contrast to water, carbon dioxide does not manifest itself in granitoid mineral assemblages. Nevertheless, the presence of CO₂ in granitoid magmas is recorded as primary inclusions in minerals of granitoids, especially, in the Precambrian high-grade terranes (Konnerup-Madsen, 1977, 1979; Santosh et al., 1991, 2005; Frezzotti et al., 1994; Safonov et al., 2014, 2018a, 2018c). These data show that the role of CO₂ in granite magmatism requires more attention.

* Corresponding author.

E-mail address: oleg@iem.ac.ru (O.G. Safonov).

A principal reason to discuss the role of CO₂ in the formation and evolution of granite magma concerns in the problem of participation of carbonic fluids during high-grade metamorphism and crustal anatexis. Dense CO₂ inclusions in minerals are a common feature of high-grade rocks (e.g. Touret, 1971; Touret and Huizenga, 2011), including UHT varieties (e.g. Tsunogae et al., 2002; Santosh et al., 2004). This fact inspired the development of the concept of “carbonic granulite metamorphism”, which considers the leading role of pervasive flushing of external (including mantle-derived) CO₂-rich fluids in the formation of granulite assemblages in the lower to middle crust (e.g. Newton et al., 1980; Santosh and Omori, 2008). Based on melting experiments in the KMASH-CO₂ system, Wendlandt (1981) and Grant (1986) proposed that CO₂ promotes the formation of orthopyroxene-bearing migmatites and charnockitic magmas at high-grade conditions. Peterson and Newton (1989, 1990) extended this conclusion by finding that melting temperatures of phlogopite-quartz and phlogopite-K-feldspar-quartz assemblages in the presence of equimolar H₂O-CO₂ fluids above 6 kbar were even lower than in the presence of pure aqueous fluid.

The concept of “carbonic granulite metamorphism” has been criticized (e.g. Clemens, 1992, 1993; Stevens and Clemens, 1993) based on different issues, including the localized action of CO₂ recorded in carbon isotopic gradients in granulites (Lamb and Valley, 1985; Vennemann and Smith, 1992) and experimental data on the limited migration of CO₂ through crystalline rocks (Watson and Brenan, 1987). The strongest point of criticism of the “carbonic model” is also the influence of CO₂ on the granite production. Carbon dioxide negatively affects the melting in the granitic system (e.g. Ebadi and Johannes, 1991). Clemens (1993) and Clemens et al. (1997) could not reproduce the results of Peterson and Newton (1990) on triggering of melting of biotite-bearing assemblages by CO₂. Low solubility of CO₂ in felsic melts (<0.9 wt% at pressures up to 10 kbar; see Ni and Keppler, 2013 for compilation of experimental data) also cast doubts on the proposed participation of CO₂ in the granite magma generation and evolution during high-grade metamorphism (e.g. Stevens, 1997).

To reconcile the conflicting models of the role of CO₂-rich fluids in granulite genesis and accompanying granite magmatism, some authors (e.g. Frost and Frost, 1987; Frost et al., 1989; Farquhar and Chacko, 1991; Santosh et al., 1991; Satish-Kumar and Santosh, 1998; Harlov et al., 2014) suggested that external felsic magmas served just as transport vehicles for such fluids. The passage of voluminous CO₂-bearing magmas could facilitate extensive CO₂ distribution through high-grade terranes, as well as formation of the anhydrous granulite assemblages via CO₂ flushing from the magmas and scavenging of H₂O by the magmas from the country rocks (e.g. Frost and Frost, 1987). The model is based mostly on studies of dehydration (orthopyroxene-bearing) zones enriched in CO₂ inclusions in minerals and of graphite around felsic bodies within high-grade terrains (e.g. Frost and Frost, 1987; Frost et al., 1989; Farquhar and Chacko, 1991; Santosh et al., 1991; Satish-Kumar and Santosh, 1998; Harlov et al., 2014).

One of the propositions of the model assuming a CO₂ supply by felsic magmas to regions of high-grade metamorphism considers that carbon dioxide was actively involved in the source of these magmas. The primary source could be CO₂-bearing basaltic magmas that provide heat to the lower crust to generate felsic melts, which either were fluid-undersaturated or coexisted with CO₂-rich fluids (Frost and Frost, 1987; Frost et al., 1989). The second source is carbonate-bearing lithologies within the crustal sequences (Holloway, 1976; Lowenstern, 2001), which produce CO₂ fluids during heating. Holloway (1976) demonstrated that if CO₂ was present in the magma source region, then there would be a fluid present throughout the whole evolutionary history of the magma. CO₂ coexisting as a free fluid phase with silicic magmas would influence its physical properties, buffer water activity and assist the ascent of the magmas (e.g. Holloway, 1976; Frost and Frost, 1987; Frost et al., 1989; Lowenstern, 2001).

The presence of CO₂ in the source of granite magmas is usually assumed on the basis of studies of fluid and melt inclusions in Fe-Mg

minerals (garnet, sapphirine, cordierite) of granulites affected by high-grade anatexis. In some cases, these inclusions also contain carbonates, the composition of which might help to speculate about the fluid sources (Bolder-Schrijver et al., 2000; Tsunogae et al., 2002; Ferrero et al., 2016; Tacchetto et al., 2018). However, carbonate-bearing inclusions from anatectic granitoids have not been reported, so far. In the present paper, we report a result of a study of carbonate-bearing poly-phase inclusions in garnets from *syn*-late-tectonic leucocratic granitoids intruding metapelitic granulites of the Neoproterozoic (2.72 Ga) Southern Marginal Zone (SMZ) of the Limpopo granulite complex, South Africa. The presence of such inclusions imply a link between the fluids in the granitoids and the carbonate-bearing greenstone sequences of the Kaapvaal Craton that underlies the SMZ (De Beer and Stettler, 1992; van Reenen et al., 2014, 2019).

2. Geological setting

2.1. General geology and metamorphic history of the Southern Marginal Zone (SMZ) of the Limpopo Complex

The high-grade metamorphic terrane of the Limpopo Complex, which is located between the Zimbabwe and the Kaapvaal cratons, is traditionally subdivided into Northern Marginal Zone (NMZ), Central Zone (CZ), and Southern Marginal Zone (SMZ) (Fig. 1). The zones are separated from each other and from the adjacent cratons by regional-scale shear zones. The material for the present study is collected from the rocks of the SMZ that is juxtaposed against the Northern Kaapvaal Craton along the steeply north-dipping crustal-scale Hout River Shear Zone (HRSZ) (Fig. 1). The HRSZ guided thrusting of the SMZ granulites against and onto the granite-greenstone terrane between ~2720 and 2690 Ma (De Beer and Stettler, 1992; Roering et al., 1992; Kreissig et al., 2001; van Reenen et al., 2011, 2019; Kramers et al., 2014; Smit et al., 2014). Two major lithological units of the SMZ (e.g. van Reenen et al., 2011, 2014, 2019), i.e. migmatized tonalitic-trondhjemitic Baviaanskloof gneisses and ultramafic, mafic, pelitic and minor BIF granulites of the Bandelierkop Formation, comprise large crustal blocks bounded by steeply dipping regional-scale high-grade shear zones (Annaskraal, Petronella, Matok; Fig. 1) (Smit et al., 1992, 2014; Smit and van Reenen, 1997). Geochemical data (Kreissig et al., 2000, 2001) and detrital zircons ages up to 3440 Ma derived from metapelites of the Bandelierkop formation (e.g. Rajesh et al., 2014) permit the interpretation that the high-grade rocks of the SMZ represent the high-grade equivalents of supracrustal rocks of the juxtaposed granite-greenstone terrane of the Kaapvaal Craton. Nevertheless, detrital zircons with ages <3000 Ma in the metapelites led Nicoli et al. (2015) to suggest that metasediments of the Bandelierkop Formation might belong to an individual block unrelated to the Kaapvaal Craton.

The peak metamorphic age of the SMZ rocks is 2720–2710 Ma (Retief et al., 1990; Belyanin et al., 2014a; Rajesh et al., 2014; Taylor et al., 2014; Nicoli et al., 2015; Vezinet et al., 2018). Various research groups indicated peak metamorphic condition in the SMZ of 800–870 °C and 7.5–11 kbar (e.g., van Reenen, 1983; van Reenen et al., 1987; Stevens and van Reenen, 1992; Perchuk et al., 1996, 2000a, 2000b; Taylor et al., 2014; Nicoli et al., 2014, 2015, 2017). According to some authors (e.g., Stevens and van Reenen, 1992; Taylor et al., 2014; Nicoli et al., 2014, 2015, 2017), these conditions have been attained via burial of the rocks at the base of the continental crust and their prograde heating during collision. Metamorphism in the SMZ was accompanied by anatectic history (Du Toit et al., 1983; Stevens and van Reenen, 1992; van Reenen et al., 2014; Taylor et al., 2014; Nicoli et al., 2014, 2015, 2017; Madlakana and Stevens, 2018). UHT conditions (>1000 °C at 11–12 kbar) reported by Tsunogae et al. (2004), Belyanin et al. (2010, 2012) and Rajesh et al. (2014) for Mg-Al-granulites of the SMZ were criticized by Taylor et al. (2014). Nevertheless, Belyanin et al. (2014b) showed that Mg-Al-rich granulites provide evidence for temperatures slightly above

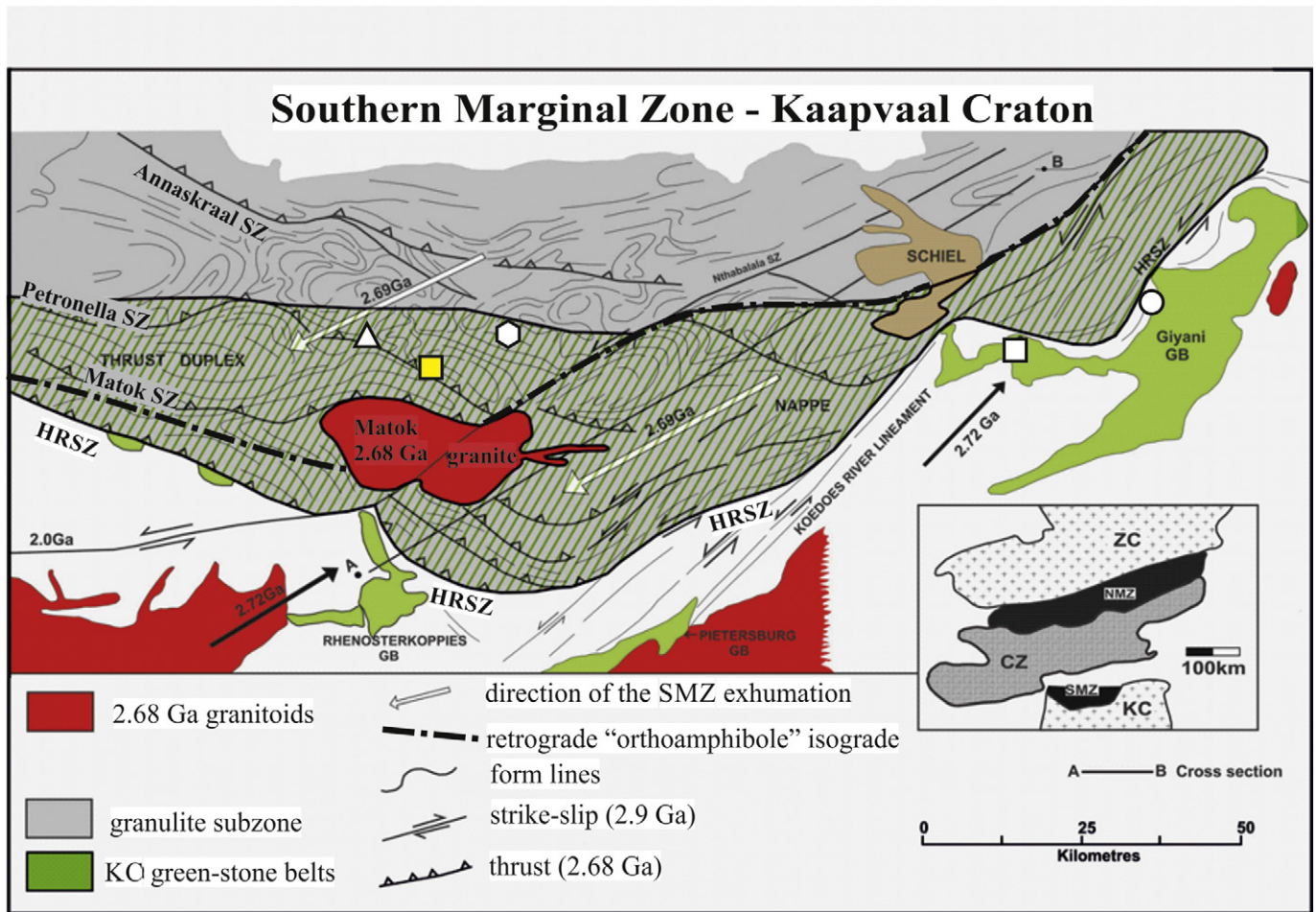


Fig. 1. Structural map of the Southern Marginal Zone (SMZ) and the adjacent Kaapvaal Craton (KC). SZ – major shear zones (Annaskraal, Petronella, Matok), HRSZ – Hout River Shear Zone, GB – greenstone belts. Hatched area indicates the portion of the SMZ, which is according to geophysical data (De Beer and Stettler, 1992) underlain by greenstone material of the NKVC. Yellow square shows a position of the studied locality at farm Klippit. Localities mentioned in the text: white hexagon - Banderlierkop quarry (Stevens and van Reenen, 1992; Taylor et al., 2014; Dubinina et al., 2015; Safonov et al., 2018a, 2018c; Madlakana and Stevens, 2018), white triangle - farm Petronella (Safonov et al., 2014, 2018b, 2018c), white square - Khavagari Hills (McCourt and van Reenen, 1992; Kramers et al., 2014), white circle - Hudson Ntsanwisi Dam spillway (McCourt and van Reenen, 1992). Abbreviations in the insert image: ZC – Zimbabwe Craton, KC – Kaapvaal Craton, NMZ – Northern Marginal Zone, CZ – Central Zone, SMZ – Southern Marginal Zone.

900 °C, but at 6.5–7.0 kbar. Safonov et al. (2014, 2018b, 2018c) related these conditions to the effect of leucocratic granitoids that intruded into the SMZ at 2667–2668 Ma after the metamorphic peak (see below and Belyanin et al., 2014a; Safonov et al., 2018b for age data).

The post-peak metamorphic evolution of the SMZ is manifested by decompression at 2691 ± 7 Ma (Kreissig et al., 2001), related to thrusting a hot allochthonous granulite nappe against and over the low-grade granite-greenstone terrain (Pietersburg block) of the Kaapvaal Craton along the HRSZ (De Beer and Stettler, 1992; Roering et al., 1992; Smit et al., 1992; van Reenen et al., 2014, 2019). Sub-isobaric cooling, which followed decompression down to 6.0–6.5 kbar, is documented in metapelites located south of the Annaskraal shear zone (van Reenen, 1983; Stevens and van Reenen, 1992; Perchuk et al., 1996, 2000a, 2000b; Smit et al., 2001, 2014; Taylor et al., 2014; Nicoli et al., 2015; van Reenen et al., 2011, 2014, 2019; Safonov et al., 2014). Sub-isobaric cooling was accompanied or followed by regional retrograde hydration at 2670–2660 Ma (Belyanin et al., 2014a), which is defined by the formation of the assemblage orthopyroxene+anthophyllite+quartz in metapelitic granulites and establishment of the “retrograde anthophyllite-in isograd” (van Reenen, 1986; van Reenen et al., 2011, 2014; Smit et al., 2014; Koizumi et al., 2014). Rehydration of the SMZ rocks was provoked by complex CO₂-rich and aqueous-salt fluids (van Reenen, 1986; van

Reenen and Hollister, 1988; Baker et al., 1992; van den Berg and Huizenga, 2001; Huizenga et al., 2014; van Reenen et al., 2014). Most authors (van Reenen and Hollister, 1988; van den Berg and Huizenga, 2001; Smit et al., 2014; van Reenen et al., 2014; Koizumi et al., 2014; Kramers et al., 2014) agree that the source of these fluids was the low-grade sequences of the Kaapvaal Craton that were buried underneath the SMZ granulites during exhumation and thrusting against and over the adjacent granite-greenstone terrane of the Kaapvaal Craton. It also has been proposed that regional hydration in the SMZ was caused by fluids released from crystallizing granitic magmas (e.g. Stevens, 1997; van den Berg and Huizenga, 2001; Safonov et al., 2018a, 2018b, 2018c).

