

**Prograde infiltration of Cl-rich fluid into the granulitic continental
crust from a collision zone in East Antarctica (Perlebandet, Sør
Rondane Mountains)**

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Abstract

Utilizing microstructures of Cl-bearing biotite in pelitic and felsic metamorphic rocks, the timing of Cl-rich fluid infiltration is correlated with the pressure-temperature-time (P - T - t) path of upper amphibolite- to granulite-facies metamorphic rocks from Perlebandet, Sør Rondane Mountains (SRM), East Antarctica. Microstructural observation indicates that the stable Al_2SiO_5 polymorph changed from sillimanite to kyanite + andalusite + sillimanite, and P - T estimates from geothermobarometry point to a counterclockwise P - T path characteristic of the SW terrane of the SRM. *In situ* laser ablation inductively coupled plasma mass spectrometry for U-Pb dating of zircon inclusions in garnet yielded ca. 580 Ma, likely representing the age of garnet-forming metamorphism at Perlebandet.

Inclusion-host relationships among garnet, sillimanite, and Cl-rich biotite ($\text{Cl} > 0.4 \text{ wt\%}$) reveal that formation of Cl-rich biotite took place during prograde metamorphism in the sillimanite stability field. This process probably predated partial melting consuming biotite ($\text{Cl} = 0.1\text{-}0.3 \text{ wt\%}$). This was followed by retrograde, moderately Cl-bearing biotite ($\text{Cl} = 0.1\text{-}0.3 \text{ wt\%}$) replacing garnet. Similar

timings of Cl-rich biotite formation in different samples, and similar $f(\text{H}_2\text{O})/f(\text{HCl})$ values of coexisting fluid estimated for each stage can be best explained by prograde Cl-rich fluid infiltration. Fluid-present partial melting at the onset of prograde metamorphism probably contributed to elevate the Cl concentration (and possibly salinity) of the fluid, and consumption of the fluid resulted in the progress of dehydration melting. The retrograde fluid was released from crystallizing Cl-bearing partial melts or derived externally. The prograde Cl-rich fluid infiltration in Perlebandet presumably took place at the uppermost part of the footwall of the collision boundary. Localized distribution of Cl-rich biotite and hornblende along large-scale shear zones and detachments in the SRM supports external input of Cl-rich fluids through tectonic boundaries during continental collision.

Keywords: fluid, brine, partial melting, Al_2SiO_5 polymorphs, chlorine, continental collision

Introduction

Low water activity fluids have been recognized as the major fluid species present under granulite facies conditions prevailing in the lower continental crust (Aranovich et al., 1987; Newton et al., 1998; Touret and Huizenga, 2011). Under such conditions, brines can immiscibly coexist with CO_2 -rich fluids (Heinrich, 2007). Direct evidence of highly saline brine, such as fluid inclusions (van den Berg and Huizenga, 2001) and/or salt crystals (e.g., Markl and Bucher, 1998) have been reported, although

they are relatively uncommon. Rare preservation of brines as fluid inclusions is attributed to the low viscosity and low wetting angle of brines (Watson and Brenan, 1987; Holness, 1997) that make it easy for brine to escape the rock. In addition, steep isochores of NaCl-H₂O fluids in pressure-temperature (*P-T*) space result in gross overpressurization of brine inclusions during heating and decrepitation or implosion during isobaric cooling (Touret et al., 2016). These features probably hindered understanding of the timing and spatial distribution of brines in high-grade metamorphic terranes.

The presence of Cl-rich biotite, hornblende and apatite is often taken as evidence for the presence of Cl-bearing fluids and brines (e.g., Harlov and Förster, 2002; Higashino et al., 2013a; Safonov et al., 2014). These minerals are known to incorporate Cl in place of OH in their crystal structures when they exchange with Cl-bearing fluids (e.g., Munoz and Swenson, 1981; Kullerud, 1996). Data on Cl partitioning between fluids and these minerals is available (e.g., Zhu and Sverjensky, 1991; 1992; Mathez and Webster, 2005); the $f(\text{H}_2\text{O})/f(\text{HCl})$ ratio of the coexisting fluid can be estimated from the composition of biotite and apatite (e.g., Selby and Nesbitt, 2000). In partially molten, migmatitic pelitic gneisses, Cl-rich biotite may coexist with nanogranite/felsite inclusions (Kawakami et al., 2016; see Hiroi et al. (2014) for ‘felsite inclusions’), and thus not only subsolidus Cl-rich aqueous fluid infiltration but also processes involving partial melting can lead to the formation of Cl-rich biotite.

This study aims to correlate the reconstructed *P-T-t* path with partial melting and Cl-rich fluid

infiltration events using microstructural observations pointing to several stages of Cl-bearing biotite formation in pelitic and felsic gneisses from Perlebandet (western Sør Rondane Mountains (SRM), East Antarctica). We discuss multiple Cl-bearing fluid infiltration events in the SRM. Mineral abbreviations are after Kretz (1983).

Geological setting

The Sør Rondane Mountains

In the SRM (22°-28°E, 71.5°-72.5°S) of eastern Dronning Maud Land, East Antarctica (Fig. 1a), the granulite facies lower continental crust of a continental collision setting is widely exposed (Shiraishi et al., 1991; Asami et al., 1992). The SRM are thought to be a part of the collision zone between East and West Gondwana during the ca. 750–620 Ma ‘East African-Antarctic Orogeny (EAAO)’ (Jacobs et al., 2003) and are also affected by the ca. 570–500 Ma ‘Kuunga Orogeny’ (Meert, 2003). Apparent depositional ages of metacarbonate rocks from Balchenfjella, Brattnipene, Menipa and Tanngarden regions in the SRM (Fig. 1b) are estimated as late-Tonian and early-Cryogenian age (880–850 Ma and 820–790 Ma) based on a Sr isotope study (Otsuji et al., 2013). Protoliths of metacarbonates are considered to have been deposited in the Mozambique Ocean that separated the continental blocks that amalgamated to form Gondwana (Otsuji et al., 2013).

The SRM is divided into the NE and SW terranes which are separated by a gently N- to

NE-dipping mylonite zone named the Main Tectonic Boundary (MTB; Osanai et al., 2013) (Fig. 1b). The NE terrane is mainly composed of amphibolite- to granulite-facies metamorphic rocks of pelitic, psammitic, and intermediate compositions (Shiraishi and Kojima, 1987; Asami and Shiraishi, 1987; Grew et al., 1989) showing clockwise P - T paths (Osanai et al., 2013; Grantham et al., 2013). In contrast, the SW terrane is composed of granulite- to greenschist-facies rocks with a large volume of meta-tonalite (Fig. 1b; Shiraishi et al., 2008; Kamei et al., 2013), showing counterclockwise P - T paths (Adachi et al., 2013; Baba et al., 2013). U-Pb ages of detrital zircon are also different between these two terranes; detrital zircons older than 1200 Ma are absent from the SW terrane (Osanai et al., 2013; Kitano et al., 2016). Based on these observations, the two different P - T paths in these adjoining terranes are explained by the collision between these two terranes, with the NE-terrane thrust over the SW-terrane during the EAAO at 650-600 Ma, followed by amphibolite-facies metamorphism at ca. 570 Ma (Osanai et al., 2013). A SE-dipping ductile extensional shear zone termed the Balchen Detachment Fault (BDF) structurally divides Balchenfjella (Fig. 1b), and the southeastward movement of the Berrheia unit (hanging wall side) with respect to the Gropeheia unit (footwall side) is inferred to represent an extensional deformation phase between ca. 600 Ma and ca. 549 Ma (Ishikawa et al., 2013), which is interpreted to result from extensional collapse after crustal overthickening.

The Main Shear Zone (Kojima and Shiraishi, 1986; Fig. 1b) that defines the boundary between older meta-tonalite and amphibolite-facies metamorphic rocks in the SW-terrane was inferred to have

limited tectonic significance by Osanai et al. (2013). However, Ruppel et al. (2015) interpreted it to be a large-scale late Pan-African strike-slip structure of ca. 560-530 Ma, representing an important lithotectonic boundary separating East African affinities from ‘Indo-Antarctic’ Rayner-age affinities presumably close to the eastern margin of the EAAO (Ruppel et al., 2015).

The SRM is also interpreted to be a part of the hanging wall of a mega-nappe complex which formed through continental collision between northern and southern Gondwana during the Kuunga Orogeny at 580–540 Ma (Grantham et al., 2008; 2013), as supported by the data from part of the NE terrane (Balchenfjella and Austhameren; Fig. 1b).

In the SRM, Cl-rich biotite, apatite and hornblende have been described in felsic and mafic gneisses along the large scale shear zones and tectonic boundaries which extend over 200 km (Higashino et al., 2013a; 2013b; 2015a; Fig. 1b). In eastern SRM (Balchenfjella; Fig. 1b), Cl-rich biotite and apatite in pelitic gneisses have been interpreted to have resulted from interaction with a Cl-rich fluid or melt that was present at near peak metamorphic condition of ca. 0.8 GPa and 800 °C (Higashino et al., 2013a). In the central SRM (Brattnipene; Fig. 1b), Cl-rich hornblende and biotite are formed along garnet-hornblende veins, and ‘diffusion-like’ profiles of Cl content in hornblende and biotite decreasing from the vein towards the wall rock are observed (Higashino et al., 2015b). Mass balance analysis revealed that elements mobile in brines rather than in melts were added to the wall rock, suggesting that brine infiltration produced the garnet-hornblende veins in Brattnipene

(Higashino et al., 2015b).

In addition to these Cl-rich minerals in metamorphic rocks, magmatic hornblende and biotite show relatively high Cl contents in some granitoids in the SRM. Li et al. (2003, 2007) reported 0.28-0.32 wt.% Cl in hornblende from the Dufek granite, and 0.31-0.41 wt.% Cl in hornblende and 0.21-0.59 wt.% Cl in biotite from the Pingvinane granite (Fig. 1b). The U-Pb zircon age determined by SHRIMP or laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) is 619 ± 7 Ma (Li et al., 2006) and 637 ± 6 Ma (Elburg et al., 2016) for the Dufek granite, and 506 ± 4 Ma (Elburg et al., 2016) for the Pingvinane granite.

Perlebandet

Perlebandet is one of the westernmost nunataks in the SRM, where granulite facies layered gneisses are exposed (Fig. 1c). It is a key area to constrain the location of the MTB, and has been considered to belong to the NE terrane (Osanai et al., 2013) in the lack of detailed information of *P-T* path of this area. However, Perlebandet is interpreted to be part of the SW terrane on the basis of magnetic surveys (Mieth et al., 2014).

The main lithologies observed in Perlebandet are garnet-biotite (Grt-Bt) gneiss, garnet-sillimanite-biotite (Grt-Sil-Bt) gneiss, hornblende-biotite gneiss, marble and skarns, pyroxene granulite, and orthopyroxene-bearing amphibolite (Fig. 1c; Shiraishi et al., 1997). Previous SHRIMP

U-Pb zircon dating of a Sil-Grt-Bt gneiss from Perlebandet gave an inherited core age of 1009 ± 13 Ma, and rim ages of 736 ± 13 Ma, 609 ± 11 Ma, and 565 ± 7 Ma (Shiraishi et al., 2008). Among the three rim ages, the latter two are considered as metamorphic, whereas the detrital or metamorphic origin of the first one remains unclear (Shiraishi et al., 2008). Sillimanite is the most common aluminosilicate mineral, and retrograde andalusite and kyanite are locally present (Kawakami et al., 2010). Otsuji et al. (2013) reported low Sr and oxygen isotope ratios from Perlebandet metacarbonates, which are not characteristic of continental settings. These low Sr isotope ratios can be attributed to interaction with low Sr-bearing magmatic fluids or to the older depositional age of Perlebandet metacarbonates compared to that from other parts of the SRM (Otsuji et al., 2013). Otsuji et al. (2016) further pointed out that Nd and Sr isotopic data from metacarbonate rocks from Perlebandet neither match the data from the rocks in the SW terrane, nor from the Balchenfjella in the NE terrane. Based on these data, they proposed that Perlebandet carbonates were deposited in an environment surrounding an isolated seamount in the Tonian to Cryogenian period, and that amalgamation of Gondwana and the final closure of Mozambique Ocean and East Antarctic Ocean took place at ca. 660-550 Ma (Otsuji et al., 2016).

Analytical methods

Quantitative analysis of rock-forming minerals and X-ray elemental mapping of thin section

samples were performed by a JEOL JXA-8105 superprobe. Analytical conditions for quantitative analyses except for apatite were 15.0 kV acceleration voltage, 10 nA beam current, and 3 µm beam diameter. The counting time for the peak and backgrounds was 30 s and 15 s for Cl, 60 s and 30 s for F, and 10 s and 5 s for other elements. Analytical conditions for quantitative analysis of apatite followed that recommended by Goldoff et al (2012). Natural and synthetic minerals (Astimex MINM25-53) were used as standards and ZAF correction was applied. Analytical conditions for X-ray elemental mappings were acceleration voltage of 15.0 kV, probe current of 50 nA, focused beam to 3 µm beam diameter, and dwell time of 25-40 milliseconds. Electron microprobe analysis of rutile was also done by a JEOL JXA-8105 superprobe, following analytical conditions recommended by Zack et al. (2004).

Cathodoluminescence (CL) images were obtained using a JEOL JXA-8105 superprobe equipped with Hamamatsu Photonics high voltage power supply C9525 and photon counting unit C9744. Analytical conditions for CL mapping were 15.0 kV acceleration voltage, 1 nA beam current, focused beam to 10 µm beam diameter, and dwell time of 1 msec.

Minerals were also qualitatively identified by a Hitachi S3500H scanning electron microscope equipped with an EDAX X-ray analytical system. Laser Raman spectroscopy (JASCO NRS 3100) was used to identify Al₂SiO₅ minerals.

In situ zircon U-Pb dating on thin section samples via LA-ICP-MS was carried out using a Nu Plasma II HR-MC-ICPMS coupled to a NWR femtosecond laser-ablation system. Backscattered

electron (BSE) and CL images were obtained prior to the analyses to identify spot positions, overlapping multiple growth zones, grain edges, cracks or damaged zircon grains. Detailed analytical conditions of the LA-ICP-MS analysis are given in Higashino et al. (2015a). Data were processed and plotted using *Isoplot 4.15* (Ludwig, 2012). All of the above analyses were done at the Department of Geology and Mineralogy, Graduate School of Science, Kyoto University.

Sample localities and sample descriptions

The samples used in this study are two Grt-Bt gneisses [samples TK2009113001B (3001B) and TK2009112601C (2601C)] and three Grt-Sil-Bt gneisses [samples TK2009113001G (3001G), TK2009113001H (3001H) and TK2009112602D (2602D)] collected during the summer season of the 51st Japan Antarctic Research Expedition (JARE51; Tsuchiya et al., 2012). Samples were collected from the northern half of Perlebandet (Fig. 1c). The common Al_2SiO_5 mineral in these gneisses is sillimanite, found as inclusions in cores of garnet and as a matrix mineral defining the gneissose structure (Fig. 2a-d). A rare sample with strong retrogression (sample 3001G) contains secondary andalusite, kyanite, and sillimanite replacing garnet (Fig. 2e-n). Detailed descriptions of the samples studied are given below, and representative mineral analyses are given in Table 1.

Garnet-sillimanite-biotite gneiss (samples 2602D and 3001H)

These gneisses consist of garnet, sillimanite, biotite, K-feldspar, quartz and plagioclase (An₁₉₋₂₃ in 2602D, and An₁₃₋₁₇ in 3001H), and subordinate rutile, ilmenite, zircon, monazite and apatite. Muscovite is only present as a secondary mineral. Sillimanite is abundant in the matrix and also present as inclusions in cores of garnet ($X_{Mg} = 0.25-0.29$ in 2602D, and $X_{Mg} = 0.25-0.32$ in 3001H) (Fig. 2a). Biotite is not included in garnet. Garnet is replaced by secondary biotite at the rim and along the cracks. It does not preserve chemical zoning, except for the rims and along the cracks affected by the retrograde re-equilibration. The highest X_{Mg} content of garnet is preserved distant from the cracks where the retrograde effects are minimal. In both samples, sillimanite and biotite partly replace garnet rim. Retrograde biotite tends to have lower TiO_2 contents compared to matrix biotite. Cracks in garnet are filled with retrograde biotite with the lowest Cl (Cl ~ 0.01 wt.%) and the lowest TiO_2 (< 0.29 wt.%) contents.

In sample 2602D, garnet rim contain inclusions of quartz and K-feldspar. Matrix biotite has moderate Cl content (0.17-0.22 wt.%, $X_{Mg} = 0.41-0.51$) and the highest TiO_2 content (2.04-3.96 wt.%). Retrograde biotite (Cl < 0.15 wt.%, $TiO_2 = 0.98-2.82$ wt.%, $X_{Mg} = 0.45-0.48$) and plagioclase (An₁₈₋₂₃) replace garnet at the rim ($X_{Mg} = 0.11-0.13$). Matrix sillimanite very rarely includes garnet ($X_{Mg} = 0.23-0.24$). Rutile in the matrix and that included in sillimanite gave Zr contents of 1125-1466 ppm (average = 1359 ppm; 8 points) and 1917-1947 ppm, respectively.

In sample 3001H, some sillimanite grains contain inclusions of green spinel. Biotite in this

sample has very low Cl content ($Cl < 0.03$ wt.%, $X_{Mg} = 0.42-0.49$) irrespective of its mode of occurrence. Garnet is replaced by biotite ($Cl < 0.02$ wt.%) and plagioclase (An16-18) at the rim ($X_{Mg} = 0.10-0.12$). Matrix sillimanite rarely includes rutile ($Zr = 1473-1636$ ppm). Rutile in the matrix has a Zr content of 1125-2162 ppm (average = 1712 ppm; 15 points).

