CHAPTER 8

FLUID EVOLUTION

Knowledge of the composition of fluid inclusions is important to understand the fluid evolution of high-grade terrane and the role of fluid in high temperature metamorphism. Fluid inclusion study was carried out on the high-grade rocks of the Phulbani domain as it provides the only direct evidence pertaining to the compositions of metamorphic fluids. It also provided important clues regarding the change of the nature of the fluid composition during peak- to post-peak metamorphic evolution of the studied rocks. Indirect evidences like composition and texture of monazite and feldspar grains put some additional clues on the type of fluid during or subsequent to the high temperature metamorphism of the Phulbani domain as the composition and textural characters of these minerals are sometimes thought to be a good proxy which indirectly helps to constrain the composition of the associated fluid.

8.1 Analytical methods

Fluid inclusions were studied in doubly polished thin wafers (approximately 200 μm in thickness) prepared from the representative samples. The nature of occurrence of inclusions, their distribution patterns, shapes, sizes and phase categories were carefully studied and documented under petrological microscope at varying magnifications using the standard techniques (Touret, 2001; van den Kerkhof and Hein, 2001; van den Kerkhof et al., 2014). Microthermometric measurements were performed with a Linkam heating/freezing system at JAMSTEC, Yokosuka, Japan. Calibrations were undertaken with standard materials. Heating rates of the samples were 0.1-0.2 °C/min for melting and 1-5 °C/min for homogenization temperatures, respectively. For isochore calculations, almost all the analyzed carbonic fluid inclusions were regarded as CO_2. Densities of the fluid inclusions were calculated using the program of FLUIDS (Bakker, 2003). The equations of state of the fluid were calculated using the program of Duan et al. (1992a, b). Mole fractions of fluid species present within the inclusions were calculated using the method outlined by Huizenga (2005).

Laser Raman spectroscopy was carried out using a Raman Touch spectrometer of Nano Photon Ltd installed at JAMSTEC, Yokosuka, Japan. An exciting radiation at 532 nm was provided by a YAG laser. Analytical accuracy of wave number measurements of the Raman spectrometer was 1 wave number (cm^{-1}). Analyses were done on relatively large inclusions (> 5 μm) in order to get good quality Raman signals. Raman data were acquired at room temperature for single phase inclusions and compared with the data listed by Burke (2001) for fluids (CO_2, H_2O, CH_4, N_2 etc.) and solid crystals found in the inclusions to identify each species. The Raman bands for the host phases were compared with the Rruff database (http://rruff.info/) for precise identification.

The EPMA analytical procedure for feldspar grains of the calc-silicate granulite, coarse-grained charnockite and the pegmatoidal metasomatic rock at the contact zone is described in Chapter 6. Monazite grains were measured by JEOL JXA 8200 Superprobe at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University. The details of the analytical procedure are described in Chapter 9.

8.2 Fluid inclusion study

Fluid inclusions are present in all the rocks located at the Phulbani domain but their population is not high. In most cases, these inclusions appear to be primary and occur as small clusters within the host crystals (Fig. 8.1a) and their abundance does not vary appreciably across the rock types.

Secondary fluid inclusions are present in these samples but these are very minor in proportion. On the other hand, the migmatitic felsic gneiss from the RSZ contain numerous secondary fluid inclusion trails (Fig. 8.1b) which are parallel to each other and dominantly cross-cut the mylonitic fabric (S_{5S}). Fluid inclusions which define these secondary trails are small in size. It is important to mention that such secondary fluid inclusions are notably absent from the rocks which are located outside the RSZ. Additionally, the migmatitic felsic gneiss xenoliths from RSZ also do not contain such secondary fluid inclusions.

Fluid inclusion densities are low in the calc-silicate granulite and dominantly present in clinopyroxene and quartz (Fig. 8.1c). Fluid inclusions present within these minerals are primary and pseudosecondary in nature and most of them are augen shaped. Although most of the inclusions are mono-phase, bi-phase inclusions are also present in some instances (Fig. 8.1d). In all the cases, the bi-phase inclusions are characterized by an additional vapor phase present in the fluid inclusion cavities. It is however, important to mention that the patches and veins of pegmatoidal rock present within the calc-silicate granulite have high fluid inclusion density. Most of the fluid inclusions of this rock are pseudosecondary in nature (Fig. 8.1e). These pseudosecondary fluid inclusions are dominantly mono-phase having square or rectangular shape and usually occur within K-feldspar grains.