2.2. Post-peak granitoid magmatism of the SMZ

The period ~2680–2640 Ma is manifested by a number of late-tectonic intrusions into the SMZ. The largest is the ~2.68 Ga diorite-granodiorite-monzogranite Matok pluton (Fig. 1), a body composed of 2686 ± 7 Ma to 2679 ± 7 Ma pyroxene-bearing, pyroxene-absent and amphibole-biotite granitoids (all U-Pb zircon ages; Barton et al., 1992; Bohlender et al., 1992; Laurent et al., 2013, 2014). Post-peak granitoid magmatism in the SMZ is also expressed in number of smaller bodies, veins and pegmatites of leucocratic granitoids, the origin of which is a

matter of controversy (Safonov et al., 2014, 2018a, 2018b, 2018c; Belyanin et al., 2014a). Various authors reported zircon ages of these granitoids from 2680 to 2640 Ma (Kreissig et al., 2001; Belyanin et al., 2014a; Nicoli et al., 2015) that are clearly younger than the peak metamorphic age (~2720 Ma), and support of field evidence that the granitoids intruded already deformed and granulite-facies metamorphosed rocks. Based on the coincidence of the ages, Safonov et al. (2014) and Belyanin et al. (2014a) suggested that the leucogranitoid bodies and veins could be a part of the same event as the emplacement of the Matok pluton (Barton et al., 1992; Laurent et al., 2013, 2014; Laurent and Zeh, 2015). Laurent et al. (2014) concluded that the Matok pluton is a complex body built both by lithospheric mantle-derived magmas, which interacted with subduction-related sedimentary material and magmas produced from the reworked crust. Thus, the leucocratic granitoids might also have been produced from a source unrelated to the Banderlierkop Formation of the SMZ. Using $\delta^{18}\text{O}$ data on a garnet-bearing pegmatitic trondhjemite vein, Vennemann and Smith (1992) concluded that the granitoids were not in isotopic equilibrium with the adjacent metapelites but were crystallized from “melts being derived from several compositionally different but finely interlayered metasediments”. Based on a correlation of $\delta^{18}\text{O}$ with the composition of trondhjemites from the Banderlierkop quarry (Fig. 1), Dubinina et al. (2015) also concluded that “the leucogranites represented partial melts derived from an external source and ... were contaminated when they intruded the host metapelite” and suggested the Baviaanskloof-type TTG gneisses as the possible source for the granitoids.

The presence of CO_2 -rich fluids of low water activity with lesser amounts of aqueous-salt fluids as recorded in fluid inclusions is the principal characteristics of the post-peak leucogranitoid magmas that intruded into the SMZ (Safonov et al., 2014, 2018a, 2018c). This feature implies that the fluids and granitoids must have been derived from a source enriched in CO_2 or carbonates. Such a source is unusual for the SMZ since granulite-facies carbonate-bearing rocks are rare in the complex. Carbonates documented from ultramafic granulites (e.g. van Schalkwyk and van Reenen, 1992) or, sporadically occurring in metapelites (Safonov et al., 2018a) are exclusively products of retrograde fluid-rock interaction. Thus, the carbonate-rich source for the leucogranitoid magmas must be searched for outside the SMZ. Recently Safonov et al. (2018a) reported $\delta^{13}\text{C}_{\text{PDB}}$ values for graphite (−6.52, −8.65 and −8.59‰) and fluid inclusions (−2.50, −4.22 and −5.58‰) from garnet granitoids from the Banderlierkop quarry. A substantial difference of these values from the carbon isotope composition for graphite from the surrounding SMZ metapelites (−12.5 to −15.2‰, Vennemann and Smith, 1992) support a source unrelated to the host metapelites. Based on the “heavy” $\delta^{13}\text{C}_{\text{PDB}}$, it is assumed that the magmas carried fluids were derived from devolatilization of mafic rocks interlayered with hydrothermal carbonate veins in granite-greenstone successions of the Kaapvaal craton that underlies large areas of the SMZ (see hatched area in Fig. 1; De Beer and Stettler, 1992). In the present paper, we report additional evidence for the link of fluids in the leucocratic granitoids of the SMZ with a carbonate-rich source, which can be related to the low-grade cratonic rocks.

2.3. The studied locality

The locality on farm Klipput (Google Earth: 23°21′46″ S; 29°42′56″ E; Fig. 1, 2a, b) is located within the Petronella shear-zone several kilometers southeast from localities described by Safonov et al. (2014, 2018b) (Fig. 1). The locality is an oval-shaped hill about 200–250 m in length and about 100 m in width comprising leucocratic granitoids (Figs. 2a, b, 3a). The granitoid body intrudes variously sheared metapelitic granulites of the Banderlierkop Formation (Fig. 3b). The Mg-rich metapelites are characterized by the principal mineral assemblage $\text{Opx} + \text{Crd} + \text{Bt} + \text{Pl} + \text{Qz}$ (all mineral abbreviations are from Whitney and Evans, 2010) with accessory sillimanite, ilmenite, apatite, monazite, zircon and sulfides (van Reenen, 1983, 1986; Stevens and van

Reenen, 1992; Perchuk et al., 1996, 2000a; van Reenen et al., 2011; Taylor et al., 2014; Safonov et al., 2014, 2018a, 2018b; Nicoli et al., 2015, 2017; Madlakana and Stevens, 2018). Garnet is usually absent in the rocks. However, isometric clusters comprising intergrowths of orthopyroxene and cordierite reflect the reaction $\text{Grt} + \text{Qz} = \text{Opx} + \text{Crd}$ and imply that garnet was present in the assemblage before the decompression-cooling stage (van Reenen, 1983; Stevens and van Reenen, 1992; Perchuk et al., 1996, 2000a; Smit et al., 2001; van Reenen et al., 2011; Taylor et al., 2014; Nicoli et al., 2015). Large garnet grains appear at the contact of metapelite blocks with the leucocratic granitoids. This situation is very similar to that described by Safonov et al. (2014) at the Petronella locality and manifests the interaction of metapelites with the granitoid magma.

3. Bulk rock characteristics, petrography, and mineral composition of granitoids

3.1. Modal and bulk chemical composition

Garnet-bearing granitoids (>20 modal % of Qz; Le Maitre et al., 2002) of the Klipput locality are leucocratic rocks (Fig. 3a) consisting predominantly of plagioclase (50–70 vol%) and quartz (25–50 vol%). At a SiO_2 content of 71–74 wt%, the studied granitoid samples are sodic ($\text{Na}_2\text{O}/\text{K}_2\text{O} > 1$) with medium K_2O content (2–3 wt%) and total $\text{Fe} + \text{MgO} + \text{MnO} + \text{TiO}_2$ content of 1.5–1.6 wt% (Table S1, Supplementary online material). They are slightly peraluminous with $\text{AlI} = \text{mol. Al}/(\text{Ca} - 1.67\text{P} + \text{Na} + \text{K})$ ratios of 1.1 to 1.12 and corundum normative (1.6–1.7 mol%); the highest values correlate with the granitoid sample with the highest garnet content. According to the normative An-Ab-Or plot (Le Maitre et al., 2002), the leucocratic granitoid rocks of the Klipput locality correspond to trondhjemites, falling close to the granite field (Fig. 4a). The studied samples are within the range of compositions of leucocratic granitoids associated with metapelites of the Banderlierkop formation (Fig. 4a; Stevens, 1997; Safonov et al., 2014, 2018a, 2018c; Taylor et al., 2014; Dubinina et al., 2015). The Na-rich nature of the Klipput leucocratic granitoids is concomitant with high Sr content and low Ba and Rb contents (Table S1, Supplementary online material).

The Klipput leucocratic granitoids show large ion lithophile element (LILE) enrichment and high-field strength element (HFSE) depletion, giving rise to negative Nb, Ta, P and Ti anomalies in primitive mantle-normalized trace element diagrams (Table S1, Supplementary online material). The chondrite-normalized (Sun and McDonough, 1989) REE patterns of the rocks show enrichment of light REE (LREE, e.g., La) relative to the middle REE (MREE, e.g., Sm) [$(\text{La}/\text{Sm})_{\text{N}} = \sim 3\text{--}5$], depletion of heavy REE (HREE, e.g., Yb) [$(\text{Gd}/\text{Yb})_{\text{N}} = \sim 1$] and variable Eu anomalies [$(\text{Eu}/\text{Eu}^*) = \sim 0.6\text{--}1.4$] (Fig. 4b; Table S1, Supplementary online material). The REE pattern of the leucocratic granitoid sample with a lower garnet content is similar to that of low-HREE TTG, defined by Halla et al. (2009) (Fig. 4b). On the other hand, the HREE pattern of the granitoid sample that is richer in garnet shows $(\text{Gd}/\text{Yb})_{\text{N}} = \sim 5$ (Fig. 4b), suggesting either strong garnet accrual in the magma or its possible contamination by the country metapelite material.

3.2. Petrography

The leucocratic granitoids are medium to coarse-grained rocks (Fig. 3a). K-feldspar is unevenly distributed in the rocks (Fig. 5a) and even at the thin section scale, some portions of the rocks contain <5 vol% of K-feldspar, whereas other portions show up to 20–30 vol% of K-feldspar. K-feldspar is present as antiperthitic inclusions. They are concentrated in the centers of plagioclase grains and clearly represent exsolution features rather than products of metasomatic replacement (Fig. 5a). K-feldspar also forms rare microveins at the boundaries of plagioclase and quartz grains (Fig. 5a), which could be interpreted as a products of the rock interaction with aqueous-salt and brine fluids

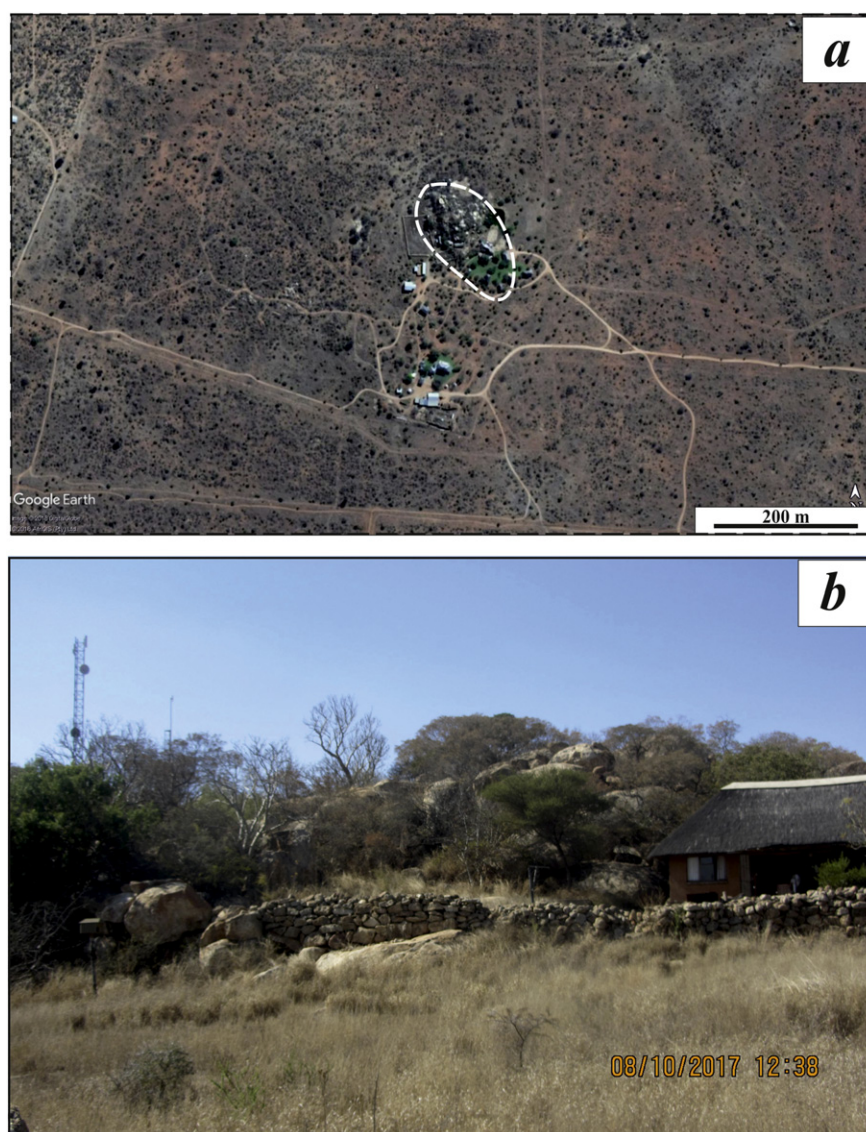


Fig. 2. The Klippit locality. (a) Google Earth image showing an oval-shaped granitoid body (approximate contours of the main outcrop are shown by dashed line) at the locality. (b) A general view of the granitoid body at farm Klippit.

(e.g. Aranovich and Safonov, 2018). With increasing modal content, K-feldspar acquires forms of anhedral grains and wide microveins in the plagioclase-quartz matrix (Fig. 5a). Some individual K-feldspar grains show perthitic tabular inclusions. At contacts with garnet, K-feldspar usually coexist with biotite (Fig. 5b).

Garnet is a major Fe-Mg mineral, although its content is below 5 vol% (Fig. 3a). It occurs as separate irregular or rounded grains with sizes 1–1.5 mm that are dispersed in the quartz-feldspathic matrix (Figs. 3a, 5b, c). Some large (up to 2–3 mm) macroscopically single grains appear under the microscope as clusters of grains of various shapes and sizes cemented by biotite (Fig. 5d). It is evident that such complex clusters represent large fractured grains rather than aggregates of individual grains. Garnet grain margins are usually clear at the contacts with plagioclase and quartz, but are extensively rimmed by biotite at the contacts with K-feldspar (Fig. 5b, c). Garnet grains also contain subhedral and euhedral inclusions of quartz, zircon and ilmenite, while plagioclase inclusions are extremely rare. In addition, garnet cores contain polyphase carbonate-bearing inclusions and “granitic” inclusions (see below; Fig. 5c, d).

Rare individual flakes of biotite are closely associated with K-feldspar in the matrix (Fig. 5a). Apparent inclusions of biotite in garnet

are only found to be attached to the polyphase inclusions (Fig. 4c). Biotite forms rims and fringes around garnet at the contacts with matrix K-feldspar and fills cracks in large fractured garnet grains (Fig. 5b–d). Biotite fringes around garnet locally contain inclusions of K-feldspar (Fig. 5b) suggesting that biotite was developed via sub-solidus K-feldspar-garnet reactions rather than reactions of garnet with residual K-rich liquid. Biotite is locally replaced by muscovite along cleavages. Secondary muscovite is dispersed in the rock matrix.

The granitoids contain accessory zircon, ilmenite, rutile and monazite.

3.3. Composition of rock-forming minerals

Cores of internally unzoned garnet grains in the granitoids show $X_{Mg} = 0.28–0.29$, $X_{Ca} = 0.02–0.03$ and $X_{Mn} = 0.02$ (Table S2, Supplementary materials). No change in X_{Mg} is observed at contacts with matrix plagioclase. However, X_{Mg} decreases to 0.22–0.19 at the contacts with late biotite surrounding garnet grains (Fig. 5b; Table S2, Supplementary materials). Variations in X_{Mg} are not accompanied by changes in X_{Ca} and X_{Mn} (Table S2, Supplementary materials).

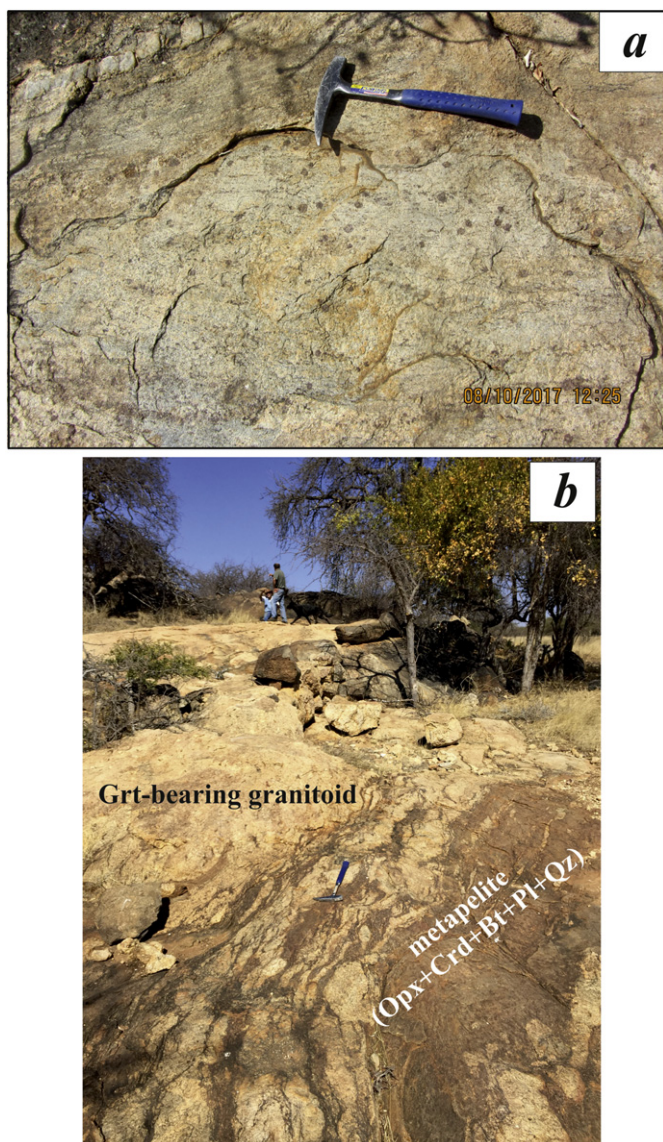


Fig. 3. Leucocratic granitoids of the Klippit locality. (a) Close view of garnet grains in the leucocratic granitoids; clusters of garnet grains is visible at the left lower corner of the image. (b) Contact of the leucocratic granitoids with country garnet-free metapelites; granitoids contain semi-dissolved blocks of metapelites.

