

## Metamorphic evolution of UHT calc-silicate rocks from Rundvågshetta, Lützow Holm Complex (LHC), East Antarctica

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**Summary** Calc-silicate boudins within the pyroxene gneiss at Rundvågshetta, Lützow-Holm Complex, East Antarctica preserve petrologic signatures of ultra-high temperature metamorphism and microstructures that gave insights to the regional metamorphic evolution. Three mineralogical zones of varying modal proportion of an assemblage of grandite-garnet + scapolite + clinopyroxene + plagioclase + titanite +/- wollastonite +/- calcite +/- quartz are observed. Meionitic scapolite coexists with anorthite suggesting a minimum peak metamorphic temperature of ~830°C. Several generations of chemically distinct garnet corona and breakdown reactions involving garnet, scapolite clinopyroxene and wollastonite are observed. Activity corrected partial retrograde grids, constructed in the CAFSV system, helped in constraining the  $P$ - $T$ - $X$ - $f_{O_2}$  evolution during peak and retrograde metamorphism. These results were then supplemented with titanite SHRIMP geochronology to consider the exhumation history of the region. Taking into account of the existing models on  $P$ - $T$ - $t$  evolution, a geodynamic evolution of the Rundvågshetta granulites within the Lützow-Holm Complex was formulated.

### Introduction

Calc-silicate rocks in high-grade metamorphic terrains have attracted a great deal of attention among petrologists in the last few decades (e.g. Valley and Essene, 1980; Harley and Buick, 1992; Dasgupta and Pal, 2005) because of its widespread occurrence as thin layers and boudins in high-grade terrains, preservation of characteristic mineral assemblages representing the peak metamorphic conditions, preservation of microstructures to changes in the  $P$ - $T$ -fluid history, mineral compositional response with changes in oxygen fugacity conditions and resistance to partial melting. Similar to many high-grade terrains worldwide, calc-silicate rocks are common in the Pan-African high-grade metamorphic terrain exposed in the Lützow-Holm Bay region, East Antarctica (Hiroi et al., 1987; Satish-Kumar et al., 2006a). During the 46<sup>th</sup> Japanese Antarctic Research Expedition, the calc-silicate boudins from Rundvågshetta, the locality where ultrahigh-temperature metamorphic conditions were reported in earlier studies (Motoyoshi and Ishikawa, 1997), was focused for systematic sampling. Based on the mineralogy and reaction textures, we deduce the metamorphic ( $P$ - $T$ - $X$ - $f_{O_2}$ ) evolution. Furthermore, titanite SHRIMP ages are reported here for the first time.

### Geology of Rundvågshetta in the Lützow-Holm Complex

The LHC in the eastern Dronning Maud Land, East Antarctica is a continuous oblique continental deep crustal section with a metamorphic gradient from east to west of late Proterozoic to early Paleozoic age, bounded in the east by the Rayner Complex and by the Yamato Belgica Complex in the west (Hiroi et al., 1991; Shiraishi et al., 1994, 2003; Hokada and Motoyoshi, 2006). Progressive metamorphism, with a clockwise  $P$ - $T$  evolution and a thermal maximum at Rundvågshetta has been accredited to this terrain (Hiroi et al., 1991; Motoyoshi and Ishikawa, 1997), where multiple stages of fluid-rock interactions could be traced from detailed geochemical and stable isotope studies (Satish-Kumar et al., 2006b and references therein). This terrain was tectonothermally active during the waning stages of Pan-African tectonothermal event, in analogy with many terrains of adjoining East Gondwana continental ensemble. A recent study focused on Sr-C-O isotopic compositions and geochemical characteristics of high-grade marbles from this region suggest that the protolith sediments in the LHC were possibly deposited in the Mozambique Ocean that separated the east and west Gondwana some time between ~600 Ma (earliest metamorphic age reported; Hokada and Motoyoshi, 2006) and 850 Ma (chemostratigraphic constraints) (Satish-Kumar et al., 2007).