Strongly retrogressed garnet-sillimanite-biotite gneiss (sample 3001G)

This is a folded, pelitic gneiss with sillimanite porphyroblasts (ca. 1cm in length). The matrix of this gneiss mainly consists of biotite, garnet, sillimanite, K-feldspar, plagioclase (An26-31), quartz and retrograde andalusite, kyanite, sillimanite and muscovite (Fig. 2b-n). K-feldspar is especially abundant in the matrix (Fig. 2e-f). Accessory minerals are ilmenite, zircon, monazite and rare rutile. Ti-oxide minerals are mostly ilmenite in the matrix, but rare rutile ($Zr = 874-1273$ ppm; average of 15 points = 1139 ppm) is preserved as inclusions in garnet (Fig. 2o) and in K-feldspar. Myrmekite is also present in the matrix. Garnet in this sample is strongly replaced mainly by biotite, plagioclase, andalusite, kyanite, and sillimanite (Fig. 2e-n).

Sillimanite is the only Al_2SiO_5 mineral included in garnet. Prismatic sillimanite porphyroblast in the matrix has an inclusion-poor core and inclusion-rich rim (Fig. 2b, c). Sillimanite porphyroblasts up to 1 cm in diameter show numerous subgrains and often includes smaller prismatic sillimanite with crystallographic orientations different from that of the host sillimanite (Fig. 2c). The core of

sillimanite porphyroblast includes plagioclase (An₃₃₋₃₇), K-feldspar and moderately Cl-bearing biotite (0.17-0.30 wt.%; Table 1). The rim of sillimanite can be recognized by the presence of abundant inclusions of Zn-bearing spinel (ZnO = 4-6 wt.%, $X_{Mg} [= Mg/(Mg+Fe_{total})] = 0.18-0.22$), plagioclase (An₃₁₋₃₅), garnet ($X_{Mg} = 0.18-0.19$), biotite (Cl < 0.32 wt.%), ilmenite, and rare quartz (Fig. 2c, d). Sillimanite that is replacing garnet (Fig. 2e, i, j) commonly includes Zn-bearing spinel crystals, resembling the rim of prismatic sillimanite in the matrix. Randomly-oriented, fibrolitic sillimanite is locally formed along the grain boundaries of matrix minerals.

Garnet is mostly xenomorphic, and includes sillimanite, Zn-bearing spinel, biotite, plagioclase, quartz, ilmenite and zircon (Fig. 2k-n). It is replaced by retrograde minerals such as biotite, andalusite, kyanite, sillimanite, muscovite, plagioclase and quartz (Fig. 2f-n). Replacement by biotite + plagioclase intergrowths is also common (Fig. 2i-j). Garnet that locally includes Zn-bearing spinel overgrows sillimanite porphyroblasts (Fig. 2b-d). Spinel included in such garnet is more Zn-rich than that included in sillimanite. Garnet that overgrows sillimanite and separate garnet grains in the matrix both show decreasing X_{Mg} from the core ($X_{Mg} = 0.15-0.21$) to the rim ($X_{Mg} = 0.10-0.14$). The $X_{Ca} [= Ca/(Fe+Mn+Mg+Ca)]$ slightly decreases towards the rim or remains constant at 0.04-0.07 (Table 1). These garnet zonings are diffuse and are strongly affected by retrograde re-equilibration.

Biotite included in garnet-overgrowth on sillimanite (Fig. 2b) shows high Cl (< 0.41 wt.% Cl) and X_{Mg} (~ 0.63) and varying TiO₂ (2.3-6.0 wt.%) (Fig. 3a, b). Biotite included in sillimanite

porphyroblast shows moderate Cl contents (0.17-0.30 wt.%) with high X_{Mg} (0.46-0.56) and varying TiO_2 (2.8-5.0 wt.%) (Fig. 3a, b). Matrix biotite shows moderate Cl contents (0.13-0.25 wt.%) with lower X_{Mg} (~ 0.40) and moderate TiO_2 (2.5-3.6 wt.%) (Fig. 3a, b). Biotite in the biotite-plagioclase intergrowth replacing garnet (Fig. 2g, i) shows moderate TiO_2 (3.2-4.2 wt.%) and Cl (0.17-0.24 wt.%) contents and X_{Mg} (~ 0.47) value (Fig. 3a, b). Apparently retrograde, crack-filling biotite in garnet (Fig. 2k-n) shows moderate to low Cl (0.09-0.16 wt.%) and low TiO_2 (1.9-2.5 wt.%) contents (Fig. 3a, b). Retrograde biotite developed at garnet rims also shows similar compositions to the crack-filling biotite (Fig. 3a, b). There is a clear tendency for prograde biotites, such as inclusions in garnet and sillimanite and some of the matrix biotite, to show Cl-rich composition and higher TiO_2 and X_{Mg} values than the retrograde ones.

Andalusite intergrown with biotite commonly replaces garnet (Fig. 2f-e). Retrograde andalusite is commonly accompanied by sillimanite and rare kyanite (Fig. 2e-n). Garnet is Fe-richer around the andalusite-bearing replacement, and andalusite in the replacement locally includes irregularly-shaped garnet and/or Zn-bearing spinel (Fig. 2k-n). Andalusite is never found as inclusions in garnet, and is in contact with the matrix phases even when it is surrounded by garnet (Fig. 2k-n).

Kyanite is rare, and tends to be finer-grained than other Al_2SiO_5 polymorphs and is never found as inclusions in garnet. It replaces garnet together with biotite, andalusite and sillimanite (Fig. 2g-j, m, n). The CL images combined with laser Raman spectroscopy are useful in identifying dispersed

fine-grained kyanite because kyanite is more luminescent than sillimanite (moderately bright) and andalusite (dark) (Fig. 2g-j). Zn-bearing spinel is also found as inclusions in some kyanite grains.

The composition of Zn-bearing spinel included in all Al_2SiO_5 polymorphs and garnet varies from $\text{ZnO} = 4.0\text{-}5.0$ wt.% and $X_{\text{Mg}} = 0.28$ to $\text{ZnO} = 11\text{-}13$ wt.% and $X_{\text{Mg}} = 0.18$.

Garnet-biotite gneiss (sample 3001B)

This gneiss mainly consists of garnet, biotite, quartz, plagioclase and K-feldspar, with accessory zircon, ilmenite, fluorapatite and minor sulfide (Fig. 4a-c). Myrmekite is present in the matrix. Biotite included in garnet (Fig. 4a-c) shows high TiO_2 (3.5-7.3 wt.%) and moderate Cl (mostly 0.20-0.34 wt.%) contents and high X_{Mg} (~ 0.6) (Fig. 3c, d). Biotite in the matrix (Fig. 4a-c) has moderate TiO_2 (3.3-4.5 wt.%) and Cl (0.11-0.25 wt.%) contents and X_{Mg} of ~ 0.4 (Fig. 3c, d; Table 1). Retrograde biotite next to garnet, and crack-filling biotite in garnet (Fig. 4a-c) both show lower Cl contents below 0.21 wt.% (Fig. 3c, d). Some of the matrix biotite and retrograde biotites (in biotite-plagioclase intergrowths and retrograde biotite next to garnet) share the same chemical characteristics of having low TiO_2 and Cl contents and low X_{Mg} (Fig. 3c, d).

Garnet-biotite gneiss (sample 2601C)

This gneiss mainly consists of garnet, biotite, K-feldspar, quartz and plagioclase (Fig. 4d-f).

K-feldspar is abundant, and randomly-oriented secondary muscovite is present in the matrix. Accessory minerals are zircon, ilmenite and fluorapatite. Minor sulfide is included in garnet and minor myrmekite is locally present in the matrix. This sample has the most Fe-rich whole-rock composition among the samples studied as suggested by the Fe-rich composition of mafic minerals (X_{Mg} of biotite and garnet = 0.06-0.22; Table 1). Separate biotite grains in the matrix (Fig. 4d-f) show the highest Cl contents (0.61-0.68 wt.%) and the highest X_{Mg} (~ 0.2) in this sample (Figs. 3e, 3f and 4d-f). Biotite replacing garnet rim as biotite-plagioclase intergrowths (Fig. 4d-f) also show high X_{Mg} (~ 0.2) and moderate to high Cl content (0.32-0.41 wt.%) (Fig. 3e, f). It shares the same chemical characteristics as retrograde biotite near garnet. Crack-filling biotite in garnet (Fig. 4d-f) shows the lowest X_{Mg} and Cl contents (Fig. 3e, f). No systematic variation in TiO_2 content (2.2-3.8 wt.%) is observed among different biotite types in this sample (Fig. 3e, f).

LA-ICPMS U-Pb zircon dating

Zircon is commonly oval-shaped, and the diameter of zircon reported below represents the length of the shorter axis. Weighted mean and lower intercept ages given below are at 95% confidence level. Unless specified, ages reported below refer to $^{206}Pb/^{238}U$ results. A summary of the results of LA-ICPMS U-Pb zircon dating is given in Supplementary Table 2.

Sample 3001G

Zircon in the matrix is commonly shorter than 100 μm in diameter, and shows oscillatory zoning (Fig. 5a-h). Analyses gave concordant U-Pb ages of ca. 1200-1100 Ma, 950-900 Ma, 750-700 Ma and 650-550 Ma. Ages older than 700 Ma are in most cases obtained from zircon cores, and the youngest ages of ca. 580 Ma are in most cases obtained from rims. Ages older than 900 Ma tend to have high Th/U ratios from 0.20 up to 1.1, while the younger age domains (750-550 Ma) give low Th/U ratios below 0.20 (Figs. 5a-h and 6a; Table 2). The weighted mean U-Pb age of zircon rims from matrix grains is 581 ± 10 Ma ($n = 5$, mean square of weighted deviates (MSWD) = 1.3, probability = 0.28).

Zircon included in garnet is commonly about 50 μm in diameter, and tends to have oscillatory zoned cores with bright- and dark-CL zones (Th/U = 0.01-0.40, mostly around 0.25), discordantly overgrown by dark-CL rims (Th/U = 0.01-0.03) (Fig. 5e, h). The lower intercept age for selected rim analyses of zircon included in garnet is 578 ± 9 Ma ($n = 6$, MSWD = 1.3, probability = 0.28), and Th/U ratios of these zircon rims with concordant ages are 0.04-0.07. Rim and mantle of a zircon grain included in the inclusion-rich rim of a sillimanite porphyroblast yielded 575 ± 13 Ma ($n = 2$, Th/U = 0.04-0.09) (Fig. 5g).

Zircon in the garnet breakdown microstructure of Cl-poor Bt + Ms $\pm$ And shows similar zoning to zircon included in garnet (Fig. 5a-d). The weighted mean U-Pb age of zircon rims (and mantles with similar age) in such microstructure is 573 ± 5 Ma ($n = 9$, MSWD = 0.83, probability = 0.57).

325

326 ***Sample 3001B***

327 Zircon in the matrix and zircon inclusions in garnet are commonly 30-70 μm in diameter, and
328 shares similar microstructural features. The inherited core and mantle of zircon show oscillatory
329 zoning under CL and BSE images, which are discordantly overgrown by relatively bright-CL rim
330 (Figs. 5i-l, 6b). Zircon in this sample yielded concordant U-Pb ages of 850-700 Ma and 630-550 Ma
331 (Fig. 6b). The youngest rim age from matrix zircon is 551 ± 14 Ma. Cores and rims of zircon included
332 in garnet gave 758-585 Ma. Among them, the weighted mean of rims is 596 ± 7 Ma ($n = 4$, MSWD =
333 0.74, probability = 0.53). Both in the matrix zircon and inclusion zircon in garnet, domains of ca. 600
334 Ma commonly correspond to the bright-CL rim, and show high Th/U ratios up to 1.6 (Fig. 5i, j).
335 However, some dark-CL parts with ca. 600 Ma age show relatively low Th/U ratios (0.05-0.38) (Fig.
336 5k).

337

338 ***Sample 2601C***

339 Zircon in the matrix and included in garnet are commonly 60-100 μm and 20-70 μm in diameter,
340 respectively (Fig. 5m-t). They share the same microstructural characteristics. The cores of zircon are
341 oscillatory zoned and bright under CL image, or unzoned and dark (Fig. 5m-t). Several- μm to ca. 10
342 μm thick, bright-CL rims are commonly developed (Fig. 5m-t except for 5o). The oscillatory zoned

cores tend to give older ages (> 600 Ma) than the unzoned dark-CL ones. Zircon in the matrix and inclusions in garnet both show concordant U-Pb ages of ca. 600-550 Ma (Figs. 5m-t, 6c). The weighted mean U-Pb age of the rims of zircon included in garnet is 583 ± 6 Ma ($n = 17$, MSWD = 1.14, probability = 0.31). No significant difference is observed between the age distribution patterns of matrix zircon and zircon inclusions in garnet. The Th/U ratios of zircon domains with 600-550 Ma ages are mostly below 0.40 (Figs. 5m-t, 6d).

Discussion

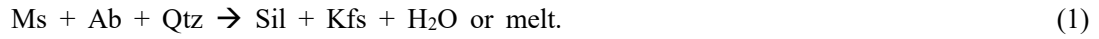
Pressure-temperature path of the pelitic gneiss from Perlebandet

Sample 3001G is strongly affected by retrograde metamorphism as suggested from the presence of retrograde andalusite and kyanite. Therefore, it is suitable for constraining the retrograde metamorphic P - T conditions. On the other hand, samples 2602D and 3001H are less affected by retrograde overprint, and thus used to estimate peak metamorphic conditions.

1. Prograde to peak metamorphic conditions

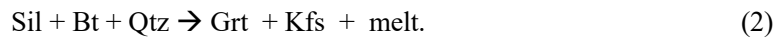
In all the sillimanite-bearing samples (3001G, 2602D and 3001H), sillimanite is commonly found as porphyroblasts in the matrix, and is considered to have been stable during peak metamorphism. The absence of prograde muscovite along the gneissose fabric together with the

presence of sillimanite + K-feldspar in the matrix suggest that peak metamorphic conditions exceeded reaction (1)

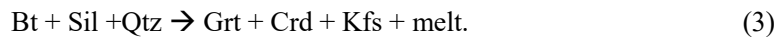


which was responsible for the formation of the core of sillimanite porphyroblasts in sample 3001G.

Sillimanite inclusions are abundant in garnet cores of samples 2602D and 3001H, and K-feldspar is also abundant in the matrix. Sillimanite in the matrix of sample 3001G is partly to completely overgrown by garnet (Fig. 2b-d), and some of the garnet overgrowths include Zn-bearing spinel grains (Fig. 2b-d), suggesting consumption of the sillimanite rims that are hosting spinel to form garnet with $X_{\text{Mg}} = 0.10\text{-}0.20$ (Fig. 7). Garnet with kyanite or andalusite inclusions is not seen in all studied samples. These are consistent with the progress of reaction (Fig. 7)



The absence of cordierite in all garnet-bearing felsic gneiss samples suggests that the *P-T* conditions did not exceed the reaction



Garnet, plagioclase, biotite and rare quartz are included in the inclusion-rich rim of a sillimanite porphyroblast in sample 3001G (Fig. 2b-d). The composition of biotite and garnet separately included in sillimanite (Table 1) are most likely to preserve compositions of entrapment, because sillimanite would hinder Fe-Mg exchange reactions between garnet and biotite after entrapment. Therefore,

prograde P - T conditions can be estimated using these minerals. The Grt-Bt (GB) geothermometer (Holdaway et al., 1997; Holdaway, 2000) and the garnet- Al_2SiO_5 -quartz-plagioclase (GASP) geobarometer (Holdaway, 2001) yielded ca. 700 °C, 0.47 GPa, which is in agreement within error of the geothermobarometry (± 50 °C and ± 0.10 GPa) with P - T conditions of reaction (2) for the observed garnet composition of $X_{\text{Mg}}^{\text{Grt}} = 0.10$ -0.20 in the NaKFMASH system (Fig. 7). The rarity of quartz inclusions in the sillimanite rims may imply local absence of quartz, in which case the result may represent the highest- P estimate. Although the Grt-Bt thermometer of Holdaway (2000) does not account for the effects of F and Cl, calculations using the Zhu and Sverjensky (1992) calibration showed that the opposing effects of F (T increase) and Cl (T decrease) on the temperature estimate canceled each other out, and thus the effects of F and Cl are negligible in this sample.

On the other hand, the absence of a significant low- P retrograde overprint in samples 2602D and 3001H suggests that such rocks preserve peak metamorphic conditions better. In these samples, garnet core with sillimanite inclusions (Fig. 2a) and matrix plagioclase core are interpreted as coexisting with sillimanite and quartz, and used in the GASP geobarometry (Holdaway, 2000). For peak temperature estimate, Zr-in-rutile thermometry (Zack et al., 2004; Tomkins et al., 2007) was applied to rutile included in sillimanite and that in the matrix. The Tomkins et al. (2007) calibration is preferred in this study since it takes pressure effect into account and is experimentally calibrated. Peak P - T conditions estimated by the intersection of Zr-in-rutile thermometry (Tomkins et al., 2007) and GASP

geobarometry (Holdaway, 2001) are ca. 768-840 °C and 0.8-1.0 GPa. The Grt-Bt geothermometry is considered less reliable than the Zr-in-rutile thermometry in this case, because the X_{Mg} of matrix biotite or inclusion biotite in garnet is more susceptible to retrograde re-equilibrium compared to rutile included in sillimanite. The peak P - T conditions above are consistent with those of reaction (2) for garnet with composition of $X_{Mg}^{Grt} \sim 0.40$, higher than that observed at the sillimanite-bearing garnet core (Table 1; Fig. 7), implying a modification of X_{Mg} of garnet during retrograde metamorphism.

Sample 3001G, affected by the low- P retrograde overprint, also preserves rutile as inclusions in garnet and K-feldspar or rarely in the matrix (Fig. 2o). The Zr-in-rutile thermometry gives temperature estimates (743-780 °C assuming 1.0 GPa) almost consistent with those of samples 2602D and 3001H. This observation strongly supports that sample 3001G shared the same peak P - T conditions as other samples before the low- P retrograde overprint.