Individual small flakes of biotite in the matrix (Fig. 5a) show $X_{Mg} = 0.43–0.44$ and contain 3–4.5 wt% TiO_2 (Table S3, Supplementary materials). In contrast, biotite fringes around garnet grains (Fig. 5b, c) show $X_{Mg} = 0.66–0.68$ and are almost TiO_2 -free (Table S3, Supplementary materials). At similar X_{Mg} , biotites filling cracks in the fractured garnets (Fig. 5d) contain up to 2.5 wt% TiO_2 . The Al content of both biotite varieties is 1.7–2.0 a.p.f.u. suggesting the presence of about 50 mol% of eastonite-siderophyllite component. All types of biotites are halogen-free (Table S3, Supplementary materials).

Feldspar chemical characteristics in the Klippit granitoids are very similar to those in other leucocratic granitoids of the SMZ (Safonov et al., 2014, 2018a, 2018c). Re-integrated compositions of plagioclase grains containing tabular K-feldspar lamellae (Fig. 5a–d) measured using a rastered electron beam show $X_{An} = 0.14–0.16$ and $X_{Or} = 0.14–0.19$ (Fig. 6; Table S4, Supplementary materials). Plagioclases without K-feldspar lamellae have $X_{An} = 0.16–0.18$ and $X_{Or} = 0.013–0.019$ (Table S4, Supplementary materials). Cores of the matrix plagioclase grains are usually slightly more calcic. Solitary small inclusions of plagioclase in garnet contain even more anorthite, $X_{An} = 0.20$.

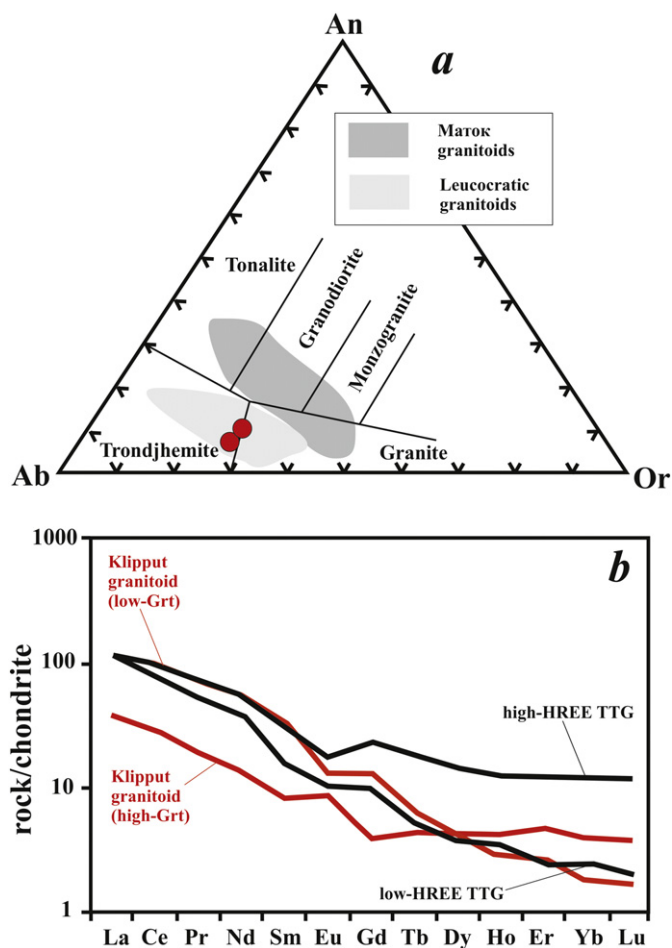


Fig. 4. Bulk rock characteristics of the studied granitoid samples of the Klippit locality. (a) The normative An-Ab-Or plot (Le Maitre et al., 2002) comparing the Klippit granitoids (red dots) with the compositions of the leucocratic granitoids from other localities in the SMZ (Stevens, 1997; Safonov et al., 2014, 2018a, 2018c; Taylor et al., 2014; Dubinina et al., 2015) and granitoids of the Matok pluton (Laurent et al., 2014). (b) The chondrite-normalized (Sun and McDonough, 1989) REE plot comparing the Klippit granitoids (red lines) with two types of TTGs (Halla et al., 2009).

Re-integrated compositions of perthitic alkali feldspar varies within $X_{Or} = 0.75–0.76$, $X_{Ab} = 0.22–0.23$ and $X_{An} = 0.02–0.03$ (Fig. 6; Table S4, Supplementary materials).

4. Fluid inclusions in the granitoids

Measurable carbonic and aqueous-salt inclusions are identified in quartz of the Klippit granitoids (Fig. 7a–c). Both compositional types of fluid inclusions are pseudosecondary, i.e. localized along healed planes, which do not cross grain boundaries. No isolated (primary) inclusions were observed in the studied samples. Some quartz grains contain short trails of both types of inclusions (Fig. 7c). However, relations between these trails are not discernible. Presence of both types of fluid inclusions in a single grain could suggest that the inclusions were trapped as a part of the same fluid inclusion assemblage.

CO_2 is the prevailing fluid inclusion type. The CO_2 inclusions are 10–15 μm in size (Fig. 7a), inclusions of up to 20 μm are rare. The inclusions show clear negative crystal shape. The homogenization temperatures of the carbonic inclusions varies from -13.8 to $+27.3^\circ C$ corresponding to densities from 1.002 to 0.671 g/cm³. Melting temperatures from $-56.7^\circ C$ to $-61.8^\circ C$ suggest a presence of additional species (CH_4 or N_2). However, the majority of the inclusions are pure CO_2 .

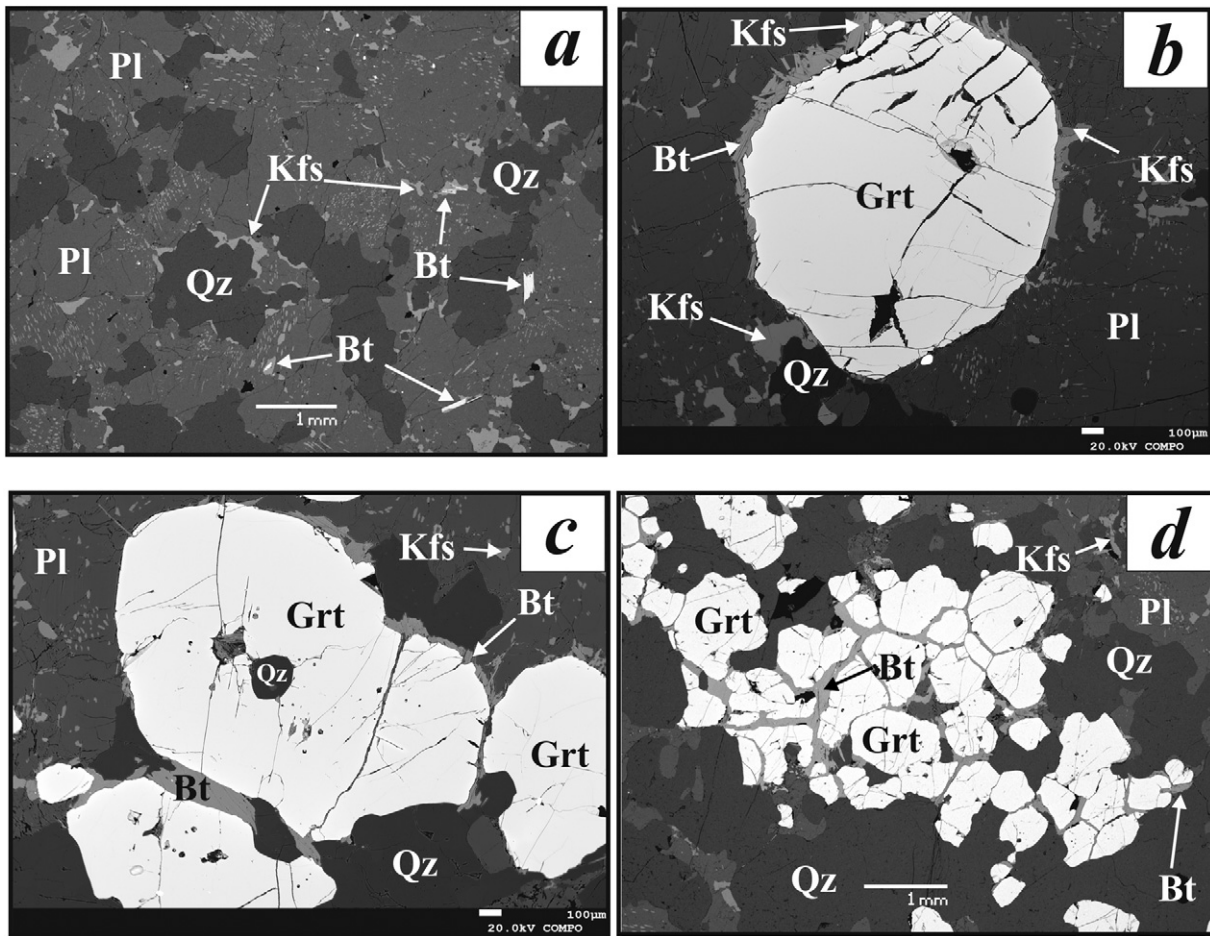


Fig. 5. Petrographic features of the leucocratic granitoids of the Klippit locality. (a) The typical texture of the granitoid: anhedral plagioclases with abundant antiperthitic inclusions, which are mostly concentrated in cores; K-feldspar forming irregular grains and microveins in contacts between plagioclase and quartz; rare small biotite flakes, which are mostly associated with K-feldspar. (b) Large inclusion-free garnet grain partially surrounded by biotite fringe; in the fringe, biotite is locally intergrown with K-feldspar; matrix plagioclase shows antiperthitic inclusions, which are mostly located in the cores of the grains. (c) Group of isometric garnet grains with inclusions of quartz and numerous polyphase silicate and carbonate-bearing inclusions; garnet grains are cemented by rims of biotite; matrix plagioclase shows antiperthitic inclusions. (d) Cluster of garnet grains cemented by biotite, probably, representing an initial strongly fractured large grain; numerous polyphase inclusions are visible in the garnet grains.

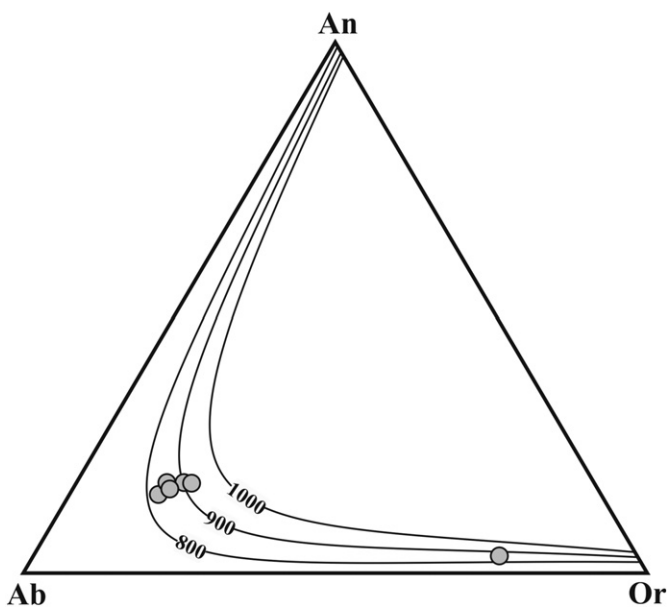


Fig. 6. Reintegrated compositions of exsolved plagioclases and alkali feldspars in granitoids plotted on isotherms in the system Ab–An–Or calculated from the ternary feldspar model of Elkins and Grove (1990).

Pseudosecondary aqueous-salt inclusions are usually of irregular shape, flat, and with sizes up to 20 μm (Fig. 7b). Reliable microthermometric data from these inclusions was not possible to obtain because of their small size and irregular shape. The monophasic inclusions are predominant. Measureable inclusions become pale-yellow during freezing down to ca. -120°C that is typical for the H_2O – NaCl – CaCl_2 fluid inclusions. This conclusion is supported by the initial melting temperature of the inclusions from -55 to -50°C , which are close to the eutectic melting of ice + hydrohalite + antarcticite and suggest a presence of NaCl and CaCl_2 in the solution (e.g. Steele-MacInnis et al., 2011). The final temperature of ice melting for several inclusions varies from -16.2 to -11.5°C corresponding to a salinity of 19.8–15.6 wt% NaCl eq. Only few aqueous-salt inclusions contain bubbles, which occupy less 5 vol%.

5. Carbonate-bearing polyphase inclusions in garnet

5.1. Internal texture, phase assemblage and composition

Carbonate-bearing inclusions occur usually in the centers of garnet grains as rounded clusters (Figs. 5c, d, 8a, b). In some grains, they are associated with inclusions of quartz and zircon, as well as silicate polyphase inclusions (see below). The inclusions are dark or even opaque in plane-polarized light (Fig. 8a, b), but at high magnification, they show a distinct polyphase structure composed of aggregates of

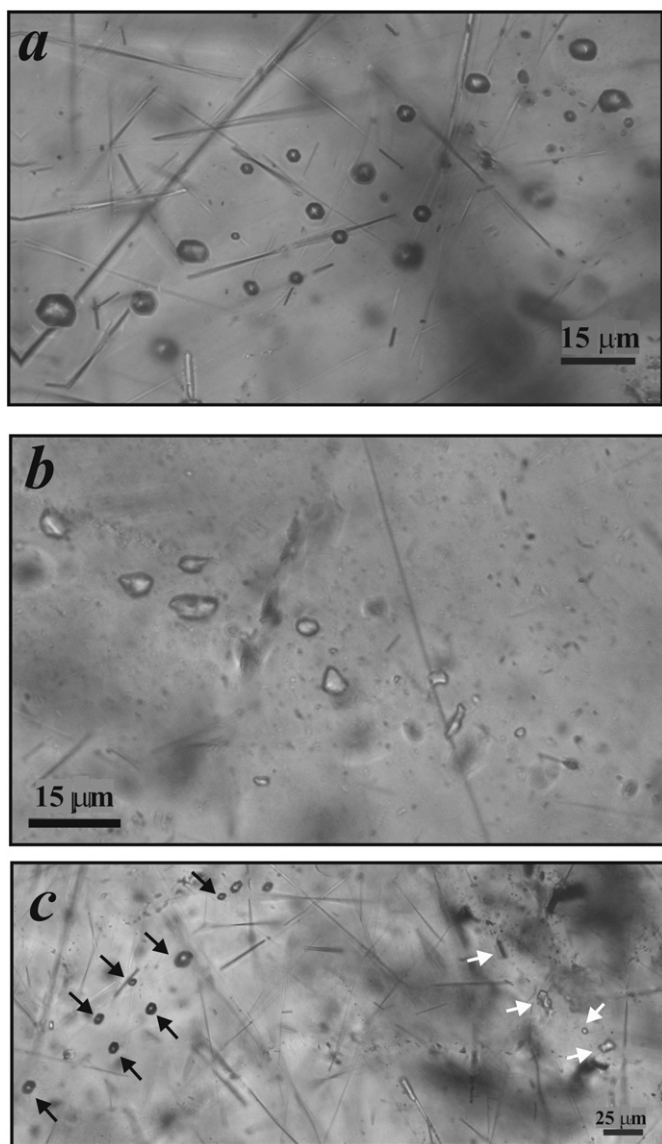


Fig. 7. Fluid inclusions in quartz of the leucocratic granitoids of the Klippit locality. (a) Trail of pseudosecondary CO_2 inclusions. (b) Trail of pseudosecondary aqueous-salt inclusions. (c) Relations between short trails of pseudosecondary CO_2 (black arrows) and aqueous-salt (white arrows) inclusions in a single quartz grain.

birefringent crystals (Fig. 8b). The polyphase structure of the inclusions is well-discerned in cross-polarized light. Usually, the inclusions are isometric (rarely, slightly elongated) and 5–20 μm in diameter, although the size of some inclusions reaches 40 μm (Fig. 8a–f). The carbonate-bearing inclusions show distinct negative crystal shape, which is close to the garnet-like hexagonal habit (Fig. 8c, e, f). Cracks and fissures are usually absent around the inclusions, and the inclusions do not show any evidence for strong decrepitation (for example, any halos). However, some inclusions are touched by thin cracks, which only slightly modify their euhedral shape (Fig. 8d, f). Inclusions are observed at different depth levels in the garnet grains, but do not show any attachment to planar structures in garnet grains (Fig. 8a, b). All such features manifest the distinct primary origin of the inclusions. Composition of garnet in contact with the inclusions does not show any compositional modifications ($X_{\text{Mg}} = 0.28\text{--}0.29$, $X_{\text{Ca}} = 0.02\text{--}0.03$ and X_{Mn} about 0.02).

