**Zirconium in rutile thermometry from garnet granulites of the Jijal complex of Kohistan arc, NW Himalaya**

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Zirconium in rutile thermometry data from the garnet granulites of the Jijal Complex of Kohistan arc, NW Himalaya are presented in this study. The garnet granulites are composed of garnet, clinopyroxene, plagioclase, quartz, symplectic augite/amphibole, rutile, ilmenite, zircon, and magnetite. Rutile grains range in size from 50 to 350 µm, occur as inclusion in garnet, clinopyroxene, and in plagioclase as well as along the grain boundaries. In total 19 rutile grains were analyzed for Zr contents using an X-ray Analytical Microscope (XGT-5000) by HORIBA. The Zr contents among the analyzed grains ranged between 450 and 920 ppm, where the analyzed spots with lower Zr contents (containing SiO₂ or Fe₂O₃), indicating some influence of host silicate or ilmenite, were removed from results. At the individual grain scale, most of the rutile grains exhibited homogeneous chemical compositions, regardless of their textural affinity. Temperature values, based on zirconium in rutile thermometry, ranged between 792 and 849 °C for rutile enclosed in garnet, 771 and 851 °C for rutile in clinopyroxene, and 784 and 862 °C for rutile in plagioclase whereas matrix rutile grains showed T values between 820 and 847 °C. Using the pressure-dependent zirconium in rutile thermometry, the T values were slightly lower (±50 to 100 °C). The maximum temperature values were consistent with the temperature data obtained from the conventional thermobarometry results (P; 1.2 ± 0.2 GPa and T; 818 ± 80 °C) whereas the lower values, likely, reflect chemical resetting of the analyzed grains during later stages of retrogression.

**Keywords:** Zirconium in rutile thermometry, Garnet granulites, Metamorphism, Jijal complex, Kohistan arc

**INTRODUCTION**

Kohistan arc, situated at the NW Himalayan range (Fig. 1a), represents an oceanic arc exposing mantle to upper crustal complete section, is welded to the Asian Plate along the Northern Suture and the Indian Plate along the Southern Suture, where the rocks from the mantle to upper crustal levels are exposed (Fig. 1b). The arc formed during the Jurassic-Cretaceous periods with some younger late-stage granitic intrusives. The arc collided with Asian Plate during 102–75 Ma and then welded to the Indian Plate during 55–50 Ma (Tahirikheli 1979; Searle et al., 1999 and references therein). The mafic-ultramafic rock unit at the base of the arc, known as the Jijal complex, is exposed above the Southern Suture. The complex is comprised of peridotites, dunites, and pyroxenites in the lower part and mafic rocks (garnet granulate with minor pyroxene granulate/gabbro) in the upper part (Fig. 1c). In this study, we analyzed rutile grains in garnet granulites of the Jijal complex for zirconium contents using an X-ray Analytical Microscope (XGT-5000) by HORIBA. The aims were (1) to check the applicability of XGT to zirconium in rutile thermometry, (2) to understand the metamorphic temperatures of the garnet granulites, and (3) to check if the results obtained from the XGT analysis on texturally different types of rutile (inclusion phase and those in the matrix) bear same or different results for the metamorphism and are comparable to the previously obtained P-T data from the conventional thermobarometry.