2. Retrograde metamorphic conditions and proposed P - T path

In sample 3001G, peak garnet is commonly replaced by three Al_2SiO_5 polymorphs (Fig. 2i-j, m-n). It is difficult to define the sequence of andalusite and kyanite formation from their microtextures (Fig. 2g-j, m-n). Some sillimanite grains surrounding retrogressed garnet and including Zn-bearing spinel grains in sample 3001G (Fig. 2i) may have been originally included in garnet and survived the garnet breakdown reactions, because Zn-bearing spinel inclusions are the typical feature for prograde

sillimanite rims (Fig. 2b, c). However, the coexistence of andalusite+sillimanite, andalusite+kyanite, and andalusite+kyanite+sillimanite in the replacement microtextures of garnet suggests garnet breakdown near the P - T conditions of the Al_2SiO_5 triple point. Since the coexistence of three Al_2SiO_5 polymorphs in the garnet breakdown microstructure is only preserved in sample 3001G, it is likely that localized fluid infiltrated this sample at P - T conditions of the Al_2SiO_5 triple point to trigger the retrograde reaction. This is also supported by the GASP geobarometry (Holdaway, 2000) and the Grt-Bt geothermometry (Holdaway et al., 1997; Holdaway, 2000) using mineral compositions of the breakdown microstructure of garnet into biotite, plagioclase, quartz and Al_2SiO_5 minerals, which yield P - T conditions of ca. 600 °C and 0.48 GPa, close to the Al_2SiO_5 triple point (Fig. 7). The almost complete cancelation of the opposite effects of F and Cl in biotite on the Grt-Bt geothermometer is confirmed by using Zhu and Sverjensky (1992) calibration, supporting the above P - T estimate. Since prograde (ca. 700 °C, 0.47 GPa) and retrograde (ca. 600 °C, 0.48 GPa) P - T conditions are estimated using the same geothermobarometers, and since the effects of F and Cl in biotite can be ignored, we consider the differences between them meaningful. Therefore, by connecting prograde, peak and retrograde P - T estimates from three samples, a counterclockwise P - T path for the Perlebandet rocks is proposed (Fig. 7).

Garnet rims are also locally replaced by the intergrowth of biotite and plagioclase in all samples. Utilizing the composition of garnet rims and biotite and plagioclase in the intergrowth, and applying

the Grt-Bt geothermometer (Holdaway et al., 1997; Holdaway, 2000) and the garnet-biotite-plagioclase-quartz (GBPQ) geobarometer (Wu et al., 2004), retrograde P - T conditions of garnet breakdown to biotite + plagioclase are estimated. These vary depending on samples, and are ca. 580 °C and ca. 0.40 GPa for sample 3001G (average of 4 estimates; Fig. 7), ca. 640 °C, 0.66 GPa for sample 3001B (average of 5 estimates; Fig. 7), and ca. 760 °C, ca. 0.97 GPa for sample 2601C (average of 5 estimates; Fig. 7). Among these, an estimate from sample 3001G is consistent with the estimate by the GB-GASP pair (Fig. 7). These P - T conditions are consistent with the proposed counterclockwise P - T path (Fig. 7).

This proposed P - T path is very similar to that estimated for Brattnipene, central SRM (Fig. 1b; e.g., Adachi et al., 2013; Baba et al., 2013), suggesting that Perlebandet belongs to the SW terrane of the SRM (Fig. 1b; e.g., Mieth et al., 2014). Our results of zircon dating (Fig. 6) are consistent with previous results from Perlebandet (Shiraishi et al., 2008) in that detrital ages older than 1200 Ma are absent. This is also true for SW terrane rocks of the SRM (Osanaï et al., 2013), and thus zircon data also support Perlebandet as being part of the SW terrane (Fig. 1b).

Timings of Cl-bearing fluid infiltration and relationship with partial melting

The presence of Cl-rich biotite has been considered as evidence for the presence of brines (e.g., Newton et al., 1998; Manning and Aranovich, 2014; Safonov et al., 2014). Although the $f(\text{H}_2\text{O})/f(\text{HCl})$

ratio of the coexisting fluid can be deduced from the composition of biotite and apatite (e.g., Selby and Nesbitt, 2000), it should be noted that the salinity of the fluid cannot be directly determined by this method (e.g., Rubenach, 2005). However, if the fluid coexists with silicate melt, the HCl concentration can be related to the total Cl concentration in the fluid by the equation $\log(\text{HCl}/\Sigma \text{Cl})^{\text{aq}} = -0.63 - 0.00035 \cdot P$ (bars) up to 0.67 GPa (Piccoli and Candela, 1994). This means that at pressures typical of the middle crust, most of the Cl forms complexes with cations other than H. Therefore, considering a case where Cl-bearing fluid coexists with melt, low $f(\text{H}_2\text{O})/f(\text{HCl})$ ratios in the fluid indicates abundant chloride salts in the fluid (i.e., high salinity). It is important, therefore, to carefully consider the melt-related processes that can increase Cl contents in biotite in addition to fluid-related processes. Several possible mechanisms to elevate Cl-contents in biotite are listed below, and their likeliness is discussed:

(a) Original Cl-rich whole-rock compositions allowed biotite to become Cl-rich.

(b) Consumption of originally Cl-bearing biotite through melting reactions caused an increase of Cl-content in remaining biotite.

(c) Retrograde consumption of H_2O by hydration reactions increased Cl content in the fluid, resulting in the increase of Cl in coexisting biotite (Kullerud, 1996; Markl and Bucher, 1998).

(d) Subsolidus Cl-rich fluid infiltration occurred (e.g., Newton et al., 1998; 2014; Higashino et

al., 2015b).

(e) Infiltration of Cl-rich fluid triggered anatexis, and preferential partitioning of H₂O into the melt resulted in enrichment of Cl in the fluid (e.g., Aranovich et al., 2013; Safonov et al., 2014).

Cases (a)-(c) assume closed system behavior of Cl, and (d)-(e) assume open system behavior of Cl.

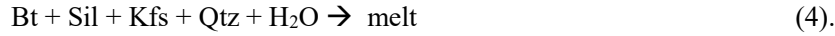
Case (b) plays an important role if the partition coefficient of Cl between granitic melt and biotite is greater than 1. Based on experiments at 0.2 GPa, $D_{Cl}(\text{biotite/melt})$ is estimated to be ~1 to 6 (Icenhower and London, 1997). Recently, Safonov et al. (2014) performed a melting experiment of a biotite-amphibole gneiss with H₂O-CO₂-(K, Na)Cl fluids at 0.55 GPa and 750-800 °C. Their compositional data of coexisting biotite ($X_{Mg} = 0.43-0.57$) and melt imply that Cl is preferentially incorporated in the melt rather than in biotite, that is, $D_{Cl}(\text{biotite/melt})$ is less than 1 at 0.55 GPa and 800 °C. Therefore, the behavior of Cl under middle crustal depths can be different from that in shallow levels of the crust, and if this is the case, case (b) alone is not likely a strong process to elevate Cl content in biotite, at least for samples 3001B and 3001G having X_{Mg} values of biotite ($X_{Mg} = 0.40-0.64$; Table 1) similar to the experiment of Safonov et al (2014).

Sample 3001G preserves Cl-rich biotite (~ 0.4 wt.%) as inclusions in garnet. Biotite inclusions in garnet tend to re-equilibrate and change X_{Mg} on cooling, while preserving their original halogen content. Biotite was already Cl-rich prior to the garnet-formation by reaction (2), because moderately

Cl-bearing biotite (< 0.30 wt.%Cl) is included in sillimanite porphyroblasts predating garnet formation (Fig. 3a). Biotite inclusions in garnet from sample 3001B show the highest Cl-content in the sample, suggesting prograde formation of Cl-enriched biotite (Fig. 3b). Therefore, case (c) can be ruled out. Although case (a) cannot be ruled out, we consider that the similar timing of Cl-enriched biotite formation in different lithologies can be best explained by the infiltration of a Cl-rich fluid. The $\log[f(\text{H}_2\text{O})/f(\text{HCl})]$ and $\log[f(\text{H}_2\text{O})/f(\text{HF})]$ values of the fluid estimated assuming its presence during prograde stage for these two samples are in good agreement (Table 1), supporting the infiltration of fluids with a similar composition. External input of Cl-rich fluid is also supported by the localized field distribution of Cl-rich minerals in the SRM as discussed in the next section.

At P - T conditions estimated for reaction (2) in Perlebandet (~ 700 °C and ~ 0.5 GPa), $a_{\text{H}_2\text{O}}$ of a pelitic gneiss undergoing partial melting can be estimated to be ~ 0.85 (Clemens and Vielzeuf, 1987). Ascribing this lowering of $a_{\text{H}_2\text{O}}$ to the addition of NaCl and KCl, $X_{\text{H}_2\text{O}}$ is estimated to be ~ 0.9 using the $a_{\text{H}_2\text{O}}$ - $X_{\text{H}_2\text{O}}$ relationship by Aranovich and Newton (1997), corresponding to ~ 26 wt% NaCl (KCl). This is the highest estimate of salinity of the fluid, because CO_2 can also contribute to lower $a_{\text{H}_2\text{O}}$. It is difficult, however, to envisage source of the voluminous high-salinity fluid. More likely case is an infiltration of smaller volume of lower salinity fluids that continually increased salinity through preferential partitioning of H_2O into anatectic melts (Aranovich et al., 2013). In such case, we may assume that the fluid-present reaction such as follows (e.g., Yardley and Barber, 1991)

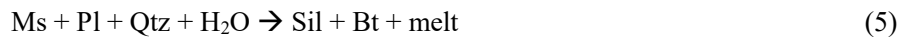
took place prior to the dehydration melting reaction (2),



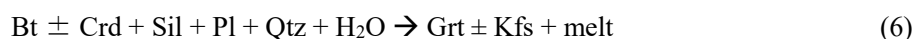
As fluid-present melting reaction proceeds by consuming H_2O , $\log[f(\text{H}_2\text{O})/f(\text{HCl})]$ and $\log[f(\text{H}_2\text{O})/f(\text{HF})]$ values of the fluid will decrease, resulting in an increase of Cl content in biotite.

Small volume of the fluid will be soon used up, resulting in cessation of the fluid-present partial melting reactions, and further melting must proceed by dehydration melting reactions (e.g., Brown, 2013) such as reaction (2) in the present case. The escape of concentrated fluids from the system with the assistance of deformation or low wetting angle of brines will also help switching the reaction from fluid-fluxed melting to dehydration melting. This process might explain why the Cl content of biotite included in peritectic garnet formed by dehydration melting reaction (2) is higher than that included in sillimanite porphyroblasts (Figs. 2b-d and 3).

On the other hand, some fluid-present melting reactions can also produce peritectic phases as sillimanite and garnet (Weinberg and Hasalová, 2015). Reactions such as



and



(Jung et al., 2000; Milord et al., 2001) are the examples reported to occur at the P - T conditions for the beginning of partial melting in this study (~ 0.5 GPa and ~ 700 °C). At medium pressure of ~ 0.5 GPa,

fluid-present melting and dehydration melting reactions take place in relatively small temperature intervals. However, observed mineral compositions and sequences of reactions are mostly consistent with the P - T diagram constructed under the scheme of dehydration melting (Fig. 7). This might suggest that fluid-present melting occurred in the Perlebandet rocks only at the onset of the prograde partial melting process, and the subsequent melting occurred through dehydration melting reactions.

In sample 3001G, matrix biotite as a remnant of reaction (2) was presumably once Cl-rich. Compositional similarity between matrix biotite and microstructurally secondary biotite (Fig. 3) suggests that moderately Cl-bearing matrix biotite is a result of recrystallization of former Cl-rich biotite, re-equilibrated with retrograde fluids possibly released from the crystallizing melt. Using the P - T conditions of retrograde metamorphism, $\log[f(\text{H}_2\text{O})/f(\text{HCl})]$ of the retrograde fluid can be estimated as 4.2-4.3, with an average of 4.3 (Table 1).

The age of metamorphism and Cl-rich fluid infiltration

In sample 3001G, rims of matrix zircon and inclusion zircon in garnet and sillimanite all yielded U-Pb ages of 580-575 Ma. Most of these zircon rims show Th/U ratios below 0.1 (Fig. 6d), typical for metamorphic zircon (e.g., Rubatto, 2002). The garnet-forming reaction was probably partial melting reaction (2). Therefore, garnet-forming, sillimanite-grade metamorphism is likely to have occurred at or after ca. 580 Ma, together with the Cl-rich fluid infiltration. Moderately Cl-bearing biotite replacing

garnet suggests that Cl-bearing aqueous fluid was present during retrograde garnet breakdown. The weighted mean U-Pb age of rims of zircon found in the microstructure of garnet replaced by Al_2SiO_5 minerals and biotite is 573 ± 5 Ma. The similarity of this age with zircon rims included in garnet implies that the retrogression took place soon after the peak metamorphism, or zircon was inert during the retrograde breakdown of garnet.

Samples 3001B and 2601C both give constraints that are consistent with the above scenario. For sample 3001B, the formation of garnet and moderately Cl-bearing biotite included in it (Fig. 3e, f) was presumably at 596 ± 7 Ma or younger. The fluid at retrograde stage shows $\log[f(\text{H}_2\text{O})/f(\text{HCl})]$ value of 4.0-5.0, with an average of 4.5 (Table 1). For sample 2601C, garnet growth would predate or coincide with 583 ± 6 Ma. Low Th/U zircon rims (Fig. 6d) supports this to be the metamorphic age. Markedly high Cl concentration of isolated matrix biotite in this sample ($\text{Cl} > 0.61$ wt.%) reflects Mg-Cl avoidance, in addition to the Cl-rich nature of the coexisted fluid, since biotite in this sample is Fe-richer than other samples (Fig. 3). The $\log[f(\text{H}_2\text{O})/f(\text{HCl})]$ of the near-peak to retrograde fluid is calculated as 3.5-4.2, with an average of 3.9 (Table 1).

To summarize, the timing of garnet-forming prograde metamorphism in Perlebandet is estimated to be ca. 580 Ma or younger. Since biotite was already enriched in Cl before the onset of reaction (2), the formation of highly to moderately Cl-bearing biotite in samples 3001G and 3001B took place before or at ca. 580 Ma during prograde metamorphism. Taking into account that estimated prograde

log[$f(\text{H}_2\text{O})/f(\text{HCl})$] and log[$f(\text{H}_2\text{O})/f(\text{HF})$] of fluid are almost the same among the samples studied, it is likely that external Cl-bearing fluid infiltration occurred, prior to or simultaneously with the sillimanite-forming reaction. On the other hand, the presence of a retrograde, Cl-bearing fluid with log[$f(\text{H}_2\text{O})/f(\text{HCl})$] = 4.0-5.0 (with one exception of 3.5) is detected from three samples. This probably lasted until ca. 550 Ma. During the retrograde decompression, log[$f(\text{H}_2\text{O})/f(\text{HCl})$] of fluids increased slightly or was almost constant (Table 1; Fig. 7).

At the outcrop scale, fluid pathways may be localized (e.g., Aranovich et al., 2010; Dubinina et al., 2015; Kusebauch et al., 2015). This is also suggested in the SRM by localized distribution of post-peak Cl-rich veins in the outcrop scale in Brattnipene (Fig. 1b; Higashino et al., 2015b). The localized distribution of prograde Cl-bearing biotite in Perlebandet shows that Cl-bearing fluid pathways may be localized during prograde metamorphism as well, but obscured by later ductile deformation.

Comparison with other areas of the SRM

The P - T - t conditions of Cl-rich aqueous fluid infiltration in the SRM have been previously determined from two other localities; the eastern part (Balchenfjella; Higashino et al., 2013a) and the central part (Brattnipene; Higashino et al., 2015a) (Fig. 1b). In Balchenfjella, the P - T conditions of Cl-rich biotite and apatite entrapment in the garnet rim are estimated to be ca. 800°C and 0.80 GPa at

603 ± 14 Ma, which corresponds to the early retrograde stage postdating a peak metamorphic event at ca. 850°C and 1.1 GPa (Higashino et al., 2013a). A subsequent Cl-poor fluid infiltration is recorded in Cl-poor matrix biotite, and estimated to have occurred at 564 ± 17 Ma from the rim age of zircon in the matrix (Higashino et al., 2013b). On the other hand, in Brattnipene, early retrograde Cl-rich fluid infiltration is estimated at ca. 700 °C, 0.75 GPa and after ca. 620 Ma (Higashino et al., 2015b). In contrast to these post-peak Cl-rich fluid activities, the present study shows that the Cl-rich biotite included in garnet was formed during prograde metamorphism possibly as a result of Cl-bearing fluid infiltration. External input of Cl-rich fluid during prograde- to peak-metamorphism possibly produced Cl-bearing partial melt, and its crystallization during decompression and cooling resulted in a release of post-peak, Cl-bearing fluid (Fig. 7).

Experimental data by Safonov et al. (2014) shows that melt can contain more Cl than coexisting biotite at 0.55 GPa and 750-800 °C. The fluid released by the crystallization of such melt would have significantly more Cl than coexisting melt (Webster, 1992; Aranovich et al., 2013). Therefore, one possible mechanism to produce Cl-rich fluid during the retrograde stage is the crystallization of Cl-bearing partial melt. However, if the partial melting and crystallization of the melt alone is the cause of Cl-rich fluid, Cl-rich biotite should be more widely distributed throughout the NE terrane of the SRM where partially molten granulites and migmatites are widely distributed (Fig. 1b). What is actually observed in the field is the localized distribution of Cl-rich biotite and hornblende along

large-scale shear zones and detachments both in felsic and mafic gneisses (Fig. 1b; Higashino et al., 2015a). The distribution of Cl-rich minerals corresponds with the boundaries of magnetic anomaly domains of Mieth et al. (2014). This trend may be obscured by a possible granite intrusion near Perlebandet that is inferred to be the source of a high-magnetic anomaly (Mieth et al., 2014), but ignoring the possible effect of this granite intrusion, Perlebandet is also located along the boundaries of magnetic anomaly domains which corresponds to the major tectonic boundaries (e.g., Mieth et al. 2014). These suggest that the input of Cl in the SRM including Perlebandet is probably external, possibly as Cl-rich fluid infiltration channeled along the tectonic boundaries (e.g., Glassley et al., 2010) during prograde metamorphism. One occurrence of Cl-rich biotite in Brattnipene is at a major shear zone containing peridotite and pyroxenite lenses (Fig. 1b; location 4 of Higashino et al. 2013), supporting this idea. Because Perlebandet and Brattnipene share the counterclockwise P - T paths, they should both belong to the footwall side of the MTB based on the tectonic model by Osanai et al. (2013) (Fig. 8). Therefore, the Cl-rich fluid infiltration presumably took place at the uppermost part of the footwall of the MTB (Fig. 8).