Most of the measured inclusions are totally filled with crystalline phases (Fig. 8c–f). Among them, carbonates occupy 40–80 vol%. However, some inclusions contain voids or are filled with cryptocrystalline semi-amorphous material. Carbonate-bearing inclusions show a

uniform phase assemblage. The predominant carbonate is magnesite-siderite, which forms crystals with euhedral facets (Fig. 8c–e). The X_{Mg} of carbonates in the studied inclusion varies widely, from 0.74 to 0.77 down to 0.35–0.40, rarely down to 0.25 (Fig. 8c–f; Table S5, Supplementary materials). In some small inclusions, either Fe-rich or Mg-rich carbonates were identified (Fig. 8c); this feature clearly depends on the degree of the inclusion exposition. BSE images of some larger inclusions reveal distinct and strong Fe-Mg zoning of the carbonate crystals (Fig. 8d–f). Cores of the zoned crystals are always more Mg-rich than outer zones, and the difference between Mg-numbers of carbonates in cores and rims of the zoned crystals can reach 45–46 mol% (Fig. 8d, e). The Ca content of these carbonates does not exceed 1 mol%. Calcite (~ 96 mol% CaCO_3) and Ca-Mg-Fe (~ 39 mol% CaCO_3) carbonate along with magnesite-siderite carbonate were identified in only a few inclusions (Fig. 8d, f; Table S5, Supplementary materials). Bands at about 1088 cm^{-1} corresponding, probably, to calcite were identified by Raman spectroscopy of unexposed inclusions. BSE images of the inclusions show that Ca-rich carbonates appear to be texturally later than Mg-Fe carbonates (Fig. 8d, f). In most cases, carbonate is never observed alone in the inclusions, but is always associated with a silicate phase. However, few individual pure carbonate inclusions were observed (Fig. 8g). These inclusions were, probably, accidentally exposed cross sections of larger carbonate-bearing polyphase inclusions.

The major silicate phase is pyrophyllite (Fig. 8c–f), presence of which was confirmed by Raman analyses. This phase forms flakes and layered aggregates among carbonate crystals suggesting that pyrophyllite crystallized after carbonate. Large pyrophyllite flakes (Fig. 8d, f) do not contain MgO and FeO (Table S5, Supplementary materials), whereas pyrophyllite-like acicular aggregates usually show 3–8 wt% MgO + FeO (Table S5, Supplementary materials) suggesting a mixture of pyrophyllite with some unidentified Mg-Fe-rich material (probably carbonate). In addition to the inclusions with discernible crystalline phases, some inclusions are filled with a cryptocrystalline material consisting, probably, of pyrophyllite and carbonates (Fig. 8g). Rutile, zircon, Zn-bearing spinel and ZnS were identified in individual carbonate-bearing inclusions (Fig. 8c–f).

5.2. Raman spectroscopy

Sixteen unexposed carbonate-bearing inclusions were analyzed using Raman spectroscopy. Spectra of most of the analyzed inclusions show vibrations in the region $1084\text{--}1090\text{ cm}^{-1}$, which can be attributed to a magnesite-siderite carbonate phase (Fig. 9). However, just two inclusions showed bands at 1089 and 1090 cm^{-1} corresponding to solid solutions with $X_{\text{Mg}} = 0.32$ and 0.41 , respectively, according to the calibration by Boulard et al. (2012), while most of measured inclusions show vibrations between 1086 and 1087 cm^{-1} corresponding to almost pure siderite. No vibrations attributed to Mg-rich carbonates ($>1092\text{ cm}^{-1}$) were identified. The discrepancy of the Raman results with the results of BSE imaging and microprobe analyses can be explained by zoning of the carbonate crystals in the inclusions: Raman spectra reflect just the outer Fe-rich zones of the crystals that protect Mg-rich cores from the laser beam. The bands at $1087\text{--}1088\text{ cm}^{-1}$ could also correspond to calcite, but this assumption is hard to check. Pyrophyllite was confirmed in the inclusions based on vibrations at 704 , 349 , 259 and 192 cm^{-1} , as well as hydroxyl-related vibrations at $3675\text{--}3676\text{ cm}^{-1}$ (Fig. 9).

Raman signals of gaseous species were not identified in all the measured inclusions. Only six of them showed a doublet vibrations at ~ 1285 and $\sim 1388\text{ cm}^{-1}$ corresponding to CO_2 (Frezzotti et al., 2012; Lamadrid et al., 2014). In addition to the CO_2 bands, Raman spectra usually contain a band at $\sim 2917\text{ cm}^{-1}$ (e.g. Frezzotti et al., 2012) corresponding to CH_4 (Fig. 9). Five measured inclusions showed a wide band in the region $2700\text{--}3600\text{ cm}^{-1}$ (Frezzotti et al., 2012) indicating liquid H_2O (Fig. 9). A wide band at about 1600 cm^{-1} could correspond to the presence of

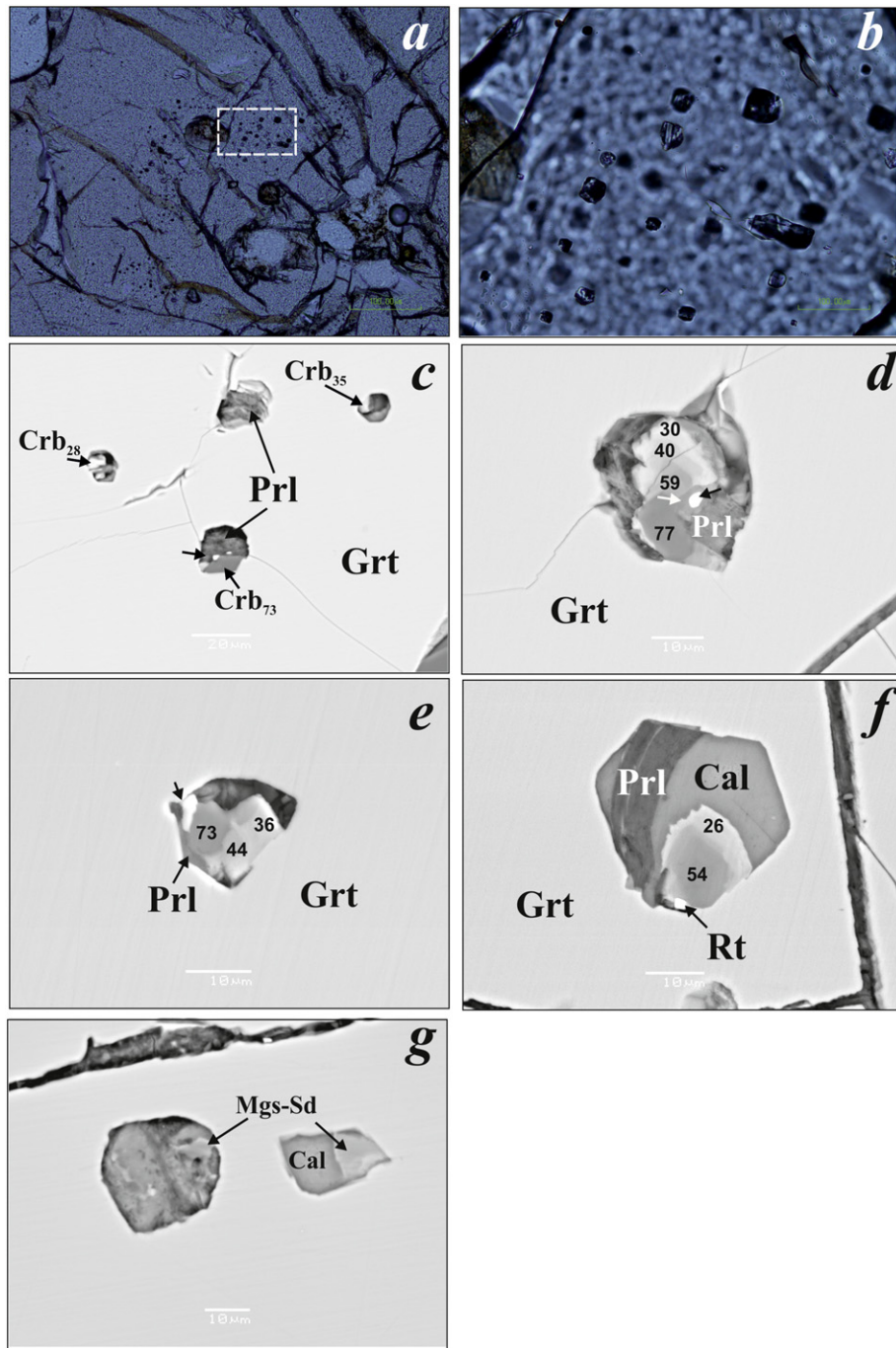


Fig. 8. Carbonate-bearing polyphase inclusions in garnet. (a) Optical image of a group of the carbonate-bearing inclusions in the core of garnet. (b) Closer view of a group of the inclusions; the polyphase structure of the inclusions is clearly seen. (c) Negative crystal shaped inclusion containing calcite and rutile along with the zoned magnesite-siderite carbonate and pyrophyllite; numbers show Mg-number of the Mg-Fe carbonate. (d) Inclusion, slightly modified by cracks, composed of strongly zoned magnesite-siderite daughter crystal and pyrophyllite; the inclusion contains Zn-Cu-Fe sulfide (black arrow), which is rimmed by Ca-Mg-Fe carbonate (white arrow) at the contact with the magnesite-siderite carbonate; left-side portion of the inclusion is filled with Fe-Mg-bearing pyrophyllite-like phase; numbers show Mg-number of the magnesite-siderite carbonate. (e) Small negative crystal shaped inclusion composed of zoned magnesite-siderite carbonate, pyrophyllite and unidentified phase containing Al, Ti, Zn, Si, Fe, Mg (probably a mixture of rutile, Zn-spinel and pyrophyllite). (f) A group of carbonate-bearing inclusions; two inclusions are slightly modified by cracks, although still preserving an euhedral shape, two inclusions are intact; subscript numbers at Crb labels show Mg-numbers of Mg-Fe carbonate; black arrow shows Zn-spinel grain inside the inclusion. (g) Inclusion consisting of calcite and magnesite-siderite and inclusion filled with a cryptocrystalline mixture of pyrophyllite, Ca-bearing and Fe-Mg-carbonates; note that the inclusions are not touched by a crack.

highly disordered low-temperature carboniferous matter in the inclusions (e.g. Beyssac et al., 2002).

5.3. Composition of the inclusions

The composition of the exposed areas of the carbonate-bearing inclusions was measured via the rastered microprobe analyses. Well-

exposed large (20–40 μm) inclusions with euhedral shapes were used. The contribution of the garnet composition to the rastered analysis has been estimated for every inclusion by means of a series of analyses over various areas either including or not including contacting garnet. For comparison, this procedure was also repeated for the exposed euhedral quartz inclusions in garnet of a size comparable to the size of the carbonate-bearing inclusions (20–40 μm). This approach showed

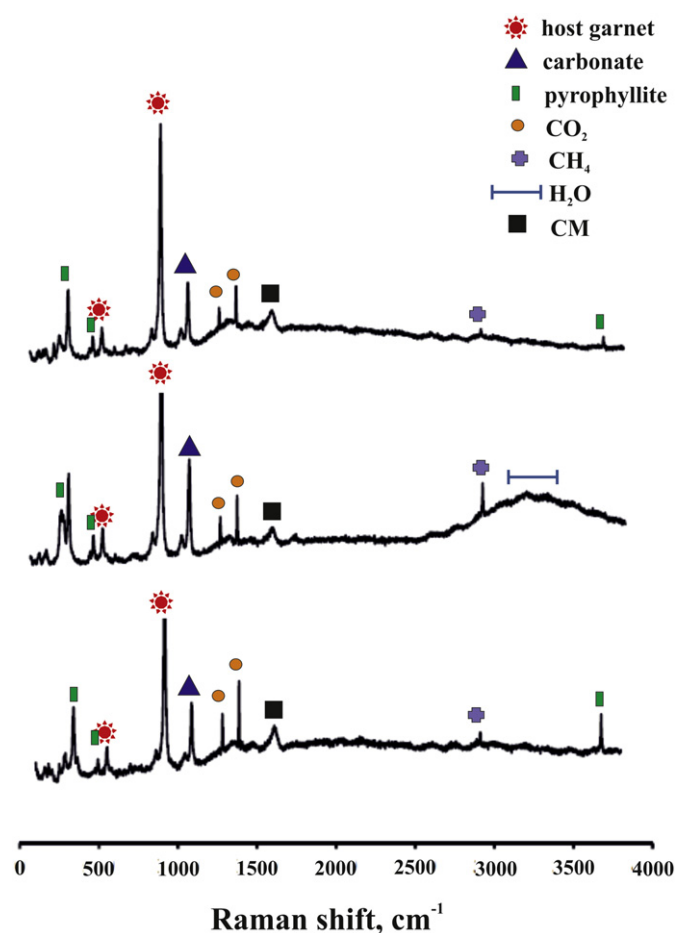


Fig. 9. Raman spectra of three unexposed carbonate-bearing polyphase inclusions in garnet showing major crystalline phases (carbonate, pyrophyllite), fluid species (CO_2 , CH_4 , H_2O) and disordered carbonaceous matter (CM).

that the garnet composition contribution was rather small and relatively constant in rastering of the area confined by outlines of an inclusion.

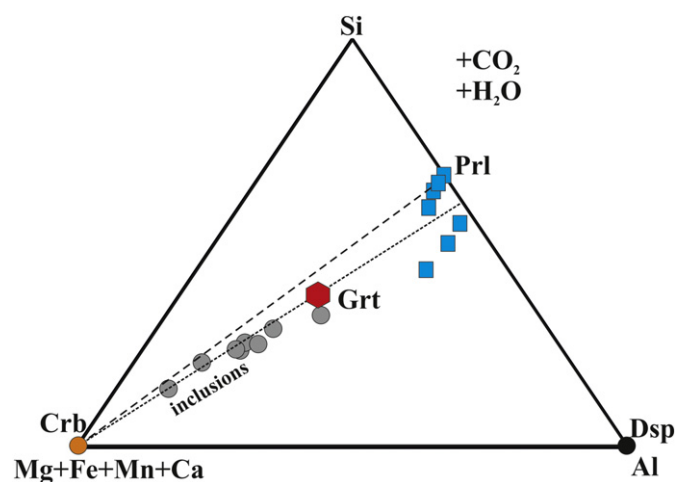


Fig. 10. Cation ratios in the area analyses of exposed inclusions (gray circles) in comparison to the composition of garnet (red hexagon), carbonate (orange circle) and pyrophyllite phase (blue rectangles).

The analyses of the variously exposed carbonate-bearing inclusions are shown in Table S6 in On-line supplementary material. Wide variations of the SiO_2 content from about 0 wt% (the individual carbonate inclusions; Fig. 8g) up to about 32 wt% (normalized to 100 wt%) show a positive correlation with Al_2O_3 , which reaches about 24 wt% in the analysis with the highest SiO_2 . The SiO_2 content is negatively correlated with the sum $\text{MgO} + \text{FeO} + \text{CaO} + \text{MnO}$. Such correlations are related to various carbonate/pyrophyllite (Crb/PrI) proportions in the measured areas. The measured compositions lie closely along a tie-line connecting carbonate (Crb) and garnet (Grt) compositions in the (Mg + Fe + Mn + Ca)-Al-Si triangle (Fig. 10). However, the tie-line is displaced from the tie-line connecting compositions of carbonate to an ideal pyrophyllite composition (PrI) suggesting an Al excess in the inclusions. Higher measured Al and Si is related to higher displacement from the tie-line, implying that the Al excess is related to the Fe-Mg-bearing pyrophyllite-like aggregates in the inclusions. Only one data point of the measured areas is located close to the Grt composition (Fig. 10). However, this area is measured in the less exposed inclusion and includes a fragment of garnet (with the same compositional characteristics as of the host garnet), which was probably rubbed into the inclusion during polishing. All other measured areas show compositions, which is notably displaced from Grt toward Crb (Fig. 10).