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GEOLoGICAL BACKGROUND

The Kohistan arc presents a classical example of a juvenile crust that was formed by the magmatic addition at an intra-oceanic convergent margin in the Neo–Tethys Ocean (Tahirkheli, 1979; Jan and Howie, 1981; Coward et al., 1987; Hamilton, 1994; Beck et al., 1995; Rehman et al. 2011 and references therein). It is exhibited by a complete section of an oceanic arc where rocks from the mantle to upper crustal volcanic and sedimentary levels are exposed (Fig. 1b). Sedimentary sequences of Aptian–Albian age (<120–99 Ma) known as the Yasin Group are exposed at the top of the arc near the Northern Suture, which suggests that the formation of arc began in the Lower Cretaceous period (Pudsey, 1986). Majority of the igneous lithologies of the arc formed between 90 and 110 Ma (Schärer et al., 1984; Petterson and Windley, 1985). Generally, the arc consists six main lithological units from bottom to top (south to north), i.e., the Jijal ultramafic–mafic complex, the Kamila amphibolites, the Chilas ultramafic–mafic complex, the Kohistan batholith, the Jurassic–Cretaceous metavolcanics and meta-sedimentary units of the Jaglot and Chalt Groups, and the Aptian–Albian volcano–sedimentary Yasin Group (Petter-
son and Windley, 1985; Pudsey et al., 1985; Petterson and Windley, 1991; Yamamoto, 1993; Dhuique et al., 2009). The Jijal complex includes peridotites, dunites, and pyroxenites in the lower part and garnet granulites with minor pyroxene granulites and gabbro in the upper part. This complex forms a tectonic wedge to the north of the Southern Suture along the Indus River (Jan and Howie, 1981; Miller et al., 1991). Yamamoto and Nakamura (2000) reported 118 ± 12 Ma age (based on Sm-Nd mineral isochron) for two-pyroxene granulite and 91 ± 6.3 Ma age for the garnet granulate of the Jijal complex. Dhuique et al. (2007) reported the formation of the Jijal complex in three stages, a 117 Ma as the protolith formation age of the ultramafic–mafic rocks, 110 Ma for the intrusion of pyroxenite dykes, and 110–95 Ma of the tholeitic magmatism. Above the Jijal complex lie the Cretaceous to Upper Jurassic Kamila amphibolite belt which mainly comprises of amphibolite facies metavolcanics, ultramafic, gabbro, diorites, tonalites, granites, trondhjemitites, and rare silicic and calcareous metasediments (Bard, 1983; Khan et al., 1993; Treloar et al., 1996). The Chilas ultramafic-mafic complex, formed during 85 Ma (Jagoutz et al., 2006, 2009), is dominantly made up of gabbronorite with some hypersthene-quartz diorite, gabbros, troctolites, anorthosites, pyroxenites, chromite-layered dunites, peridotite, and retrograde amphibolites (Khan et al., 1997). North of Chilas Complex, the Kohistan batholith covers a wide area. It is comprised of plu- tons of calc–alkaline gabbro, diorites, granodiorites, and tonalities of 102 ± 12 Ma that were intruded by a basic dyke swarm around 75 Ma (the Jutal–Numal dykes) which further were intruded by 62–40 Ma granites and 34 ± 14 and 26 ± 1 Ma late-stage aplitic/pegmatitic sheets (Petterson and Windley, 1985; Treloar et al., 1989; Petterson and Windley, 1991; George et al., 1993; Treloar et al., 1996; Jagoutz et al., 2009). The Jaglot Group meta-sediments and metavolcanics overlie the Kohistan batholith towards the north, which represent Eocene volcanics and back-arc basin sediments (Tahirkheli, 1979; Treloar et al., 1996; Khan et al., 1997). Some of the sediments (Gilgit Formation) are metamorphosed into gneisses and schists reaching up to the sillimanite grade (Khan et al., 1997). Above these lie the Chalt volcanics and the Yasin Group sediments comprised of carbonates, siliciclastic and volcaniclastic turbidites of the Aptian–Albian age (Pudsey, 1986).

In this study, we mainly focus on garnet granulites of the Jijal complex and provide a brief description of the samples (further details can be found in past publication, e.g., Yamamoto, 1993; Yamamoto and Yoshino, 1998; Yamamoto and Nakamura, 2000). Yamamoto (1993) reported that garnet granulites of the Jijal complex were derived from gabbroic to ultramafic rocks and were metamorphosed under P-T conditions of 831 °C at 1.15 GPa and 949 °C at 1.7 GPa. The above author inferred that the metamorphic equilibration reaction was: Clinopyroxene + plagioclase = garnet + quartz (after Green and Ringwood, 1967).

ANALYTICAL PROCEDURES

Nineteen rutile grains from garnet granulites from the Jijal complex, Kohistan arc, were analyzed using an X-ray Analytical Microscope (XGT-5000) by HORIBA, situated at the Kagoshima University Instrumental Analytical Center. Two textural varieties of rutile were identified as inclusions in garnet, clinopyroxene, plagioclase, and grains in the matrix or along the grain boundaries. In-situ analysis on two textural varieties of rutile was conducted for seven oxide elements (SiO2, CaO, TiO2, Fe2O3, Nb2O5, Ta2O5, and ZrO2) using the XGT microscope with an acceleration voltage of 50 kV, beam current of 100 nA, and beam diameter of 10 μm. Counting time for analysis was 200 s. The lower limits of detection of the XGT for the analyzed elements are <10 ppm. To check the analytical precision of the instrument, we analyzed two homogenous rutile grains from the Itabara mine, Brazil for the above-mentioned elements (n = 42), all the results showed an analytical error of less than 5%. Past publications reported zirconium—in rutile thermometry of rutile grains that were mainly analyzed by EPMA or LA–ICP–MS (e.g., Zack et al., 2002, 2004; Watson et al., 2006; Zack and Luizottot, 2006; Ferry and Watson, 2007; Tomkins et al., 2007; Luvizotto et al., 2009; Luvizotto and Zack, 2009; Zhang et al., 2009; Kooijman et al., 2012; Ewing et al., 2013; Kohn et al., 2016; Pape et al., 2016; Cruz-Uribe et al., 2018; Pape et al., 2016; Zack and Kooijman, 2017; Rehman et al., 2019 and references therein). In this study, we tried to analyze rutile for zirconium contents using the XGT for the first time. In addition, major phases (garnet, clinopyroxene, plagioclase, and symplectic amphibole) were analyzed using the EPMA (JEOL JXA-8230) at the Kagoshima University Instrumental Analytical Center, with an acceleration voltage of 15 kV, beam current of 100 nA, and beam diameter of 2 μm. The quantitative data were corrected using the metal PR–ZAF method (Reed, 1993).