Based on this tectonic constraint, there are several candidates for the origin of the Cl-rich fluids. Because the Mozambique Ocean is considered to have been located between the NE and SW terranes of the SRM before collision (Otsuji et al., 2016), sea water introduced into the depth and fluids released from the mantle are the likely candidates, and should be examined in future studies. High Cl

content in biotite, hornblende and apatite is a measure of low $\log[f(\text{H}_2\text{O})/f(\text{HCl})]$ of fluids, implying that the origin of Cl-rich fluids in the SRM can be also related to the magmatic activity during collision.

Multiple episodes of zircon growth within single orthogneissic samples from the NE terrane with ages from ca. 630 Ma to ca. 535 Ma described by Grantham et al. (2013) and the result of this study from the SW terrane indicate a long history of metamorphism, magmatism and deformation that affected both terranes (e.g., Elburg et al., 2016), and multiple Cl-rich fluid infiltrations took place in the SRM during this period (e.g., Higashino et al., 2013; 2015a).

Conclusion

Chlorine-rich fluid infiltration into the upper-amphibolite- to granulite-facies middle continental crust at the prograde stage of counterclockwise P - T path is likely at Perlebandet (western SRM, East Antarctica). This presumably occurred in the uppermost part of the footwall of the continental collision boundary at ca. 580 Ma. The localized distribution of Cl-rich biotite and hornblende along large-scale shear zones and detachments in the SRM supports the external input of Cl-rich fluids through tectonic boundaries during continental collision.

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References

- Adachi, T., Hokada, T., Osanai, Y., Nakano, N., Baba, S., Toyoshima, T., 2013. Contrasting metamorphic records and their implications for tectonic process in the central Sør Rondane Mountains, eastern Dronning Maud Land, East Antarctica. In: Harley SL, Fitzsimons LCW, Zhao Y (ed) Antarctica and Supercontinent Evolution. Geological Society, London, Special Publication 383, 113-133.
- Aranovich, L.Y., Shmulovich, K.I., Fedkin, V.V., 1987. The H₂O and CO₂ regime in regional metamorphism. International Geology Review 29, 1379-1401.
- Aranovich, L.Y., Dubinina, E.O., Avdeenko, A.S., Lebedeva, Y.M., Bushmin, S.A.,

649 Dolivo-Dobrovolskii, D.D., 2010. Oxygen isotopic composition of coexisting minerals of
 650 sillimanite-hypersthene rocks from the Por'ya bay area: Evidence of fluid involvement in
 651 granulite-facies metamorphism. *Geochemistry International* 48, 739-751.

652 Aranovich, L.Y., Newton, R.C., Manning, C.E., 2013. Brine-assisted anatexis: Experimental melting
 653 in the system haplogranite–H₂O–NaCl–KCl at deep-crustal conditions. *Earth and Planetary
 654 Science Letters* 374, 111-120.

655 Asami, M., Shiraishi, K., 1987. Kyanite from the western part of the Sør Rondane Mountains, East
 656 Antarctica. *Proceedings of the NIPR symposium on Antarctic Geosciences* 1, 150-168.

657 Asami, M., Osanai, Y., Shiraishi, K., Makimoto, H., 1992. Metamorphic evolution of the Sør Rondane
 658 Mountains, East Antarctica. In: Yoshida, Y., Kaminuma, K., Shiraishi, K. (Eds.), *Recent
 659 Progress in Antarctic Earth Science*. Terra Scientific Publishing Company, Tokyo, pp. 7–15.

660 Baba, S., Osanai, Y., Nakano, N., Owada, M., Hokada, T., Horie, K., Adachi, T., Toyoshima, T., 2013.
 661 Counterclockwise P–T path and isobaric cooling of metapelites from Brattnipene, Sør Rondane
 662 Mountains, East Antarctica: Implications for a tectonothermal event at the proto-Gondwana
 663 margin. *Precambrian Research* 234, 210–228.

664 Brown, M., 2013. Granite: From genesis to emplacement. *GSA Bulletin* 125, 1079–1113.

665 Dubinina E.O., Aranovich, L.Y., van Reenen, D.D., Avdeenko, A.S., Varlamov, D.A., Shaposhnikov,
 666 V.V., Kurdyukov, E.B., 2015. Involvement of fluids in the metamorphic processes within

667 different zones of the Southern Marginal Zone of the Limpopo complex, South Africa: An
 668 oxygen isotope perspective. *Precambrian Research* 256, 48-61.

669 Elburg, M.A., Andersen, T., Jacobs, J., Läufer, A., Ruppel, A., Krohne, N., Damaske, D., 2016. One
 670 Hundred Fifty Million Years of Intrusive Activity in the Sør Rondane Mountains (East
 671 Antarctica): Implications for Gondwana Assembly. *The Journal of Geology* 124, 1-26.

672 Glassley, W.E., Korstgård, J.A., Sørensen, K., 2010. K-rich brine and chemical modification of the
 673 crust during continent–continent collision, Nagssugtoqidian Orogen, West Greenland.
 674 *Precambrian Research* 180, 47–62.

675 Goldoff, B., Webster, J.D., Harlov, D.E., 2012. Characterization of fluor-chlorapatites by electron
 676 probe microanalysis with a focus on time-dependent intensity variation of halogens. *American
 677 Mineralogist* 97, 1103-1115.

678 Grantham, G.H., Macey, P.H., Ingram, B.A., Roberts, M.P. Armstrong, R.A., Hokada, T., Shiraishi,
 679 K., Jackson, C., Bisnath A., Manhica V., 2008. Terrane correlation between Antarctica,
 680 Mozambique and Sri Lanka; comparisons of geochronology, lithology, structure and
 681 metamorphism and possible implications for the geology of southern Africa and
 682 Antarctica..*Geological Society, London, Special Publications* 308, 91-119.

683 Grantham, G.H., Macey, P.H., Horie, K., Kawakami, T., Ishikawa, M., Satish-Kumar, M., Tsuchiya,
 684 N., Graser, P., Azevedo, S., 2013. Comparison of the metamorphic history of the Monapo

685 Complex, northern Mozambique and Balchenfjella and Austhameren areas Sør Rondane,
686 Antarctica: Implications for the Kuunga Orogeny and the amalgamation of N and S.
687 Gondwana. Precambrian Research 234, 85–135.

688 Grew, E.S., Asami, M., Makimoto, H., 1989. Preliminary petrological studies of the metamorphic
689 rocks of the eastern Sør Rondane Mountains. Proceedings of the NIPR symposium on Antarctic
690 Geosciences 3, 100-127.

691 Harlov, D.E., Förster, H.J., 2002. High-grade fluid metasomatism on both a local and a regional scale:
692 the Seward Peninsula, Alaska, and the Val Strona di Omegna, Ivrea-Verbano Zone, northern
693 Italy. Part 1: Petrography and silicate mineral chemistry. Journal of Petrology 43, 769-799.

694 Heinrich, W., 2007. Fluid immiscibility in metamorphic rocks. Fluid-fluid interactions. Reviews in
695 Mineralogy and Geochemistry 65, 389-430.

696 Higashino, F., Kawakami, T., Satish-Kumar, M., Ishikawa, M., Maki, K., Tsuchiya, N., Grantham,
697 G.H., Hirata, T., 2013a. Chlorine-rich fluid or melt activity during granulite facies
698 metamorphism in the Late Proterozoic to Cambrian continental collision zone- An example
699 from the Sør Rondane Mountains, East Antarctica. Precambrian Research 234, 229-246.

700 Higashino, F., Kawakami, T., Satish-Kumar, M., Ishikawa, M., Tsuchiya, N., Grantham, G.H., 2013b.
701 Multi-stage Cl-rich fluid activity and behavior of REE-bearing minerals in a Neoproterozoic
702 granulite terrane. Goldschmidt 2013 abstract, Mineralogical Magazine 77, 1298.

703 Higashino, F., Kawakami, T., Tsuchiya, N., Satish-Kumar, M., Ishikawa, M., Grantham, G.H., Sakata,
 704 S., Hattori, K., Hirata, T., 2015a. Geochemical behavior of zirconium during Cl-rich aqueous
 705 fluid infiltration under upper amphibolite facies metamorphism – A case study from
 706 Brattnipene, Sør Rondane Mountains, East Antarctica. *Journal of Mineralogical and*
 707 *Petrological Sciences* 110, 166-178.

708 Higashino, F., Kawakami, T., Tsuchiya, N., Satish-Kumar, M., Ishikawa, M., Grantham, G.H., 2015b.
 709 Mass transfer in mafic gneiss during upper-amphibolite facies chloride brine infiltration.
 710 *Goldschmidt 2015 abstract*, 1268.

711 Hiroi Y., Yanagi A., Kato M., Kobayashi T., Prame B., Hokada T., Satish-Kumar M., Ishikawa M.,
 712 Adachi, T., Osanai Y., Motoyoshi Y., Shiraishi GK., 2014. Supercooled melt inclusions in
 713 lower-crustal granulites as a consequence of rapid exhumation by channel flow. *Gondwana*
 714 *Research* 25, 226–234.

715 Holdaway, M.J., 2000. Application of new experimental and garnet Margules data to the garnet–
 716 biotite geothermometer. *American Mineralogist* 85, 881–892.

717 Holdaway, M.J., 2001. Recalibration of the GASP geobarometer in light of recent garnet and
 718 plagioclase activity models and versions of the garnet-biotite geothermometer. *American*
 719 *Mineralogist* 86, 1117-1129.

720 Holdaway, M.J., Mukhopadhyay, B., Dyar, M.D., Guidotti, C.V., Dutrow, B.L., 1997. Garnet-biotite

721 geothermometry revised: New Margules parameters and a natural specimen data set from
 722 Maine. *American Mineralogist* 82, 582-595.

723 Holness, M.B., 1997. Surface chemical controls on pore-fluid connectivity in texturally equilibrated
 724 materials. In: Jamtveit, B., Yardley, B.W.D. (Eds.), *Fluid Flow and Transport in Rocks*.
 725 Chapman and Hall, London, pp. 149–169.

726 Holness, M.B., Cesare, B., Sawyer, E.W., 2011. Melted rocks under the microscope: Microstructures
 727 and their interpretation. *Elements* 7, 247–252.

728 Ishikawa, M., Kawakami, T., Satish-Kumar, M., Grantham, G.H., Hokazono, Y., Saso, M., Tsuchiya,
 729 N., 2013. Late Neoproterozoic extensional detachment in eastern Sør Rondane Mountains, East
 730 Antarctica: Implications for the collapse of East African Antarctic Orogen. *Precambrian*
 731 *Research* 234, 247-256.

732 Icenhower, J., London, D., 1997. Partitioning of fluorine and chlorine between biotite and granitic
 733 melt: experimental calibration at 200 MPa H₂O. *Contributions to Mineralogy and Petrology*
 734 127, 17-29.

735 Jacobs, J., Bauer, W., Fanning, C.M., 2003. Late Neoproterozoic/Early Palaeozoic events in central
 736 Dronning Maud Land and significance for the southern extension of the East African Orogen
 737 into East Antarctica. *Precambrian Research* 126, 27-53.

738 Jacobs, J., Elburg, M., Läufer, A., Kleinhanns, I.C., Henjes-Kunst, F., Estrada, S., Ruppel, A.S.,

739 Damaske, D., Montero, P., Bea, F., 2015. Two distinct Late Mesoproterozoic/Early
 740 Neoproterozoic basement provinces in central/eastern Dronning Maud Land, East Antarctica:
 741 The missing link, 15–21°. *Precambrian Research* 265, 249-272.

742 Jung, S., Hoernes, S., Mezger, K., 2000. Geochronology and petrology of migmatites from the
 743 Proterozoic Damara Belt — importance of episodic fluid-present disequilibrium melting and
 744 consequences for granite petrology. *Lithos* 51, 153–179.

745 Kamei A., Horie K., Owada M., Yuhara M., Nakano N., Osanai Y., Adachi T., Hara Y., Terao M.,
 746 Teuchi S., Shimura T., Tsukada K., Hokada T., Iwata C., Shiraishi K., Ishizuka H., Takahashi Y.,
 747 2013. Late Proterozoic juvenile arc metatonalite and adakitic intrusions in the Sør Rondane
 748 Mountains, Eastern Dronning Maud Land, Antarctica. *Precambrian Research* 234, 47-62.

749 Kawakami, T., Hokada, T., Sakata, S., Hirata, T., 2016. Possible polymetamorphism indicated by
 750 monazite and zircon dating and isotope mapping of garnet, and significance of Cl-rich biotite
 751 coexisted with melt in the garnet-sillimanite gneiss, Skallevikshalsen, Lützow-Holm Complex,
 752 East Antarctica. *Journal of Mineralogical and Petrological Science* 111, 129-143.

753 Kawakami, T., Satish-Kumar, M., Tsuchiya, N., Ishikawa, M., Higashino, F., Grantham, G.H.,
 754 Yoshida, K., 2010. Pelitic metamorphic rocks from Perlebandet and Balchenfjella, Sør Rondane
 755 Mountains, East Antarctica. Abstract of the First Symposium on Polar Science. GO008.

756 Kitano, I., Osanai, Y., Nakano, N., Adachi, T., 2016. Detrital zircon provenances for metamorphic

757 rocks from southern Sør Rondane Mountains, East Antarctica: A new report of Archean to
 758 Mesoproterozoic zircons. *Journal of Mineralogical and Petrological Science* 111, 118-128.
 759 Kojima, S., Shiraishi, K., 1986. Note on the geology of the western part of the Sør Rondane
 760 Mountains, East Antarctica. *Memoirs of National Institute of Polar Research, Special Issue*, 43,
 761 116-132.
 762 Kretz, R., 1983. Symbols for rock-forming minerals. *American Mineralogist* 68, 277-279.
 763 Kullerød, K., 1996. Chlorine-rich amphiboles: interplay between amphibole composition and an
 764 evolving fluid. *European Journal of Mineralogy* 8, 355-370.
 765 Kusebauch, C., John, T., Barnes, J.D., Klügel, A., Austrheim, H.O., 2015. Halogen element and stable
 766 chlorine isotope fractionation caused by fluid–rock interaction (Bamble Sector, SE Norway).
 767 *Journal of Petrology* 56, 299-324.
 768 Li, Z., Tainosho, Y., Shiraishi, K., Owada, M., 2003. Chemical characteristics of fluorine-bearing
 769 biotite of early Paleozoic plutonic rocks from the Sør Rondane Mountains, East Antarctica.
 770 *Geochemical Journal* 37, 145–161.
 771 Li, Z., Du, Z., Yang, S., Chen, H., Song, B., Liu, D., 2006. First report of zircon SHRIMP U–Pb dating
 772 from the Dufek granite in the Sør Rondane Mountains, East Antarctica. *Journal of Zhejiang*
 773 *University Science A (Suppl. II)*, 315–319.
 774 Li, Z.L., Chen, H., Yang, S., Tainosho, Y., Shiraishi, K., Owada, M., 2007. Fluid components in

775 accessory minerals of Pan-African granitoids in the Sør Rondane Mountains, East Antarctica.
 776 Journal of Zhejiang University Science A 8, 1004-1010.
 777 Ludwig, K.R., 2012. User's manual for Isoplot 3.75. A geological toolkit for Microsoft Excel.
 778 Berkeley Geochronology Center Special Publication No.5 (revision of January 30, 2012. 75
 779 pp.).
 780 Manning, C.E., Aranovich, L.Y., 2014. Brines at high pressure and temperature: Thermodynamic,
 781 petrologic and geochemical effects. Precambrian Research 253, 6-16.
 782 Markl, G., Bucher, K., 1998. Composition of fluids in the lower crust inferred from metamorphic salt
 783 in lower crustal rocks. Nature 391, 781-783.
 784 Mathez, E.A., Webster, J.D., 2005. Partitioning behavior of chlorine and fluorine in the system
 785 apatite-melt-fluid. Geochimica et Cosmochimica Acta 69, 1275-1286.
 786 Meert, J., 2003. A synopsis of events related to the assembly of eastern Gondwana. Tectonophysics
 787 362, 1-40.
 788 Mieth, M., Jacobs, J., Ruppel, A., Damaske, D., Läufer, A., Jokat, W., 2014. New detailed
 789 aeromagnetic and geological data of eastern Dronning Maud Land: Implications for refining the
 790 tectonic and structural framework of Sør Rondane, East Antarctica. Precambrian Research 245,
 791 174-185.
 792 Milord, I., Sawyer, E.W., Brown, M., 2001. Formation of diatexite migmatite and granite magma

793 during anatexis of semi-pelitic metasedimentary rocks: an example from St. Malo, France.
794 *Journal of Petrology* 42, 487-505.

795 Munoz, J.L., Swenson, A., 1981. Chloride-hydroxyl exchange in biotite and estimation of relative
796 HCl/HF activities in hydrothermal fluids. *Economic Geology* 76, 2212-2221.

797 Munoz, J.L., 1992. Calculation of HF and HCl fugacities from biotite compositions: revised equations.
798 Geological Society of America, Abstract with Programs 24, A221.

799 Newton, R.C., Aranovich, L.Y., Hansen, E.C., Vandenheuve, B.A., 1998. Hypersaline fluids in
800 Precambrian deep-crustal metamorphism. *Precambrian Research* 91, 41-63.