Four samples were selected for fluid inclusion analyses. Fluid inclusions from these samples are thought to represent the peak- to post-peak fluid evolutionary history of the studied area. The samples of the aluminous granulite (sample PH 10A), the migmatitic felsic gneiss (sample PH 10GM) and the coarse-grained charnockite (sample PH 10C) were collected from the N-S trending ductile shear zone (Fig. 8.2). Another sample of the felsic gneiss (sample PH

40) was collected from the marginal part of the same shear zone where intensity of shearing is less prominent. All the analyzed data are presented in Table 8.1.

8.2.1 Aluminous granulite (Sample PH 10A)

Fluid inclusions are present within quartz, sillimanite and garnet. Almost all the measurable inclusions are primary, while a few pseudosecondary inclusions are also present. Primary inclusions are small (5-10 µm along maximum dimension), oblong augen type, while few are irregular (Fig. 8.3a). These are either locally concentrated or disseminated within the host grain. Pseudosecondary inclusions are even smaller (1-2 µm along maximum dimension). Some secondary trail-bound inclusions transgress grain boundaries but these are extremely fine (< 1 µm). Primary inclusions are mono-phase liquid, while in a few cases, the pseudosecondary inclusions are bi-phase. Inclusions in quartz are abundant compared to other phases. For primary inclusions, the melting temperature (T_m) ranges between -57.9°C and -61.6°C (Fig. 8.4a). The temperature of homogenization (T_h) for these inclusions could not be measured precisely. T_m values for the pseudosecondary inclusions could not be determined because of their finer size but one suspected pseudosecondary inclusion in K-feldspar yields T_h value of 27.2°C. Raman spectral characters show strong bands at 1277 and 1380 cm^{-1} (Fig. 8.4b), indicating the presence of CO_2 in the mono-phase fluid.

8.2.2 Coarse-grained charnockite (Sample PH 10C)

Fluid inclusions are present within K-feldspar, quartz and garnet. Almost all the measurable inclusions are primary with variable size (2-20 µm maximum), circular to oblong type (Fig. 8.3b). These are locally concentrated or disseminated within the host grain. Halite crystals are present in rare occasions within quartz, K-feldspar and orthopyroxene grain (Fig. 8.3c). Primary inclusions are mono-phase and distributed as clusters within garnet and feldspar grains. The estimated T_m for the inclusions varies within -57.4°C to -59.2°C (Fig. 8.4c) and calculated density ranges between 0.82-1.00 gm/cm^3. One suspected pseudosecondary inclusion in garnet shows T_m of 58.7°C. T_h values for the primary inclusions range between 22°C and -18°C, while the suspected pseudosecondary inclusion yields T_h of 21°C (Fig. 8.4d). The calculated density of this inclusion is 0.76 gm/cm^3. The calculated isochores of the primary and the secondary inclusions are presented in figure 8.5a. Raman spectral characters show strong bands at 1284 cm^{-1} and 1386 cm^{-1} (inset of Fig. 8.4d), implying the presence of CO_2 in the mono-phase fluid. Low intensity band at 2331 cm^{-1} indicates the presence of N_2. Out of the nine analyzed inclusions, one primary inclusion in garnet shows Raman band at 3625 and 3655 cm^{-1}, possibly indicating the presence of H_2O.

8.2.3 Migmatitic felsic gneiss (Samples PH 10GM and PH 40)

In the sheared variety of the migmatitic felsic gneiss (Sample PH 10GM), fluid inclusions are present within K-feldspar, quartz and garnet. These inclusions are primary with variable size (2-20 µm maximum) and shape (Fig. 8.3d). These are mono-phase and distributed as clusters within garnet, quartz and K-feldspar grains. Estimated T_m varies within -58.2°C to -59.2°C (Fig. 8.4e) with a calculated density range of 0.90-1.02 gm/cm^3. T_h values vary within 7.6°C and -17.8°C (Fig. 8.4f) with the suspected pseudosecondary inclusion having T_h of 7.6°C. The calculated density of this inclusion is 0.88 gm/cm^3. Isochores calculated from the inclusions are shown in figure 8.5b. Raman spectral characters show strong bands at 1282 cm^{-1} and 1386 cm^{-1} (inset of

Fig. 8.4f) with minor band at 2324 cm^{-1}, indicating the presence of CO_2 (+ minor N_2) in the mono-phase fluid. Presence of minor CH_4 (2943 cm^{-1}) was noted in a few cases.