In the absence of an individual Ca-bearing phase, all measured inclusions show 0.5–2.4 wt% CaO (Table S6 in On-line supplementary material). The CaO content in the calcite-bearing inclusions (Fig. 8c) reaches 34 wt%. The analyses indicate the presence of P_2O_5 (0–0.7 wt%), TiO_2 (0.01–1.9 wt%), SO_3 (0–1.2 wt%), ZnO (0.03–0.8 wt%) and MnO (0.6–1.4 wt%). The alkali content is low, 0.08–0.29 wt% (Table S6 in On-line supplementary material).

6. Silicate polyphase inclusions in garnet

Two morphological types of carbonate-free polyphase inclusions are distinguished in garnets. Large (up to 200 μm) irregularly shaped inclusions are usually surrounded by numerous cracks (Fig. 11a). The inclusions usually show cusped offshoots filled with material similar to that in the inclusions. This feature is very similar to decrepitated melt inclusions (e.g. Cesare et al., 2015). Predominant phases in these inclusions are biotite, quartz, and plagioclase. K-feldspar and aluminum silicate are sporadically present in some inclusions (Fig. 11a). Some smaller inclusions (<20 μm) containing quartz and biotite show negative-crystal shape (Fig. 11b). These inclusions usually accompany larger ones (Fig. 11a). They might be interpreted either as individual inclusions or as accidentally exposed cross sections of larger polyphase silicate inclusions. In general, textural features and phase composition of the inclusions are similar to those characteristic for “granitic” melt inclusions in peritectic minerals from migmatites (e.g. Cesare et al., 2015).

In addition to the silicate inclusions filled with discernible crystalline aggregates, garnets contain rare inclusions filled with cryptocrystalline material and containing locally flakes of biotite (Fig. 11a, c). These inclusions show negative crystal shape, characteristic for melt inclusions. Concentric fissures around these inclusions (Fig. 11c) suggest contraction of a material inside the inclusions during solidification. The cryptocrystalline material shows a high SiO_2 content, and, thus, this type of inclusions can be classified as silicate melt inclusions as well.

Biotite in the polyphase inclusions is TiO_2 -poor (<0.5 wt%), but shows much higher $X_{\text{Mg}} = 0.74$ –0.76 than biotite from the rock matrix. The Al content of the biotite is about 2.0 a.p.f.u., i.e. ~50 mol% of the eastonite-siderophyllite component. The inclusion-hosted biotite is F-free and contains 0.01–0.02 wt% Cl. Plagioclase in the polyphase inclusions shows $X_{\text{An}} = 0.21$ –0.22.

Silicate polyphase inclusions coexist with the carbonate-bearing polyphase inclusions in a single garnet grain suggesting their coeval entrapment (Fig. 11a).

7. Geochronology

Zircons were separated from a sample of trondhjemite (GAB95b). Single spot analyses were performed for 36 individual zircon grains, whereas one large grain was analyzed in three different spots (Fig. 12a, left upper image). Among 39 measurements, 27 were corrected for 0.05–4.2% common lead using the [Stacey and Kramers \(1975\)](#) values for common Pb at the time of the uncorrected $^{206}\text{Pb}/^{238}\text{U}$ age of the zircon. All geochronological data are presented in Table S7 in the On-line supplementary material. The age data for zircons are clustered in three groups.

- (1) Cores of 6 grains yielded the oldest concordant ages ranging from 2838 ± 6 Ma to 2750 ± 7 Ma (2σ) (Fig. 13a, b). Four of these grains have the highest Th/U ratios (0.20–0.24).
- (2) The largest age cluster consists of cores of 29 analyzed zircons with ages varying from 2729 ± 7 Ma to 2651 ± 3 Ma, with the majority of these age data being concordant with exception of two measurements (Fig. 13a, b). It is difficult to distinguish separate populations in this cluster, since neighboring age values are within 2σ error. Th/U ratios are more uniform and generally lower than in the older cluster (most of them ranging from 0.02 to 0.07).
- (3) Cores of three small zircon grains as well as a rim of large grain show the youngest age cluster. The concordant ages vary from 2632 ± 6 Ma to 2476 ± 7 Ma (Fig. 13a, b). Th/U ratios are similar to the second cluster (0.05–0.08).

Monazites were analyzed directly in a thin section of sample GAB95b (Fig. 12b). Nine single spot analyses were performed on nine individual grains and three separate analyses were done for one large grain. BSE images of four selected monazites with analytical spots are shown in Fig. 12b. Analyzed monazite grains yielded concordant ages varying from 2749 ± 5 Ma to 2667 ± 5 Ma (Fig. 13c) closely corresponding to the range obtained for the second age cluster of zircons. A weighted average age of 2698 ± 40 Ma (MSWD = 1.9) is calculated for 12 separate monazite analyses supporting the concordia age.

8. P-T conditions of the granitoid crystallization

8.1. Conventional thermobarometry

Granitoids of the Klippit locality contain no assemblages of Mg-Fe minerals suitable for calculations of P-T conditions of the high-temperature stage of their evolution. The only approach to estimate temperatures of granite crystallization is to use re-integrated compositions of antiperthite plagioclases and perthite alkali feldspars from the rocks. Fig. 6 compares these compositions with isotherms in the ternary system albite-orthoclase-anorthite calculated using the equations by [Elkins and Grove \(1990\)](#) for a pressure of 6.5 kbar (see below). The data points mainly fall between the 800 and 900°C isotherms.

Cooling of the granitoids is reflected in the formation of biotite in the rocks. Small biotite flakes dispersed in the matrix are predominantly associated with K-feldspar (Fig. 5a), which is the late mineral in the granitoids. Individual flakes are characterized by higher FeO content, implying that this biotite was probably not equilibrated with garnet. Formation of the biotite veins in fractured garnet and fringes around garnet grains is accompanied by a decrease of X_{Mg} in garnet. We applied the winTWQ (version 2.32) software ([Berman, 2007](#)) with self-consistent end-member mineral properties according to [Berman \(1988\)](#) and solid solution models for garnet and biotite of [Berman and Aranovich \(1996\)](#) to estimate temperatures for compositions of contacting biotite and garnet. For the biotite veins in fractured garnet (Fig. 5d), this procedure gave a temperature around 540 °C.

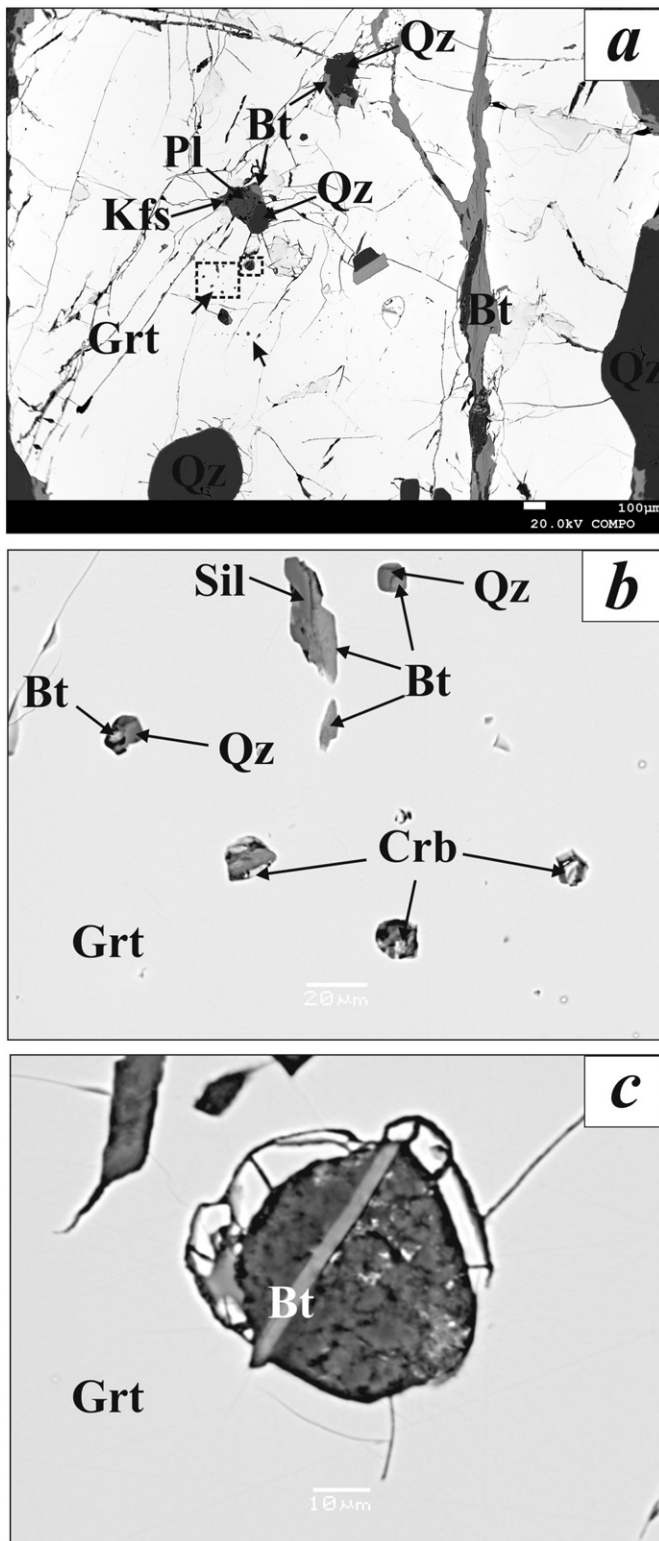


Fig. 11. Silicate polyphase inclusion in garnet. (a) Large irregular polyphase “granitic” inclusions (Bt + Qz + Pl ± Kfs ± Sil) surrounded by smaller silicate and carbonate-bearing inclusions (see detailed images b and c); note numerous cracks, as well as offshoots, around the polyphase inclusions; dashed frames show locations of images b and c; black arrows show location of carbonate-bearing inclusions; (b) Small polyphase “granitic” inclusions coexisting with the carbonate-bearing inclusions; some inclusions show negative crystal shape; (c) Silicate inclusion filled with cryptocrystalline aggregate with a biotite needle surrounded by concentric fissures.

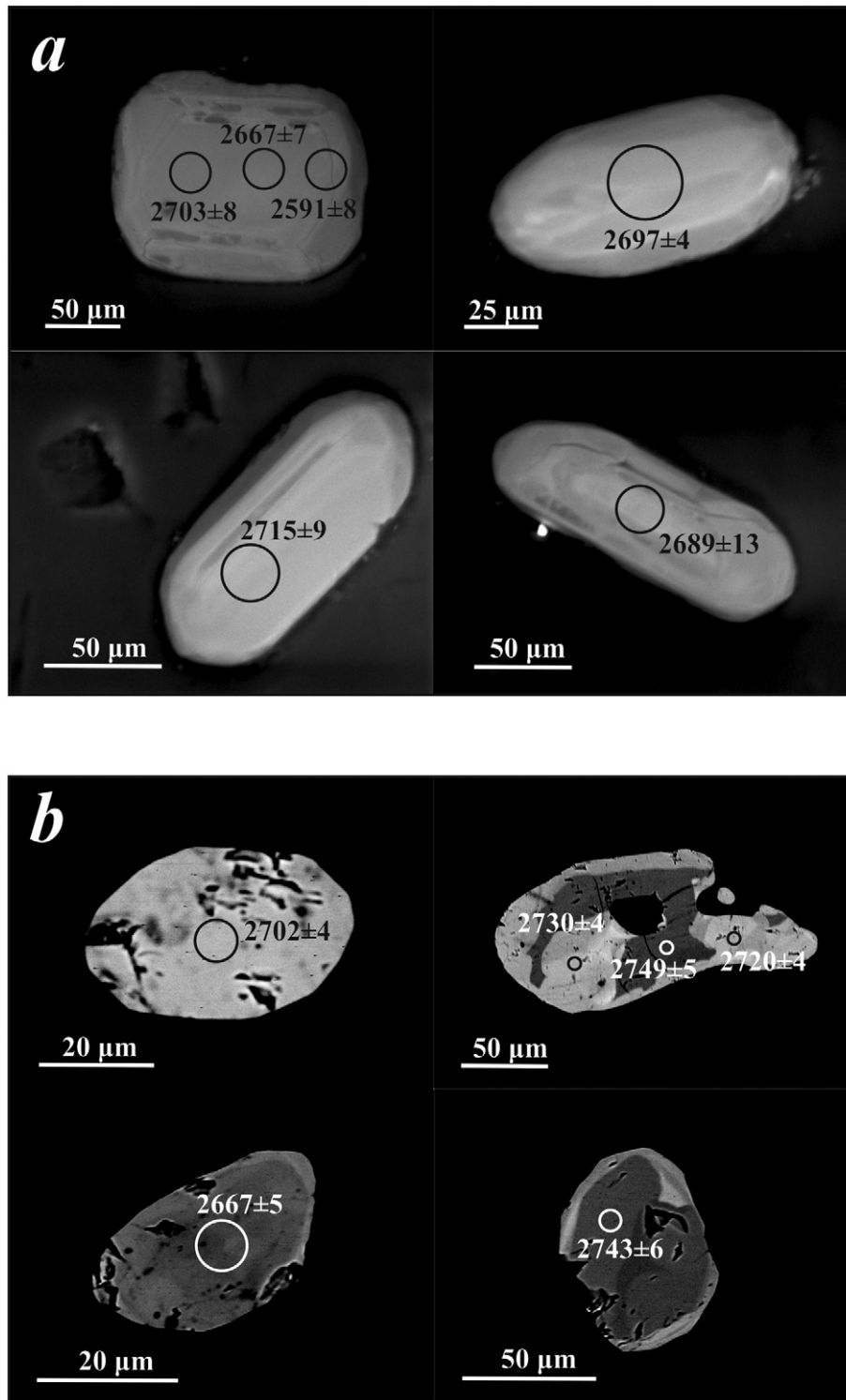


Fig. 12. Representative images of zircons and monazites showing analytical spots and corresponding ages. (a) CL images of four analyzed zircon grains (beam size is 25 μm), (b) BSE images of four analyzed monazite grains (beam size is 7 μm).

Compositions of fringes of Ti-poor biotite around garnet (Fig. 5b, c) correspond to temperatures of 480–500 °C. Using reactions involving the anorthite component of plagioclase, an average pressure of 6.5 kbar was computed for these temperatures. The calculated garnet-biotite temperatures are far below the granite solidus, especially in presence of H₂O–CO₂ fluid. Thus, biotite in the granitoids of the Klipput locality was produced, probably, after solidification via reactions of garnet and

K-feldspar in presence of a fluid. This is reflected in biotite fringes around garnet containing relics of K-feldspar (Fig. 5b).