801 Newton, R.C., Touret, J.L.R., Aranovich, L.Y., 2014. Fluids and H₂O activity at the onset of granulite
802 facies metamorphism. *Precambrian Research* 253, 17-25.

803 Osanai, Y., Shiraishi, K., Takahashi, Y., Ishizuka, H., Tainosho, Y., Tsuchiya, N., Sakiyama, T.,
804 Kodama, S., 1992. Geochemical characteristics of metamorphic rocks from the central Sør
805 Rondane Mountains, East Antarctica. In: Yoshida, Y., Kaminuma, K., Shiraishi, K. (Eds.),
806 Recent Progress in Antarctic Earth Science. Terra Scientific Publishing Company, Tokyo, pp.
807 17-27.

808 Osanai, Y., Nogi, Y., Baba, S., Nakano, N., Adachi, T., Hokada, T., Toyoshima, T., Owada, M.,
809 Satish-Kumar, M., Kamei, A., Kitano, I., 2013. Geologic evolution of the Sør Rondane
810 Mountains, East Antarctica: Collision tectonics proposed based on metamorphic processes and

811 magnetic anomalies. *Precambrian Research* 234, 8-29.

812 Otsuji, N., Satish-Kumar, M., Kamei, A., Tsuchiya, N., Kawakami, T., Ishikawa, M., Grantham, G. H.,
813 2013. Late-Tonian to early-Cryogenian apparent depositional ages for metacarbonate rocks
814 from the Sør Rondane Mountains, East Antarctica. *Precambrian Research* 234, 257-278.

815 Otsuji, N., Satish-Kumar, M., Kamei, A., Takazawa, E., Tsuchiya, N., Grantham, G. H., Kawakami, T.,
816 Ishikawa, M., Osanai, Y., 2016. Sr and Nd Isotopic evidence in metacarbonate rocks for an
817 extinct Island arc - ocean system in East Antarctica. *Journal of Mineralogical and Petrological*
818 *Sciences* 111, 170-180.

819 Piccoli, P., Candela, P., 1994. Apatite in felsic rocks: a model for the estimation of initial halogen
820 concentrations in the Bishop Tuff (Long Valley) and Tuolumne intrusive suite (Sierra Nevada
821 Batholith) magmas. *American Journal of Science* 294, 92-135.

822 Rubatto, D., 2002. Zircon trace element geochemistry: partitioning with garnet and the link between
823 U–Pb ages and metamorphism. *Chemical Geology* 184, 123-138.

824 Rubenach, M.J., 2005. Relative timing of albitization and chlorine enrichment in biotite in Proterozoic
825 schists, Snake Creek anticline, Mount Isa inlier, Northeastern Australia. *The Canadian*
826 *Mineralogist* 43, 349-366.

827 Ruppel, A.S., Läufer, A., Jacobs, J., Elburg, M., Krohne, N., Damaske, D., Lisker, F., 2015. The Main
828 Shear Zone in Sør Rondane, East Antarctica: Implications for the late-Pan-African tectonic

829 evolution of Dronning Maud Land. *Tectonics* 34, 1290-1305.

830 Safonov, O.G., Kosova, S.A., Van Reenen, D.D., 2014. Interaction of biotite-amphibole gneiss with
831 H₂O-CO₂-(K, Na)Cl fluids at 550MPa and 750 and 800°C: Experimental study and applications
832 to dehydration and partial melting in the middle crust. *Journal of Petrology* 55, 2419-2456.

833 Selby, D., Nesbitt, B.E., 2000. Chemical composition of biotite from the Casino porphyry Cu-Au-Mo
834 mineralization, Yukon, Canada: evaluation of magmatic and hydrothermal fluid chemistry.
835 *Chemical Geology* 171, 77-93.

836 Shiraishi, K., Kojima, S., 1987. Basic and intermediate gneisses from the western part of the Sør
837 Rondane Mountains, East Antarctica. *Proceedings of the NIPR symposium on Antarctic
838 Geosciences* 1, 129-149.

839 Shiraishi, K., Asami, M., Ishizuka, H., Kojima, H., Kojima, S., Osanai, Y., Sakiyama, T., Takahashi,
840 Y., Yamazaki, M., Yoshikura, S., 1991. Geology and metamorphism of the Sør Rondane
841 Mountains, East Antarctica. In: Thomson, M.R.A., Crame, J.A., Thomson, J.W. (Eds.),
842 *Geological Evolution of Antarctica*. Cambridge University Press, Cambridge, pp. 77–82.

843 Shiraishi, K., Osanai, Y., Tainosho, Y., Takahashi, Y., Tsuchiya, N., Kojima, S., Yanai, K., Moriwaki,
844 K., 1992. Geological map of Widerøefjellet. *Antarctic Geological Map Series*, sheet 32, scale
845 1:100,000, National Institute of Polar Research, Tokyo.

846 Shiraishi, K., Osanai, Y., Ishizuka, H., Asami, M., 1997. Geological map of the Sør Rondane

847 Mountains, Antarctica. Antarctic Geological Map Series, sheet 35, scale 1:250,000, National
848 Institute of Polar Research, Tokyo.

849 Shiraishi, K., Dunkley, D.J., Hokada, T., Fanning, C.M., Kagami, H., Hamamoto, T., 2008.
850 Geochronological constraints on the Late Proterozoic to Cambrian crustal evolution of eastern
851 Dronning Maud Land, East Antarctica: a synthesis of SHRIMP U-Pb age and Nd model age
852 data. Geological Society of London, Special Publications 308, 21–67.

853 Spear, F.S., Kohn, M.J., Cheney, J.T., 1999. P-T paths from anatectic pelites. Contributions to
854 Mineralogy and Petrology 134, 17-32.

855 Tomkins, H.S., Powell, R., Ellis, D.J., 2007. The pressure dependence of the zirconium-in-rutile
856 thermometer. Journal of metamorphic Geology 25, 703-713.

857 Touret, J.L.R., Huizenga, J.M., 2011. Fluids in granulites. The Geological Society of America Memoir
858 207, 25-37.

859 Touret, J.L.R., Santosh, M., Huizenga, J.M., 2016. High-temperature granulites and supercontinents.
860 Geoscience Frontiers 7, 101-113.

861 Toyoshima, T., Osanai, Y., Baba, S., Hokada, T., Nakano, N., Adachi, T., Otsubo, M., Ishikawa, M.,
862 Nogi, Y., 2013. Sinistral transpressional and extensional tectonics in Dronning Maud Land,
863 East Antarctica, including the Sør Rondane Mountains. Precambrian Research 234, 30-46.

864 Tsuchiya, N., Ishikawa, M., Satish-Kumar, M., Kawakami, T., Kojima, H., Kaiden, H., Miura, H.,

865 Suganuma, Y., Abe, M., Sasaki, D., Chiba, M., Okada, Y., Hashizume, F., Grantham, G.,
 866 Goderis, S., 2012. Report on geological fieldwork in the Sør Rondane Mountains, Eastern
 867 Dronning Maud Land, 2009–2010 (JARE-51). *Antarctic Record* 56, 295–379.
 868 Van den Berg, R., Huizenga, J.M., 2001. Fluids in granulites of the Southern Marginal Zone of the
 869 Limpopo Belt, South Africa. *Contributions to Mineralogy and Petrology* 141, 529–545.
 870 Watson, E.B., Brenan, J.M., 1987. Fluids in lithosphere, 1. Experimentally determined wetting
 871 characteristics of CO₂-H₂O fluids and their implications for fluid transport, host-rock physical
 872 properties and fluid inclusion formation. *Earth and Planetary Science Letters* 85, 594–615.
 873 Webster, J.D., 1992. Fluid-melt interactions involving Cl-rich granites: Experimental study from 2 to 8
 874 kbar. *Geochimica et Cosmochimica Acta* 56, 659–678.
 875 Weinberg, R.F., Hasalová, P., 2015. Water-fluxed melting of the continental crust: A review. *Lithos*
 876 212–215, 158–188.
 877 Wu, C.-M., Zhang, J., Ren, L.-D., 2004. Empirical garnet-biotite-plagioclase-quartz (GBPQ)
 878 geobarometry in medium- to high-grade metapelites. *Journal of Petrology* 45, 1907–1921.
 879 Yardley, B.W.D., Barber, J.P., 1991. Melting reactions in the Connemara Schists: the role of water
 880 infiltration in the formation of amphibolite facies migmatites. *American Mineralogist* 76, 848–
 881 856.
 882 Zack, T., Moraes, A.R., Kronz, A.A., 2004. Temperature dependence of Zr in rutile: empirical

calibration of a rutile thermometer. *Contributions to Mineralogy and Petrology* 148, 471-488.

Zhu, C., Sverjensky, D.A., 1991. Partitioning of F-Cl-OH between minerals and hydrothermal fluids.

Geochimica et Cosmochimica Acta 55, 1837-1858.

Zhu, C., Sverjensky, D.A., 1992. F-Cl-OH partitioning between biotite and apatite. *Geochimica et*

Cosmochimica Acta 56, 3435-3467.

Figure captions

Figure 1. (a) Gondwana amalgamation model by Neoproterozoic orogens. East African Orogen and

Kuunga Orogen (Meert, 2003) are shown. Position of the Sør Rondane Mountains is shown by

a star. (b) Geological map of the Sør Rondane Mountains, East Antarctica (modified after

Shiraishi et al., 1997, 2008; Osanai et al., 1992; 2013; Toyoshima et al., 2013; Ishikawa et al.,

2013), showing the location of Perlebandet. Chlorine concentrations of biotite (circles) and

amphibole (squares) in pelitic and mafic gneisses (Higashino et al., 2013a; 2015a) are also

shown. Warm color represents biotite or hornblende with higher-Cl contents. Note that Cl-rich

biotite and hornblende are localized near tectonic boundaries and shear zones. location 4;

location 4 of Higashino et al. (2013). The Main Tectonic Boundary (O) is after Osanai et al.

(2013) and the Main Tectonic Boundary (M) is after Mieth et al. (2014). (c) Geological map of

Perlebandet after Shiraishi et al. (1992). Sample localities are also shown.

Figure 2. (a) Garnet porphyroblast including abundant sillimanite needles in the core. Sillimanite is also arranged along the gneissose structure of the matrix (top). Sample 2602D. Plane polarized light (PPL). (b)-(o) Mode of occurrence of metamorphic minerals in a garnet-sillimanite-biotite gneiss (sample 3001G). (b) Sillimanite including Zn-bearing spinel overgrown by garnet. This microstructure is interpreted to represent staurolite breakdown. Crossed polarized light (CPL). (c) Sillimanite porphyroblast with the inclusion-poor core and inclusion-rich rim. Subgrain boundaries can be clearly observed. CPL. (d) Enlargement of the dotted square in (c). Zn-bearing spinel is included in the inclusion-rich rim of the sillimanite porphyroblast. Cl-rich biotite and ilmenite are included in the inclusion-poor core of the sillimanite. PPL. (e) Sillimanite, andalusite and biotite replacing garnet. PPL. (f) Garnet rim replaced by biotite + andalusite intergrowth with minor fibrolitic sillimanite. PPL. (g) BSE image of breakdown microstructure of garnet replaced by biotite, plagioclase, andalusite + quartz intergrowth, kyanite and muscovite. Outlines of kyanite grains are indicated by red lines. (h) Panchromatic CL image of the same area as (g). Warm colors indicate higher CL intensity. Note the high CL intensity of kyanite compared to low CL intensity of andalusite. (i) BSE image of breakdown microstructure of garnet replaced by biotite, plagioclase, quartz, andalusite, kyanite and sillimanite. Sillimanite includes Zn-bearing spinel grains. Outline of kyanite grains are indicated by red lines. (j) Panchromatic CL image of the same area as (i).

919 Warm colors indicate higher CL intensity. Note the high CL intensity of kyanite compared to
 920 moderate and low intensity of sillimanite and andalusite, respectively. (k) Garnet including
 921 sillimanite and Zn-bearing spinel, which is partly replaced by the aggregate of Bt + And + Sil +
 922 Crn + Spl + Ms at the rim. PPL. (l) CPL of (k). Sillimanite is separately included in garnet,
 923 whereas andalusite and sillimanite are found in the replacement microstructure of garnet. (m)
 924 Garnet that is including Zn-bearing spinel is partly replaced by the retrograde aggregate of Bt +
 925 And + Ky + Sil + Spl. PPL. (n) CPL of (m). Note that andalusite and kyanite (right), as well as
 926 andalusite and sillimanite (center) are in direct contact. (o) A BSE image of rutile partly
 927 replaced by ilmenite. Both of them are included in garnet.

928 Figure 3. Plots showing the variations of biotite composition depending on the mode of occurrence. (a)
 929 TiO_2 (wt.%) vs X_{Mg} plot for sample 3001G. (b) Cl (wt.%) vs X_{Mg} plot for sample 3001G. (c)
 930 TiO_2 (wt.%) vs X_{Mg} plot for sample 3001B. (d) Cl (wt.%) vs X_{Mg} plot for sample 3001B. (e)
 931 TiO_2 (wt.%) vs X_{Mg} plot for sample 2601C. (f) Cl (wt.%) vs X_{Mg} plot for sample 2601C.

932 Figure 4. X-ray elemental mappings and BSE images showing the mode of occurrence of Cl-rich
 933 biotite from samples 3001B (a-c) and 2601C (d-f). (a) BSI of garnet including Cl-rich biotite
 934 and apatite. Garnet is partly replaced by retrograde biotite at the rim and along the cracks. (b)
 935 X-ray elemental map of Cl for the area including (a). Cl-rich biotite (yellow to yellowish green)
 936 is present as inclusions in garnet and as a matrix phase (especially at the top of the map).

Retrograde biotite replacing garnet has lower Cl content (light blue). Apatite included in garnet is enriched in Cl. (c) X-ray elemental map of Mg for the same area as (b). Some of the Cl-rich biotite grains included in garnet show higher Mg content (red) than the matrix biotite (greenish yellow). (d) BSI of garnet partly replaced by biotite-plagioclase intergrowths. (e) X-ray elemental maps of Cl for the area including (d). Cl-rich biotite is present as an isolate matrix phase (yellowish green). Moderately Cl-bearing biotite is present as a biotite-plagioclase intergrowth replacing garnet (light blue). (f) X-ray elemental map of Mg for the same area as (d).

Figure 5. CL images of zircon from Perlebandet. (a)-(h) Sample 3001G. (i)-(l) Sample 3001B. (m)-(t) Sample 2601C. Red circles represent the pits of the LA-ICPMS U-Pb dating (5 μ m) and numbers given are the $^{206}\text{Pb}/^{238}\text{U}$ age $\pm$ 2S.D. error [better than 95-105% concordance, where concordance = $(^{206}\text{Pb}/^{238}\text{U} \text{ age}) * 100 / (^{207}\text{Pb}/^{235}\text{U} \text{ age})$] and Th/U ratio. *in Grt bd*; zircon present in garnet breakdown microstructure developed around garnet. *matrix*; zircon present in the matrix. *in Grt/Sil rim*; zircon included in garnet/sillimanite rim. *** Ma; discordant data point.

Figure 6. (a)-(c) Concordia diagrams and probability density plot (inset) for the LA-ICPMS U-Pb zircon dating. Concordant data (concordance = 95-105%) are used to construct the probability density plot. Color variation of the error ellipses represents Th/U ratio of the dated spots. Note that ages older than ca. 1200 Ma is absent in all samples. (a) Sample 3001G. (b) Sample 3001B.

(c) Sample 2601C. (d) A plot showing the relationship between concordant age vs Th/U ratio of the analyzed spots.

Figure 7. Pressure-temperature diagram showing a P - T - t path (red arrows) for Perlebandet rocks.

