Petrology and possible significance of barroisite-bearing metabasite from the Kebara Formation in NW Kii Peninsula

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We report the new finding of barroisite (Brs)–bearing metabasites within a metabasite layer from the Kebara Formation, a unit exposed between the Sanbagawa and the Chichibu belts in NW Kii Peninsula. The dominant lithotype of the metabasite layer shows pale-green colors and is mainly composed of sodium amphibole, actinolite, pumpellyite and epidote. It is in agreement with reported mineral assemblages in the Kebara Formation which document pumpellyite–actinolite (PA) or pumpellyite–blueschist (PBS) facies conditions (<340 °C and 0.8 GPa), and with geothermometry based on the Raman analysis of carbonaceous material from metapelite samples which give peak metamorphic temperatures of 300–340 °C. Brs grains are identified from metabasites with dark-green color in the layer, and are closely associated with epidote, chlorite, white mica, albite and quartz, but not with pumpellyite. Brs grains are replaced by sodium amphibole and/or winchite at the rim with a distinct compositional gap. Thermodynamic calculation suggests that the Brs + epidote + chlorite + albite + quartz assemblage is stable at P–T conditions higher than 450 °C and 0.4 GPa. The abovementioned data suggest that the Brs–bearing metabasites suffered an early higher temperature (>450 °C) metamorphism and then overprinted by PA or PBS facies metamorphism along with the main constituents of the Kebara Formation. In the Besshi area of the Sanbagawa belt, the earlier subducted higher grade rocks are considered to juxtapose to the newly subducted rocks and overprinted retrograde metamorphism during their exhumation stage. Our new finding suggests that the similar phenomenon was took place in the lower grade part of the Sanbagawa belt.

Keywords: Barroisite, Kebara Formation, Sanbagawa metamorphic belt

INTRODUCTION

In the Sanbagawa metamorphic belt of central Shikoku, the composition of amphibole group minerals in hematite–bearing metabasites changes from actinolite (Act), winchite (Wnc), and/or sodium amphibole (Na–amp) in the lower-grade part, i.e., chlorite and lower-grade garnet zones, to barroisite (Brs) or hornblende in the higher-grade part, i.e. higher-grade garnet, albite–biotite, and oligoclase–biotite zones (e.g., Otsuki and Banno, 1990; Nakamura and Enami, 1994). Similar compositional variations in amphiboles with increasing metamorphic grade have been reported in New Caledonia (e.g., Yokoyama et al., 1986). These observations suggest that variations of Na in amphibole mainly reflect a pressure change, whereas variations in the tschermakite component indicate a change in temperature conditions.

Furthermore, the composition of amphibole formed at peak P–T conditions is commonly modified by retrograde reactions and newly grown rims may record the P–T conditions of the exhumation stage. In the case of the Sanbagawa belt, Brs and hornblende in metabasites of the garnet and albite–biotite zones in the Asemi-gawa and Dozan-gawa areas are commonly rimmed by Wnc and/or Act (e.g., Otsuki and Banno, 1990; Okamoto and Toriumi, 2004), and these compositional changes in amphibole interpreted to have formed by isothermal decompression at an early stage of exhumation (Okamoto and Toriumi, 2004). On the other hand, amphibole grains with a Brs core, a Na–amp mantle and a Wnc and/or Act rim are reported from the albite–biotite zone in the Saruta-gawa area by Banno (2000), who interpreted this zoning pattern as in terms of decompression associated with significant cooling at an early stage of exhumation. These findings clearly suggest that the exhumation path of San-
bagawa metamorphic rocks in central Shikoku is not uniform.

In this study, we report the first finding of amphibole grains with a Brs core rimmed by magnesioriebeckite (Mrbk) and/or Wnc in metabasites from the Kebara Formation in NW Kii Peninsula, the P–T conditions of which are considered to be equivalent to those of the chlorite zone based on mineral assemblages in both metapelites and metabasites (Kurimoto, 1986a; Tomiyoshi and Takasu, 2009). In this report, we describe the mode of occurrence of Brs-bearing metabasites and the compositional variation of the zoned amphiboles and discuss their possible significance.

GEOLOGICAL AND PETROLOGICAL BACKGROUND

The Kebara Formation is a fault-bounded tectonometamorphic unit, about 5 × 1 km in the NE–SW direction, exposed between the Sanbagawa metamorphic belt and the Chichibu belt (Kurimoto, 1986a, 1986b: Fig. 1A). The Kebara Formation is mainly composed of pelitic schist and a minor amount of lenses or layers of metabasite, siliceous schist, and marble (e.g., Kurimoto, 1986a, 1986b; Tomiyoshi and Takasu, 2009). The dominant schistosity in pelitic schist strikes NE–SW to ENE–WSW and steeply dips. K–Ar white-mica ages for pelitic schist and metabasite samples and whole-rock 40Ar/39Ar ages for pelitic schist samples indicate metamorphism of the Kebara Formation at 103–89 Ma (Isozaki et al., 1992; Kurimoto, 1993; De Jong et al., 2000). These ages are slightly older than those reported for the Sanbagawa belt of the Kii Peninsula (85–72Ma with two exceptions; Kurimoto, 1993, 1995, 2013). This explains why the origin of the Kebara Formation is still under debate in the framework of the Sanbagawa metamorphism.