The Rundvågshetta region is dominated by layered orthopyroxene-gneiss. Thin layers of metapelitic rocks comprising equilibrium orthopyroxene+sillimanite and sapphirine+quartz assemblages were reported from this region, suggesting peak metamorphic  $P$ - $T$  condition of around 1000°C at c. 11 kbar (Yoshimura et al., 2007 and references therein). The peak metamorphism is dated at around 517±9 Ma (Fraser et al., 2000), although recent studies reported older metamorphic imprints at around 600 Ma. Further, Fraser et al. (2000), based on a detail K-Ar and Ar-Ar dating, suggested a rapid isothermal decompression in the Rundvågshetta region span for about 20±10 My, starting at around 520 Ma.

Calc-silicate rocks at Rundvågshetta occur as boundins up to 2 m thick and several meters in length, enclosed in pyroxene-gneiss with thin layers of garnet-sillimanite-gneiss and garnet-biotite-gneiss. A granitic vein intrudes between the lower contact of the boudin and the pyroxene gneiss. The major mineral assemblage is garnet + scapolite + clinopyroxene + plagioclase + titanite ± calcite ± quartz. Two important mineralogical zones could be identified within the boudins, one with garnet prophyroblasts and other with fine-grained garnet intergrowths. Thin (few centimeters) rim zones are garnet free and mainly comprises plagioclase and clinopyroxene.

## **Calc-silicate mineralogy, microstructures and mineral chemistry**

The mineralogical variation observed within the calc-silicate boudin suggests the presence of distinct mineral zones. The rim zone of the calc-silicate boudin is characterized by a mineral assemblage of plagioclase + quartz + clinopyroxene. This assemblage commonly shows granular texture. However, thin seams containing clinopyroxene porphyroblasts are observed. Plagioclase is zoned with cores having higher albite content.

A thin layer of coarse-grained scapolite-rich domain occurs between the rim zone and the intermediate zone. The scapolite-rich domain contains subordinate amounts of quartz and clinopyroxene. Scapolite + garnet intergrowth texture is a common feature in the intermediate zone of the calc-silicate boudin in Rundvågshetta. Minor amounts of clinopyroxene and titanite occur within these intergrowths. These domains occur alternating with equigranular plagioclase + garnet + clinopyroxene throughout the intermediate zone of the boudin.

The core portion of the calc-silicate boudin is composed of garnet porphyroblasts, which are up to 5 cm in diameter. Medium grained (up to few millimeters) scapolite + quartz, with subordinate amounts of clinopyroxene forms the matrix. Titanite occurs in minor amounts, both as inclusions in porphyroblasts as well as in the matrix.

Wollastonite is rarely observed. It occurs either as a relict surrounded by granular calcite and quartz or as intergrowths with plagioclase, after garnet. Titanite is ubiquitously present as accessory phase in the matrix or as thin blebs microstructurally related to the reactions.

### ***Early intergrowths***

Several metamorphic intergrowth microstructures are observed in the Rundvågshetta calc-silicate rocks. Coarse-grained intergrowths of scapolite + grandite garnet +/- clinopyroxene or plagioclase + grandite garnet +/- clinopyroxene are characteristic in the intermediate zone. Large scapolite grains enclose garnet that often exhibit resorbed grain boundaries. These microstructures possibly represent mineral reactions that have progressed during high-temperature metamorphism.

### ***Garnet coronas***

Several stages of retrograde microstructures are identified, of which the garnet corona formation is the prominent one. Garnet corona surrounding clinopyroxene or calcite is commonly observed. Thin rinds and corona of garnet are also observed surrounding scapolite, which show partial alteration to plagioclase.

### ***Retrograde symplectites***

Scapolite in some zones is replaced by plagioclase, calcite and minor amounts of quartz. Thin rinds of garnet are observed in the anorthite + calcite +/- quartz intergrowth, suggesting garnet formation after the breakdown of scapolite. Wollastonite, found as a relict in one sample, is surrounded by retrograde calcite and quartz. In addition, wollastonite+plagioclase symplectitic intergrowth is observed, which replaces early garnet. In one sample, scapolite+quartz symplectitic intergrowth, after feldspar, is observed, indicating metasomatic activity accompanied with an influx of CO<sub>2</sub>-rich fluids (Harley and Santosh, 1995)