Evolution of microstructure for sample 3001G is given as sketches (1)-(3) and change of fluid compositions along the P - T - t path is also indicated. Note that Cl-rich fluid is present from prograde metamorphism. Petrogenetic grid for the NaKFMASH system with contours of $Mg/(Fe+Mg) = 0.1$ - 0.4 in garnet in divariant Als + Grt + Bt assemblage are from Spear et al. (1999). Prograde, peak and retrograde P - T estimates by the Grt-Bt geothermometer (GB) (Holdaway et al., 1997; Holdaway, 2000) and the GASP geobarometer (Holdaway, 2001) are shown as gray, red and black squares, respectively. Peak P - T estimate by the Zr-in-rutile geothermometer (Tomkins et al., 2007), the Grt-Bt geothermometer (Holdaway et al., 1997; Holdaway, 2000) and the GASP geobarometer (Holdaway, 2001) is shown by a red broken diamond. Zr-in-rutile₁₅₅₀ represents a result of the Zr-in-rutile geothermometer (Tomkins et al., 2007) for 1550 ppm Zr, and Zr-in-rutile₂₂₀₀ represents that for 2200 ppm Zr. Retrograde P - T estimates by the Grt-Bt geothermometer (Holdaway et al., 1997; Holdaway, 2000) and the GBPQ geobarometer (Wu et al., 2004) using compositions of garnet rims and biotite and plagioclase in the biotite-plagioclase intergrowths are shown as solid squares, where green, blue and brown squares are from samples 3001B, 3001G and 2601C, respectively. These

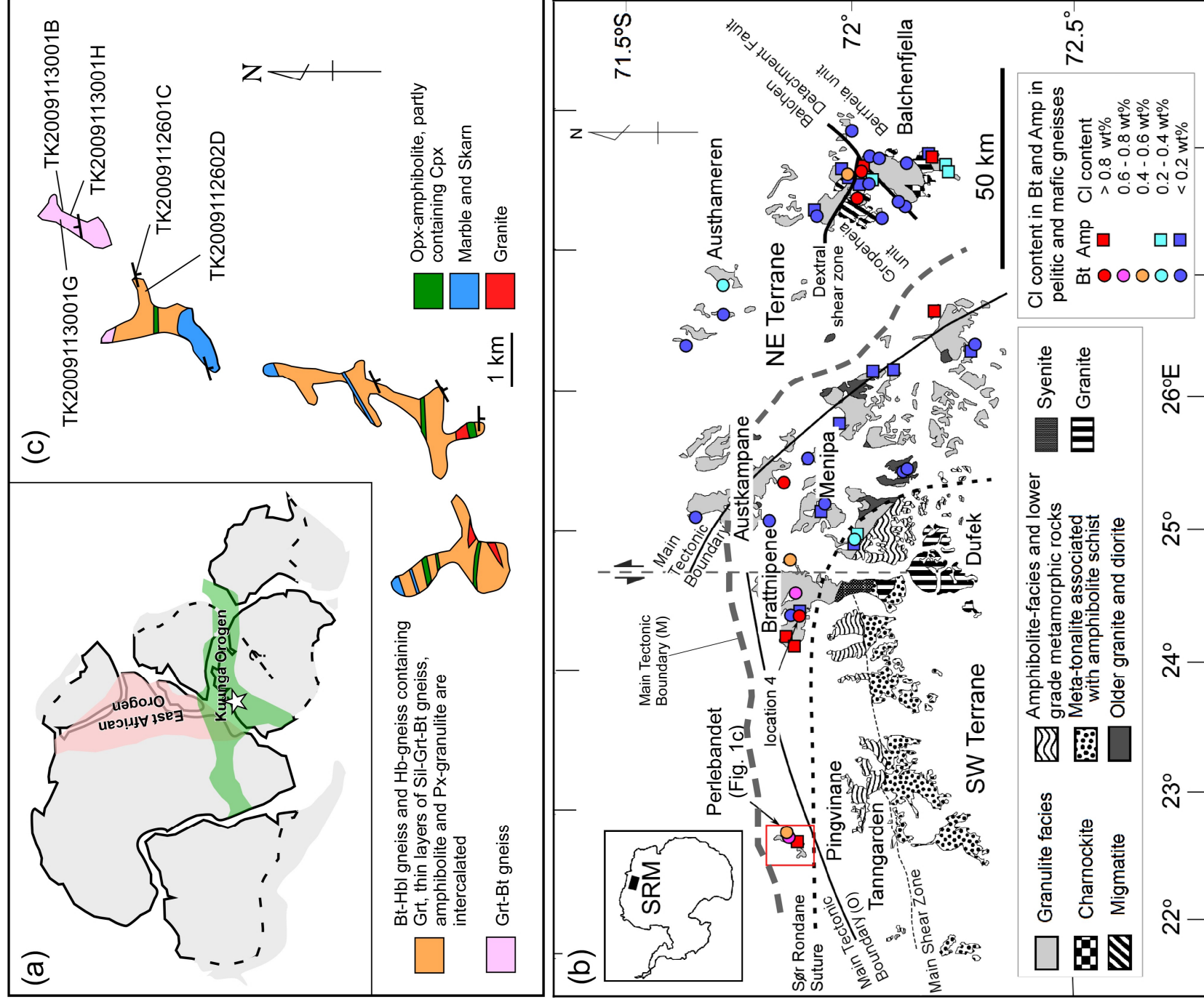
estimates would accompany errors of ± 50 °C and ± 0.1 GPa, which are not shown for simplicity. Numbers of the reactions correspond to those in the text. Reactions (4)–(6) are not shown.

Figure 8. Simplified cross section showing the tectonic model for the continental collision in the SRM, modified after Osanai et al. (2013). Chlorine-rich fluid infiltration in Perlebandet presumably took place at the uppermost part of the footwall of the MBT. Chlorine-rich fluid infiltration in Balchenfjella is dated to be at ca. 603 Ma (Higashino et al., 2013), and would be an older event than that in Perlebandet (ca. 580 Ma). BDF: Balchen Detachment Fault (Ishikawa et al., 2013).

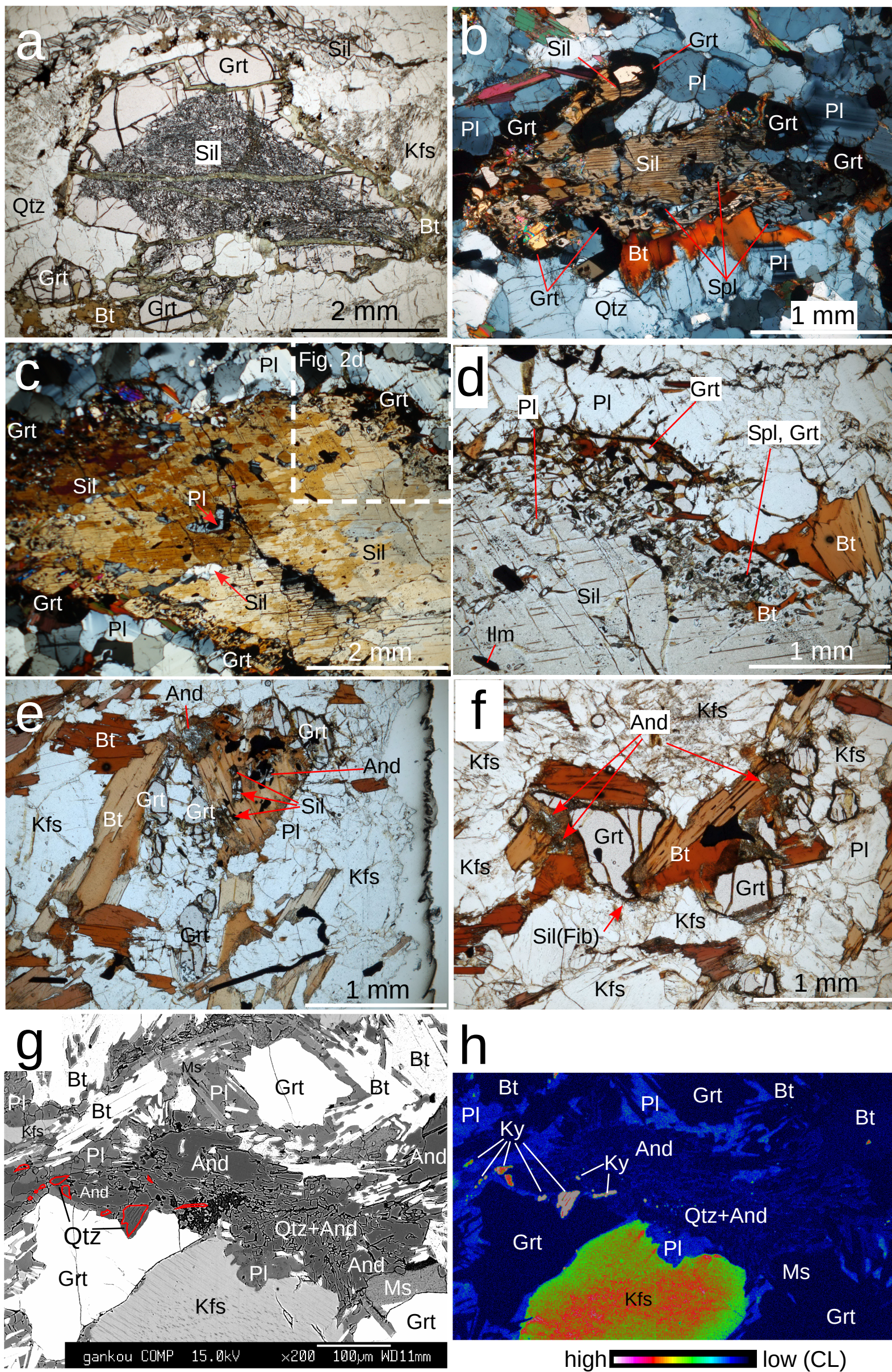
^{*1} This study, ^{*2} Higashino et al. (2015a), ^{*3} Higashino et al. (2013).

Table 1. Representative mineral analysis of biotite, garnet and plagioclase from samples 3001G, 3001B and 2601C. The $\log[f(\text{H}_2\text{O})/f(\text{HCl})]$ and $\log[f(\text{H}_2\text{O})/f(\text{HF})]$ values of the fluid that possibly coexisted with Cl-bearing biotite (Munoz, 1992) are also shown. ^{*1} Based on Munoz (1992). ^{*2} Temperature used in calculating $\log[f(\text{H}_2\text{O})/f(\text{HCl})]$ and $\log[f(\text{H}_2\text{O})/f(\text{HF})]$ values of the fluid possibly coexisted with biotite. Temperature was estimated using the Grt-Bt geothermometer (Holdaway et al., 1997; Holdaway, 2000) and the GASP (Holdaway, 2001) and Grt-Bt-Pl-Qtz (Wu et al., 2004) geobarometers. ^{*3} Temperature was estimated using Zr-in-rutile geothermometer by Tomkins et al. (2006) and GASP geobarometer (Holdaway, 2001).

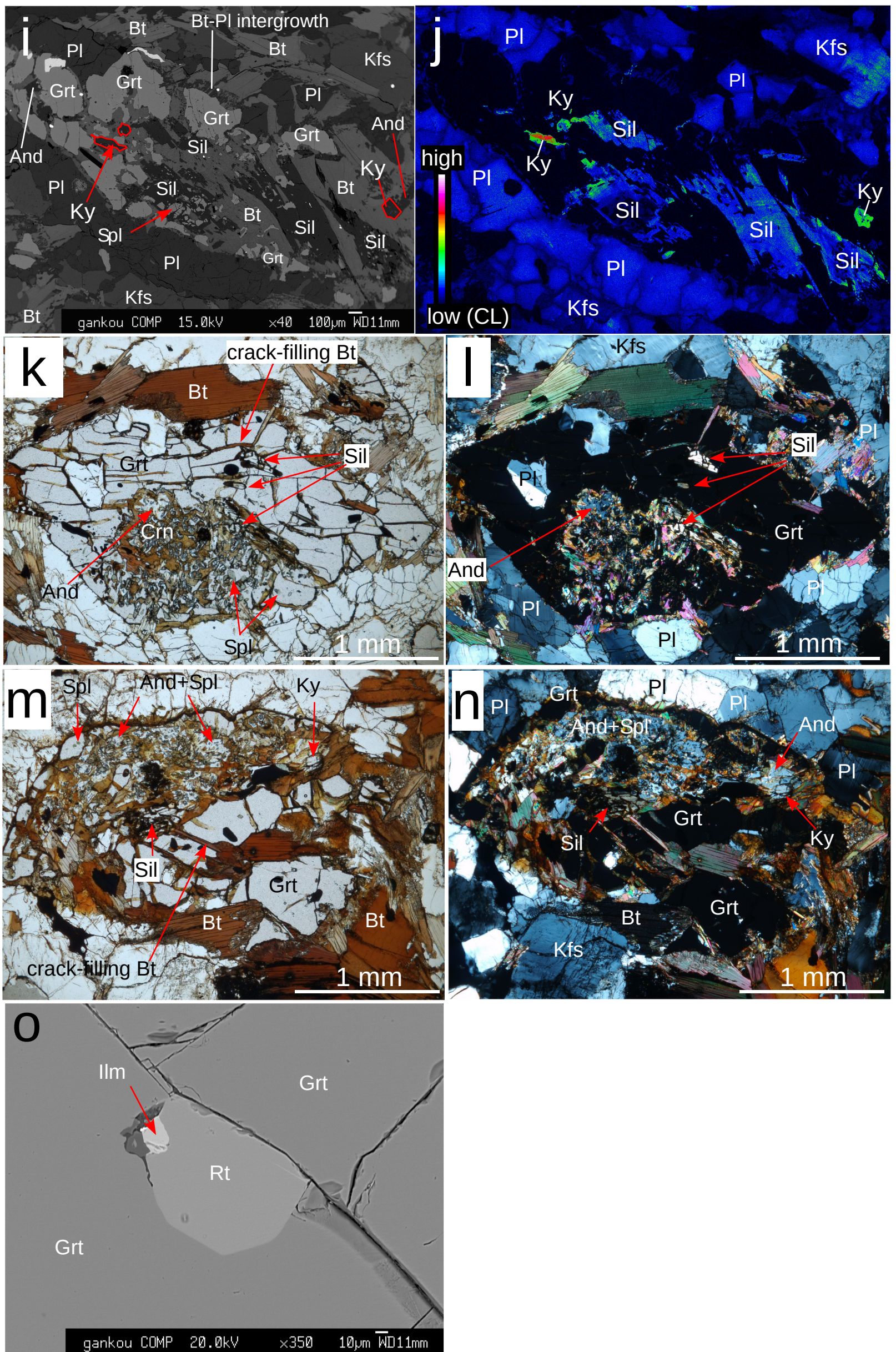
991 Supplementary Table 2. Summary of the results of LA-ICPMS U-Pb zircon dating.



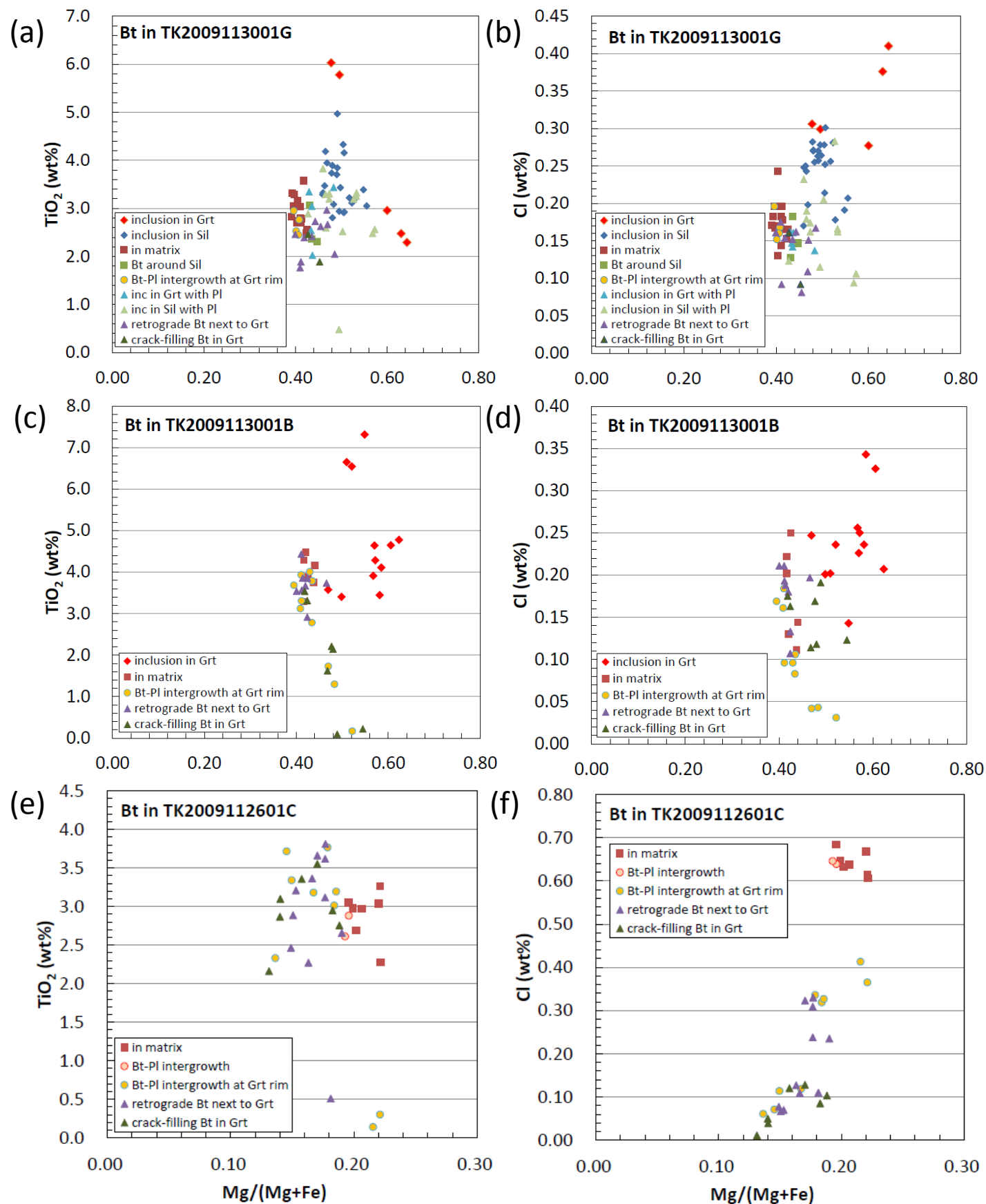
Kawakami et al. Fig. 1



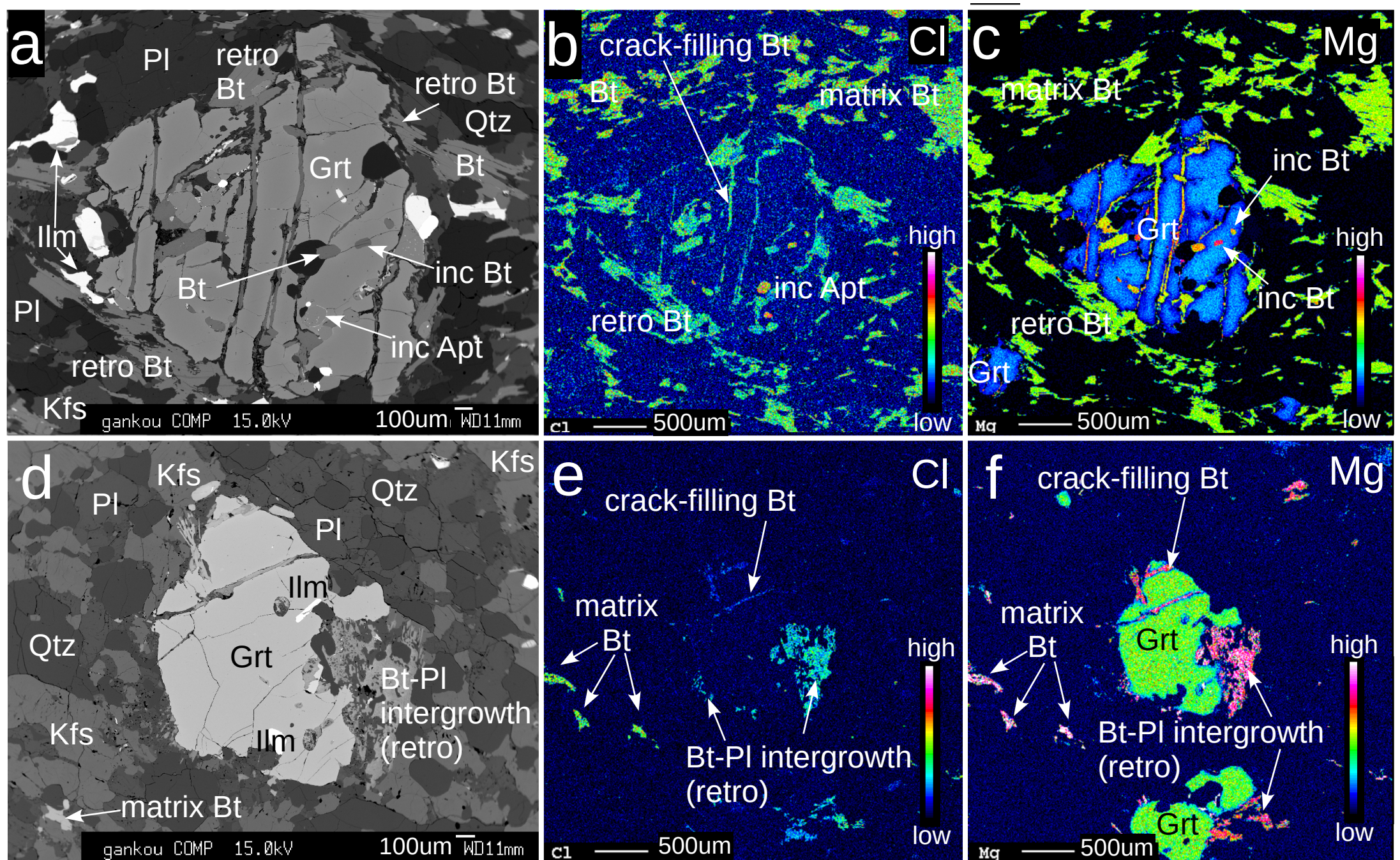
Kawakami et al. Fig. 2



Kawakami et al Fig 2 (continued)