The following diagnostic mineral assemblages are identified from metabasite of the Kebara Formation (Kurimoto, 1986a; Tomiyoshi and Takasu, 2005): lawsonite + Act + pumpellyite (Pmp) and Na-amp + Pmp in metabasites with excess of chlorite (Chl), albite (Ab), and quartz (Qz). These assemblages are stable under the pumpellyite-actinolite (PA) or pumpellyite-blueschist (PBS) facies (Banno, 1998; Katzir et al., 2000; Sato et al., 2017). The mineral assemblage is reported from pelitic schist of the Kebara Formation (Tomiyoshi and Takasu, 2009) and a similar mineral assemblage is reported from pelitic schist of the Sanbagawa metamorphic belt in the Ise area, eastern Kii Peninsula. For this assemblage, P–T conditions of <340 °C and 0.8 GPa are proposed based on thermodynamic calculations (Ueno, 1999, 2001). In pelitic rocks, geothermometry using the analysis of carbonaceous material (CM) by Raman spectroscopy yielded metamorphic temperatures of 302–340 °C (Yoshida et al., 2016). Temperature estimates based on different methods all indicate that the Kebara Formation was metamorphosed at low temperature conditions.

ANALYTICAL METHOD, SAMPLE OUTCROP DESCRIPTION, AND PETROLOGY

Quantitative analysis of minerals was performed using a JEOL JXA-8105 superprobe at the Department of Geology and Mineralogy, Kyoto University. Analytical conditions for quantitative analyses were an acceleration voltage of 15.0 kV and a beam current of 10 nA with a diameter of 3 μm. The counting times for the peak and backgrounds were 10 and 5 s, respectively. Natural and synthetic minerals were used as standards and ZAF correction was applied. The ferric iron content of amphibole is calculated on the basis of 13 cations exclusive of Ca, Na, and K after Leake et al. (1997), and iron of epidote (Ep) is considered as all ferric.

Brs-bearing metabasites are identified from two parts of a metabasite layer in N-S trending 30 m-long outcrop which stretches from the Takino-gawa to the side of a forest road in the SW part of the Kebara Formation (Figs. 1A and 1B). The metabasites layer is mainly composed of pale-green rocks, but Brs grains are identified from dark-green ones (Figs. 1B–1C and 2). The pelitic schist crops out at the southern end of the outcrop. The dominant schistosity of pelitic schist is concordant with that observed in the metabasite; it strikes ENE–WSW and steeply dips to the S (Fig. 1B). This orientation is consistent with that of the main schistosity observed in the Kebara Formation. No clear fault–bounded contact is observed in the outcrop.

Five metabasite samples collected from the northern part of the outcrop, i.e., along the forest road, are mainly composed of Pmp, Act, Ep [Y_Fe = Fe³⁺/(Fe³⁺ + Al) = 0.29–0.32], Chl, and Ab with or without Na-amp and Qz (Figs. 1B and 3A). Those mineral assemblages have been reported in the Kebara Formation and suggest PA or PBS facies conditions.

Figure 1C shows the field view of the southern end of the 30 m thick metabasites layer. All thin sections made from the dark-green part (KB05, KB89U, and KB89S) contain Brs. Those made from the other colored rocks (KB89N, KB89O, and KB89R) are free from Brs; the main constituent of Brs-free metabasites are Act, Wnc, Na-amp, Ep, Chl, Ab, and Qz (Fig. 3A). Brs is mainly associated with Ep (Y_Fe = 0.26–0.32), Chl, white mica, hematite, Ab, and Qz along with a minor amount of calcite,
Ep occurs as columnar or rounded shape crystals up to 300 μm in length and has a slight compositional zoning with a Fe$^{3+}$-poor core (Y$\text{Fe}^3$ = 0.26–0.29, average = 0.27) and a Fe$^{3+}$-rich rim (Y$\text{Fe}^3$ = 0.27–0.32, average = 0.30) in KB05. Ep included in the Brs core shows a zoning pattern which is similar to that of matrix Ep. Some hematite grains are identified in the matrix of KB05. If we assume that the Ep core formed in equilibrium with hematite, the observed zoning pattern can be thought to reflect a decrease in metamorphic grade (e.g., Nakajima, 1982; Otsuki and Banno, 1990).