In the migmatitic felsic gneiss sample collected away from the shear zone (Sample PH 40), fluid inclusions occur within K-feldspar, quartz and garnet with variation in size (up to 20 µm in garnet and up to 40 µm in quartz) and shape (Fig. 8.3e). Those inside K-feldspar are usually finer and could not be measured. Few inclusions show negative crystal shape. Primary inclusions are mono-phase and distributed as clusters within garnet, quartz and feldspar grains. One inclusion in quartz shows presence of mono-phase vapor. Estimated T_m for the inclusions varies within -59.7°C to -57.7°C (Fig. 8.4g). The mono-phase vapor inclusion shows T_m and T_h values of -58.2°C and 19.7°C respectively. T_h values for inclusions within quartz vary from 5.2°C to -19.0°C, while those in garnet show a wider range of -2.7°C to 22.5°C (Fig. 8.4h). The calculated density of the primary inclusions ranges between 0.89-1.03 gm/cm^3. Pseudosecondary inclusions within garnet have T_m of -57.8°C, while T_h varies in the range 18.7-22.5°C. The calculated density of such pseudosecondary inclusions varies within the range of 0.74-0.79 gm/cm^3. Isochores of the fluid inclusions are presented in figure 8.5c. Raman spectra show strong bands at 1282 cm^{-1} and 1386 cm^{-1} (inset of Fig. 8.4h), indicating presence of CO_2 in the mono-phase fluid. Minor bands at 2348 cm^{-1} and 3651 cm^{-1} suggest the presence of N_2 and H_2O, respectively.

The changes in fluid densities are presented in the constructed isochores for three samples (Fig. 8.5a, b,c). Primary fluid inclusions in all the samples imply their entrapment at pressure 4.5-7.5 kbar at a temperature ~1000ºC. These values are lower than the pressure estimated from the conventional barometers and phase diagram modeling (~ 8-8.5 kbar).

8.3 Fluid-induced textural and chemical changes in the RSZ

Fluid-induced textural and chemical changes were studied from the rocks of the RSZ. Apart from the minerals like feldspar, accessory mineral like monazite in this rock shows diagnostic features of fluid-rock interaction. Such changes in monazite are significant as these affect the age information since Pb and Th are commonly found to be mobilized in alkali-rich fluids (cf. Hetherington et al., 2010; Harlov et al., 2011; Didier et al., 2013). In shear zones, hydrous fluids (with or without a brine component) play a key role in strain localization by infiltrating along discrete brittle fractures offering increased permeability and fast fluid pathways. Infiltrating fluids promote alteration and catalyze metamorphic reactions within previously metastable mineral assemblages (Austrheim, 1987; Marsh et al., 2011; Getsinger et al., 2013; Goncalves et al., 2012; Jamtveit et al., 2016; Condit and Mahan, 2018). This eventually leads to strain softening (Wintsch et al., 1995; Oliot et al., 2014), or even strain hardening in some cases (Finch et al., 2016). This also shifts the deformation mechanisms that are active during fluid flow. Thus, the interplay between fluids and deformation can fundamentally influence the temporal evolution of deep crustal rheology (Diaz et al., 2007; Jamtveit et al., 2016).

Monazite grains from the aluminous granulite and the migmatitic felsic gneiss from Phulbani domain are characterized by Th-rich interiors and Y-rich patches and overgrowths (Fig. 8.6a). This character is notably absent in the monazite grains of the migmatitic felsic gneiss and felsic augen gneiss samples collected near the RSZ. Most monazite grains of the latter rocks have conspicuous Th-rich overgrowths and Th-poor, Y-rich patches that constitute the major portion of the interiors. Moreover, some monazite grains of these rocks have Th-rich veins (Fig. 8.6b and c) which are sometimes stemmed to the Th-rich overgrowth portions. These Th-rich veins cross-cut the original grains in a random manner. Along such Th-rich veins small micro-pores occur which are occasionally interconnected to produce relatively large pores. The implication of such zoning on the geochronological results will be described later (Chapter 9).