RESULTS

Petrography and mineral chemistry

The Jijal complex garnet granulites occur as layers or domains intercalated with two-pyroxene granulites and are
surrounded by amphibolites (Figs. 2a and 2b). Garnet granulites are composed of garnet, clinopyroxene, plagioclase, symplectic hornblende after clinopyroxene, quartz, rutile, ilmenite, rare zircon, and magnetite (Fig. 2). Detai
tailed descriptions of the granulites of the Jijal complex are presented elsewhere (Yamamoto, 1993; Yamamoto and Yoshino, 1998; Yoshino et al., 1998; Yamamoto and Nakamura, 2000). Here, we provide a brief description of the rocks used in this study. Well-developed garnet porphyroblasts are surrounded by elongated clinopyroxene and plagioclase grains (Fig. 2c). Two garnet grains were analyzed by EPMA that showed chemical composition in the range of Almandine44–48, Pyrope32–36, Grossular15–22, and Spessartine0.9–1.2, showing weak chemical zoning (Fig. 5 and Table 1). In addition, we also analyzed the adjacent clinopyroxene and plagioclase grains, and the results are shown in Table 1. One spot was analyzed for the symplectic amphibole also. Rutile grains are widespread in garnet granulites (Figs. 3 and 4). They occur as inclusions in garnet, clinopyroxene, and plagioclase, and some grains are located along the grain boundaries. Several grains are overgrown by ilmenite, seen as darker rims around (Fig. 4) whereas a few grains contained exsolution lamellae of ilmenite too (Fig. 3).

**Zirconium in rutile analysis**

In total nineteen rutile grains from garnet granulites were analyzed for zirconium contents. Representative rutile grains with analysis are shown in Figures 3 and 4, and a summary of the results are shown in Table 2 (details of the individual analyzed spots are shown in Supplementary Table S1 available online from https://doi.org/10.2465/jmps.191226). Some of the analyzed spots with higher Fe₂O₃ contents were discarded from the calculations because those spots may have incorporated the Fe component from the overgrown ilmenite. Rutile grains that were larger than 100 μm were analyzed for multiple spots covering the entire grain (rim–core–rim, along the longer axis as well as across the grain). Smaller grains were analyzed for one or two spots.

Zirconium contents in the analyzed grains ranged between 450 and 920 ppm, with a majority of grains showing >700 ppm (Fig. 6a and Table S1).

Temperature values, based on the zirconium–in-rutile thermometry method of Zack et al. (2004), ranged between 792 and 849 °C for rutile enclosed in garnet, 771 and 851 °C for rutile in clinopyroxene, and 784 and 862 °C for rutile in plagioclase whereas matrix rutiles showed T values between 820 and 847 °C (Fig. 6b). We also applied the pressure–dependent zirconium–in-rutile thermometry of Tomkins et al. (2007) and the temperature values obtained were slightly lower (±50 to 100 °C) for the analyzed spots (Fig. 6b and 6c). Based on the conventional geothermobarometry, applied to the coexisting phases such as garnet-clinopyroxene-plagioclase-am-
average $P$–$T$ calculations using the Thermocalc with its internally consistent thermodynamic data set of Holland and Powell (1998) were obtained: $P; 1.2 \pm 0.2$ GPa and $T; 818 \pm 80$ °C from the garnet core composition and $P; 1.3 \pm 0.1$ GPa and $T; 841 \pm 77$ °C from the garnet rim composition (Fig. 7). The average $P$–$T$ results were consistent within the error range with the zirconium in rutile thermometry and those previously reported for the same granulites (~1.1 to 1.7 GPa and 831 to 949 °C, Yamamoto, 1993).