Most white micas occur as fibrous crystals up to 100 μm in length and up to 20 μm in width in KB05 and are commonly surrounded by Chl. The Si content of white mica ranges from 3.36 to 3.53 pfu (O = 11), but no significant zoning pattern is detected. Chl is the main matrix phase; it is clinochlore with X$\text{Fe}^2$ = Fe$^{2+}/$(Fe$^{2+}$ + Mg) of 0.37–0.42.

**DISCUSSION**

In order to constrain the stability conditions of Brs, we performed thermodynamic calculations of amphibole compositions coexisting with Ep, Chl, Ab, Qz, and water in the P–T range 400–600 °C and 0.1–1.2 GPa in the system SiO$_2$–Al$_2$O$_3$–Fe$_2$O$_3$–FeO–MgO–CaO–Na$_2$O–H$_2$O, using the ‘phase diagram calculation’ mode of THERMOCALC 3.33 (Powell and Holland, 1988) (Fig. 4). Thermodynamic models of Ep and Chl are after Holland and Powell (1998), and that of amphibole after Diener et al. (2007). Ab and Qz are considered as pure phases. X$\text{Fe}^3$ of Chl and Y$\text{Fe}^3$ of Ep are fixed to 0.4 and 0.26, respectively. Amphibole compositions refer to the calculation outputs and the names are based on the nomenclature of Leake et al. (1997), ignoring $^4$Na to simplify the discussion.

The investigated P–T range can be divided into three fields separated by discontinuous compositional changes...
Barroisite–bearing metabasite from the Kebara Formation

...amphibole (Fig. 4); Na–amp is stable in the HP/LT field, Act is stable in the LP/LT one, and Brs /tschermatite (Ts)/’magnesiotarmite’ (’Mtm’) is stable in the HT field. Amphibole composition in the HT field changes continuously from Ts through ’Mtm’ to Brs with increasing pressure. Brs is stable in a narrow field between Na–amp and ’Mtm’, at >450 °C and 0.4 GPa (Fig. 4). Higher XFe of Chl and YFe of Ep can expand the Brs stability field to lower T and P side, but this effect is not significant. These calculation results are consistent with those of Otsuki and Banno (1990) and Okamoto and Toriumi (2004), except for the absence of the Wnc stability field.

The reported metamorphic conditions of the Kebara Formation belong to the PA or PBS facies (Kurimoto, 1986a; Tomiyoshi and Takasu, 2009; Yoshida et al., 2016), which means that the metamorphic temperature of the Kebara Formation is lower than 340 °C (Fig. 4). Therefore, there is a significant temperature gap between...
the main constituents of the Kebara Formation and the newly found Brs-bearing metabasites (>450 °C). Most of Brs grains are rimmed by Mrbk and/or Wnc at various degrees. These rim amphiboles are stable at PA and PBS facies conditions.

The above-mentioned amphibole-zoning pattern is similar to the report by Banno (2000), who found it in the albite-biotite zone, equivalent to the epidote-amphibolite (EA) facies, in the Saruta-gawa area. Banno (2000) concludes that the observed amphibole zoning pattern reflects the decompression with a significant cooling path during the early stage of the exhumation. However, our finding of Brs-bearing metabasite is in the lower-grade part of the Sanbagawa belt. One possible scenario is that all constituents of the Kebara Formation once suffered EA facies metamorphism, and then most of them recrystallized under the lower temperature conditions of the PA or PBS facies. However, this scenario is rejected, because the irreversible nature of Raman spectra of CM geothermometry suggests that the matrix forming major lithotype, i.e., pelitic schist, of the Kebara Formation never experienced temperatures higher than ~ 400 °C (Yoshida et al., 2016).

Therefore, the abovementioned data suggest one possible scenario that: (1) The Brs-bearing metabasites suffered EA facies at an early stage of the subduction. (2) Subsequent exhumation of the Brs-bearing metabasite caused the juxtaposition with newly subducted materials, which are the main constituents of the Kebara Formation. (3) Both of them suffered PA or PBS facies metamorphism.

In the eclogite terrain of the Sanbagawa belt in central Shikoku, the earlier subducted higher grade rocks (e.g., eclogite facies rocks) are considered to be juxtaposed to the newly subducted lower grade rocks (e.g., oligoclase-biotite grade pelitic schist) during their exhumation stage (e.g., Takasu, 1989; Wallis and Aoya, 2000; Aoya, 2001). Our new finding may become evidence for supporting that similar phenomenon can be observed in the lower grade part, such as chlorite zone, of the Sanbagawa belt. This unexpected finding suggests that further geological and petrological studies are necessary for understanding the material cycling process in the subduction zone.

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**SUPPLEMENTARY MATERIALS**

Color version of Figures 1 and 3, Figure S1 (the X-ray maps of the Brs grain shown in Fig. 2B), and Table S1 (the representative microprobe data of amphibole, Ep, Chl, phengite, and Ab) are available online from http://doi.org/10.2465/jmps.160719a.

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