8.4 Feldspar composition and texture

8.4.1 Fluid-induced textures in aluminous granulite and migmatitic felsic gneiss

In some aluminous granulite and migmatitic felsic gneiss, K-feldspar micro-veins are present around the plagioclase and garnet grains (Fig. 8.7a). These micro-veins are commonly interconnected to form larger veins solely composed of K-feldspar. Granular and vermicular quartz grains are frequently observed at the contacts between the plagioclase grains and the K-feldspar veins to form myrmekite intergrowth (Fig. 8.7b).

8.4.2 Fluid-induced textures at calc-silicate granulite and coarse-grained charnockite contact

Myrmekite-like intergrowths are ubiquitous at the contact zone of calc-silicate granulite and coarse-grained charnockite (Figs. 6.3a, b, c). Plagioclase in such intergrowth shows patchy zoning defined by variations in Ca and Na (Figs. 6.3d, e, f). It is additionally important to note that the plagioclase grains with patchy zoning maintain the grain shapes that appear to be similar to that of the coarse-grained charnockite located several micro-meters away from the contact zone. Orthopyroxene grains of the coarse-grained charnockite located at the contact zone are rimmed by clinopyroxene (Fig. 6.3l).

The pegmatoidal metasomatic rock which occurs at the immediate vicinity of the contact between the calc-silicate granulite and coarse-grained charnockite contains K-feldspar, clinopyroxene and plagioclase with minor amount of quartz, titanite and apatite (Fig. 6.3m). The boundaries between these two types of feldspar are always ornamented with myrmekite intergrowth. However, myrmekite is also present at the boundaries of the K-feldspar grains where plagioclase is absent (Fig. 6.3o). The myrmekitic intergrowth is invariably associated with micro-pores and has conspicuous transgressive fronts which appear to invade into the K-feldspar grains (Fig. 6.3o). Thin films of albitic plagioclase exist at the contacts between the recrystallized K-feldspar grains and these films are sometimes connected to the albitic lamellae present within the host K-feldspar (Fig. 6.3r).

The most plausible fluid that is responsible to form such textures could be hypersaline brine which has the ability to transfer elements in lower crustal condition (Aranovich, 2017; Newton et al., 1998; Newton and Manning, 2010; Touret and Huizenga, 2012; Harlov and Wirth, 2000). The coarse-grained charnockite is thought to be the source of this brine solution as the textures described above are present only at the contacts of the coarse-grained charnockite and the calc-silicate granulite. Although fluid inclusions containing such brine solution was not found in the coarse-grained charnockite but rare occurrences of halite crystals suggest that it was certainly present in this rock but not preserved because of its high mobility.

8.5 Summary

The major outcomes of the fluid evolution study of Phulbani domain is summarized below:

1. Micro-thermometric measurements of the primary fluid inclusions present in the studied rocks suggest that a high density (up to 1.03 gm/cm^3) CO_2-rich fluid was present at UHT condition. Low density (up to 0.76 gm/cm^3) of the secondary CO_2-rich fluid inclusions in some samples possibly vindicate modification of the fluids during upliftment.

2. Wide variation of the melting temperature (T_m from -56°C to -61°C) of all the samples implies presence of other fluid species other than CO_2. In some of the cases, Raman bands of CH_4 and N_2 species have been identified which possibly was responsible for depression of the melting temperature (Hall and Bodnar, 1990) during upliftment.
3. Th-rich overgrowths and veins in monazite indicate that alkali-bearing fluid could be a potential fluid which dissolve Th from the monazite structure and reprecipitate it in the overgrowth domains during coupled dissolution-repreciptation process.
4. K-feldspar micro-veins around plagioclase and garnet grains, slightly Na-rich rim of the plagioclase and associated myrmekite texture suggest the presence of Na-rich brine solution which otherwise remained undetected during fluid inclusion analyses.
5. Patchy Ca-rich zones present in the plagioclase grains that belong to the myrmekite-like intergrowth and clinopyroxene corona over orthopyroxene located at the contact of the calc-silicate granulite and the coarse-grained charnockite suggest that addition of Ca occurred into the latter rock. Calc-silicate granulite is interpreted to be the source of such Ca. At the same time Na and K were transferred towards calc-silicate granulite from the coarse-grained charnockite to produce the pegmatoidal metasomatic rock. Myrmekite texture present in the latter rock could have been developed by such element movement in micrometer-scale and produced porosity due to change in molar volume. Thin films of albitic plagioclase at the grain boundaries of K-feldspar of the pegmatoidal rock suggest that movement of Na along grain boundaries possibly through a fluid phase.