8.2. Phase equilibria modeling of granitoid assemblage

Mineralogical data, fluid inclusions and re-integrated composition of feldspars indicate that the crystallization of granitoids at the Klipput

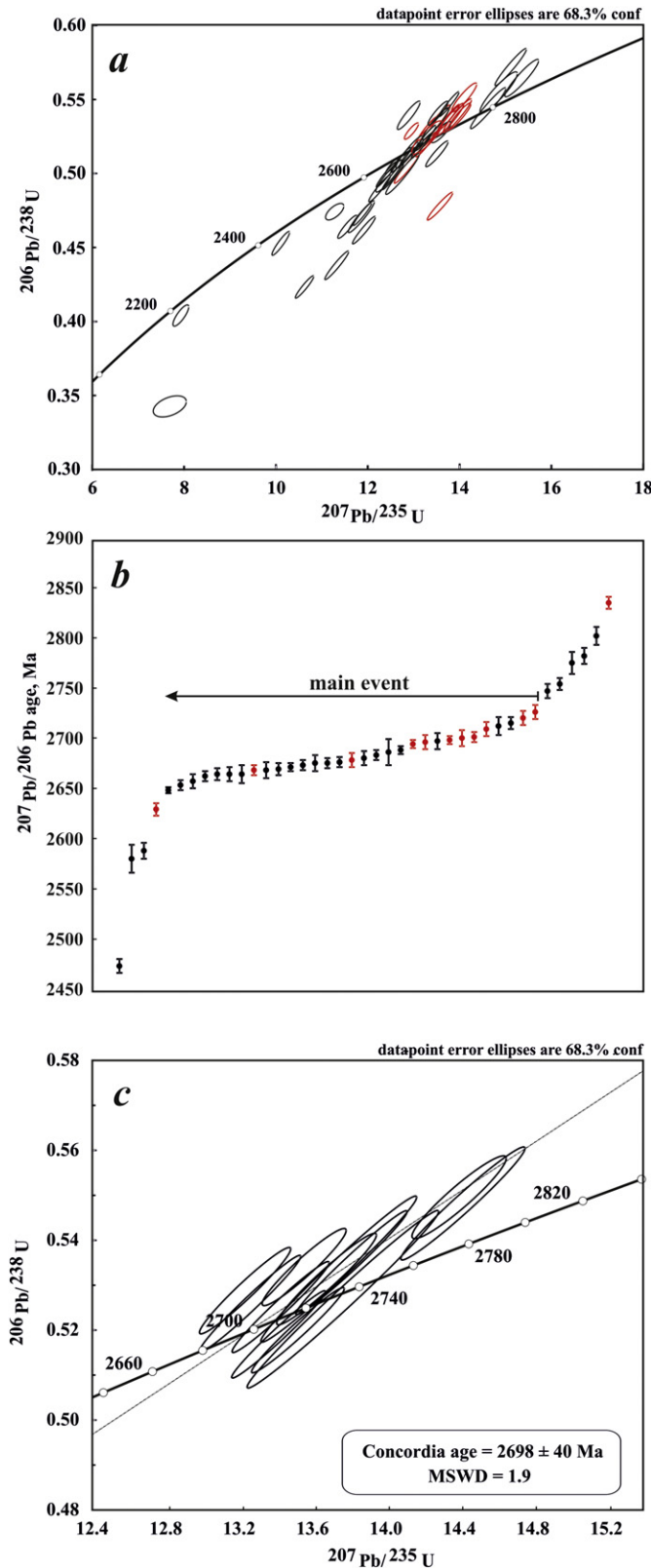


Fig. 13. U-Pb data plots for zircons and monazites from the trondhjemitic sample GAB95b of the Klippitz locality. (a) U-Pb concordia diagram for all the analyzed zircons. Black ellipses show analyses corrected for common lead, red ellipses show CPb-free analyses. (b) $^{207}\text{Pb}/^{206}\text{Pb}$ zircon ages in order of increasing age showing a continuous event at $\sim 2.73\text{--}2.65$ Ga (29 analyses). (c) U-Pb concordia diagram for monazites showing a weighted average age of 2698 ± 40 Ma.

locality began at temperatures around 900 °C in the presence of a CO₂-bearing fluid. In order to model the mineral assemblages of the granitoids and to demonstrate their dependence on P, T and fluid composition, we constructed P-T and T-X_{CO₂} pseudosections for the representative bulk composition (wt%): SiO₂ – 73.84, TiO₂ – 0.02, Al₂O₃ – 14.87, FeO – 1.044, MnO – 0.023, MgO – 0.28, CaO – 1.06, Na₂O – 5.06, K₂O – 2.86. A “free” O₂ (as a monitor of Fe₂O₃) content of 0.001 wt% was taken arbitrarily based on the following observations. Garnet containing relatively low Fe³⁺ concentrations is the only principle Fe³⁺-bearing phase in the granitoids. Its low modal content imposes a low Fe³⁺ content on the rock bulk composition. Stability of pyrite instead of pyrrhotite in the granitoids also implies low Fe₂O₃ (i.e. “free O₂”) content in the rocks.

Phase equilibria were modelled via Gibbs free energy minimization in the system $\text{MnO}-\text{Na}_2\text{O}-\text{CaO}-\text{K}_2\text{O}-\text{FeO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{TiO}_2-\text{O}_2$ (MnNCKFMASHTO) using the PERPLE_X software (Connolly, 2005) in version 6.7.7 for Windows. The updated standard properties database hp11ver.dat (Holland and Powell, 2011) and solution model database solution_model.dat (<http://www.perplex.ethz.ch>) were applied for modeling. The following models from White et al. (2014) were applied for mineral and melt solutions: “Gt(W)” for Fe^{3+} -bearing Ca-Mg-Fe-Mn garnet, “Bi(W)” for Ti and Fe^{3+} -bearing biotite, Ilm(WPH) for the Mg-Mn- Fe^{3+} -bearing ilmenite. The model “feldspar”, based on the solution model of Fuhrman and Lindsley (1988), was taken for ternary feldspar. The model melt(W) from White et al. (2014) was used for the NCKFMASH silicate melt. In addition, we used model Mica (W) (White et al., 2014) for the white mica solid solution and Cc(AE) (Anovitz and Essene, 1987) for the Ca-Mg-Fe carbonate solid solution to model low temperature assemblages of the rock.

The T- X_{CO_2} pseudosection was computed for the system saturated with a H_2O - CO_2 fluid with variable X_{CO_2} . The pseudosection predicts relatively high liquidus for the leucogranite. This feature is related to either entrainment of peritectic minerals in the magma (e.g. [Taylor and Stevens, 2010](#)) or contamination of the magma with metapelitic

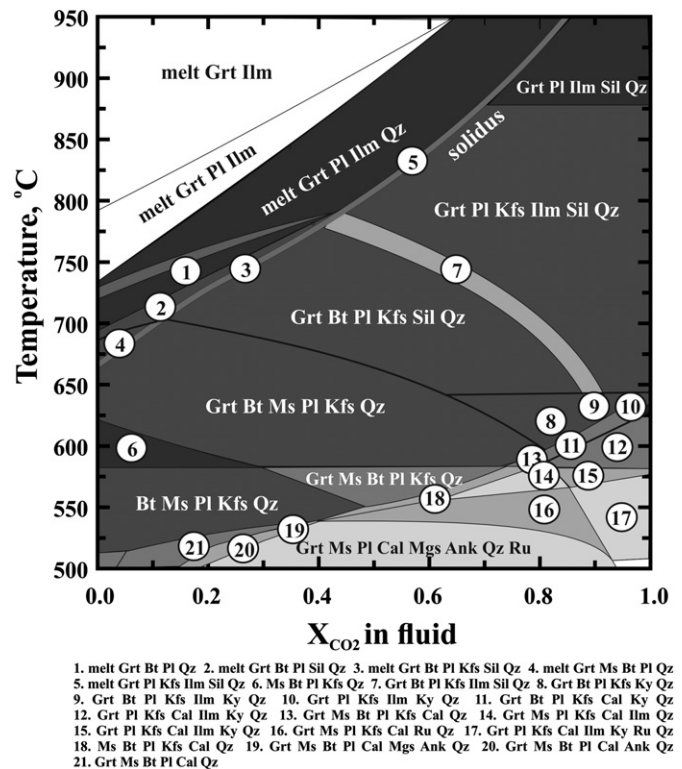


Fig. 14. T-X_{CO2} pseudosection at 6.5 kbar computed for the representative bulk composition of the granitoid from the Klippit locality (see text for the composition).

material. The granitoid melt begins crystallization with garnet and ilmenite, which are followed by quartz and plagioclase (Fig. 14). K-feldspar coexists with a melt only at the solidus (Fig. 14). This feature is consistent with the appearance of K-feldspar predominantly as rims at plagioclase and quartz grain boundaries (Fig. 5a–d). Solidus temperatures are extremely dependent on X_{CO_2} , increasing from about 670 °C in the absence of CO_2 up to 1000 °C at $X_{\text{CO}_2} > 0.8$. K-feldspar extensively forms in the sub-solidus region via exsolution from plagioclase solid solution on cooling, consistent with the petrographic observations (Fig. 5a–d). The subsolidus assemblage at $X_{\text{CO}_2} > 0.45$ is Grt + Pl + Kfs + Qz + Sil + Ilm (Fig. 14). The sillimanite content predicted for the above bulk composition is about 1 vol%. Biotite coexists with the melt only at $X_{\text{CO}_2} < 0.45$ and its stability becomes more inhibited at lower temperatures with increasing CO_2 content in the fluid (Fig. 14). At $X_{\text{CO}_2} > 0.45$, biotite appears only in the subsolidus region on cooling, reflecting the absence of biotite-forming melt-involving reactions in the studied granitoids. According to conventional thermometry, biotite began to form in the rock at temperatures around 600 °C. According to the pseudosection, the formation of biotite at this temperature could occur at $X_{\text{CO}_2} > 0.7$ in the fluid (Fig. 14). Such high content of CO_2 does not prevent the appearance of muscovite at lower temperatures. This mineral locally occurs in the rock matrix and replaces late biotite.

In the T- X_{CO_2} pseudosection (Fig. 14), isopleths $X_{\text{Ca}}^{\text{Grt}} = 0.02$ –0.03, $X_{\text{Mg}}^{\text{Grt}} = 0.28$ –0.29 and $X_{\text{An}}^{\text{Pl}} = 0.14$ –0.17, characteristic for the rock, are subparallel to each other and to the solidus line. They overlap within the phase field melt + Grt + Pl + Ilm + Qz very close to the solidus. The plagioclase isopleths indicate that X_{An} in plagioclase increases with increasing temperature above solidus. This regularity is consistent with higher $X_{\text{An}}^{\text{Pl}}$ in cores of matrix plagioclase as well as the presence of rare plagioclase inclusions with $X_{\text{An}}^{\text{Pl}} = 0.20$ in garnet.

In order to specify P-T conditions for the granitoids, the P-T pseudosection (Fig. 15) and corresponding isopleths for garnet and plagioclase were computed at $X_{\text{CO}_2} = 0.7$. The P-T pseudosection demonstrates that the sequence of mineral crystallization is practically independent of pressure (phase field boundaries are sub-vertical). The

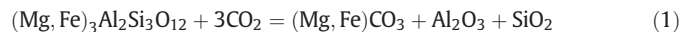
assemblage Grt + Pl + Ilm + Qz coexists with the melt within the whole pressure range. Similar to the T- X_{CO_2} pseudosection, isopleths $X_{\text{Ca}}^{\text{Grt}} = 0.02$ –0.03, $X_{\text{Mg}}^{\text{Grt}} = 0.28$ –0.29 and $X_{\text{An}}^{\text{Pl}} = 0.14$ –0.17 are subparallel to each other and overlap within this phase field very close to the solidus within 850–900 °C. This interval is consistent with the ternary feldspar thermometry (Fig. 6). However, the isopleths do not allow pressure evaluation.

9. Discussion

9.1. Nature of the carbonate-rich inclusions

Magnesite-siderite and other carbonate phases associated with CO_2 -rich fluid inclusions in various Mg-Fe minerals were previously reported in high-grade rocks (Herms and Schenk, 1992, 1998; Srikantappa et al., 1992; Bolder-Schrijver et al., 2000; Tsunogae et al., 2002; Lamadrid et al., 2014; Ferrero et al., 2016; Tacchetto et al., 2018). Three points of view on the origin of carbonates in the inclusions exist. Bolder-Schrijver et al. (2000) reported magnesite and rare pyrophyllite in fluid inclusions in garnet from sapphirine-bearing granulites from central Sri Lanka. From the constant solid/bulk inclusion volume (about 0.15) ratio in large inclusions, the authors concluded that magnesite was not an incidental captured solid but a true daughter mineral (Bolder-Schrijver et al., 2000, p. 265–266). Because of the rarity of the phase, the formation of pyrophyllite was not discussed in detail. Based on the observation that the size of the solid phase is substantially larger than the coexisting fluid phase in the inclusions, Tsunogae et al. (2002) interpreted magnesite inclusions in sapphirine in high-temperature granulites of Tonagh Island, Antarctica, as discrete mineral inclusions trapped along with fluids during the growth of sapphirine. Thus, in these studies, magnesite was considered to be precipitated directly from a homogeneous carbonic fluid with dissolved MgCO_3 rather than formed via post-entrapment reactions between CO_2 -rich fluid inclusion and host Mg-Fe mineral.

In contrast, Herms and Schenk (1992) interpreted Fe-Mg carbonate in fluid inclusions in cordierite from metapelites of Southern Calabria, Italy, as a product of the reaction cordierite + CO_2 = magnesite + Al-silicate + quartz at the inclusion walls at temperatures beyond the cordierite stability. A similar interpretation was proposed by Tacchetto et al. (2018) for the carbonate-bearing inclusions in peritectic garnets in felsic granulites from the Upper Deck domain of the Athabasca granulite terrane, Canada. Magnesite-siderite carbonate (calcite is extremely rare) in these inclusions is associated with quartz, graphite, corundum and minute amount of pyrophyllite, Zn-spinel and sulfides. The inclusions contain abundant CO_2 with traces of CH_4 and N_2 . The high CO_2 content and its low density (0.5–0.7 g/cm³) of the fluid in the carbonate-bearing inclusions was a major argument in favor of interpretation of carbonates as the daughter crystals formed by a post-entrapment reaction (Tacchetto et al., 2018)



Association of corundum with quartz was explained by sluggish kinetics of the reaction in the small inclusion volume.

The inclusions described in the above studies are substantially different from the inclusions reported by Ferrero et al. (2016) in garnets of migmatites in the Oberpfalz, Bohemian Massif. The predominant carbonate phase in the inclusions is calcite, while hydrous phases are clinochlore and white mica. Mg-Fe carbonate and pyrophyllite were identified only in the CO_2 -rich fluid inclusions associated with the calcite-bearing inclusions. This is the evidence that calcite-bearing and magnesite-siderite-bearing inclusions represent the crystallization products of different substances. Calcite-bearing inclusions were interpreted as crystallized droplets of carbonatitic melt generated along with the granitic melt (which was found as polyphase Bt + Pl + Qtz inclusions) during anatexis of heterogeneous pelitic sequences

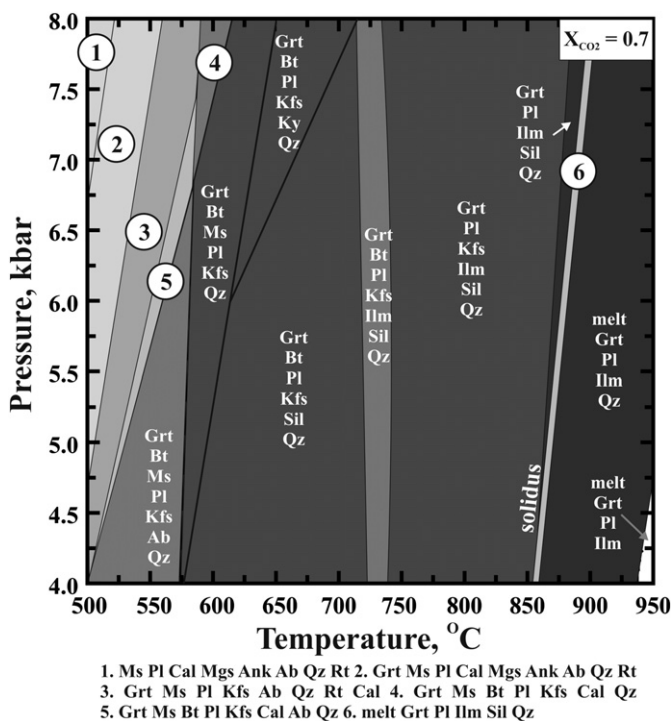


Fig. 15. P-T pseudosection computed for the representative bulk composition of the granitoid from the Klippit locality (see text for the composition) at $X_{\text{CO}_2} = 0.7$.

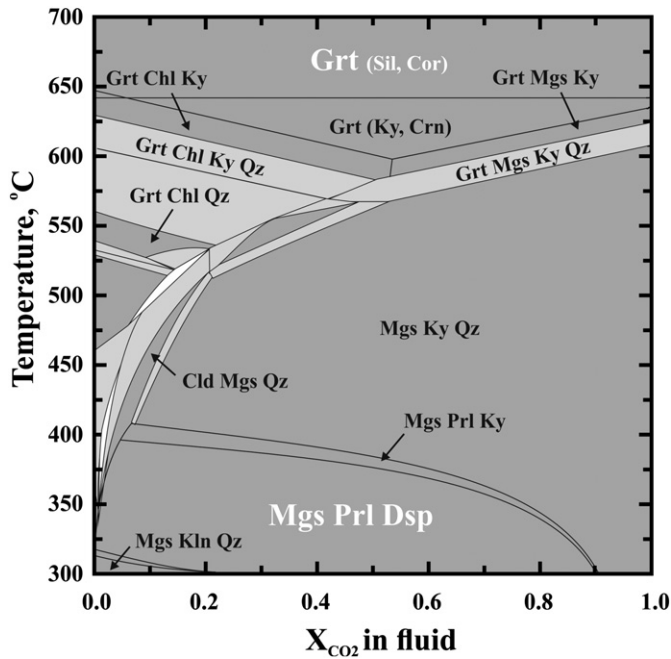


Fig. 16. T- X_{CO_2} pseudosection at 6.5 kbar illustrating phase assemblages forming via interaction of host garnet (see text for the composition) with the H_2O - CO_2 fluid trapped as inclusion. The assemblage Mgs (magnesite-siderite carbonate; $X_{\text{Mg}} = 0.29$) with pyrophyllite (+diaspore) characteristic for the polyphase inclusions is highlighted.