### ***Mineral chemistry***

Garnet compositional variation is principally restricted to the grossular-andradite solid solution, with minor (<10 mol.%) other components. Early formed porphyritic garnet (Gr<sub>I</sub>) is nearly pure grossular in composition. Only minor chemical zoning is observed with a decrease in Al content and an increase in Fe<sup>3+</sup> content toward rim. Gr<sub>II</sub> is matrix garnet, which coexists with clinopyroxene, anorthite and scapolite, which has andradite component in the range of 5-15%. Gr<sub>III</sub> forms intergrowth with scapolite and minor clinopyroxene, with andradite component of up to 20%. Gr<sub>IV</sub> is garnet that forms corona surrounding other minerals. Although there are several microstructural types of garnet coronas, in this study we group them together. This type of garnet shows large variation in chemical composition, ranging from almost pure grossular to andradite component up to 50%.

Three microstructural types of clinopyroxene could be identified in Rundvågshetta calc-silicate boudins. Cpx<sub>I</sub> is matrix clinopyroxene, which is almost pure diopside. Cpx<sub>II</sub> that form thin intergrowth with garnet or scapolite has appreciable CaTs component (Al < 0.5afpu). Cpx<sub>III</sub> are inter-grown with garnet and has slightly higher hedenbergite content.

Irrespective of microstructural positions, scapolite is meionite-rich in composition, with EqAn values in the ranging between 75 and 90. Scapolite co-existing with anorthite has slightly higher EqAn values between 80 and 90, whereas scapolite without co-existing anorthite has lower EqAn values between 75 and 85. Two generations of plagioclase are observed in the calc-silicate boudins. First one is the granular type, which co-exists with all other major minerals and the second one form intergrowths within symplectites. However, both microstructural types of plagioclase are anorthite-rich in chemical composition (>An<sub>90</sub>).

## **Metamorphic evolution of calc-silicate rocks**

Scapolite phase equilibria provide a mean to estimate the minimum metamorphic temperature condition in calc-silicate rocks. The vapor absent equilibria Scp = 3An + Cc, between coexisting plagioclase and scapolite, suggests minimum temperature of formation of scapolite around 830°C for the Rundvågshetta calc-silicate rocks. This minimum estimate is supportive of the ultrahigh-temperature peak metamorphic conditions recorded in the metapelite rocks

(~1000°C; Motoyoshi and Ishikawa, 1997).

Grandite garnet+scapolite and grandite garnet+plagioclase intergrowth with subordinate amounts of clinopyroxene is commonly found in the intermediate portions of the boudins. In addition, co-existing scapolite + quartz and calcite + quartz assemblages are also observed. These assemblages suggest that a high-pressure and/or high- $X_{\text{CO}_2}$  conditions prevailed during peak metamorphism (Harley and Buick, 1992). Computation of T- $X_{\text{CO}_2}$  partial petrogenetic grid for the metamorphic assemblages and microstructures observed was carried out using an internally consistent thermodynamic data set of Holland and Powell (1998) employing the computer software THERMOCALC v.3.1 (Powell and Holland, 2001). Measured mineral compositions of garnet and scapolite were used for activity computations following the procedure described in Harley and Buick (1992). The grid was constructed at a pressure condition of 11 kbar, considered as optimum for Rundvågshetta region (Motoyoshi and Ishikawa, 1997). In the simplified CASV system (Mg and Fe-free), the scapolite-dominant wollastonite-free assemblage should have equilibrated at moderate to high  $X_{\text{CO}_2}$  conditions (0.3 ~ 0.7) and temperatures between 850 and 1000°C. Relict wollastonite is indicative of either high temperature conditions or low  $X_{\text{CO}_2}$  fluid composition. The plagioclase-dominant (wollastonite-, calcite- absent) assemblages indicate the  $X_{\text{CO}_2}$  conditions at peak P-T might have been low to moderate (<0.45).