Kawakami et al. Fig. 3



Kawakami et al Fig 4

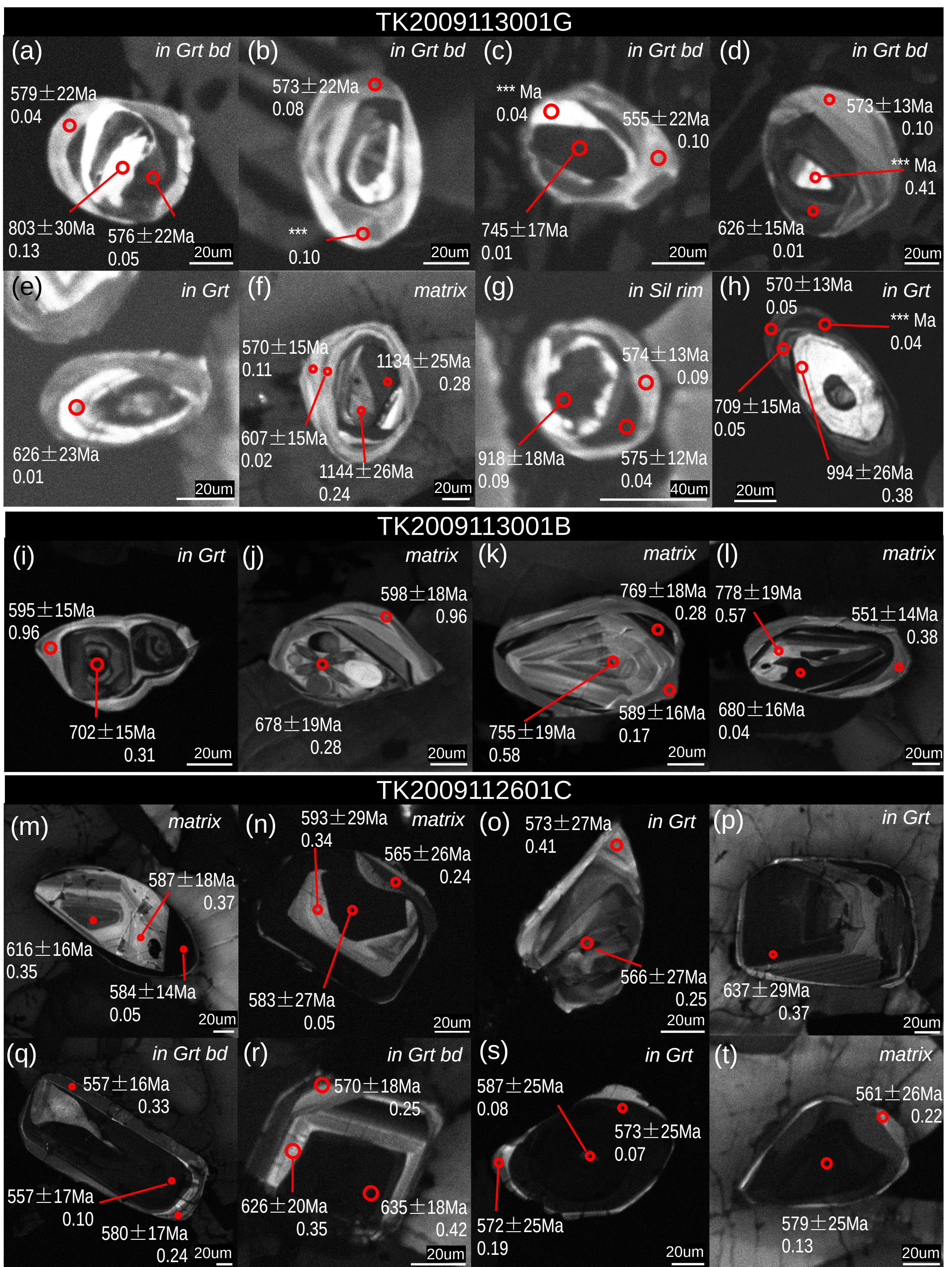
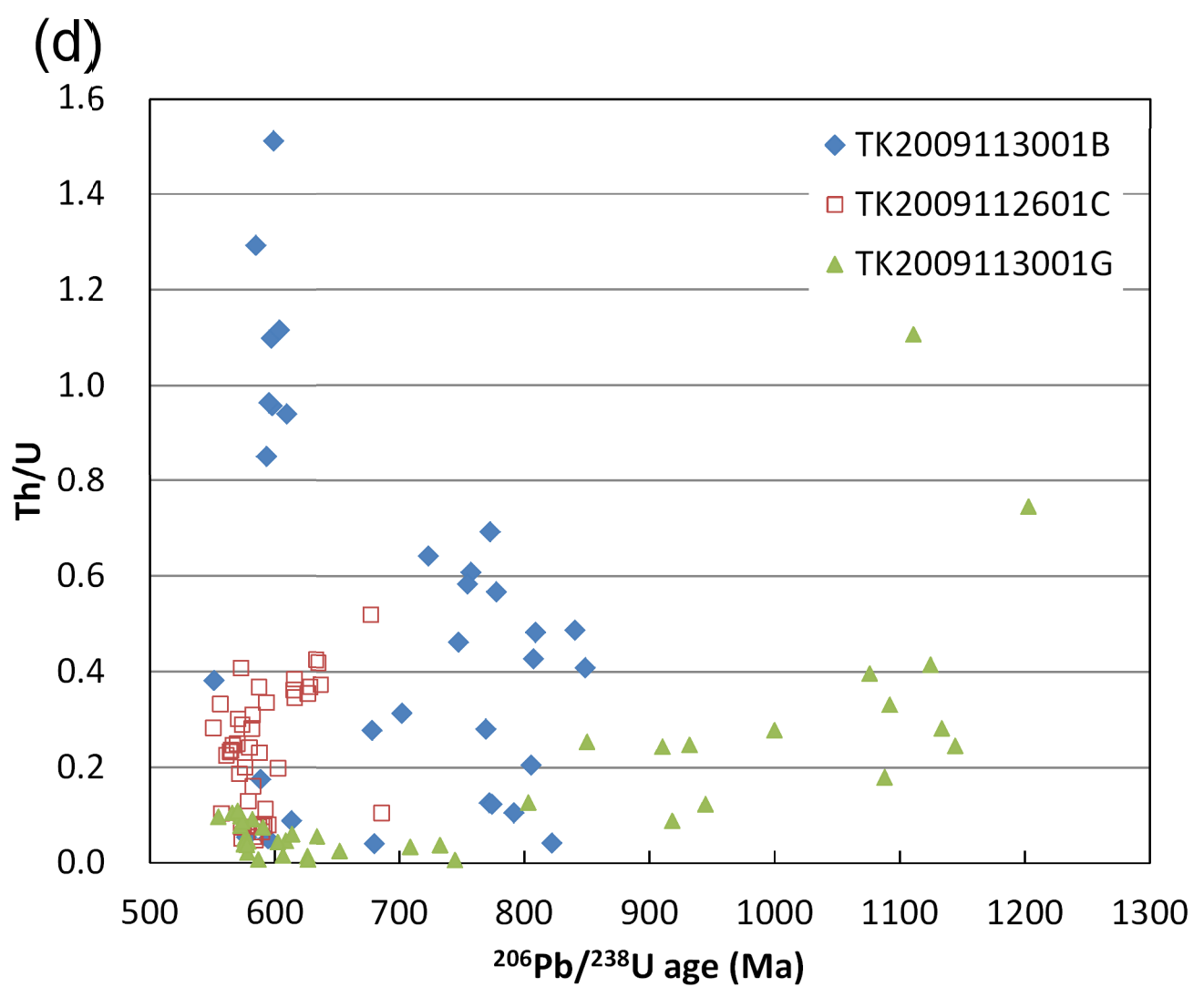
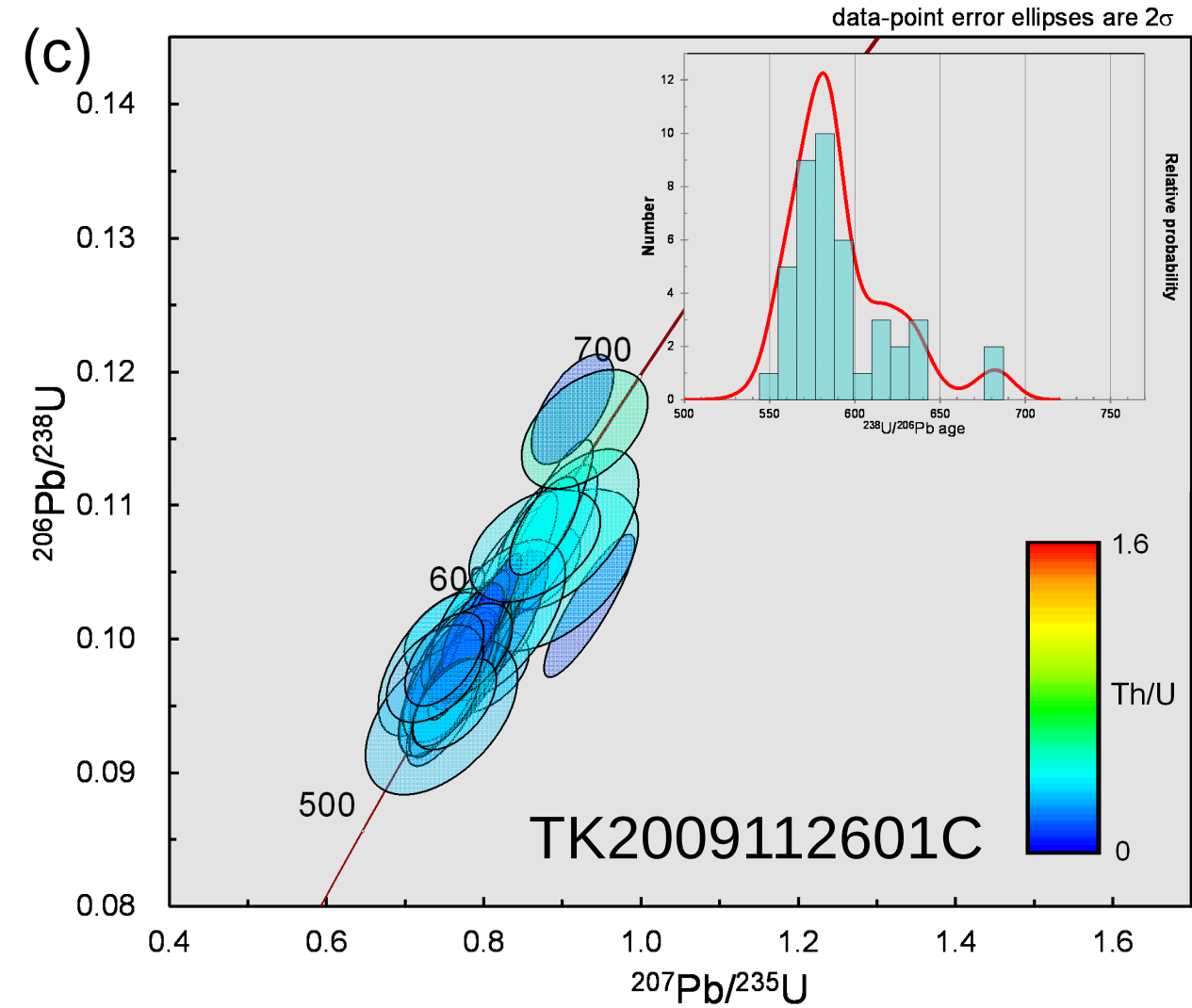
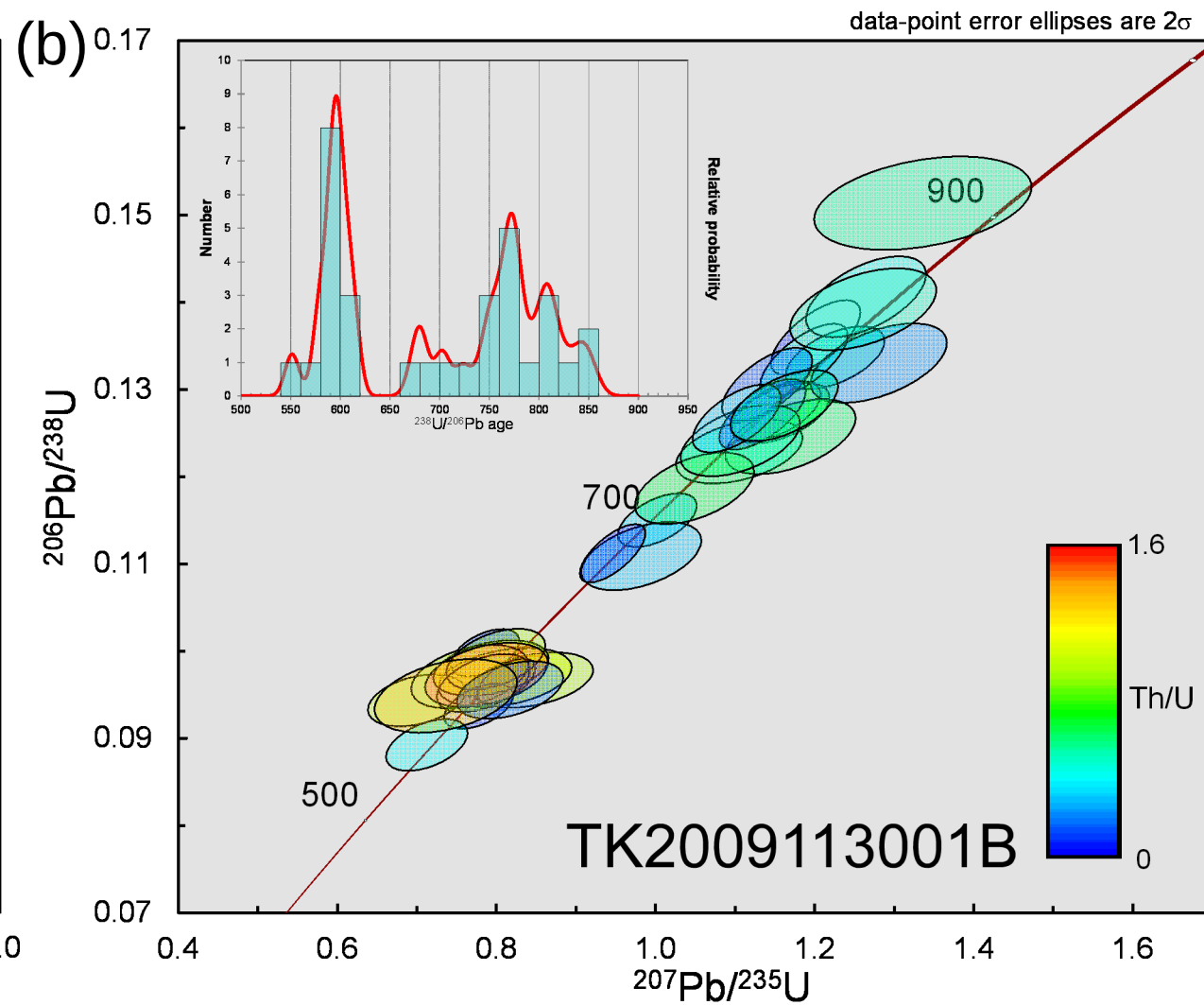
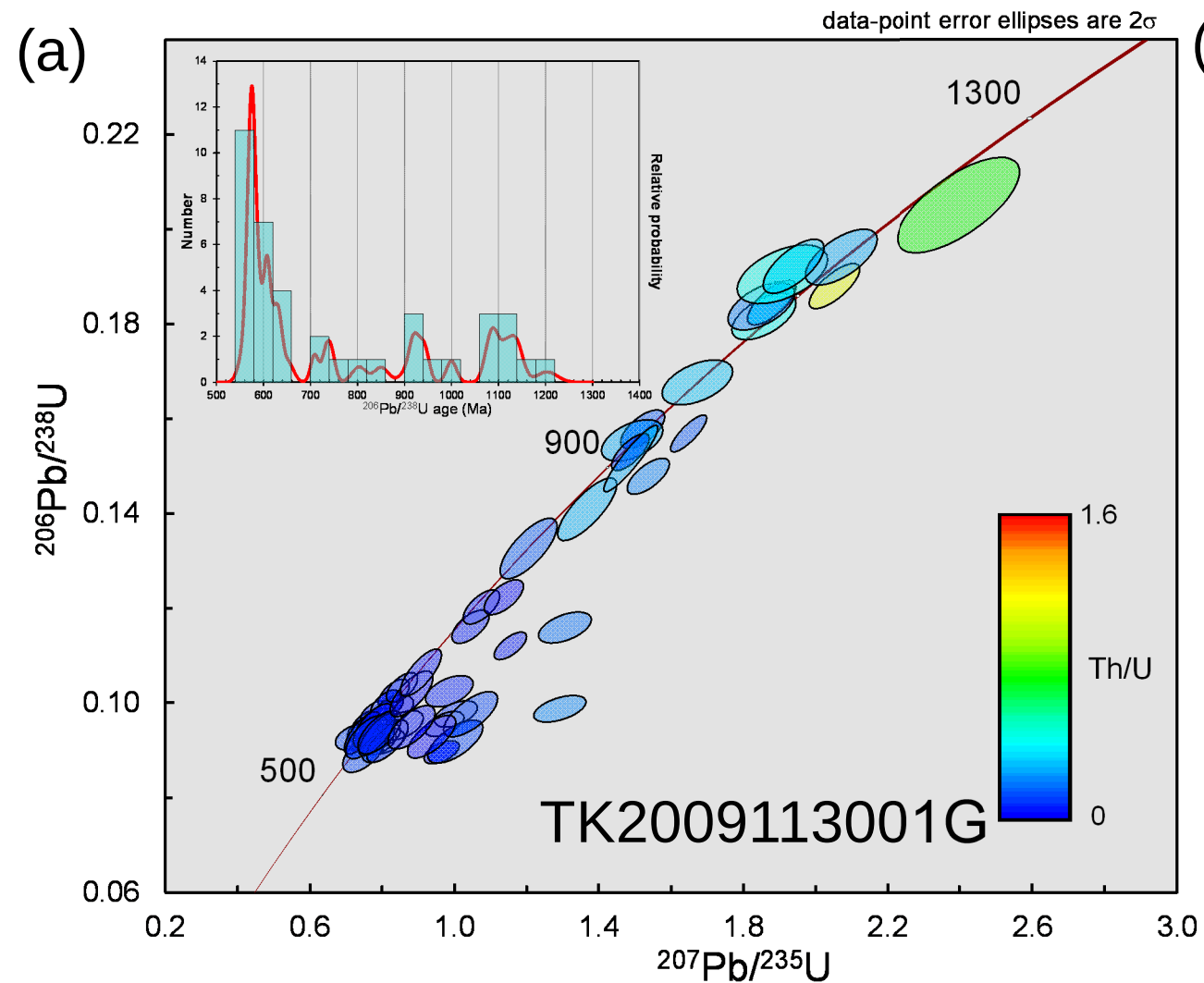