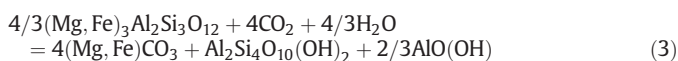
intercalated with marbles at high CO_2 activity (Ferrero et al., 2016). Mg-Fe carbonates and pyrophyllite seemed to be precipitated from the CO_2 - H_2O fluid or formed via reactions of this fluid with the inclusion walls.

The carbonate-bearing inclusion in the garnets of the Klippit locality can be subdivided into two groups: (1) the predominant inclusions consisting of magnesite-siderite and pyrophyllite and (2) inclusions involving Ca-bearing carbonates in addition to Mg-Fe-carbonates and pyrophyllite. In order to model these phase assemblages, the T- X_{CO_2} pseudosection for the system garnet- H_2O - CO_2 has been computed for 6.5 kbar and 700–300 °C (Fig. 16). The following composition of garnet (slightly corrected after the microprobe analysis) was assumed (wt%): SiO_2 – 37.8, Al_2O_3 – 21.39, FeO – 31.42, MgO – 6.93, CaO – 1.11, which gives $X_{\text{Mg}} = 0.28$, similar to the garnet cores in the granitoid. The system was assumed to be saturated with the aqueous-carbonic fluid. The model Cc(AE) (Anovitz and Essene, 1987) for the Ca-Mg-Fe carbonate solid solution was applied, models for chlorite Chl(W) and chloritoid Cld(W) solid solutions (White et al., 2014) were included in the calculation since these phases appear in the H_2O -rich portion of the pseudosection (Fig. 16).

The pseudosection (Fig. 16) demonstrates that garnet of the above composition is stable with the H_2O - CO_2 fluid down to about 600 °C (at $X_{\text{CO}_2} \sim 0.5$) (insignificant amounts, 0.01 vol% each, of Crn and Ky appear because of slight deviation of the starting garnet composition from ideality). Below this temperature, garnet decomposes to the assemblage Ca-bearing Fe-Mg-carbonate (49.8 vol%), kyanite (24.8 vol%) and quartz (25.4 vol%):

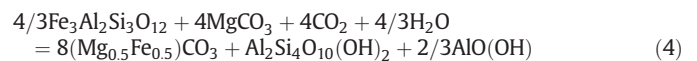


At temperature below 400 °C, the assemblage of carbonate (45.8 vol%) with pyrophyllite (49.6 vol%) and diaspore (4.7 vol%) appears via the reaction



This assemblage with the above volume ratio of phases exists within a wide fluid composition range. No traces of diaspore were identified in the inclusions both using both microprobe and Raman. Nevertheless, Fig. 10 indicates that all measured compositions of the inclusions are displaced from the Crb-Prl tie-line toward the higher-Al side. This shift of composition is attributed to the Al excess in the cryptocrystalline aggregates, which are common in the inclusions (e.g. Fig. 8d).

Thus, reaction (3) and the pseudosection (Fig. 16) adequately reproduce the major assemblage inside the inclusions. No higher-temperature aluminous phases, i.e. corundum, kyanite, or quartz, nor their relics, were identified in the inclusions. This feature distinguishes the studied inclusions from those described by Tacchetto et al. (2018), who found corundum and quartz in the carbonate-bearing inclusions as a result of reaction (1). This suggests that the assemblage of the inclusions from the Klippit locality precipitated directly at temperatures below 400 °C without any evidence for higher-temperatures reactions with the host garnet. Ca-rich carbonate is not predicted by the pseudosection at the CaO bulk content imposed by the composition of the starting garnet. Therefore, Ca-rich carbonates observed in some inclusions (Fig. 8d, f, g) were precipitated directly from the substance trapped in the inclusions rather than via reactions with garnet or exsolution from the carbonate solid solution on cooling. The bulk $X_{\text{Mg}} = \text{Mg}/(\text{Mg} + \text{Fe} + \text{Mn})$ of the inclusions is always above 0.40 (Table S5 in Supplementary material). It is much higher than 0.29, which is expected if the assemblage carbonate + pyrophyllite ($\pm$ diaspore) was produced by carbonation of the host garnet. Fig. 10 shows that despite variable proportions of carbonates and pyrophyllite in the exposed inclusions (Fig. 8a–g), all obtained analyses (Table S6 in On-line supplementary material) represent compositions, which are notably shifted from garnet (Grt) toward the carbonate apex (Crb). This suggests that the inclusions initially contained the carbonate constituent before the reactions of the inclusions with the host garnet. Due to the high $\text{Mg}/(\text{Mg} + \text{Fe} + \text{Mn})$ ratio, it might be assumed that this constituent is MgCO_3 . This is supported by zoning of the carbonate daughter crystals (Fig. 8d–f) suggesting that Mg-rich carbonate was the first to precipitate in the inclusions, whereas Fe-rich varieties crystallized later. Such zoning is expected on crystallization of the Ca-Mg-Fe carbonate melts and is known in carbonates from carbonatites (e.g. Woolley and Buckley, 1993). Enrichment of carbonate in Fe and formation of pyrophyllite (below 400 °C) are the results of this fluid/melt-garnet reaction, which can be represented, for instance, as



where MgCO_3 , CO_2 and H_2O are components of the initial fluid/melt.

The above observations suggest that carbonate-rich inclusions in garnets from the granitoids of the Klippit locality initially were trapped as a substance, which involved Ca-Mg-Fe carbonate components, H_2O and CO_2 . This substance could be either aqueous-carbonic fluid with dissolved carbonates or water-bearing carbonate melt. Both substances are possible taking into account the high H_2O solubility in carbonate melts (Keppler, 2003) and elevated solubility of carbonates in an aqueous fluid equilibrated with the carbonate melts (e.g. Veksler and Keppler, 2000). Experiments in the systems CaO - MgO - CO_2 - H_2O and CaO - MgO - SiO_2 - CO_2 - H_2O at 4–10 kbar revealed the existence of eutectic carbonate melts equilibrated with aqueous fluids at temperatures of 560–600 °C (Boettcher et al., 1980 and references therein). Although there are no experimental data on systems involving FeO and alkalis, these components could further suppress the formation temperature of the carbonate melts, as is observed for carbonatite melts at upper-mantle pressures (see Hammouda and Keshav, 2015 for review of experimental data).

9.2. Origin of the carbonate-bearing fluids

The above discussion implies that MgCO_3 -saturated fluid or melt that crystallized as polyphase inclusions in garnet must have been equilibrated initially with a MgO and CO_2 -rich source. This compositional feature can be realized in carbonated (magnesite and/or dolomite-bearing) ultramafic rocks. However, granulite-facies ultramafic rocks in the SMZ do not include carbonates in their prograde assemblages (orthopyroxene + olivine + calcic amphibole + spinel; van Schalkwyk and van Reenen, 1992). Carbonates observed in these rocks are exclusively products of interaction with a CO_2 -rich fluid ($X_{\text{CO}_2} > 0.67$) during the retrograde cooling stage near 670°C (van Schalkwyk and van Reenen, 1992). Thus, ultrabasic rocks within the granulite complex cannot serve as the source for the MgO and CO_2 -rich fluids, and a source must be searched for from outside the SMZ. The $\delta^{13}\text{C}_{\text{PDB}}$ values for graphite and fluid inclusions from garnet granulites of the SMZ (Safonov et al., 2018a) are within the range of values for hydrothermal carbonates of greenstone lithologies (Burrows et al., 1986; Kerrich et al., 1987; Kerrich, 1989, 1990; Sarangi et al., 2012). Based on this similarity, Safonov et al. (2018a) assumed that carbonate-bearing rocks in the adjacent granite-greenstone successions of the Kaapvaal craton, buried underneath the SMZ served as a source of the fluids accompanying granulites in the SMZ. The carbon isotopic composition of carbonates from the ultrabasic granulites of the SMZ is also within this range (van Schalkwyk and van Reenen, 1992), suggesting a common source of fluids acting in the SMZ during the retrograde stage.

Ultramafic metavolcanic rocks are an important constituent of greenstone belts juxtaposed against the SMZ along the north-dipping (south-verging) Hout River Shear Zone (Fig. 1). As an example, in the Gyani greenstone belt (Fig. 1), the ultrabasic (chlorite-tremolite, talc-chlorite-tremolite, chlorite-anthophyllite etc.) schists strongly dominate in the Khavagari limb of the belt in the immediate footwall of the HRSZ (Fig. 1; McCourt and van Reenen, 1992; Kramers et al., 2014; van Reenen et al., 2014, 2019). These rocks often contain high proportions of carbonates. In order to model the formation of a fluid by devolatilization of ultrabasic schist, we have constructed a P-T pseudosection for an ultrabasic schist (Fig. 17a) from the Hudson Ntsanwisi Dam spillway (Fig. 1), the locality representative of the metavolcanic-metasedimentary succession of the Gyani greenstone belt (e.g. McCourt and van Reenen, 1992). The rock is composed of subhedral crystals of low-Ca, Na and Al amphibole within the chlorite-carbonate schistose matrix (Fig. 17a). Amphibole crystals contain lamellae, which differ in Na and Al contents, and contain domains of Al-bearing tremolite. Chlorite contains about 19 wt% Al_2O_3 and 1.2–1.8 wt% Cr_2O_3 . Carbonate is dolomite-ankerite with $X_{\text{Mg}} = 0.40\text{--}0.45$. The bulk composition is typical for such kind of rock (wt%): $\text{SiO}_2 - 44.46$, $\text{TiO}_2 - 0.27$, $\text{Al}_2\text{O}_3 - 5.26$, $\text{FeO} - 9.16$, $\text{MnO} - 0.154$, $\text{MgO} - 26.09$, $\text{CaO} - 5.05$, $\text{Na}_2\text{O} - 0.11$, $\text{K}_2\text{O} - 0.02$, $\text{P}_2\text{O}_5 - 0.03$, $\text{Cr} - 1881$ ppm, $\text{Ni} - 1393$ ppm. The LOI value is 7.7 wt% suggesting a high content of $\text{H}_2\text{O} + \text{CO}_2$. Phase equilibria modeling was done using the PERPLE_X software (Connolly, 2005) in version 6.7.7 for Windows. The following models for mineral solutions were used to model the rock assemblage: Chl(W) for Fe^{3+} and Mn-bearing chlorite (White et al., 2014), Amph(DHP) for actinolite-tremolite amphibole (Dale et al., 2000), oAmph(DP) for low-Ca Fe-Mg-amphibole (Diener et al., 2007) and Do(AE) (Anovitz and Essene, 1987) for the Ca-Mg-Fe carbonate solid solution. The models Cpx(HP) for clinopyroxene, Opx (W) (White et al., 2014) for orthopyroxene and Ol(HP) for olivine solid solutions were introduced to model assemblages forming by dehydration and decarbonation of the rock.

For simplicity, K_2O and P_2O_5 were excluded from the calculations, whereas 0.3 wt% of free O_2 was introduced to account for Fe_2O_3 and formation of hematite-bearing ilmenite. Preliminary calculations with 7.7 wt% of $\text{H}_2\text{O} + \text{CO}_2$ showed that volatile content did not ensure formation of the assemblage chlorite + amphibole + carbonate at

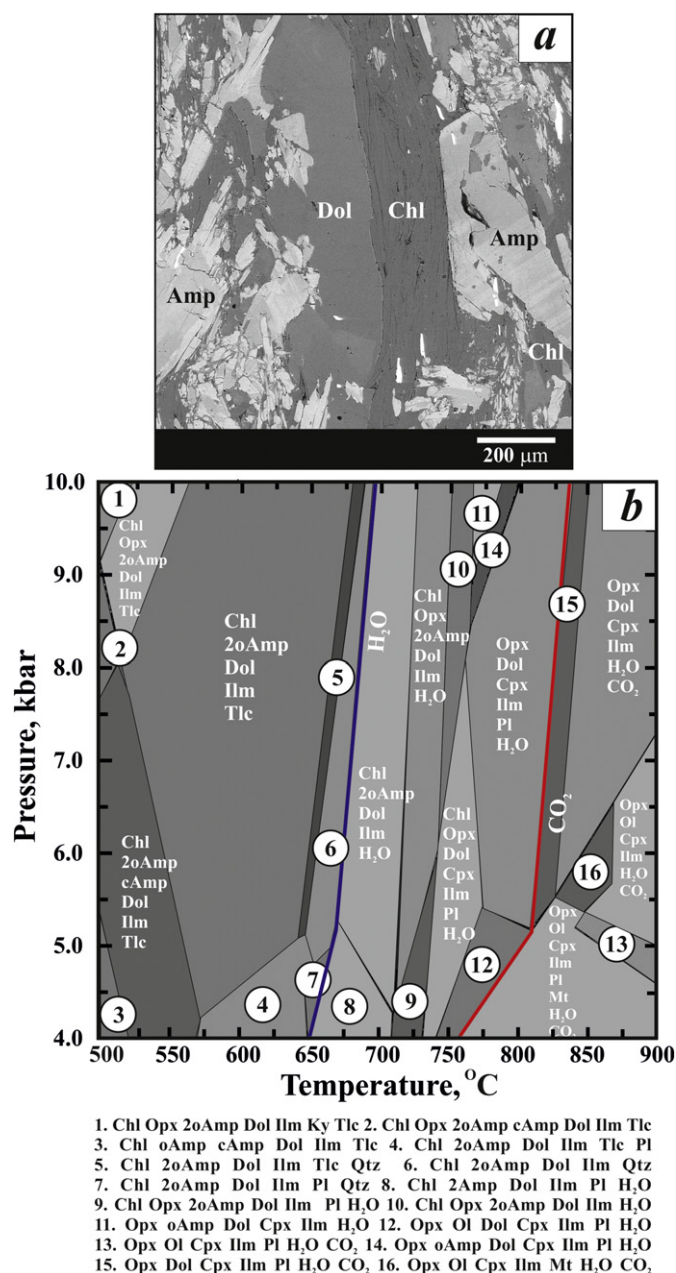


Fig. 17. Ultrabasic chlorite-amphibole-carbonate schist from the Hudson Ntsanwisi Dam spillway as a potential source for the carbonate-bearing fluids. (a) BSE image of the mineral assemblage of the schist; inhomogeneity of amphibole crystals is clearly seen (see text for explanation). (b) The P-T pseudosection computed for the bulk composition of the ultrabasic schist (see text for the composition). Dark blue line shows an appearance of aqueous fluid, red line shows appearance of aqueous-carbonic fluid.

temperatures below 600°C , and either olivine or orthopyroxene appeared. Further calculations suggested that a minimum of 8.4 wt% of volatiles was able to produce the necessary assemblage. Equal wt% of gaseous components, i.e. 4.2 wt% H_2O and 4.2 wt% CO_2 , were taken for the calculation. The assemblage chlorite (~25 vol%) + coexisting Mg-Fe and Ca-amphiboles (~64 vol%) + Mg-Fe-Ca carbonate (~9 vol%) + ilmenite (~1.5 vol%) and minor talc, at temperatures below $550\text{--}570^\circ\text{C}$ within the pressure range 4–8 kbar closely reproduced the ultrabasic schist assemblage (Fig. 17b). However, aqueous fluid begins to form via decomposition of chlorite and amphiboles at temperatures above

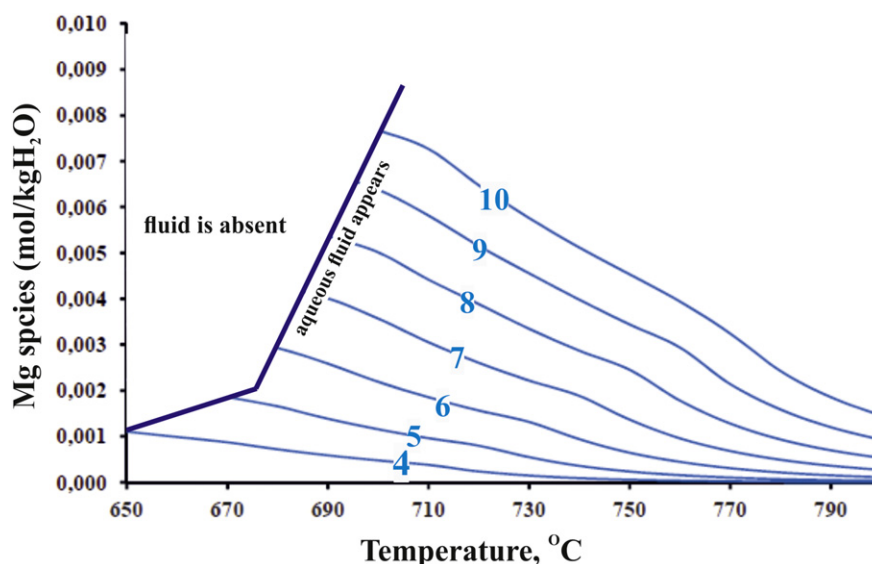


Fig. 18. Total concentration (mol per kg H₂O) of Mg-bearing species (Mg^{2+} , MgOH^+ , MgCO_3 and MgHCO_3^+) in the fluid coexisting with the assemblages of the ultrabasic schist from the Hudson Ntsanwisi Dam at the bulk wt. ratio $\text{H}_2\text{O}/\text{CO}_2 = 1/1$. Thick dark blue line shows an appearance of aqueous fluid according to Fig. 16b.