### ***Retrograde P-T-fluid evolution***

Petrogenetic T- $X_{\text{CO}_2}$  grids calculated with retrograde mineral compositions of garnet with respect to various microstructures were used to evaluate the P-T-fluid conditions of Rundvågshetta calc-silicate boudins during exhumation. Wollastonite+plagioclase intergrowth is indicative of isothermal decompression. This is consistent with the decompression microstructures observed in the metapelitic rocks (Ishikawa and Motoyoshi, 1997). Scapolite+quartz symplectitic intergrowth, after feldspar, can be interpreted as resulting from an increase in carbonic component in the fluids. Garnet corona formation might have resulted from an increment in the hydrous component in the fluid composition during retrogression. Further, scapolite breakdown occurred during cooling (e.g. Harley and Buick, 1992), whereas subsequent garnet corona formation resulted from an increase in hydrous component in the fluid. This last stage of hydrous fluid ingress may be correlated with the fluids released from the crystallization of pegmatites and granitic veins.

### ***$f_{\text{O}_2}$ -constraints***

Compositional spread observed in the grandite garnet and clinopyroxene help us to constrain the oxygen fugacity variations during the P-T evolution of the calc-silicate rocks (Sengupta and Raith, 2002; Dasgupta and Pal, 2005). Preliminary computations of  $f_{\text{O}_2}$  conditions suggest that the peak metamorphism register low  $f_{\text{O}_2}$  conditions, whereas the decompression is accompanied by an increase in  $f_{\text{O}_2}$  conditions. The final stage of retrogression, i.e. the cooling stage, resulted in lowering of  $f_{\text{O}_2}$ , possibly due to the ingress of aqueous fluids.

### ***Titanite Geochronology***

Titanite, ubiquitously present in calc-silicate rocks, is a potential mineral chronometer. However, titanite has a lower closure temperature (~660-700°C; Frost et al., 2000) than zircon and monazite. SHRIMP in situ analyses were carried out on several microstructural types of titanite. Matrix titanite from two samples gave ages of 492±8 Ma and 493±8 Ma (all ages are weighted means of  $^{204}\text{Pb}$ -corrected  $^{206}\text{Pb}/^{238}\text{U}$  spot ages). Titanite that is microstructurally related to garnet forming reactions gave a spread in ages ranging from 510 to 490 Ma, with the largest grain preserving a mean  $^{206}\text{Pb}/^{238}\text{U}$  age of 510±7 Ma. Interestingly, titanite in one sample which is microstructurally related with scapolite+quartz symplectite gave a younger age of 474 ± 8 Ma.

### **Toward a unified geodynamic evolution of LHC**

In summary, we infer that the Rundvågshetta ultrahigh-temperature granulites equilibrated at around 1000°C and >11 kbar during peak metamorphism. In general, the peak metamorphism was accompanied by moderate  $X_{\text{CO}_2}$  fluid under low  $f_{\text{O}_2}$  conditions. Whether the peak metamorphism occurred at around 520 Ma or earlier (c.600 Ma Monazite ages; Hokada and Motoyoshi, 2006) need to be resolved in future studies. Isothermal decompression was accompanied by high  $X_{\text{CO}_2}$  and  $f_{\text{O}_2}$  conditions. This decompression event continued possibly until 490 Ma or 474 Ma, as recorded in titanite. We propose that the Rundvågshetta granulites were still hot (>660°C) at 490 Ma (or even until 474 Ma), and cooling might have started subsequently. This observation is in contrary to the existing P-T-t models of Fraser et al. (2000), where the Rundvågshetta rocks were supposed to have cooled up to 300°C at around 500 Ma. The 474 Ma ages recorded in the titanite might, alternatively, be interpreted as a subsequent event of fluid influx and associated metasomatism during the crystallization of pegmatitic/granitic activity. The multiple generations of microstructures observed in the calc-silicate rocks has to be coupled with fluid influx events that resulted in variations in the  $X_{\text{CO}_2}$  and  $f_{\text{O}_2}$  conditions. Integrating titanite SHRIMP geochronology with microstructures, we might be able to further advance our understanding of protracted and complex continental crustal regimes under changing P-T-X- $f_{\text{O}_2}$  conditions. Further geochronologic assessment is in progress to define the P-T-t evolution of the Rundvågshetta region and the LHC as a whole, in comparison with the adjoining east Gondwana terrains.

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