Fig. 5 Kawakami et al.



Kawakami
et al. Fig. 6

Perlebandet
(prograde Cl-rich fluid
infiltration at ca. 580 Ma^{*1})

Brattnipene
(retrograde brine
infiltration ^{*2})

MTB

BDF

Balchenfjella
(near-peak Cl-rich fluid
infiltration at ca. 603 Ma^{*3})

amphibolite- &
greenschist-facies

SW terrane (footwall)

granulite-facies

NE terrane
(hanging wall)

amphibolite
-facies

Fig. 8 Kawakami et al.

sample	TK2009113001G																	TK2009112601C				
mineral	Pl	Pl	Pl	Pl	Grt	Grt	Grt	Grt	Spl	Bt	Bt	Bt	Bt	Bt	Bt	Bt	Bt	Grt	Grt	Pl	Pl	Pl
occurrence	inclusion in Sil	inclusion in Sil	Pl moat around Sil (Sil side)	Pl moat around Sil (Kfs side)	overgrowth on Sil	overgrowth on Sil	in matrix	in matrix	inclusion in Sil rim	inclusion in Grt	inclusion in Sil	in matrix (isolated)	in matrix (isolated)	Bt-Pl intergrowth replacing Grt	retrograde Bt next to Grt	crack-filling Bt in Grt		in matrix	in matrix	in matrix	in matrix	Bt-Pl intergrowth replacing Grt
core/rim	core	rim			core	rim	core	rim										rim	core	rim	core	
SiO ₂	59.65	59.71	61.01	62.14	38.95	37.76	37.81	37.48	0.14	37.70	34.78	36.68	35.85	35.29	34.92	35.44		38.00	38.33	61.41	61.19	61.89
TiO ₂	0.00	0.06	0.00	0.10	0.00	0.02	0.05	0.00	0.00	2.29	4.19	3.15	3.58	2.76	2.39	1.89		0.01	0.08	0.01	0.00	0.03
Al ₂ O ₃	26.02	25.63	24.76	23.72	22.00	21.18	21.72	21.26	61.03	19.12	18.50	18.91	19.30	19.04	18.94	20.28		21.23	21.10	23.93	24.06	23.88
Cr ₂ O ₃	0.00	0.00	0.00	0.00	0.02	0.08	0.00	0.06	0.11	0.00	0.06	0.10	0.05	0.07	0.09	0.01		0.00	0.04	0.00	0.00	0.00
FeO	0.11	0.05	0.00	0.02	32.31	36.58	35.68	36.04	27.07	13.57	19.09	20.20	20.43	20.39	21.17	18.59		33.74	31.81	0.06	0.02	0.38
ZnO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.	n.d.
MnO	0.01	0.00	0.02	0.00	0.62	1.44	0.84	1.83	0.06	0.11	0.04	0.02	0.06	0.04	0.14	0.05		0.77	0.82	0.03	0.00	0.02
MgO	0.00	0.00	0.00	0.00	4.90	2.38	3.26	2.48	5.56	13.74	9.33	7.68	8.21	7.89	7.90	8.64		1.48	1.95	0.01	0.00	0.02
CaO	7.78	6.92	6.54	5.52	2.29	1.49	2.27	1.44	0.00	0.08	0.02	0.00	0.00	0.01	0.00	0.00		6.36	7.17	5.90	5.94	5.60
BaO	0.15	0.06	0.09	0.02	0.11	0.06	0.11	0.00	0.06	0.30	0.08	0.16	0.05	0.00	0.00	0.00		0.09	0.00	0.02	0.00	0.00
Na ₂ O	7.24	7.65	7.95	8.69	0.00	0.02	0.04	0.02	0.00	0.19	0.05	0.12	0.10	0.11	0.12	0.16		0.07	0.00	8.14	8.20	8.35
K ₂ O	0.23	0.19	0.25	0.16	0.02	0.01	0.00	0.00	0.04	9.13	9.58	9.63	9.56	10.01	9.77	9.87		0.01	0.03	0.28	0.15	0.15
F	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.36	0.08	0.06	0.09	0.16	0.07	0.16		n.d.	n.d.	n.d.	n.d.	n.d.
Cl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.41	0.24	0.24	0.17	0.17	0.15	0.09		n.d.	n.d.	n.d.	n.d.	n.d.
-O≡F	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.15	0.03	0.03	0.04	0.07	0.03	0.07		n.d.	n.d.	n.d.	n.d.	n.d.
-O≡Cl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.09	0.05	0.05	0.04	0.04	0.03	0.02		n.d.	n.d.	n.d.	n.d.	n.d.
Total	101.18	100.26	100.62	100.37	101.22	101.03	101.78	100.61	100.04	96.51	96.16	96.80	97.48	95.87	95.60	95.09		101.76	101.32	99.78	99.56	100.31
number of O	8	8	8	8	12	12	12	12	4	22	22	22	22	22	22	22		12	12	8	8	8
Si	2.64	2.66	2.70	2.75	3.03	3.02	2.98	3.01	0.00	5.50	5.28	5.52	5.37	5.40	5.37	5.40		3.01	3.03	2.73	2.73	2.74
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.25	0.48	0.36	0.40	0.32	0.28	0.22		0.00	0.00	0.00	0.00	0.00
Al	1.36	1.34	1.29	1.24	2.02	2.00	2.02	2.01	2.00	3.29	3.31	3.35	3.41	3.43	3.43	3.64		1.98	1.96	1.26	1.27	1.25
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.00		0.00	0.00	0.00	0.00	0.00
Fe	0.00	0.00	0.00	0.00	2.10	2.45	2.36	2.42	0.63	1.66	2.42	2.54	2.56	2.61	2.72	2.37		2.23	2.10	0.00	0.00	0.01
Mn	0.00	0.00	0.00	0.00	0.04	0.10	0.06	0.12	0.00	0.01	0.00	0.00	0.01	0.00	0.02	0.01		0.05	0.05	0.00	0.00	0.00
Mg	0.00	0.00	0.00	0.00	0.57	0.28	0.38	0.30	0.23	2.99	2.11	1.72	1.83	1.80	1.81	1.96		0.17	0.23	0.00	0.00	0.00
Ca	0.37	0.33	0.31	0.26	0.19	0.13	0.19	0.12	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00		0.54	0.61	0.28	0.28	0.27
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
Zn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.12	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.	n.d.
Na	0.62	0.66	0.68	0.74	0.00	0.00	0.01	0.00	0.00	0.05	0.02	0.03	0.03	0.03	0.04	0.05		0.01	0.00	0.70	0.71	0.72
K	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	1.70	1.85	1.85	1.83	1.95	1.92	1.92		0.00	0.00	0.02	0.01	0.01
F	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.17	0.04	0.03	0.04	0.08	0.04	0.08		n.d.	n.d.	n.d.	n.d.	n.d.
Cl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.10	0.06	0.06	0.04	0.04	0.04	0.02		n.d.	n.d.	n.d.	n.d.	n.d.
Total cation	5.00	5.00	5.00	5.01	7.96	7.98	8.01	7.99	2.99	15.48	15.51	15.39	15.45	15.56	15.60	15.55		8.01	7.99	5.00	5.00	5.00
Mg/(Fe _{total} +Mg)					0.21	0.10	0.14	0.11	0.27	0.64	0.47	0.40	0.42	0.41	0.40	0.45		0.07	0.10			
An	37.0	33.0	31.0	25.7																28.2	28.3	26.8
log(f _{SiO2} /f _{H2O}) of fluid *1										3.65	3.94			4.24	4.28							
log(f _{SiO2} /f _{H2O}) of fluid *2										0.12	1.19			2.19	2.25							
log(f _{SiO2} /f _{H2O}) of fluid *1										4.31	5.07			5.12	5.46							
Temperature (°C)										800 ⁺⁴	700 ⁻³			580 ⁻³	580 ⁻³							

sample	TK2009112601C						TK2009113001B													
mineral	Bt	Bt	Bt	Bt	Bt	Bt	Grt	Grt	Pl	Pl	Bt	Bt	Bt	Bt	Bt	Bt	Bt	Bt	Bt	
occurrence	in matrix	in matrix	Bt-Pl intergrowth replacing Grt	Bt-Pl intergrowth replacing Grt	retrograde Bt to Grt	crack- filling Bt in Grt	in matrix	in matrix	in matrix	Bt-Pl intergrowth replacing Grt	inclusion in Grt	inclusion in Grt	in matrix	in matrix	in matrix (near Grt)	Bt-Pl intergrowth replacing Grt	retrograde Bt to Grt	crack- filling Bt in Grt		
core/rim							core	rim	core											
SiO ₂	35.22	34.90	34.57	34.90	34.77	33.93	38.63	37.82	59.05	54.60	37.27	38.17	37.25	37.06	36.33	37.24	35.79	36.52		
TiO ₂	2.28	3.12	3.72	0.30	0.51	2.95	0.06	0.11	0.04	0.07	4.11	3.91	4.16	3.75	4.29	0.17	3.56	0.09		
Al ₂ O ₃	17.88	16.62	16.87	18.70	19.64	17.22	22.05	21.69	25.41	28.26	16.65	15.82	16.24	16.59	16.91	18.54	17.58	19.49		
Cr ₂ O ₃	0.04	0.01	0.03	0.04	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.04	0.01	0.03	0.02	0.05	0.00	0.02		
FeO	27.96	31.02	31.10	28.37	27.47	29.95	32.35	33.11	0.05	0.33	15.95	17.35	20.95	21.62	22.84	19.80	22.46	21.06		
ZnO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
MnO	0.16	0.00	0.07	0.02	0.00	0.08	0.74	0.92	0.04	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.18		
MgO	4.47	3.74	2.97	4.52	3.41	3.76	4.70	2.99	0.01	0.00	12.61	12.77	9.24	9.44	9.14	12.12	8.82	11.30		
CaO	0.00	0.03	0.01	0.11	0.02	0.04	3.45	4.48	7.48	11.12	0.05	0.01	0.00	0.01	0.00	0.04	0.00	0.05		
BaO	0.13	0.06	0.12	0.00	0.00	0.17	0.00	0.01	0.00	0.09	0.34	0.13	0.14	0.13	0.17	0.00	0.00	0.00		
Na ₂ O	0.05	0.04	0.03	0.08	0.04	0.09	0.00	0.02	7.34	5.24	0.08	0.12	0.10	0.08	0.04	0.05	0.02	0.06		
K ₂ O	8.19	7.49	7.92	7.51	9.53	7.20	0.00	0.00	0.19	0.14	8.07	8.12	8.27	8.12	7.88	8.18	8.16	8.23		
F	0.06	0.00	0.00	0.18	0.00	0.00	n.d.	n.d.	n.d.	n.d.	0.20	0.30	0.08	0.04	0.00	0.12	0.00	0.10		
Cl	0.61	0.24	0.07	0.37	0.11	0.09	n.d.	n.d.	n.d.	n.d.	0.34	0.26	0.14	0.11	0.22	0.03	0.19	0.19		
-O≡F	0.03	0.00	0.00	0.08	0.00	0.00	n.d.	n.d.	n.d.	n.d.	0.09	0.13	0.03	0.02	0.00	0.05	0.00	0.04		
-O≡Cl	0.14	0.05	0.02	0.08	0.02	0.02	n.d.	n.d.	n.d.	n.d.	0.08	0.06	0.03	0.03	0.05	0.01	0.04	0.04		
Total	96.87	97.22	97.45	94.94	95.47	95.46	101.98	101.14	99.62	99.91	95.52	96.79	96.50	96.93	97.77	96.28	96.54	97.20		
number of O	22	22	22	22	22	22	12	12	8	8	22	22	22	22	22	22	22	22		
Si	5.49	5.47	5.42	5.53	5.49	5.40	3.00	2.99	2.65	2.47	5.55	5.63	5.61	5.56	5.44	5.55	5.42	5.44		
Ti	0.27	0.37	0.44	0.04	0.06	0.35	0.00	0.01	0.00	0.00	0.46	0.43	0.47	0.42	0.48	0.02	0.41	0.01		
Al	3.29	3.07	3.12	3.49	3.66	3.23	2.02	2.02	1.34	1.51	2.92	2.75	2.88	2.93	2.99	3.26	3.14	3.42		
Cr	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00		
Fe	3.65	4.07	4.08	3.76	3.63	3.99	2.10	2.19	0.00	0.01	1.99	2.14	2.64	2.71	2.86	2.47	2.85	2.62		
Mn	0.02	0.00	0.01	0.00	0.00	0.01	0.05	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02		
Mg	1.04	0.87	0.69	1.07	0.80	0.89	0.54	0.35	0.00	0.00	2.80	2.81	2.07	2.11	2.04	2.69	1.99	2.51		
Ca	0.00	0.00	0.00	0.02	0.00	0.01	0.29	0.38	0.36	0.54	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.01		
Ba	0.01	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.01	0.01	0.01	0.01	0.00	0.00	0.00		
Zn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
Zn	0.01	0.01	0.01	0.02	0.01	0.03	0.00	0.00	0.64	0.46	0.02	0.03	0.03	0.02	0.01	0.01	0.01	0.02		
K	1.63	1.50	1.59	1.52	1.92	1.46	0.00	0.00	0.01	0.01	1.53	1.53	1.59	1.55	1.51	1.56	1.51	1.56		
F	0.03	0.00	0.00	0.09	0.00	0.00	n.d.	n.d.	n.d.	n.d.	0.10	0.14	0.04	0.02	0.00	0.06	0.00	0.05		
Cl	0.16	0.06	0.02	0.10	0.03	0.02	n.d.	n.d.	n.d.	n.d.	0.09	0.06	0.04	0.03	0.06	0.01	0.05	0.05		
Total cation	15.41	15.38	15.37	15.46	15.58	15.38	7.99	8.00	5.00	5.01	15.31	15.34	15.29	15.33	15.34	15.58	15.39	15.63		
Mg/(Fe+Mg) An	0.22	0.18	0.15	0.22	0.18	0.18	0.21	0.14			0.59	0.57	0.44	0.44	0.42	0.52	0.41	0.49		
log(f _{CO2} /f _{H2O}) of fluid *1									35.6	53.6										
log(f _{CO2} /f _{H2O}) of fluid *2													3.70	3.82			4.95	4.09		
log(f _{CO2} /f _{H2O}) of fluid *1													0.31	0.47			2.32	1.74		
log(f _{CO2} /f _{H2O}) of fluid *1			-	-	-	-							4.52	4.33			5.17	-		
Temperature (°C)			760 ⁻³	760 ⁻³	760 ⁻³								800 ⁻⁴	800 ⁻⁴			640 ⁻³	640 ⁻³		

Table 2 Kawakami et al.