650–670 °C (Fig. 17b). CO_2 addition into the fluid via decomposition of carbonate only happens at temperature above 750–800 °C (Fig. 17b).

In order to demonstrate the solubility of various species in the aqueous fluid formed via initial dehydration of the schist, we applied the HCh software and associated Unitherm database (Shvarov, 2008, 2015), which is based on the Gibbs free energy minimization that accounts for activities of the species in aqueous solution using the extended Debye–Hückel equation. Thermodynamic properties of silicate, oxide and carbonate end-members in this software are taken from the Holland and Powell (2011) database, whereas solid solutions are described using ideal mixing-on-site models. The calculation shows that the total content of Mg-bearing species, involving Mg^{2+} , MgOH^+ , MgCO_3 and MgHCO_3^+ , strongly dominates over Fe, Ca and Al-bearing species in equilibrium with the assemblages of the carbonate-bearing ultrabasic schist at temperatures of 650–670 °C. Their concentration in the fluid increases with pressure and reaches up to 8×10^{-3} mol/kgH₂O at 10 kbar (Fig. 18). The total concentration of Mg-species in the fluid drops with temperature (Fig. 18).

9.3. Participation of the carbonate-bearing fluids in granitoid magma formation

Age data for the Klippit granitoids fall into three clusters. Excluding the youngest one at 2632 ± 6 Ma to 2476 ± 7 Ma (Fig. 13a, b), which, probably, represents late post-magmatic and metasomatic processes, there are two major clusters. The oldest concordant ages lie between 2838 ± 6 Ma and 2750 ± 7 Ma (Fig. 13a, b). The zircon cores showing these ages can be interpreted as detrital similar to the <3000 Ma-old zircons reported by Rajesh et al. (2014) and Nicoli et al. (2015) from metasediments of the Banderierkop Formation of the SMZ. However, these values are also close to the metamorphic age (ca. 2860 Ma) measured for zircons from garnet-bearing metabasites in the Lwaji limb of the Giyani greenstone belt (Kramers et al., 2014) and younger zircons from granitoids of the Giyani and Pietersburg greenstone belts (Kröner et al., 2000; Laurent et al., 2013; Zeh et al., 2013; Kramers et al., 2014). The largest age cluster that continuously range from 2729 ± 7 Ma to 2651 ± 3 Ma for zircons (Fig. 12a, b) and from 2749 ± 5 Ma to 2667 ± 5 Ma for monazites (Fig. 13c) cannot be subdivided in detail. The spread of age data seems to represent a continuous event related to intrusion and crystallization of the granitoids. The upper span of

this cluster includes values 2720–2710 Ma known as ages of peak metamorphism in the SMZ (Retief et al., 1990; Belyanin et al., 2014a; Rajesh et al., 2014; Taylor et al., 2014; Nicoli et al., 2015; Vezinet et al., 2018). The lower span of this cluster involves ages from 2680 to 2640 Ma reported for leucocratic granitoids similar to the Klippit locality (Kreissig et al., 2001; Belyanin et al., 2014a; Nicoli et al., 2015). In addition, this population lies within the interval 2720–2690 Ma, which is accepted as the time of thrusting of the SMZ granulites against and over greenstone rocks of the Kaapvaal Craton (e.g. van Reenen et al., 2011, 2014, 2019; Kramers et al., 2014) and regional retrograde hydration at 2670–2660 Ma (Belyanin et al., 2014a). Thus, geochronological data for the Klippit granitoids imply both the involvement of the “cratonic” component in the Klippit granitoids (first age cluster) and a close relation of the granitoid magma evolution with interaction of the SMZ granulites with the Kaapvaal Craton (second age cluster).

The conclusion that fluids produced by devolatilization of the ultrabasic greenstone rocks participated in the generation of the granitoid magmas, which crystallized as the Klippit granitoids, support the conclusions from the age data. The coexistence of the carbonate-bearing inclusions with silicate polyphase inclusions of granitic composition (Figs. 5c, d, 11a, b) suggest that the fluids accompanied granitoids magmas during their evolution. The coexistence of the CO_2 -rich fluids with granitic melts is also reflected in dense carbonic inclusions in quartz from the granitoids. Thus, both types of inclusions, carbonic inclusions in quartz and polyphase inclusions in garnet, represent fluids immiscible with the granitoid melt. Such immiscibility is imposed by the very low solubility of CO_2 in silicate melts (e.g. Ni and Keppler, 2013). The immiscibility can easily produce CO_2 -rich fluid inclusions coexisting with inclusions of CO_2 -saturated melts (e.g. Kamenetsky, 2006). “Granitic” melt inclusions coexisting with immiscible CO_2 -rich fluid inclusions have numerous been reported in peritectic minerals from partially molten crustal rocks (e.g. Cesare et al., 2007, 2015; Ferrero et al., 2011, 2014; Tacchetto et al., 2018 and more references in these papers).

The above discussion implies that, in the specific case of the Klippit granitoids, the Mg-carbonate-enriched fluids were probably related to devolatilization of underthrust ultrabasic carbonate-bearing rocks. The temperatures necessary for this process are above 650 °C (Fig. 17b). This temperature is much higher than the peak temperatures of the prograde metamorphism of rocks from

the Gyani greenstone belt at the contact with the SMZ (maximum 600–610 °C; e.g. [Perchuk et al., 2000b](#)). According to [Perchuk et al. \(2000b\)](#), the rocks of the Gyani greenstone belt were buried underneath the SMZ granulites to pressures of 5.5–7.2 kbar. It is hard to judge whether these P-T conditions are the upper limit for the greenstone rocks buried underneath the granulites. It cannot be excluded that the P-T conditions reported by [Perchuk et al. \(2000b\)](#) from the Khavagari area in the footwall of the HRSZ ([Fig. 1](#)) might be representative of only shallower blocks, which were exhumed along the craton-SMZ boundary. In fact, geophysical data indicate a large volume of cratonic rocks buried under the SMZ ([Fig. 1](#)), metamorphic degree of which is unknown. For example, [Miyano et al. \(1990\)](#) reported much higher P-T conditions, up to 700 °C at pressures up to 8 kbar, for unique sapphirine-bearing rocks of the Rhennosterkoppies greenstone belt ([Fig. 1](#)), which is also located in the footwall of the HRSZ. These conditions are enough to generate fluids by devolatilization of the ultrabasic rocks ([Fig. 17b](#)). However, they are not sufficient to produce granitoid melts, especially in presence of the CO₂-rich fluid. Thus, sites of fluid generation and melt generation were likely spatially separated. After production, the fluid penetrated into the much hotter overlying granulites within the contact between the SMZ and the craton. It is difficult to resolve from the present data, whether this fluid served as a trigger for the granitoid magma generation. However, surely, the fluid surely coexisted with the magma during its uplift into the SMZ and also participated in the modification of the SMZ granulites during the cooling stage.

10. Conclusions

Carbonate-bearing polyphase inclusions in garnets from the high-temperature (800–900 °C) leucocratic granitoids of the Klippit locality in the Southern Marginal Zone of the Limpopo high-grade complex represent relics of aqueous-carbonic fluid that coexisted with the granite melts during their generation and emplacement into the SMZ granulites. The present mineral and chemical composition of the polyphase inclusions are products of interaction of the fluid with the host garnet. Despite strong modification during cooling, the inclusions still bear evidence for initial saturation of the fluid with a dissolved Mg-carbonate components. This fact serves as an evidence for generation of the fluids from a Mg-rich carbonate-rich source. The potential candidate is carbonate-bearing ultrabasic schists of the greenstone belts of the adjacent Kaapvaal craton. The fluid can be extensively generated at temperatures above 650 °C by devolatilization of these rocks during their burial underneath SMZ granulites, penetrated into granulites and subsequently participated in anatexis related to the uplift of the granulites. Thus, in this case, the low-grade carbonate-bearing rocks of adjacent craton serve as an alternative source of CO₂-rich fluids in granulites during exhumation and retrograde evolution. The present data is yet another vivid illustration of active dynamic and fluid-magmatic interaction of the granulite complex with the ancient craton at their juxtaposed borders.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gr.2019.07.012>.

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Appendix A. Analytical procedures

A.1. Bulk-rock analysis

Samples for bulk chemistry analysis were crushed to a fine powder using a jaw crusher and tungsten carbide swing mill. Glass disks were prepared for XRF analysis as a mixture of high-purity fused anhydrous flux (Li₂B₄O₇ + LiBO₂ + LiBr), the rock powder (preliminary dried at 105 °C) and LiNO₃. Whole-rock major element compositions were determined using PW 2400 (Philips Analytical with SuperQ, PANalytical software) X-Ray Fluorescent Spectrometer equipped with robotic sample changer at the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry RAS (Moscow, Russia). For standards of known composition, typical deviation from the reference value is <1% for major elements present at a concentration of >1 wt%. LOI was not measured. Measurements below 0.05 wt% were considered to be zero.

A.2. BSE and microprobe analyses

Analyses of minerals were performed using the SEM Jeol 6480 LV equipped with EDS detector INCA – Energy 350 and WDS detector INCA Wave 500 (Oxford instruments) at the Laboratory of Local Methods of Analysis at the Department of Petrology of the Moscow State University. Analytical conditions for the analyses were 15 kV acceleration voltage, 15 nA beam current, counting times of 100 s. The ZAF matrix correction was applied. Reintegration of compositions of perthitic K-feldspar was carried out using scanning over areas of 180–20 μm² depending on coarseness and density of plagioclase lamellae. Usually, zones with fine perthite lamellae (2–5 μm thick) were taken for reintegration. In order to estimate possible Na loss during analyses, counting times of 100 and 40 s were applied. It was found that scanning over areas does not produce measureable Na loss from K-feldspars.

The Jeol Superprobe JXA-8230 at the same laboratory was used to analyze both major and some trace elements (Ti, Sc, Y, P, Cr) in garnet. The analytical conditions for the Superprobe analyses were 20 kV acceleration voltages and 60 nA beam current. The slit size was 500 μm for all spectrometers. The garnet standards USNM 143968 (Mg- Kα₁, Al- Kα₁ and Si- Kα₁ – TAP crystal; Fe- Kα₁ – LiF crystal) and USNM 87375 (Ca- Kα₁ – PET-J crystal) were used for calibration of the major elements ([Jarosewich et al., 1980](#)). Counting times for major elements were similar both for the standards and the sample: Mg, Ca and Fe – 40 s.; Al and Si – 20 s. The dispersion of the measured concentration during the major element analyses using the above conditions did not exceed 0.5%. The following crystalline standards were used for the minor element analyses: MnTiO₃ for Ti-Kα₁ and Mn-Kα₁; Cr₂O₃ for Cr-Kα₁; ScPO₄ for P-Kα₁ and Sc-Kα₁; Y₃Al₅O₁₂ for Y-Lα₁. The Ti, Mn, Cr measurements (crystal LiF) and P (crystal PET-J) were performed using spectrometers with a 140 mm radius Rowland circle, whereas Sc and Y (crystal PET-H) were measured using the 100 mm radius H-type spectrometer. The position of maxima for the trace elements in garnets was specified by means of slow scanning of the corresponding spectral intervals. Counting time was set to attain the detection limit of 0.005 wt%: 30 s. for Ti and Mn, 40 s. for Cr, 60 s for P and Y and 80 s for Sc. ZAF correction was applied for analyses. Analytical conditions for the elemental mapping at the Jeol Superprobe JXA-8230 were the same as for individual spot analyses. Elemental maps were constructed on the basis of 10 scans with a resolution of 256 × 192 pixels and dwell time 10 ms. All mineral analyses used in this study (see below) are presented in tables in the supplementary materials.

A.3. Fluid inclusion analysis

Fluid inclusions were investigated in double-polished sections (200 to 300 μm thick) using the LINKAM THMSG 600 heating-freezing stage at the Korzhinskii Institute of Experimental Mineralogy. The stage works within the temperature range from -196°C to 600°C with automatic heating/cooling at a rate of $0.1\text{--}90^\circ\text{C}/\text{min}$. Accuracy of the thermometric measurements is about $\pm 0.1^\circ\text{C}$. Systematic calibration of the stage was performed using natural (CO_2 , Camperio, Alps) and synthetic (H_2O) inclusions in quartz. Data on fluid inclusions were treated using the FLINCOR software (Brown, 1989). Isochores for the CO_2 fluid inclusions were calculated using EOS by Sterner and Pitzer (1994).

A.4. Raman spectroscopy

Qualitative identification of crystalline phases and gaseous species in the polyphase inclusions in garnet was performed by means of Raman spectroscopy using the JY Horiba XPlora Jobin spectrometer equipped with a polarized Olympus BX41 microscope at Department of Petrology, Moscow State University. Spectra were obtained using a 532-nm laser within the range $100\text{--}4000\text{ cm}^{-1}$ during 30 s. To better resolve band of volatile species, additional spectra were collected within the range $1200\text{--}1300\text{ cm}^{-1}$ with longer exposition time. The spectra were refined with LabSpec (version 5.78.24) software. Assignment of the Raman bands for gaseous species was carried out using a compilation by Frezzotti et al. (2012). Crystalline phases were identified using the ruff.info database.

A.5. Laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICPMS)

Zircons and monazites from the granitoids were analyzed using LA-MC-ICPMS on polished crystals utilizing an ASI RESOLUTION SE 193 nm Excimer laser ablation system, coupled to a Nu Plasma II multi-collector ICP mass spectrometer, at the Spectrum Analytical Facility of the University of Johannesburg. Ablations were carried out in a Laurin Technic dual-volume cell under a helium atmosphere (flow of 0.25 l/min) mixed with argon (ca. 0.84 l/min) before entering the MC-ICPMS. The blank was measured on-peak in the 25 s before ablation, and the ablation measurement itself took 50 s. An integration time was 0.2 s. ^{232}Th and ^{238}U were measured on Faraday cups, while ^{208}Pb , ^{207}Pb , ^{206}Pb , $^{204}(\text{Pb} + \text{Hg})$ and ^{202}Hg were measured on ion counters. Ratios and ages were computed with reference to external standards using an in-house data reduction program based on VB Excel. The Excel add-in Isoplot (v. 3.6; Ludwig, 2008) was used for age calculations.

For the zircons spots of 25 μm diameter were ablated at 2 Hz. Laser fluence was around $1.3\text{ J}/\text{cm}^2$, which is a nominal energy of 3 mJ at an attenuator setting of 12.5%. The following reference materials were used: OG1 ($3465 \pm 1\text{ Ma}$, Stern et al., 2009), A382 and A1772 ($1877 \pm 2\text{ Ma}$ and $2712 \pm 1\text{ Ma}$ respectively, Huhma et al., 2012). Analyses with detectable common Pb were corrected following the crustal lead evolution line of Stacey and Kramers (1975). Zircon (CD)QNG ($1850 \pm 1\text{ Ma}$, Black et al., 2003) was measured as an unknown to check accuracy. Apart from two analyses with very high U contents, which gave discordant ages, ten analyses of this reference material gave a concordia age of $1851 \pm 5\text{ Ma}$ (2σ), which is within error of the accepted value (Schoene et al., 2006).

Monazites were ablated with a 9–11 μm spot size, at an ablation rate of 1.2–1 Hz. Corrections for instrumental drift and mass bias were performed by multiple measurements of monazites B0109 (Hisøy, Norway, $1136 \pm 2\text{ Ma}$, Bingen et al., 2008) and A49H ($1876 \pm 2\text{ Ga}$, Salli, 1983).

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