**CONCLUSION**

Generally, the majority of researchers apply electron probe micro-analyzer or Laser–Ablation–Inductively Coupled Plasma Mass Spectrometry for zirconium in rutile analysis. In this study, we used X-ray Analytical Microscope (XGT) to analyze rutile grains for zirconium contents. The thermometry results based on zirconium contents in rutile show slightly lower but consistent temperature values for the studied samples of the Jijal complex of Kohistan arc. Domains with ilmenite exsolution...
lamellae within rutile also yielded similar temperature results to those that were free of exsolutions, hence, those lamellae were likely formed under similar $P$-$T$ conditions to the host rutile. Some of the grains that had ilmenite overgrown around the rutile grains, yielded lower $T$ values compared to the majority of the results. Those values suggest that the outer domains of rutile might have been affected by later stages of retrogression.

Figure 3. Photomicrographs [(a)-(c)] and backscattered electron images [(d)-(f)] of rutile crystals from garnet granulite. Rutile occurs as inclusion in garnet [(a)] in clinopyroxene [(b) and (c)]. Note the ilmenite exsolution lamellae (straight lines across the entire rutile grain). Also, rutile grains are overgrown by ilmenite [(c) and (f)].
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Figure 4. (a) Photomicrographs [(a) and (b)] of garnet granulites showing the textural features of main mineral assemblage and occurrence of rutile (as inclusions in other phases as well as along the grain boundaries). (c)-(k) Photomicrographs of rutile with zirconium in rutile analysis spots. Digits on the grains are the analysis numbers (details are shown in Supplementary Table S1 available online from https://doi.org/10.2465/jmps.191226).
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Table 2. Textural types of rutile and the calculated values of temperature

| Type         | Method          | $T_{\text{min}}$ ($^\circ$C) | $T_{\text{max}}$ ($^\circ$C) | Average $T$ ($^\circ$C) | at $P$ (GPa) |
|--------------|-----------------|-------------------------------|-------------------------------|--------------------------|--------------|
| $Rt_{\text{Grt}}$ | $T_{\text{Zack}}$ | 792                           | 849                           | 826                      |              |
|              | $T_{\text{Tomkins1}}$ | 703                           | 744                           | 727                      | 1.1          |
|              | $T_{\text{Tomkins2}}$ | 733                           | 775                           | 758                      | 1.7          |
| $Rt_{\text{Cpx}}$ | $T_{\text{Zack}}$ | 771                           | 851                           | 821                      |              |
|              | $T_{\text{Tomkins1}}$ | 689                           | 745                           | 723                      | 1.1          |
|              | $T_{\text{Tomkins2}}$ | 719                           | 777                           | 755                      | 1.7          |
| $Rt_{\text{Pl}}$ | $T_{\text{Zack}}$ | 784                           | 862                           | 832                      |              |
|              | $T_{\text{Tomkins1}}$ | 698                           | 753                           | 731                      | 1.1          |
|              | $T_{\text{Tomkins2}}$ | 728                           | 786                           | 763                      | 1.7          |
| $Rt_{\text{Matrix}}$ | $T_{\text{Zack}}$ | 820                           | 847                           | 835                      |              |
|              | $T_{\text{Tomkins1}}$ | 722                           | 742                           | 734                      | 1.1          |
|              | $T_{\text{Tomkins2}}$ | 754                           | 774                           | 765                      | 1.7          |
| EPMA data   |                 |                               |                               |                          |              |
| $Gr_{\text{Core}}+Cpx+Pl+Qtz+Hbl$ | 738                           | 898                           | 818                      | 1.0-1.4      |
| $Gr_{\text{Rem}}+Cpx+Pl+Qtz+Hbl$ | 764                           | 918                           | 841                      | 1.2-1.4      |

Yamamoto (1993) data 831 949 865 1.1-1.7

Temperature values marked as $T_{\text{Zack}}$ are calculated after the method of Zack et al. (2004), while temperature values calculated after the $P$-dependent thermometry ($\beta$-phase of quartz) of Tomkins et al. (2007) are marked as $T_{\text{Tomkins1}}$ for minimum and $T_{\text{Tomkins2}}$ for maximum $P$ values of 1.7 GPa, respectively (from Yamamoto, 1993).

Figure 5. Backscattered electron image of garnet granulites with main mineral assemblage. Locations of the analysis by electron probe micro-analyzer are shown as given in Table 1.

Figure 6. (a) Diagram displaying the distribution of zirconium contents (ppm) in the analyzed rutile grains. (b) Zirconium in rutile thermometry results for the analyzed samples. Note the highest $T$ values obtained from the Zack et al. (2004) method, compared with the lower $T$ values (±50 to 100 °C) obtained from the method of Tomkins et al. (2007). (c) Zirconium in rutile thermometry range obtained from the analyzed rutile. The shaded vertical box represents the temperature range previously determined by conventional thermobarometry (Yamamoto 1993).
SUPPLEMENTARY MATERIALS

Supplementary Tables S1 is available online from https://doi.org/10.2465/jmps.191226.

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